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EFFLUENT DECOLORIZATION TECHNOLOGIES
FOR THE PULP AND PAPER INDUSTRY

BY

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DISCLAIMER STATEMENT

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ABSTRACT

The discharge of color from pulp and paper mills is a serious aesthetic problem. Recently, the color-causing organic compounds have also been implicated in the appearance of algal blooms in the Chowan River, North Carolina.

The pulp and paper industry has long sponsored research to find cost-effective means to remove color from its effluents. Although many color removal technologies have been proposed, none is widely accepted.

This report is a compilation of the research literature, primarily since 1975, relevant to color removal technology.

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SUMMARY

The discharge of color from pulp and paper mills has long been thought to be a nuisance in that the brownish effluent from mills is considered polluted by the public. More recently, there is some evidence to support the contention that pulp and paper mill effluents are involved in blue-green algae blooms. At present, there are no U.S. governmental restrictions on the discharge of color.

This report is a review of the research literature concerning color removal technologies for the pulp and paper industry. The literature since 1975 is emphasized since several reviews of color removal technologies prior to that time are available.

At this point, no one specific color removal technology has been identified as the most cost effective. In fact, there are no mills in the U.S. which have installed a color removal technology for full-time service. There are no technologies which would not have an extremely adverse economic impact on the mill involved.

The pulp and paper industry has long investigated color removal technologies. Research into these technologies continues and new processes are proposed each year. However, they have all been found to have serious technical (on a full-scale basis) or economic problems.

It would appear that oxygen-based bleach plants hold the most promise for color removal. A substantial portion of the total color from a pulp mill comes from the bleach plant; these effluents cannot be recycled due to their content of chloride ions which promotes corrosion in the mill. Oxygen-based bleaching liquors can, however, be recycled. Such recycling would prevent the discharge of a significant portion of the color now being discharged.

Not all technologies can be applied to all mills. Interferences with pulp and paper production schemes, insufficient space, or process incompatibilities all may preclude acceptability of a specific technology.

It would appear that color removal technologies cost on the order of \$10-20/ton of pulp produced. This compares with a market price of \$250-400/ton of bleached kraft softwood pulp.

INTRODUCTION

General Background

The pulp and paper industry is the nation's third largest industrial consumer of water (The Kline Guide to the Paper Industry, 1980). An estimated two trillion gallons of wastewater are discharged annually by the pulp and paper industry, much of which is highly colored. This color is mainly attributable to lignin degradation products formed during various pulping and bleaching operations and is related to the color in streams which comes from decaying vegetation (Christman and Ghassemi, 1966).

The pulp and paper industry is one of the largest businesses in North Carolina. Several of the larger mills in North Carolina are shown in Table 1 with the number of employees and annual payroll. In addition to those persons employed directly by the paper companies, many others are needed for services and, in particular, to supply pulpwood to the mills. A complete listing of paper manufacturing facilities in North Carolina is presented in Table 2.

Since the advent of environmental legislation, wastewater treatment has referred primarily to BOD and suspended solids removal. Color was not thought to be a major problem, being classified as a nonconventional pollutant. There are still no federal regulations concerning color discharge, but some states and Canadian provinces have established permissible limits of color discharge for a few select pulp mills. The reasons for color regulations at these locations are said to be protection of fisheries or for aesthetic considerations, the public associating color with pollution. In addition, several Eastern Europe and Scandanavian countries and Japan have a limitation on COD discharge; this is tantamount to a color discharge regulation since

Table 1. Economic Importance of Some Major Pulp Mills in North Carolina

| <u>Location</u> | <u>Owner</u> | <u>Number of Employees</u> | <u>Annual Payroll, \$ x 10⁶</u> |
|-----------------|---------------|--------------------------------|--|
| Riegelwood | Federal Paper | 1500 | 45 |
| Roanoke Rapids | Champion | 585 | 15.1 |
| New Bern | Weyerhaeuser | 457 | 13.7 |
| Canton | Champion | 2288 | 56.9 |

Table 2. Pulp and Paper Mills in North Carolina

| <u>Location</u> | <u>Owner</u> | <u>Pulping Process</u> | <u>Production (tons/day)</u> | <u>Products</u> |
|-----------------|----------------------------|------------------------------|------------------------------|---|
| Canton | Champion Papers | Kraft | 1,540 | Envelope, Tablet, Offset, Bond, Mimeo, Duplicator, Poster, Milk Carton, Sanitary Food Container |
| Charlotte | Carolina Paper Board Corp. | NP | 115 | Plain and Bending Chip, Vat Lined, White Wood, Pure White, Bending News, Mist Grey, Bleached Manilla Lined Box Boards |
| Conway | Georgia-Pacific Corp. | Defiberated Wood | 200 | Hardboard |
| Goldsboro | Celotex Corp. | Defiberated Wood | 430 | Roofing Felt, Asphalt Saturated Felts, Prepared Roofing |
| Lumberton | Alpha Cellulose Corp. | Cotton Linter | 100 | Custom Made Cotton Linter Pulps |
| Maxton | Leggett & Platt Inc. | NP | 33 | Cellulose Wadding for Packing and Cushioning |
| Moncure | Weyerhaeuser Co. | Defiberated Wood | 110 | Medium Density Fiberboard |
| New Bern | Weyerhaeuser Co. | Kraft | 800 | Bleached Hardwood and Softwood Pulp |
| Patterson | Cellu Products Co. | NP | 20 | Creped Cellulose Wadding and Facial Tissue, Twisting Papers |
| Pisgah Forest | Olin Corp. | Modified Kraft Bleached Flax | 300 | Cigarette, Lightweight Printing and Bible, Fine and Technical Specialty, Endless Woven Belts |

Table 2. Pulp and Paper Mills in North Carolina (cont'd)

| | | | | |
|----------------|---------------------------------|---------------------|-------|--|
| Plymouth | Weyerhaeuser Co. | Kraft NSSC | 1,290 | Kraft Linerboard, NSSC Corrugating Medium, Milk Carton Board, Polyethylene Coated Board |
| | Weyerhaeuser Co. | NP | 795 | Fine Printing and Writing Papers |
| Riegelwood | Federal Paper Board Co. Inc. | Kraft | 975 | Coated and Uncoated Bleached Board, Food Board, Folding Carton Boxboard, Foil Laminating, Coated Cover, Coated Bristol |
| Roanoke Rapids | Champion Packaging | Kraft | 1,025 | Bleached Hardwood and Softwood Market Pulps |
| | | | 1,100 | Kraft Bag, Asphaltting, Laminating, and Other Converting, Wrapping, Waxing Papers, Linerboard |
| | Halifax Paper Board Co. Inc. | NP | 78 | Plain Chip, Pasted Chip, White Lined Chip, News Board, Book and Specialty Lining, Ream and Rotary Cutting |
| Roaring River | Abitibi-Price Corp. | Defiberated Wood | 330 | Exterior Hardboard Siding |
| Rockingham | Jerry L. Goodwin Inc. | NP | 7 | Meat and Poultry Pads |

NP = No Pulping

conventional biological treatment systems cannot remove color.

Even though there are no well-established color discharge regulations, the industry itself has attempted to address the color problem for many years. Previous reviews of the color problem have been prepared by Gillespie and Berger (1971), Tyler and Fitzgerald (1972), Gehm (1973), Timpe, et al (1973), Gallay (1973), Vincent (1973), Gellman and Berger (1974), and Rush and Shannon (1976).

It is the purpose of this document to review state-of-the-art of color removal technologies and to assemble information concerning the color problem which has recently been published.

The Manufacture of Paper

The manufacture of paper from trees or other woody plants first requires the destruction of the naturally occurring fiber-to-fiber structures. A flowsheet for the manufacture of paper is presented in Figure 1. These well-defined, rigid structures consist of the papermaking fibers held together in organized patterns by lignin; lignin is the cement which bonds the fibers together and imparts structural rigidity to the plant. A proposed structure of lignin is presented in Figure 2. Complete fiber separation is essential to the formation of a good paper sheet. This can be accomplished by either physical or chemical means, or a combination of both. Physical pulping processes do not actually remove the lignin from the wood fiber. The lignin remaining in association with the fibers inhibits fiber-to-fiber bonding; this results in a weak sheet. Chemical pulping processes do, however, dissolve the lignin by making it soluble in aqueous solutions. The increased availability of fiber surface for bonding due to the absence of lignin results in a stronger, more flexible sheet.

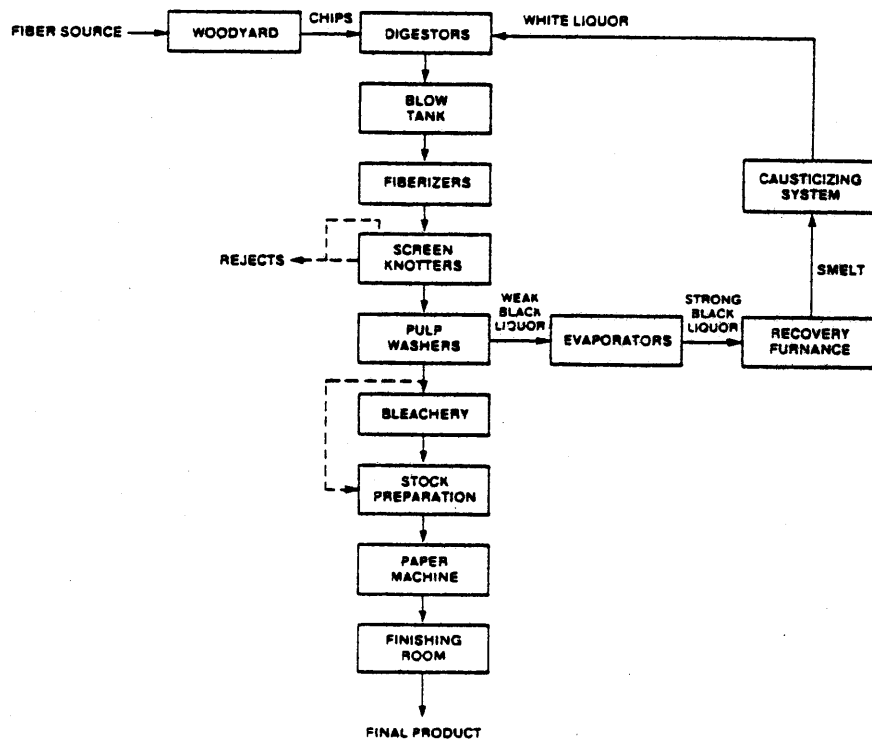


Figure 1. Flow Chart of the Manufacture of Paper

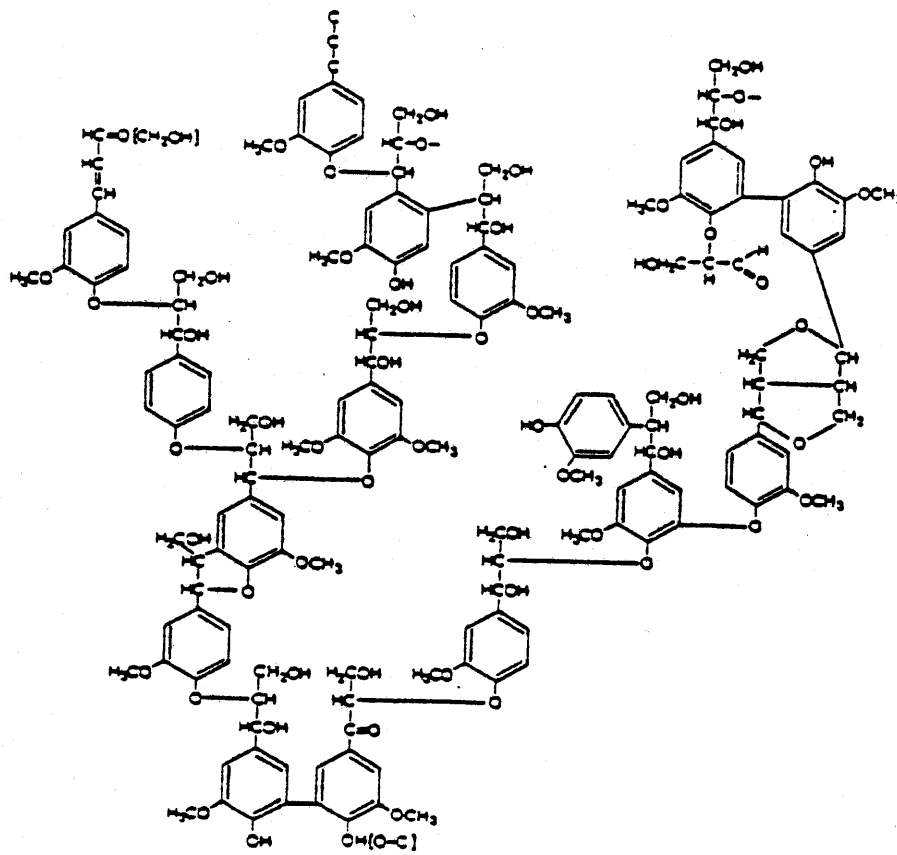


Figure 2. Portion of Lignin Polymer [after (Sjöström, 1981)]

The most common pulping process in use today is the kraft, or sulfate, process. This process is by far the most common, accounting for some 95% of the total pulp produced (Bureau of the Census, 1979). The principal pulping chemicals used in this process are sodium hydroxide (NaOH) and sodium sulfide (Na_2S). Pulps made from the kraft process are characterized by their excellent strength properties; kraft means "strong" in German. Other advantages of the kraft pulping process include the ability to recover and recycle pulping chemicals and the ability to pulp virtually any fiber source, even those containing a high percentage of resinous compounds. The differences in composition between hardwood and softwood species (Table 3) create problems for other pulping processes. This has given rise to the dominance of kraft mills in the South, where softwoods available for pulping are abundant.

Fiber is obtained for the pulp mill in the form of logs of various sizes and also as chips. The first step in converting the fiber source into paper occurs in the wood room. Long logs are reduced to a size more easily handled by cutting them on a slasher deck. Logs still too large for the ensuing equipment must be further reduced using a log splitter or other similar equipment. The logs are then sent to a debarking process which removes most of the dirt and bark from them. Either wet or dry debarking processes may be used. With more and more mills utilizing bark as a fuel, dry debarking is becoming the more common method. Dry debarking does not add moisture to the bark which reduces its fuel value; it also reduces the quantity of wastewater which must be treated. The debarked logs are then sent to the chippers where they are further reduced to chips which are usually less than one inch in length.

Table 3. Chemical Composition of Some Extractive-Free Woods

| <u>Softwoods</u> | | | | |
|------------------|---------------------|-------------------------|------------------|---------------|
| | <u>Cellulose, %</u> | <u>Hemicellulose, %</u> | <u>Lignin, %</u> | <u>Ash, %</u> |
| Loblolly Pine | 42-46 | 20.5-27.5 | 27-30 | 2.5-4.5 |
| Slash Pine | 43-45 | 20.5-24.5 | 26-30 | 2.5-4.5 |
| White Spruce | 41 | 31 | 27 | 1 |
| <u>Hardwoods</u> | | | | |
| | <u>Cellulose, %</u> | <u>Hemicellulose, %</u> | <u>Lignin, %</u> | <u>Ash, %</u> |
| Red Maple | 43.4 | 29.9 | 26.2 | 0.5 |
| Paper Birch | 40.5 | 35.4 | 22 | 2.1 |
| Blue Gum | 52 | 25.5 | 22.2 | 0.3 |

Chips are screened to insure a uniform size and are then charged into the digester. Screening allows a more consistent pulp quality to be realized from the cooking process. Oversized chips removed by the screens are sent to a rechipper and are subsequently returned to the screens. Undersized chips and fines removed by the screens can be utilized as a fuel along with the bark.

The cooking cycle can be carried out in either continuous or batch digesters. As the name implies, the batch digester pulps a specific amount of chips and then discharges them before being recharged. The continuous digester operates under conditions of continuous flow. The chips are placed in the digester along with the desired amount of cooking chemicals referred to as "white liquor" (see Table 4 for typical white liquor composition). This mixture can be heated either directly or indirectly with steam. The steam flow is regulated such that a pre-specified time-temperature curve for the cook is followed; the shape of the curve is determined by the desired pulp qualities. A pressure relief is used on the digesters to provide for the discharge of non-condensable gases and the recovery of turpentine. Once the maximum temperature is attained, it is held constant for the remainder of the cook. The pulp is finally discharged from the digester after the appropriate cooking time has elapsed; this is referred to as "blowing the digester."

The pulp is next screened to remove any oversize or undercooked constituents, such as knots. These rejects can be re-introduced into the digester for further cooking, refined and rescreened, or disposed of as fuel or refuse. The accepted pulp, along with the black liquor from the cook, is then sent to the brown stock washers.

The brown stock washers are used to separate as much of the black liquor from the pulp as possible without causing too much dilution of the black

Table 4. Typical White Liquor Composition

| <u>Chemical</u> | <u>g/l as Na₂O</u> | <u>g/l of Chemical</u> |
|---------------------------------|-------------------------------|------------------------|
| NaOH | 27 | 35 |
| Na ₂ S | 12 | 15 |
| Na ₂ CO ₃ | 6 | 11 |

30% sulfidity $[\text{Na}_2\text{S}] / [\text{NaOH}] + [\text{Na}_2\text{S}]$
 39 g/l Active Alkali as $[\text{Na}_2\text{S}]$ $[\text{NaOH}] + [\text{Na}_2\text{S}]$
 33 g/l Effective Alkali as $[\text{Na}_2\text{S}]$ $[\text{NaOH}] + 1/2 [\text{Na}_2\text{S}]$

All [] Expressed as Na₂O

liquor. The black liquor is composed of the spent and residual cooking chemicals and the dissolved solids removed from the chips during cooking. A typical black liquor composition is presented in Table 5. Washing is necessary to recover the cooking chemicals and to clean the pulp. A countercurrent water flow, utilizing a series of vacuum or pressure washers, is usually employed. The recovered black liquor is sent to the recovery system while the clean pulp proceeds to either the bleach plant or directly to the paper mill.

Bleaching is used as an extension of the cooking stage to further brighten the pulp by removing more lignin and other coloring bodies. The resulting product is a white pulp. A chemical oxidant is used for this purpose. The colored compounds to be removed from unbleached pulp must be converted to a water-soluble form; they can then be extracted from the pulp. Multiple stage bleaching is necessary to bleach kraft pulps to desired brightness levels. Many different chemicals can be used in the various bleaching stages.

A common bleaching sequence is C-E-D-E-D. A flow sheet of the conventional bleach plant is presented in Figure 3. The letters are abbreviations for chlorination (C), alkaline extraction (E), and chlorine dioxide addition (D). The first stage utilizes elemental chlorine which results in an acid chlorination step. Under proper reaction conditions the chlorine will not attack the cellulose, only the residual lignin. The second stage is an alkali extraction. This stage removes the now water-soluble, chlorinated lignin products of the first stage along with any other alkali soluble impurities. Chlorine dioxide is used in the third stage due to the ability to better control the extent of bleaching and an overall chemical

Table 5. Typical Black Liquor Composition (Pine Kraft)

| <u>Component</u> | <u>Dry Solids, %</u> |
|------------------|----------------------|
| Lignin | 47 |
| Hydroxy Acids | 28 |
| Formic Acid | 7 |
| Acetic Acid | 4 |
| Extractives | 5 |
| Other | 9 |

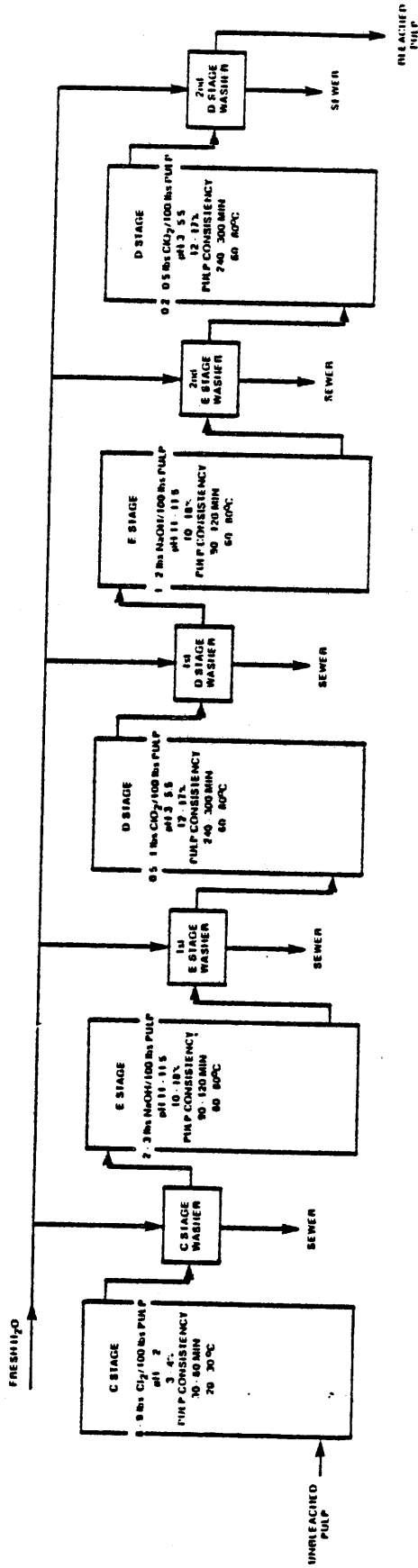


Figure 3. Conventional Bleach Plant [after (Libby, 1962)]

savings. The pulp is further brightened by the oxidation and subsequent removal of the remaining lignin. The fourth and fifth stages are the same as the second and third. They are employed to achieve an incremental increase in the pulp brightness. A complete listing of mills in North Carolina which practice pulp bleaching is presented in Table 6.

The bleached and/or unbleached fibers to be made into paper are further treated before being made into a sheet. To impart strength and drainage properties to the pulp, a beating or refining process is used. This process tears and ruptures the fibers causing fiberization which results in better bonding and a more dense sheet. Fillers such as clays, CaCO_3 , talc, and TiO_2 may be added to improve such characteristics as opacity, smoothness, and brightness. Sizing agents such as rosins, waxes, or synthetics are used to inhibit the penetration of particular liquids through the final product. Other additives such as dyes, wet or dry strength resins, and retention aids may also be used to impart desired qualities to the pulp or the finished product. Portions of these additives will appear in the wastewater treatment system due to inadvertent loss from the paper machine.

The paper sheet is formed by discharging a stream of pulp slurry onto a moving wire. A fiber mat is formed on the wire as the water is drained off. This mat leaves the wire and is introduced to the press section where additional water removal and some modifications in the paper qualities are accomplished. From the presses, the sheet enters the dryer section where indirect steam heating is used to dry the sheet to its final moisture content, usually about 5%. The sheet may also pass through a calender stock. The calender stock is a vertical stack of rolls used to impart gloss and finish to the paper surface.

Table 6. MILLS IN NORTH CAROLINA UTILIZING PULP BLEACHING

| <u>Location</u> | <u>Owner</u> | <u>Digesters</u> | <u>Bleach Sequence</u> | <u>Production of Bleached Pulp (T/D)</u> |
|-----------------|---------------------|------------------|---------------------------------|--|
| Canton | Champion Papers | 18 Batch | Pine:C-E-H-E-D-H- and C-E-H-D-H | 840 |
| | | | HWD:C-E-H-E-D | 550 |
| New Bern | Weyerhaeuser | 8 Batch | C-E-H-D-E-D | 725 |
| Pisgah Forest | Olin | 13 Rotary | C-E-H | 300 |
| Plymouth | Weyerhaeuser | 19 Batch | C/D-E-D-E-D-D | 525 |
| | | 1 Continuous | 2:C-E-H-P and 1:C-E-H-E-D-P | 435 |
| Riegelwood | Federal Paper Board | 16 Batch | 3:C-E-H-D-E-D and 2:C-E/H-D-E-D | 1,875 |
| | | 1 Continuous | | |

C = Chlorine (Cl₂), D = Chlorine dioxide (ClO₂), E = Alkaline extraction (NaOH)

H = Hypochlorite (NaOCl + NaOH), P = Peroxide (Na₂O₂)

The large rolls of paper from the paper machine are usually not suitable for customer wants or needs. These rolls are further processed into suitable form for subsequent end uses by individual customers.

The recovery system of the kraft process (Figure 4) makes this process an economically feasible means of paper production. The black liquor recovered from the cooked pulp contains the spent cooking chemicals along with the compounds removed from the chips. The liquor removed from the bleaching stage contains organic compounds that could be recovered or utilized for fuel, but the corrosiveness of the chlorides in this liquor presents too many problems to be included in the recovery system. For this reason, the industry trend is toward bleaching with oxygen, hydrogen peroxide or other oxidizing reagents which do not contain chlorides. These alternative bleaching compounds allow the recycle of portions of the bleaching liquors. This results in a decrease of the wastewater to be treated and an increase in the quantity of chemicals recovered.

The black liquor to be burned in the recovery furnace is too dilute to support combustion as it comes directly from the washers. Multiple effect evaporators concentrate the liquor to about 50-55% dissolved solids. However, this is still not concentrated enough for the recovery furnaces. Direct or indirect contact evaporators further concentrate the liquor to 60-65% dissolved solids. At this concentration, the black liquor can be burned without auxiliary fuel.

When direct contact evaporators are used, an oxidation stage for the black liquor is employed. The oxidation of black liquor prior to the direct contact evaporators decreases the amount of sulfur compounds emitted to the atmosphere. This results in a reduction of odor from the mill and a decrease

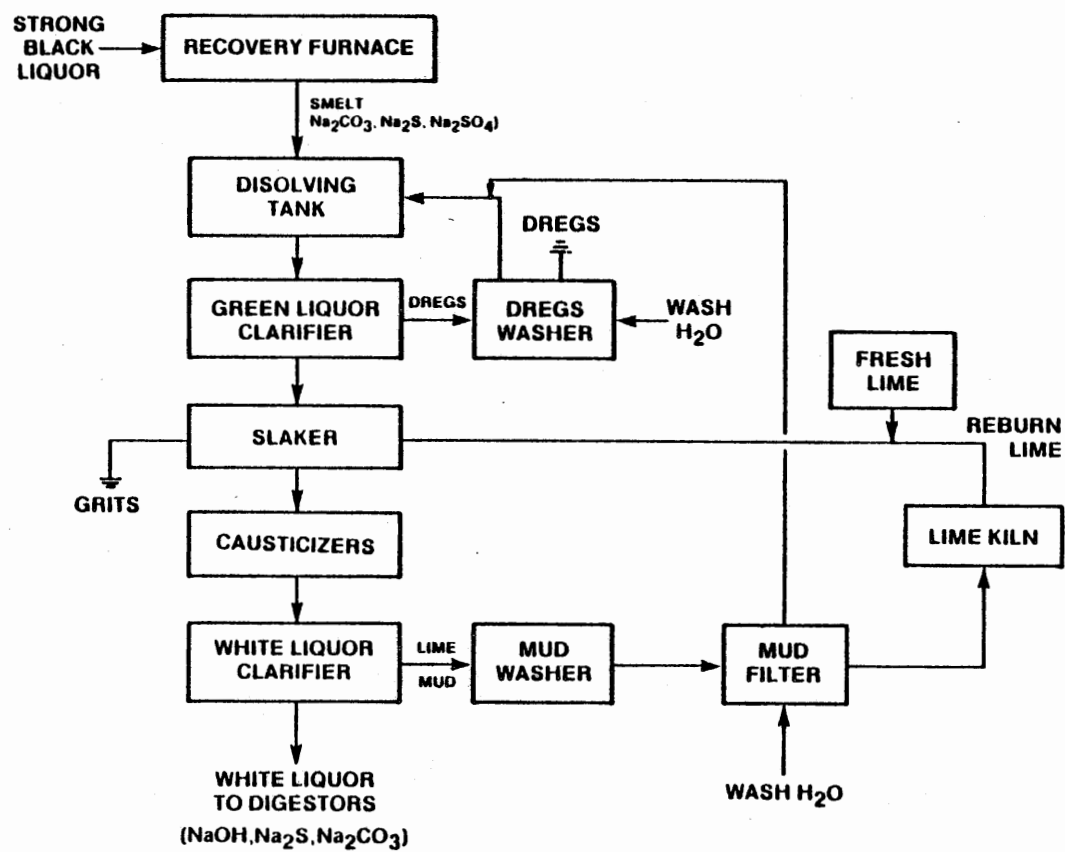


Figure 4. Kraft Recovery System

in the amount of make-up sulfur needed to maintain the desired sulfidity levels in the white liquor.

Concentrated black liquor is injected into the recovery furnace and the organics are burned as a fuel. The heat from the combustion reduces the spent cooking chemicals and they leave the furnace as a solid "smelt". This smelt is dissolved in the smelt tank and forms "green liquor".

Clarified green liquor is slaked with lime and retained in causticizing tanks. After causticizing, the "white liquor" is clarified. This is the cooking liquor used in the kraft cooks. The solids removed from the white liquor are washed, filtered, and burned in the lime kiln. The lime resulting from this process is recycled to the slaker to be mixed with the green liquor.

Effluents, or spills, from the mill which cannot be recycled or recovered must be treated. Bleach plant and paper mill effluents provide a large portion of this flow. Wastewater treatment facilities differ greatly from mill to mill. Each mill has its own special problems and the facilities are designed to handle these on a case by case basis. These designs however, must also be able to meet the effluent guidelines established for each mill.

The Nature of Color

Color is a term which has several different meanings. As it pertains to the pulp and paper industry, color is defined as the absorption of light in the visible range. The visible light range covers wavelengths of 400-700 nanometers. One additional distinction must also be made. Color can be measured in two forms, true and apparent color. True color is measured when any turbidity present initially has been removed from a sample. The observation of color prior to the removal of turbidity is referred to as apparent color. This distinction is necessary because the suspended solids in

a sample can cause scattering and reflectance of light. In this situation, reflectance can be mistaken for absorbance. This will cause the report of erroneously high color levels.

Several different methods are available for the measurement of color. These include visual comparison with platinum-cobalt standards, spectrophotometric analysis, and tristimulus filter methods. The National Council of the Paper Industry for Air and Stream Improvement, Inc. (1971) has developed a method of color measurement specifically for pulp and paper industry effluents. This method involves adjusting the pH of the sample to 7.6 using either HCl or NaOH. The sample is then filtered through a 0.8 micron porosity membrane filter to remove turbidity. It was found that the 0.8 micron filter was small enough to remove colloidal particles, but large enough not to remove lignin macromolecules. The color values are obtained by comparing spectrophotometric readings of the samples to those of platinum-cobalt standards. The spectrophotometric analyses are carried out at 465 nanometers.

The color observed in paper industry effluents is pH dependent. As the pH increases, the color value also increases for a given sample. This is not a linear relationship and varies depending on the source of the color. Resonating double bonds are generally held to be responsible for the color caused by organic compounds. As the pH increases, the resulting chemical configurations permit more resonance, thereby increasing the color. This is also the reason it is necessary to test for color at a specific pH. To make meaningful comparisons of color measurements between mills or even between samples from the same mill, the tests must have been made at the same pH.

Although seen primarily as an aesthetic concern, color may also be

responsible for several other problems. The phenolics which are an integral part of many color-causing compounds can pose a potential taste problem. Algal or bacterial activity may increase due to the availability of nutrients bound to the color-causing organic compounds. The size of some of the color bodies can cause fouling of ion-exchange resins. Other problems may include interference with coagulation at water treatment plants, increased chlorine demand, and chelation of metals. Light transmittance may be reduced in natural waters, resulting in decreased productivity and interference with colorimetric analyses done on the waters.

Recently, it has been proposed (Paerl, 1982) that algal blooms (Kuenzler, et al, 1982, and Witherspoon and Pearce, 1982) are related to the discharge of pulp and paper mill effluents into the Chowan River, North Carolina. It was hypothesized that the well-known metal chelating capability of lignin was responsible for upsetting the balance between green and blue-green algae. Essentially the same argument was made for the disturbance of the natural balance between floc-forming and filamentous bacteria in waste treatment plants (Joyce, 1979). Filamentous bacteria and blue-green algae have a high surface to volume ratio which permits them to more effectively capture nutrients from solution.

Lignin and its degradation products are the major contributors to color in mill effluents. Some of the color chromophores are shown in Figure 5. Lignin, a polymer of phenylpropane units, acts to impart structural rigidity to individual fibers and to the plant as a whole. This necessitates the removal or breakdown of some of this lignin to provide the individual fibers necessary for paper manufacture. Lignin also acts as an inhibitor to microbial attack. This is evidenced by its resistance to most organisms

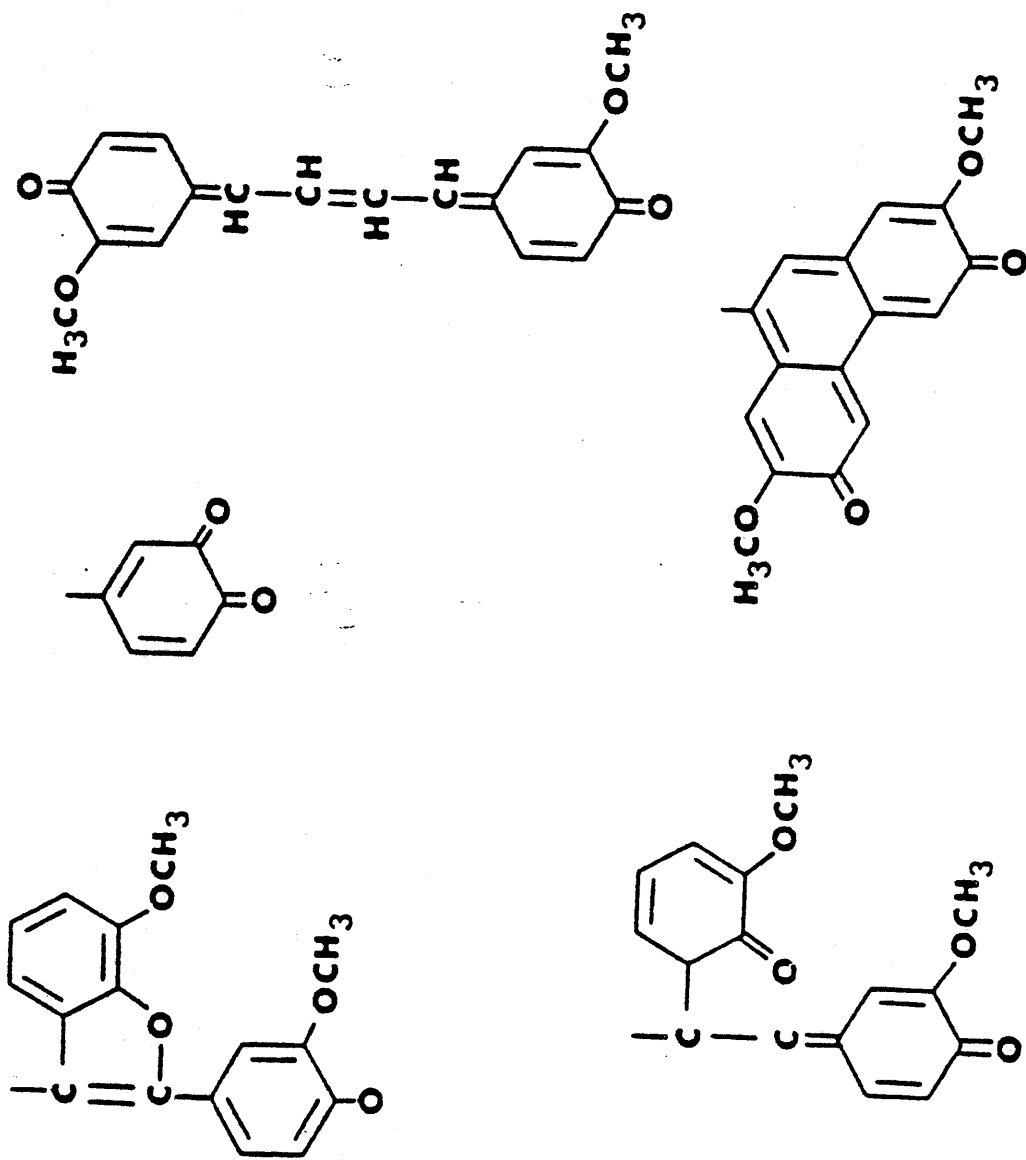


Figure 5. Some Proposed Chromophoric Structures [after (Sjöström, 1981)]

responsible for natural decay. The intricate structure of lignin allows for considerable double bond resonance, which correlates to the dark color of lignin.

The quantity of color produced by each operation in a mill can be traced almost directly to the amount of lignin released during that operation. Approximate color concentrations in several waste streams are presented in Table 7. However, the pulp mill, which releases the largest amount of lignin, is not responsible for the largest portion of color in the effluent (Figure 6). This is due to the recovery of the cooking chemicals. The color released in the pulping cycle is burned in the recovery furnace to recover the inorganic chemicals used for pulping. Therefore, most of the color released during pulping never reaches the final mill effluent. The bleach plant, which releases the next largest amount of lignin, subsequently becomes the major color source. These waste liquors cannot be treated in the same manner as the pulping wastes. The corrosiveness of the chlorides usually present in bleaching wastes prohibits the burning of these liquors. The bleach plant can be responsible for more than two-thirds of the total color load while contributing less than one-half of the effluent volume.

The color bodies associated with the bleach plant are not precisely the same as those associated with the pulp mill. There are general distinctions that can be made between the chromophores of different liquors. Although they are both mainly derivatives of lignin, the additional chemical treatments in the bleach plant cause further lignin degradation and create chemical configurations different from those found in the waste pulping liquor. These bleach plant chromophores are possibly of more interest in color reduction since the majority of the pulping chromophores will be destroyed during the recovery process.

Table 7. Approximate Color Concentrations in Various Waste Streams from Bleached Kraft Pulp Production
 [After (Rush and Shannon, 1976)]

| <u>Source</u> | <u>Color, Pt-Co Units*</u> |
|-----------------------|----------------------------|
| Pulp Mill Effluent | 700 - 3,700 |
| Bleach Plant Effluent | |
| Chlorination | 600 - 2,300 |
| Alkaline Extraction | 4,400 - 23,000 |
| Whole Mill Effluent | 1,200 - 3,700 |
| Other Liquids | |
| Coffee | 10,000 - 15,000 |
| Beer | 1,000 - 1,200 |

* Platinum - Cobalt Standard (NCASI, 1971)

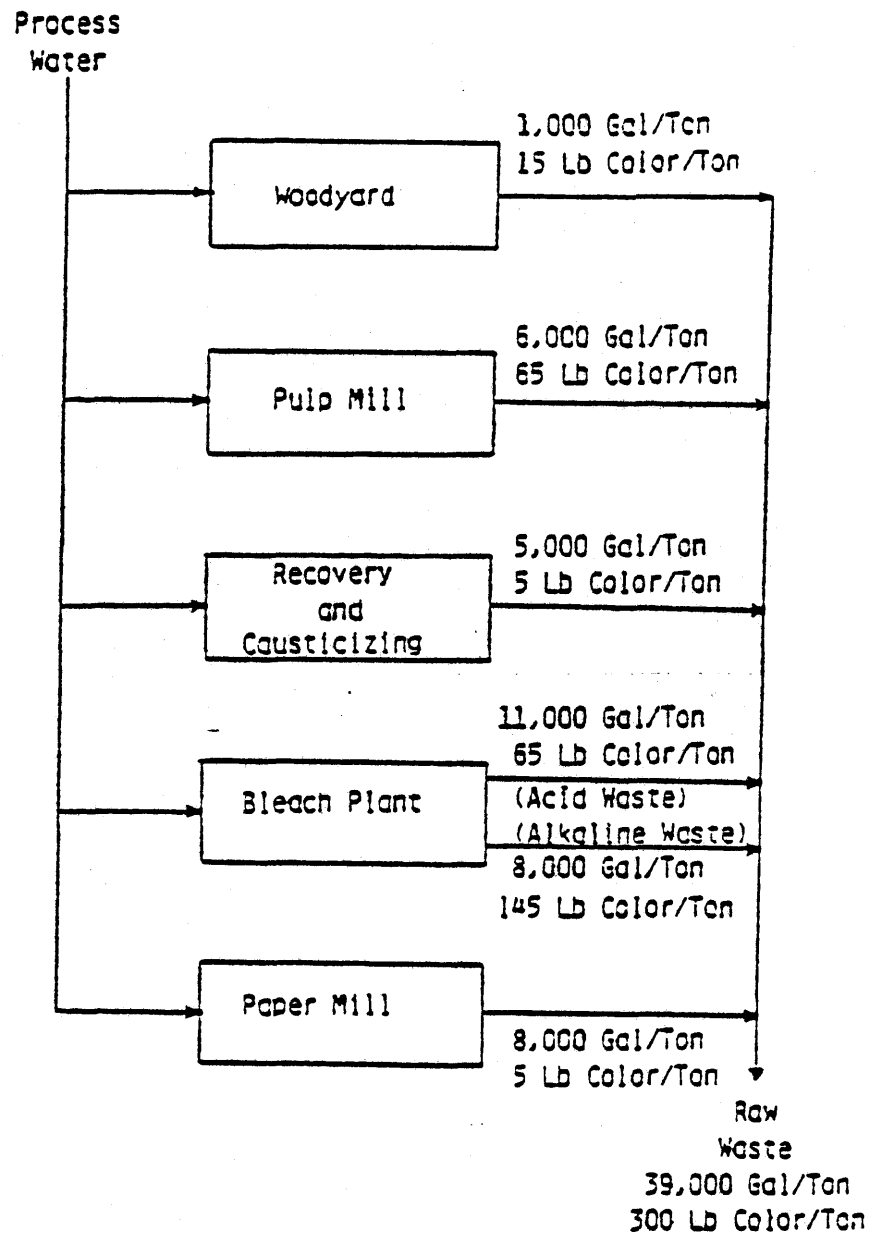


Figure 6. Sources of Pollutants in Bleached Kraft Mill [after (EPA, 1976)]

COLOR REMOVAL TECHNOLOGIES

Introduction

There are two general strategies for the removal of color from the effluent of a pulp and paper mill. The first is the conventional end-of-the-pipe treatment. While this strategy usually has the least impact on the manufacturing facilities, it is typically the most expensive. Additionally, most of the technologies which are in this category merely concentrate the color; a means of chromophore destruction must ultimately be used. The second strategy attempts to modify the manufacturing process so that less color bodies are produced or so that the waste liquors may be recycled internally and be destroyed within the process. Obviously, process modifications cannot be made in all mills because of lack of flexibility within the mill or a basic incompatibility between the proposed process modification and the desired end product.

Effluent Treatment

Color Removal by Secondary Treatment

The industry's current practice of clarification of the total mill wastewater followed by biological treatment, commonly aerated lagoons or activated sludge units, can eliminate conventional pollutants such as BOD and COD at efficiencies of up to 95%. However, these biological systems are capable of color reductions of only 0-30% (Rush and Shannon, 1976, and Obiaga and Ganczarczyk, 1974). This resistance of color bodies to biological treatment is largely due to the inability of the microbial population to metabolize lignin-derived chromophores. Joyce, et al (1979) attempted to manipulate the sludge age in an activated sludge reactor to enhance color removal, but without success.

A direct approach to improving the color reduction ability of biological processes has recently been reported (Dogherty, 1982). The Sybron Corp. has attempted to augment the natural microbial population of an aerated lagoon with a mutant strain of the bacterium, Pseudomonas aeruginosa. This organism, mutated from normal inhabitants of the treatment system, is reportedly able to metabolize "color lignins," and it is claimed to be able to remove 40% of effluent color and considerable BOD₅ in laboratory studies. Mill-scale evaluation is presently being conducted at a Canadian bleached kraft mill.

The MyCoR Process

White-rot wood decay fungi have active ligninolytic systems that will degrade even heavily modified lignin such as kraft lignin and chlorinated lignin. Thus, these fungi could conceivably be used in wastewater treatment applications to degrade lignin-derived chromophores produced during the bleaching of pulp. Exploratory experiments have demonstrated that bleach plant effluents from the first alkali extraction stage could be decolorized with the white-rot fungus, Phanerochaete chrysosporium Burds (Joyce, et al, 1981, and Eaton, et al, 1982).

The U. S. Forest Products Laboratory and North Carolina State University are working to develop and evaluate a color removal process based on P. chrysosporium. The process has been termed the FPL/NCSU MyCoR (Mycelial Color Removal) Process. Based on the results of a preliminary study with various stirred fermentors and fixed film reactors, the rotating biological contactor (RBC) was chosen for bench scale experiments because it provides a large surface area for fungal contact with both oxygen and the effluent without excessive agitation, which is deleterious to lignin degradation and decolorization. The RBC also offers unique operating features such a high

surface area per unit volume, low maintenance costs, low energy requirements, simple construction and operation, and commercial availability.

The RBC MyCoR reactor may be operated either as a batch reactor or as a continuous, plug-flow reactor (Campbell, 1983). Batch studies allowed monitoring of color and pH changes as a function of time, providing a means of studying the kinetics of chromophore destruction by draining effluent from the RBC after 24 hours and immediately refilling the reactor with a fresh effluent to be decolorized; the effluent contained all nutrients except nitrogen. The rate of color removal increased as the initial color concentration was increased until a maximum rate of chromophore destruction was reached at an initial color of approximately 6,000 color units. Above 6,000 color units, the rate of decolorization was independent of the initial color concentration. At this saturation point, the rate of fungal decolorization in the RBC MyCoR reactor was approximately 2,000 color units/L/day (Gerrard, 1983).

Since the active lifespan of the fungus in the MyCoR reactor decreases with increasing initial effluent color concentration, it was considered likely that some low molecular weight compounds present in the first extraction stage (E_1) effluent and/or the fungal degradation products may be toxic to the fungus, especially those chlorinated organic compounds known to be present in the bleach plant effluent. To determine the fate of these low molecular weight compounds in the MyCoR reactor, the E_1 effluents before and after MyCoR decolorization were extracted with chloroform after adjusting the pH to 2.5. The extracts were subsequently examined by gas chromatography/mass spectrophotometry (GC-MS). The gas chromatograms of the chloroform extracts before and after fungal decolorization and the major components that have been identified by the GC-MC analyses are shown in Figure 7. Chlorinated phenols

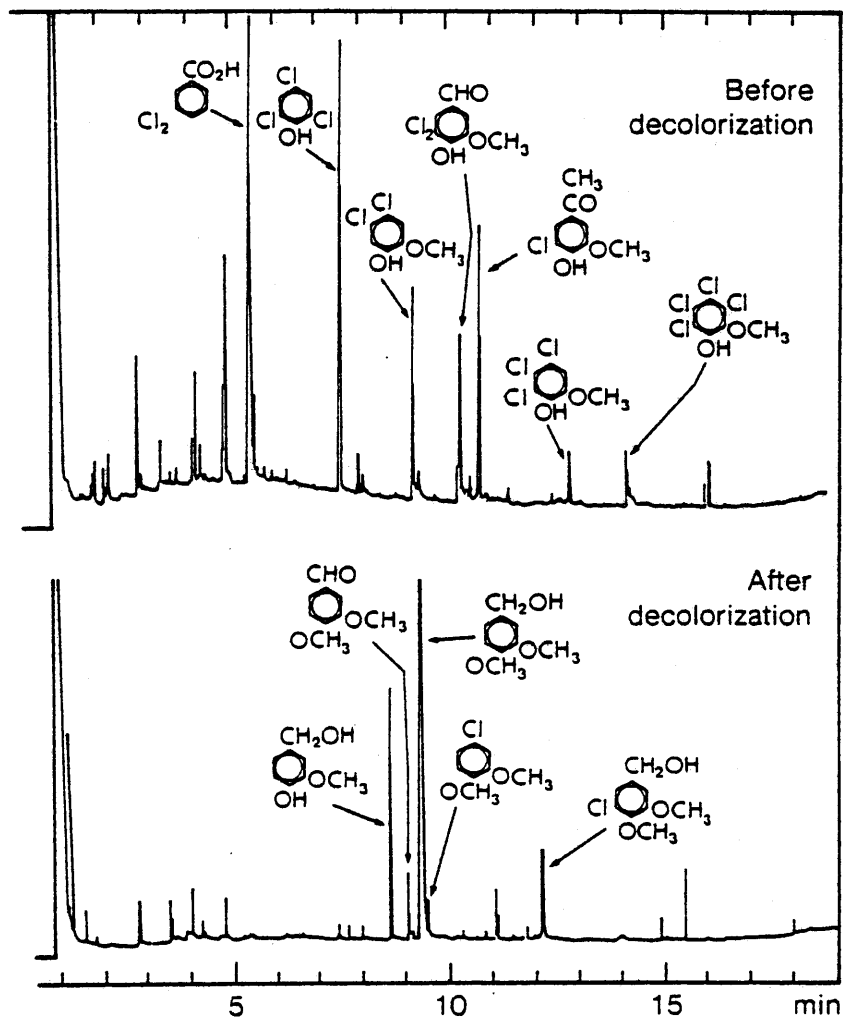


Figure 7. Destruction of Chlorinated Compounds by the MyCoR Process

were the dominant low molecular weight components in the E₁ effluents. Surprisingly, these chlorinated phenols completely disappeared after fungal treatment. This finding may be significant, because most of the identified chlorinated phenols are known to be toxic to aquatic life.

The suggested integration of the MyCoR Process into a pulp and paper mill is shown in Figure 8.

Metal Ions

One of the more promising color removal processes that has been examined on a mill scale is lime precipitation (Figure 9). Early studies on removal of color from pulp and paper mill effluents utilized the existing chemical treatment technology of municipal water supply decolorization. Screening of over thirty metal ion coagulants and adsorbants demonstrated varying degrees of effectiveness (Moggio, 1955). Lack of recovery methods, or other technological difficulties, such as corrosion problems, prevented many from further consideration. Lime addition was considered to have the greatest potential for application in the industry. Among the factors recognized as favoring use of lime were:

1. lime is comparatively low in cost and is readily available (especially in treatment of kraft mill effluent, where lime is produced as part of the chemical recovery system, i.e., causticizing of green liquor),
2. recovery methods are already well-developed, and,
3. personnel at kraft mills have experience with lime production and recovery.

The fact that lime is an integral part of the kraft pulping process offered an opportunity for both recovery of lime used for decolorization and for destruction of the color by combustion in the lime kiln. Since this early

RBC MYCOR PROCESS

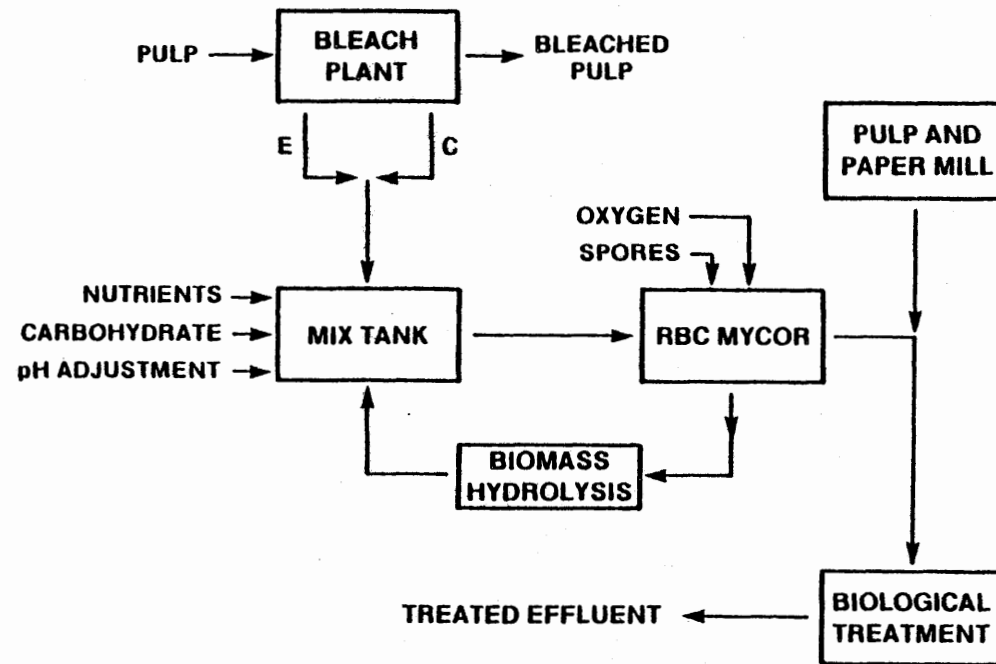


Figure 8. MyCoR Process

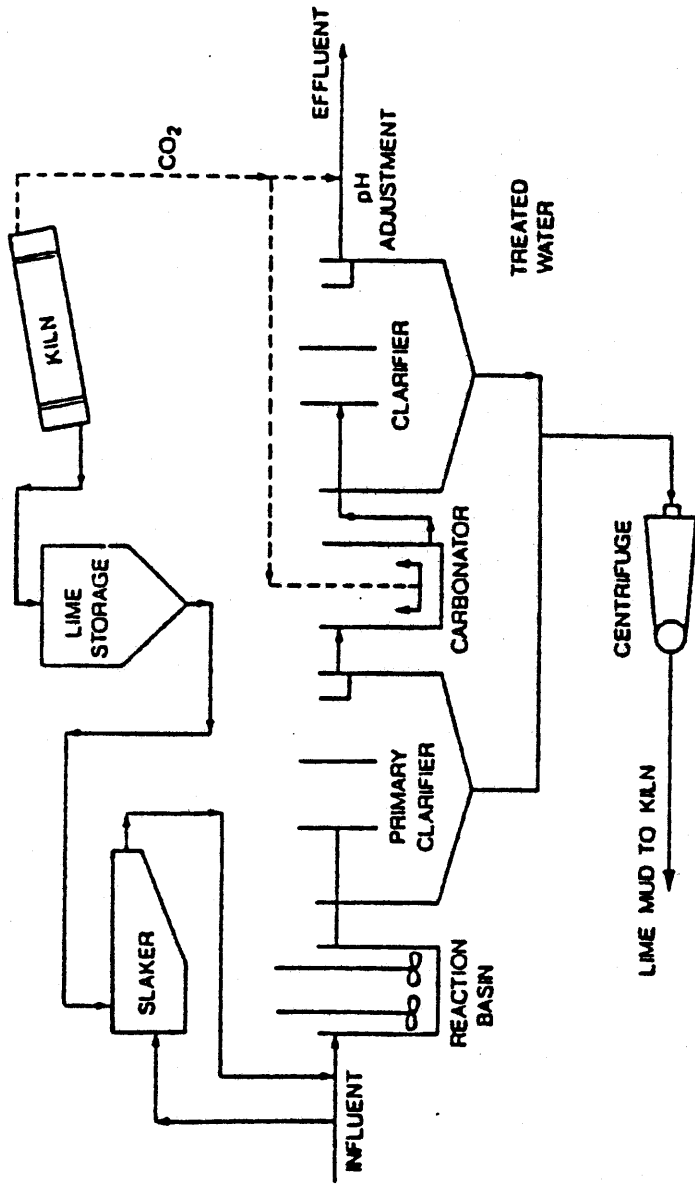


Figure 9. Mini-Lime Process [after (Rush and Shannon, 1976)]

study, lime precipitation has been one of the most widely investigated color removal processes in the pulp and paper industry. Although problems remain to be solved (Lathia and Joyce, 1978), it is generally considered to be the most readily applicable of the various physical and chemical methods studied (Rush and Shannon, 1976).

The mechanism of lime precipitation of color has been studied (Bennett, et al, 1971). Color removal was found to be a chemical reaction in which insoluble calcium-organic salts formed, rather than a physical adsorption or absorption of color onto lime particles. The process was found to be a function of two main factors: the enolic and phenolic hydroxyl content of the effluent and the molecular weight distribution of the color bodies. The reaction exhibited a pH dependence, requiring a pH of about 12 for complete ionization of the phenolic hydroxyl groups which react with the calcium ion.

Effluents studied were those from the chlorination and extraction stages of the bleach plant. The organic solids of each effluent were subjected to elemental and functional group analyses and molecular weight determination. The solids in the spent liquors were mainly characterized as acidic chlorine-substituted lignin oxidation products of relatively low molecular weight. Spectroscopic analysis revealed very little aromaticity. Attention was directed to carboxyl, phenolic, and enolic groups in developing a theory to explain the mechanism of color removal by lime. Experiments were performed utilizing selective chemical blocking of specific functional groups, followed by lime addition. It was concluded that for chlorination and extraction stage effluents, enolic hydroxyl groups are most likely the predominant groups involved in precipitation by lime.

However, in a solution of commercially-available lignin ("Indulin")

obtained from kraft pulping, phenolic hydroxyl groups appeared to have the major role in the lime reaction. Selective modification of functional groups was utilized here also. Furthermore, the phenolic hydroxyl content of kraft lignin was considerably greater than in spent bleaching liquors.

The scheme outlined in Figure 10 represents the reaction sequences proposed for color removal by lime or other metal ions. The formation of keto-enols in molecules containing chromophoric groups is shown, with alkaline conditions shifting the equilibrium to the enolic form. Alkali is also required for ionization of enolic or phenolic hydroxyls. The resulting anion then forms an insoluble salt with calcium. It was noted that, in the study of lime precipitation of acidic chlorination stage color, it could not be determined whether lime reacted with original functional groups or with ones produced by hydrolysis of chloro-substituted by alkali in the lime solution. Joyce and Beshire (1981) found that softwood and hardwood effluents reacted differently because the lignins were different.

The apparent influence of molecular weight on the lime decolorization process was seen when attempts were made to understand why approximately 15% of the original color could not be precipitated. This problem was approached by treating liquor from the caustic extraction stage with lime and recovering the precipitated and non-precipitated organic solids by ion exchange techniques. The compositions of the two fractions were similar, each containing the functional groups that had been established as capable of producing insoluble salts with calcium. The average molecular weights, however, were significantly different. The value for solids which precipitated was estimated to be about 500, whereas it was less than one-half, or 210, for the non-precipitated solids. Later work (Dugal, et al, 1975)

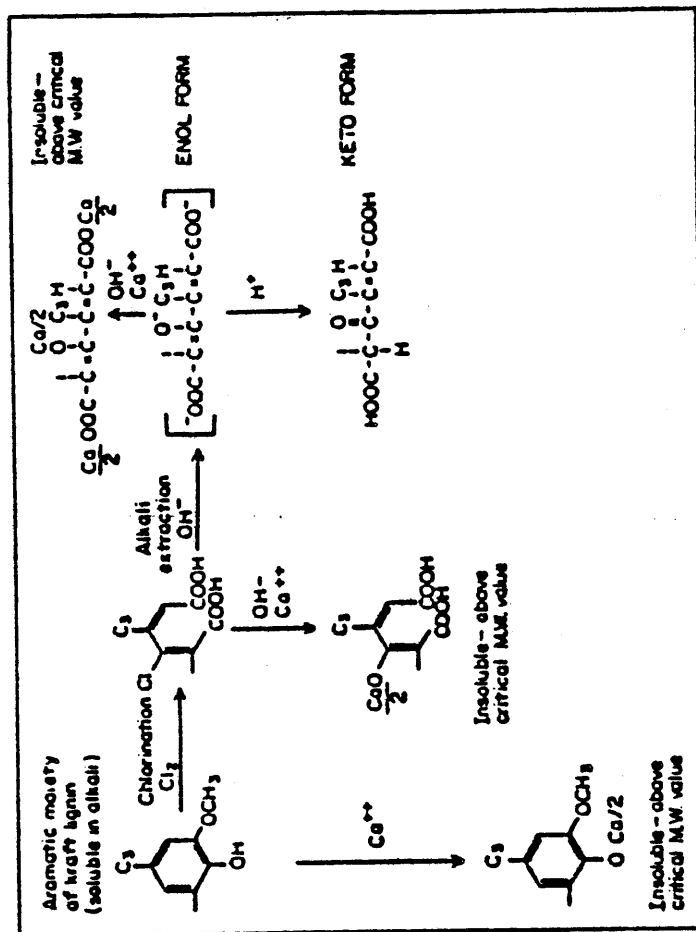


Figure 10. Chemical Reactions in the Lime Precipitation Process [after (Bennett, et. al., 1971)]

substantiated these implications. It was determined that lime will precipitate almost all high molecular weight color bodies, i.e., those greater than 5,000, partially remove those from molecular weight 400 to 5,000, but generally cannot precipitate species below molecular weight 400.

A basic scheme is common to all lime precipitation processes for color removal from pulp and paper mill effluents. Effluent and slaked lime are mixed and sent to a clarification basin where the lime-organic sludge settles. The various processes developed for lime treatment generally differ according to lime dosage, effluent type, and methods of handling the lime-organic sludge and decolorized effluent.

Processes have been developed along two avenues, termed massive lime and minimum ("mini") lime processes. The first employs lime application rates much greater than that required for stoichiometric reaction with the color bodies. In early work, problems were encountered in dewatering the lime-organic sludge when a minimum lime dose was used (Moggio, 1955), leading to further experimentation with greater lime doses. In laboratory tests, levels of 10,000 to 30,000 mg/L lime produced the most dense and most easily dewatered sludge because of the great excess of calcium hydroxide particles (Rush and Shannon, 1976). A one-year study by International Paper Company evaluated the incorporation of a massive lime system for color removal at a demonstration mill in Springhill, La. (Wright, et al, 1974). The facility produced bleached kraft pulp at about one-fifth of usual full scale. A dosage of 10,000 mg/L lime was applied to alkaline extraction stage and unbleached decker (pulp thickener) effluents. In this design, the dewatered lime-organic sludge was used for recausticizing the mill's green liquor to produce white liquor, since most of the lime was still available as calcium hydroxide. All

of the alkaline extraction stage and most of the unbleached decker effluent could be treated without exceeding the lime kiln capacity for lime production in the quantity required for causticizing. The total mill color load was thus lowered by about 70%. Further work with this process was not pursued, however, due to several serious difficulties. Foaming in causticizers and lime mud washers was a constant problem, and the white liquor concentration was about 15% lower than when produced in the conventional manner with fresh lime. Implications for full scale use included requirements for a larger volume of white liquor for wood digestion and, consequently, increased capacity in the chemical preparation and recovery systems.

There have been several versions of the mini-lime process (Davis, 1971; Gould, 1973; Spruill, 1973); these have been able to overcome the problem of lime sludge dewatering to a large degree. Perhaps the most successful is the full-scale system operated by Continental Can Company at Hodge, La. (Spruill, 1973). This mill had been under pressure from the state of Louisiana to lower the color in wastewaters discharged into a low flow stream. Most of the 15 million gallons of wastewater produced per day by combined kraft and NSSC boardmill effluents could be treated. In this scheme, a small dose of about 1,000 mg/L lime is slaked and mixed with waste liquor. After primary clarification, the decolorized overflow is sent to a recarbonator for removal of remaining dissolved calcium. In the recarbonator, lime kiln stack gas is introduced as a source of CO_2 which promotes the formation of insoluble calcium carbonate. After settling in a clarifier, the sludge is routed to the primary clarifier to aid in the formation of a dewaterable precipitate. This combined, somewhat fibrous sludge, is dewatered on a solid bowl centrifuge to approximately 35% solids before entering the kiln for lime recovery and

incineration. Color removal efficiency depended upon the proportion of NSSC effluent. The original color of 1,200 Pt-Co units was reduced to 300-400 (70% average removal) when NSSC effluent was included; 80 to 90% reduction was obtained on kraft waste alone. A major problem, probably related to lack of pH control, occasionally developed in the recarbonation system. Although color removal was usually about 85% after primary clarification, color sometimes increased during recarbonation to around 35 to 40% of the original; thus, process modifications have been necessary (Rush and Shannon, 1976). A brief report on the system (Moll, 1976) stated that decolorization had averaged 80% in the preceding year.

A process somewhat similar to that at Hodge, Louisiana, has been described for two Georgia-Pacific bleached kraft mills at Woodland, Maine, and Crossett, Arkansas (Gould, 1973). Alkaline extraction stage effluent is treated with slaked lime at 2,000 to 3,000 mg/L. In a two-year period at the Woodland mill, initial color of 10,000-15,000 Pt-Co units was generally lowered by 85-90%, and a BOD₅ reduction of 45% was possible. About 80% of the spent lime was reclaimed. The system at the Crossett mill was designed for use during the summer months, when mill effluent is nearly the entire flow of the small receiving stream (Rush and Shannon, 1976).

Lime coagulation has been investigated as a general treatment for producing an effluent which could meet Canadian regulations on toxicity, COD, BOD, and TOC, as well as color (Naish and Sandilands, 1977). This lab scale study, supported by the Canadian Government's CPAR (Cooperative Pollution Abatement Research) Program, resulted in a design proposal and cost estimate for a softwood bleached kraft mill. The combined bleach plant seal tank overflows would be treated with 2,000 mg/L lime, the optimal level for

pollutant removal, in a scheme similar to that at the Hodge plant. Bench scale results showed various parameters to be reduced as follows: toxicity, 86%; color, 85%; and COD, BOD, and TOC approximately 60%. It was felt that consideration of lime for pollution control at a given mill would depend upon comparison with other possible methods for that particular site.

Eaton, et al (1982) reported that calcium, aluminum, and iron ions could act synergistically to remove more color than either one could alone. This would allow a relatively small dosage of ions which could even be recovered and recycled.

Enzyme Pretreatment

Schmidt and Joyce investigated the feasibility of utilizing peroxidase to improve precipitation of color by lime from pulping and bleaching effluents (Schmidt and Joyce, 1980). Because one of the major factors influencing the precipitability of color bodies lime is molecular weight, it was reasoned that any process capable of increasing the average molecular weight should be able to effect corresponding increases in color removal with lime. The ability of peroxidase to polymerize phenolics made this enzyme a candidate for treating color bodies; these molecules are derived from lignin with some phenolic groups being retained. Enzyme use was, therefore, envisioned as a pretreatment prior to lime addition.

Two types of wastewater were studied. One was pulping effluent that had previously undergone biological treatment. The other consisted of color bodies that had survived lime precipitation from combined alkaline extraction and decker effluents. This last material represented molecules resistant to removal, due, in part, to their having a low molecular weight.

The effect of enzyme treatment on molecular weight distribution in

effluents was first examined. Treatment with 25 mg/L horseradish peroxidase and 9 mM H_2O_2 for 12 hours at pH 6 caused a slight but significant shift toward the higher molecular weight range ($MW < 5,000$), as determined by gel permeation chromatography, for both effluent types. Lime can almost completely remove color bodies with molecular weights greater than 5,000 (Dugal, et al, 1975). This shift was 5.5% of the total peak area for biologically-treated material, and 8% in lime-treated samples. For the latter, the transfer was mainly from the middle molecular weight range ($1,000 < MW < 5,000$). Lime precipitation was conducted on samples of biologically-treated pulping effluent, pretreated with 2.5 mg/L peroxidase and 2.5 mM H_2O_2 . This pretreatment allowed 94% color removal at a lime dosage that gave only about 10% removal from non-pretreated samples.

It was concluded that this work was encouraging in demonstrating that the lime precipitability of color bodies of pulp mill effluents can be enhanced by an enzymatic treatment that increases the proportion of higher molecular weight species. Such a treatment might be considered either for achieving greater color removal at a specific lime addition or for reducing the amount of lime required for a specific color removal. The study did not attempt to evaluate the technical or economic feasibility of a mill-scale process. Because of the difficulties encountered in the use of H_2O_2 and the added expense of the chemical, the recommendation was made that further work utilized the similar enzyme laccase.

Campbell and Joyce (1983) continued these studies using the laccase enzyme. It was found that the application of the enzyme resulted in a weak response and that, in general, addition of the enzyme could not be accomplished economically.

Resin Separation and Ion Exchange

Resin separation and ion exchange have proven to be effective color removal processes. They both rely on adsorption for their treatment success, although by different mechanisms. Ion exchange utilizes the differences in attractive forces between ions to remove substances. A given ion is displaced from an insoluble exchange material by a different ion in solution. The attractive forces between the new ion and the exchange material being greater than those between the displaced ion and the exchange material. Resin separation does not use any ionic attraction forces; it relies on true non-ionic adsorption. The organics are removed from the waste stream principally by van der Waal's forces.

The operation of both processes is similar. The waste stream is passed through a bed of the resin material, treated effluent is then removed while the unwanted substances remain in the bed (Figure 11). Since these are column-type resin adsorption processes, the waste stream must first be clarified to remove any materials which might plug or inhibit the flow of wastewater through the resins. Other pretreatments might include temperature or pH alterations depending on the type and characteristics of the resin being employed, along with the characteristics of the waste stream being treated.

A resin separation process was developed by Rohm and Haas Co. in which a polymeric adsorbant was used for the treatment of a combination of the caustic extract and chlorination effluent from a kraft mill's bleach plant. Rock, et al (1974) reported results of the testing of this system. Color removals of 70-95%, BOD reductions of 31-55%, COD reductions of 31-57%, and suspended solids removal averaging 78% were observed. The system employed sand filters for suspended solids removal followed by the resin treatment. When the

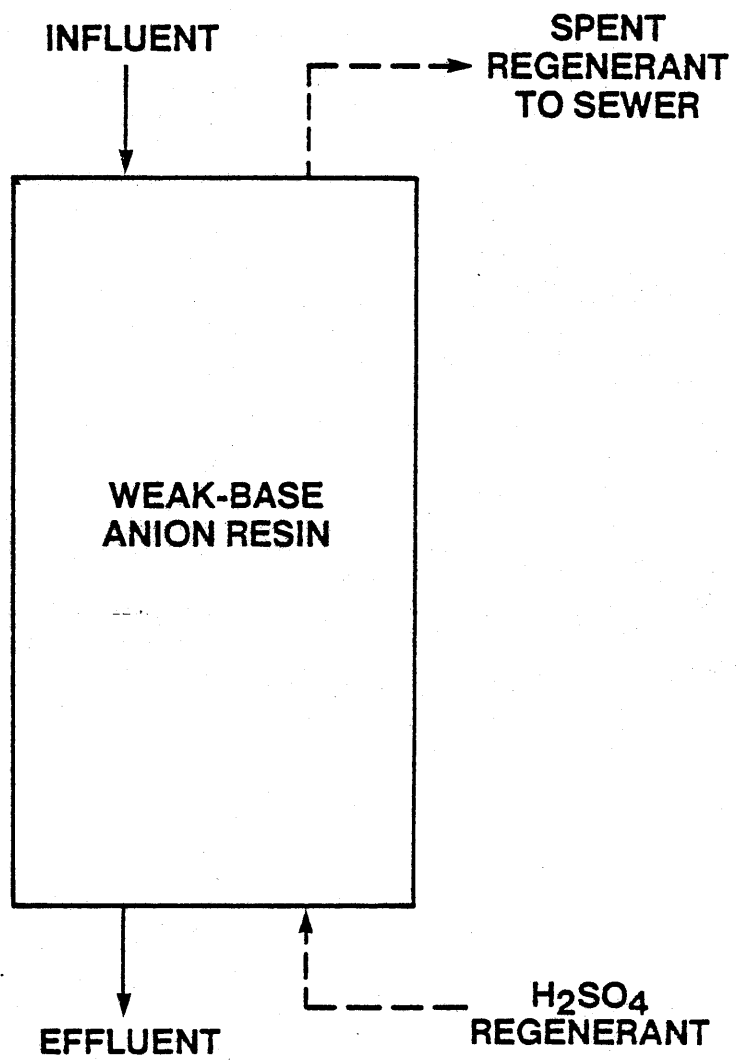


Figure 11. Resin Separation Tower

adsorptive capacity of the resin was reached, it was backwashed with filtered effluent and regenerated with the mill's white liquor. The spent regenerant was then used in the pulping system and the colored organics were eventually burned in the recovery furnace. The bleach plant chlorination and extraction waste streams were mixed to allow treatment of the more highly colored extraction stage by reducing the pH to less than 3.0 as was required by this process.

A similar system was developed by Broddevall (1976) using a phenolic ion exchange resin. Sufficient acidic chlorination stage effluent was mixed with the caustic extraction stage effluent to reach a pH of 2.0. This solution was retained in tanks until approximately 50% of the lignin degradation products had precipitated due to insolubility in low pH solutions; flocculation agents were sometimes added. The precipitate was then separated, dissolved by a convenient alkali solution from the mill and incorporated into the recovery system either at the evaporators or directly at the recovery furnace. The acidic effluent from the separation process was fed through one or more phenolic-based resin columns. The resins could be washed with aqueous Na_2SO_4 to remove chlorides prior to elution with a mill-generated alkali stream. This allowed recirculation through the recovery system without the chlorides. The reported results claimed a color reduction, on an initial color level of 15,000 Pt-Co Units/l, of 99+%.

A bleached kraft mill in Skogall, Sweden, has been operating a full-scale ion exchange system for treating bleaching wastes since 1978. Excellent results have been reported in both decolorization and detoxification by Lindberg and Lund (1980) and Borjeson and Lindberg (1981). A unique treatment system was utilized. In the C-E-H-D-E-D bleaching sequence, the plant is a

closed system from the hypochlorite stage to the last chlorine dioxide stage. Using countercurrent washing the E₁ stage wash was filtered to remove fines and fibers, passed through an ion exchanged resin, and then used as wash water for the chlorination stage. The chlorination stage effluent was also treated by an ion exchange resin. This system resulted in a decreased volume of effluent, a 90% reduction in color, and an almost 100% reduction in toxicity. The resin bed system was operated in a very unique manner, a semicontinuous system being used. The resin bed itself was transported from one location to another for the individual steps involved in the elution, chlorination stage adsorption, extraction stage adsorption, and backwashing. This system was thus cyclic and had many advantages over a system utilizing stationary resin beds (Figure 12).

Sethuraman and Raymahashay (1975) tested clays for possible applications as ion exchange material for color removal. The clays tested were kaolinite and montmorillonite. Initial adsorption of cationic dye was similar for both clays but the montmorillonite continued adsorption at a reduced rate, possibly due to interlayer cation exchange. Adsorption was found to be controlled by the nature and capacities of the available ion exchange sites. The results indicated cationic exchange sites were more abundant than anionic sites on both clays.

A study of color removal by adsorption on crosslinked polymers was performed by Samuelson and Wennergren (1977). The study included anion exchange resins as well as non-ionic resins. A decrease in color removal was reported for all the resins studied as the flow was increased through the resin bed. Increases in efficiency were noted as particle size was decreased. The anion exchange resin was found to be the most effective of the

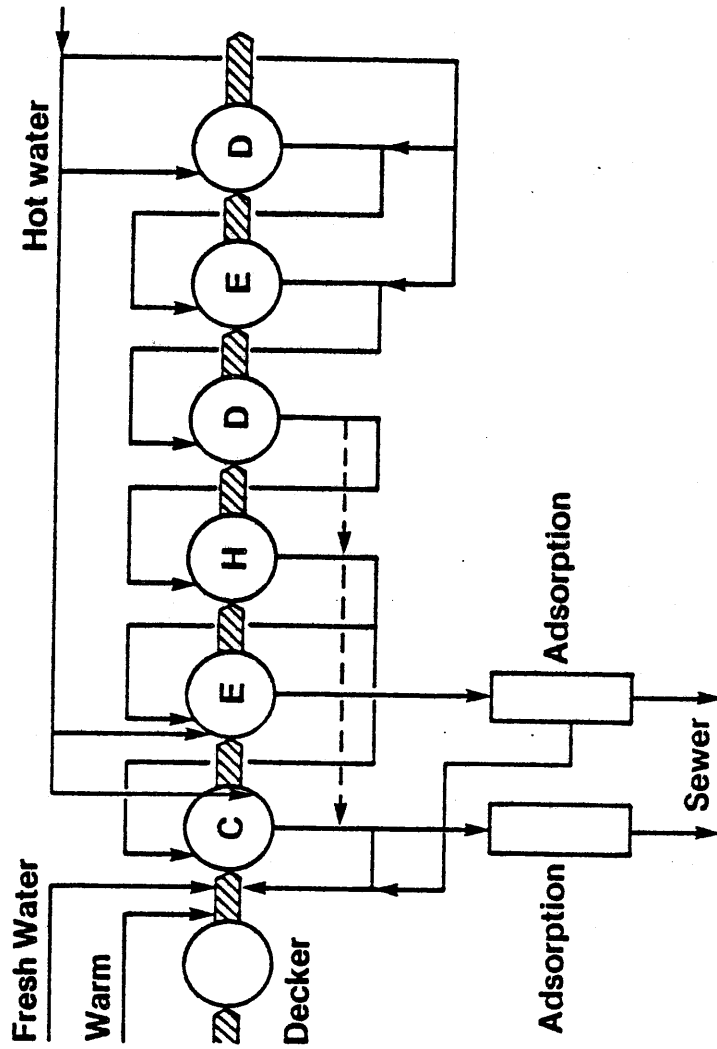


Figure 12. Resin Adsorption Treatment of Bleach Plant Effluent
 [after (Börjeson and Lindberg, 1981)]

resins studied. A disadvantage of this resin was that it required an additional treatment after elution to lower the pH to depress the sorption of chloride ions.

Aluminium Oxide

A bisulphate mill operating in West Germany (Figures 13 and 14) is presently operating a full-scale aluminium oxide adsorption system for treatment of the pulping and bleaching wastes. Ullrich (1978) discussed the start-up and operation of this plant. The effluent from the C-E-P-H bleaching sequence was clarified of fibers and other solid matter. The pH was adjusted using dilute HCl and then the waste stream was sent to the adsorption towers. The towers were filled with granular activated alumina (γ -Al₂O₃). The fluid followed an upflow pattern and, after decolorization, it was sent to the biological treatment plant, which utilized activated sludge. The aluminium oxide was regenerated by burning off the organics in an indirectly heated rotary kiln. It was found that the color removal from the effluent was caused not only by adsorption, but also by lignin precipitation caused by manipulation of the pH in the towers. If the temperature did not exceed 800°C in the kiln, the regenerated adsorbent had the same adsorptive power as fresh aluminium oxide. Results reported were 96% color removal, and 35% and 71% reduction in BOD and COD, respectively.

Adsorption on Wood

Poots, et al (1978) took a novel approach to the problem of color removal. Shavings of spruce wood were used as an adsorbant. Tests using a basic dye were carried out at different dye concentrations and different wood particle sizes. The tests indicated that the mechanism of adsorption is complex. Fairly large quantities of wood were required compared to other

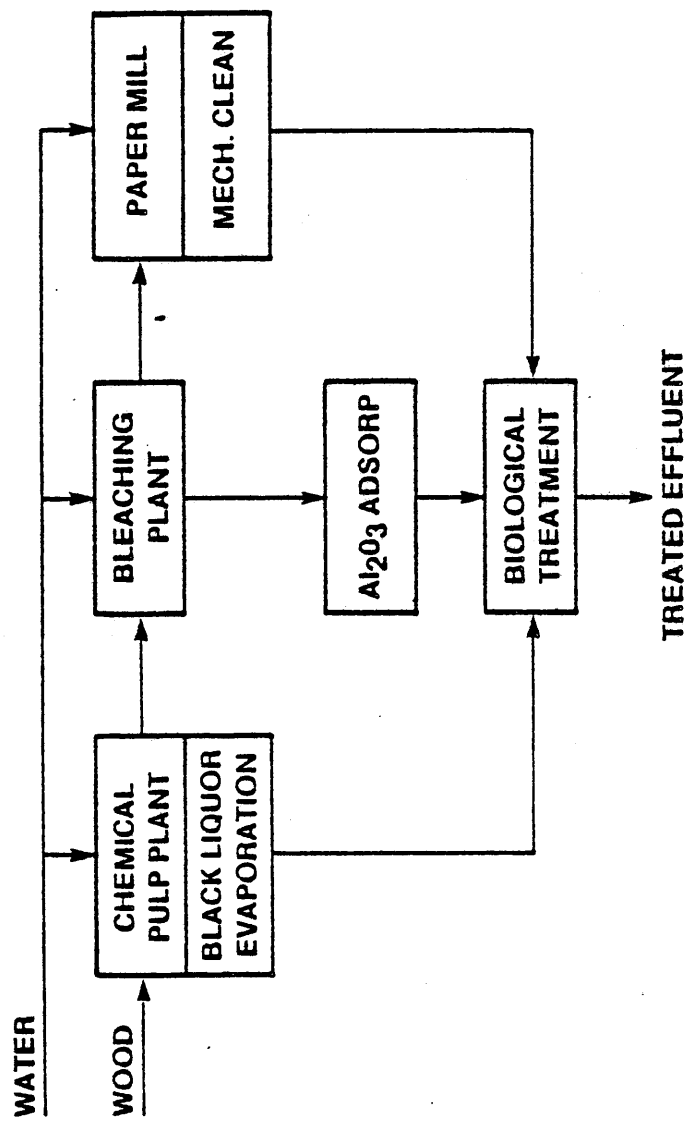


Figure 13. Activated Alumina Process Scheme [after (Ullrich, 1978)]

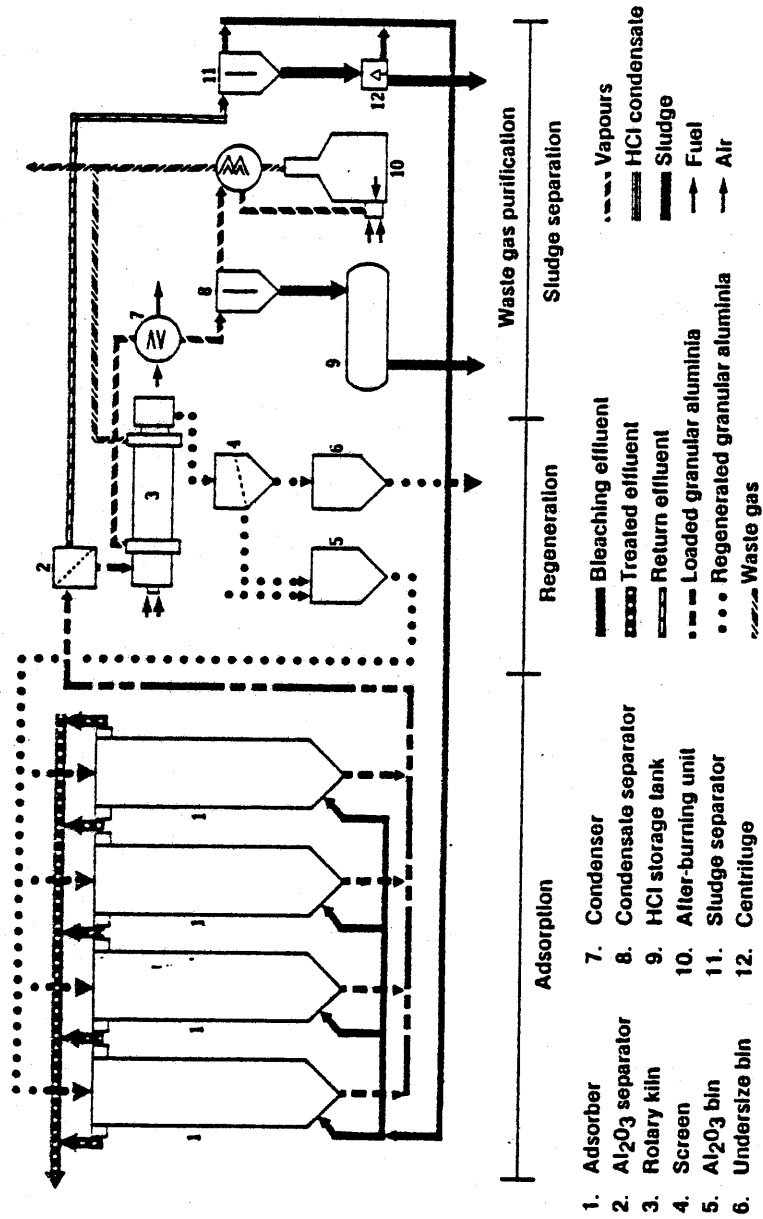


Figure 14. Activated Alumina Adsorption Plant [after (Ullrich, 1978)]

adsorbants, but it was still relatively inexpensive due to the much higher cost of other adsorbants. Another advantage was that, since it was not necessary to regenerate the adsorbant, there was no additional waste stream to be treated and the wood could be burned as a fuel.

Membrane Processes

Membrane processes involve passing the wastewater stream to be treated over a membrane filter (Figures 15 and 16). The membrane allows the water and other substances of low molecular weight to pass through, but retains the molecules of higher molecular weight. This is essentially a process of separation and concentration. The substances of large molecular weight are concentrated in one stream while the more dilute stream of treated water holds most of the low molecular weight chemicals. The rejection efficiency of these processes is dependent on the pore size of the membranes being used and the pressure at which the system is being operated. Tight membranes; i.e., those with relatively small pores, reject a larger fraction of the molecules in the waste stream than do loose membranes. However, the tighter membrane must be operated under higher pressures to obtain satisfactory water flux rates.

Although the operational principles are the same, there is a distinction made within the category of membrane processes. Excluding the dialysis processes, the membrane processes are separated into ultrafiltration, characterized by loose membranes and low operating pressures, and reverse osmosis, characterized by tight membranes and high operating pressures. Reverse osmosis (RO) membranes may be designed for salt rejection, the looser ultrafiltration membranes (UF) are not capable of very high salt rejection. Thus, chlorides are passed through the UF membrane with the filtrate. This permits the concentrate from UF systems to be directly fed into the recovery

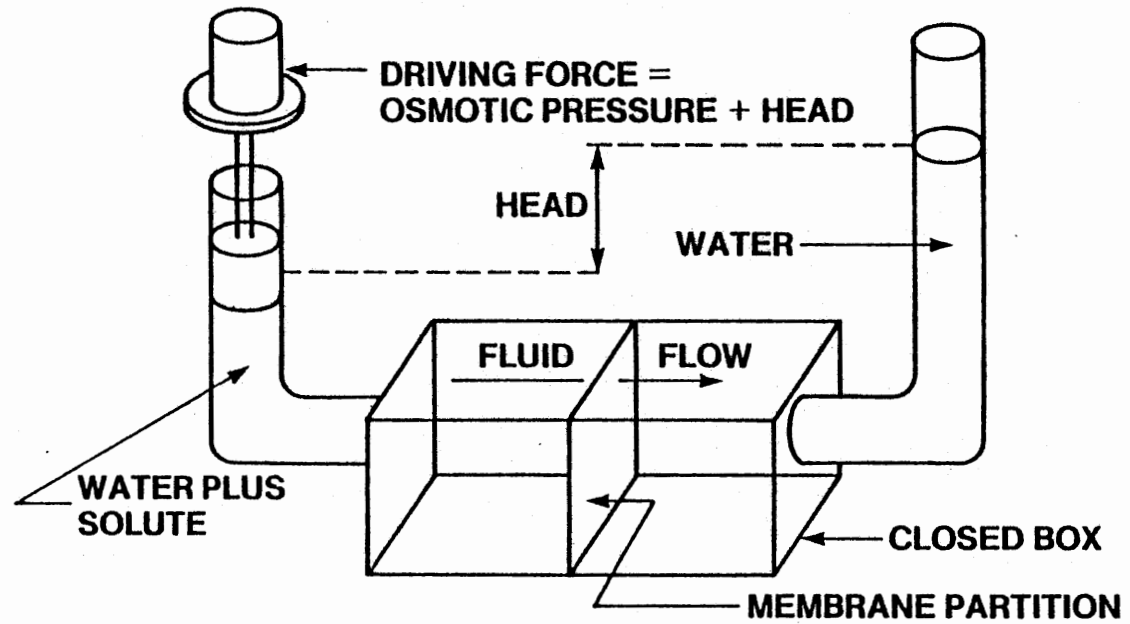


Figure 15. Principles of Membrane Separation [after (Culp, et al, 1980)]

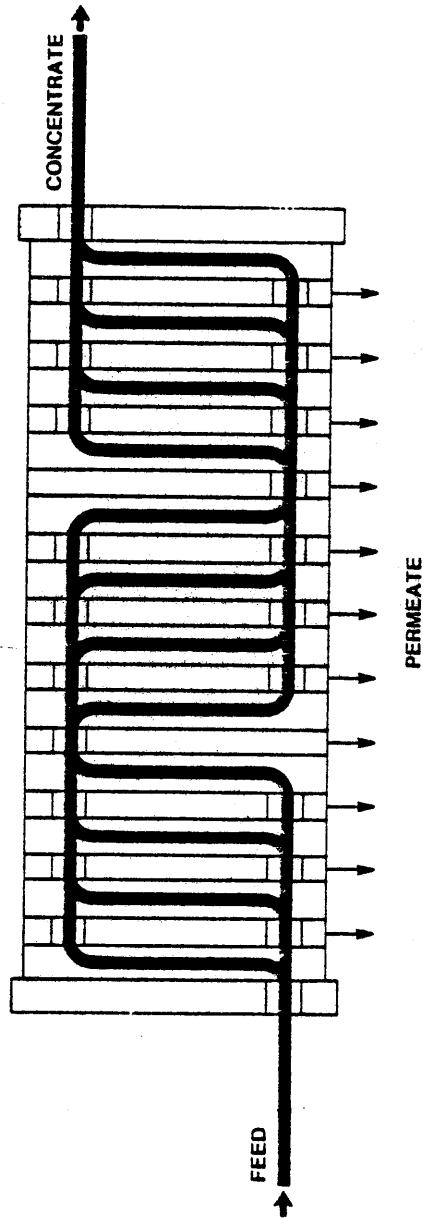


Figure 16. Ultrafiltration Module [after (Claussen, 1978)]

process without the problem of corrosion commonly associated with chlorides.

A major disadvantage to membrane processes has been the need for pre-treatment to adjust pH and temperature to protect the sensitive membranes. Mutamore, et al (1975) described operating efficiencies of a polymeric ultrafiltration membrane which did not require the pre-treatment necessary for most cellulose acetate membranes. Pilot plant data yielded COD and color removals of 60% and 70%, respectively. Calculations for computer simulation to obtain optimum operating parameters were also mentioned. Fremont (1980) developed a UF system that utilized a polysulfone membrane coated with a polyethylenimine for color removal from pulp and paper effluents. Color removals for a full-scale operation were estimated to be 92% at 44 psi and 94% at 100 psi, with flux rates increasing with pressure.

Two zirconium-based RO membranes and a polysulfone UF membrane were compared by Porter and Edwards (1977). It was noted that as particles built up on the membrane surface, the effective pore size was reduced and the membrane functioned similar to one of a tighter design. This caused a decrease in flux and an increase in particle rejection. Stream velocity was usually relied upon to disrupt particle build up, but backwashing was needed routinely to keep the membrane functioning as designed. While all membranes offered good color rejection, this comparison served to highlight differences based on membrane design.

Pfister and Sjöström (1978) used ultrafiltration to characterize the size of color molecules from each stage of several three-stage bleaching sequences. The sequences evaluated were C-E-H, O-C-E, and O-D-E. Very little of the color associated with the bleach plant was of a molecular weight of less than 1,000. The only exception reported was in the chlorination stage of

the C-E-H sequences. The data illustrated the effect that proper membrane selection can have on the efficiency of a treatment system, depending on the characteristics of the waste stream. Claussen (1978) described the applications and effectiveness of UF and RO processes in a sulphite mill. UF and RO processes were discussed as separate systems and as integrated operations. A treatment system was modeled that was capable of 60-80% color removal, depending on UF membrane selection (Figure 17).

Lundahl and Mansson (1979, 1980) described a UF system (Figure 17) that has been installed to treat the alkali-extraction stage of a softwood kraft bleach plant. This system, installed in Sweden, uses a cascade of ultrafiltration modules equipped with polysulfone membranes. The cascade resulted in a lower flux rate for each subsequent UF module, due to increases in the concentration from each previous module. The capacity of the system was increased 7% by increasing the temperature from 60°C to 65°C. Resins and fines accumulated in the system and were washed out by an automatic filtrate control system. Fibers had to be removed prior to UF to prevent clogging of the system, less than 10 ppm were permissible in the preconcentration stage. The treated effluent could be reused as wash water in the bleach plant. The recycled water was also detoxified by the ClO_2 in the bleach plant during the washing process. Recirculation of some of the filtrate to the UF system allowed reduction of color by 90%. Without recirculation the maximum obtainable reduction in color was 86%. In addition to color removal, BOD was reduced by 25%, COD was reduced by 70%, and acute toxicity was reduced by 50%. It was estimated that, in conjunction with an aerated lagoon, reductions of up to 90% should be possible for BOD, COD, and color of a total kraft mill effluent.

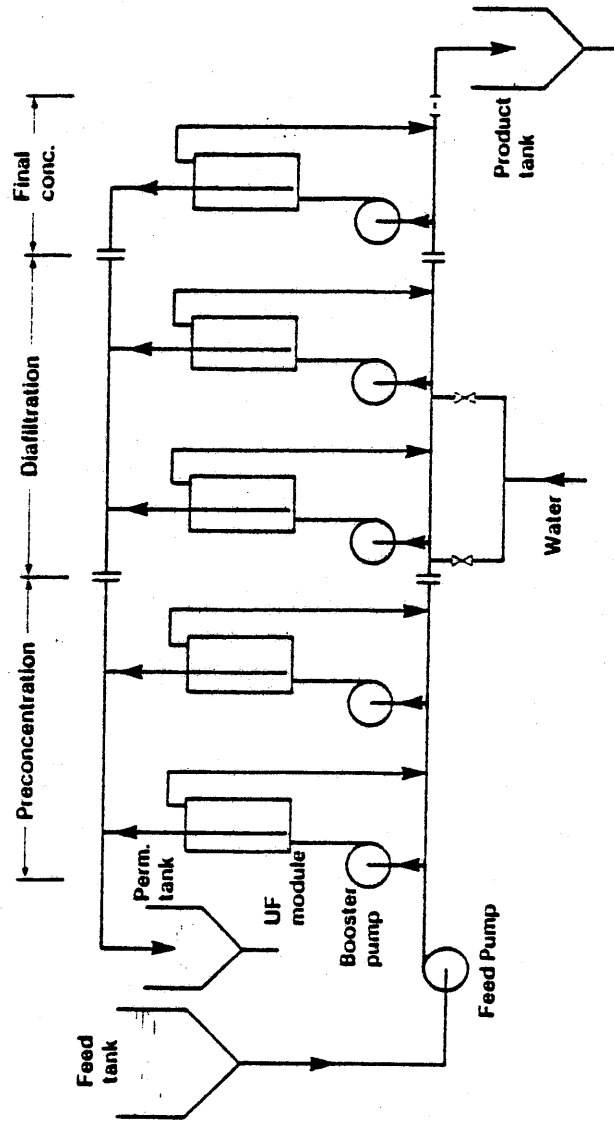


Figure 17. Ultrafiltration Treatment System [after (Claussens, 1978)]

Irradiation

Color removal by irradiation is obtained by initiating chemical reactions and chromophore breakdown with radiation. Hofreiter and Fecht (1979) found that the sedimentation properties of some hard to settle papermaking effluents could be enhanced by gamma irradiation. The depolymerization of starches with high dispersive power was accomplished with cobalt 60 radiation. This resulted in reduced treatment in other steps of the system to maintain an acceptable quality effluent.

Sameshima, et al (1975) studied color reduction on nine pulping and bleaching wastes using irradiation. An ultraviolet mercury lamp was used as the source of radiation. It was observed that the color of kraft and sulfite wastes darken upon initial exposure, but the color decreased as exposure time continued. Also, the pH of all of the wastes initially dropped and then gradually rose. It was hypothesized that this indicated the formation of acids initially and then their subsequent degradation. The rate of color reduction was faster for sulphite wastes than sulphate wastes. A decrease in COD values was also observed.

Effects on irradiation performance by oxygen or air bubbling and the reaction dependency on pH and temperature were discussed by Meguro, et al (1976). In studies using a high pressure UV-lamp for irradiation, it was reported that oxygen bubbling was the most effective. Acidic and alkaline solutions both exhibited increased color removal efficiencies as compared to a neutral pH of the same solution. The rate of removal was also shown to increase with temperature. The highest color removal, 90%, occurred at 60°C and a pH of 12 using oxygen bubbling. A decrease in COD of 40% was also

recorded. Additions of rose bengal and periodate or acetylacetone and hydrogen peroxide showed increased color removal efficiency as well.

Electrolytic Processes

Electrolytic processes operate by passing a current through a solution using an anode and a cathode (Figure 18). Oxidation and reduction reactions occur which alter the chemical nature of the electrolyte. Herer and Woodard (1976) reported on an electrolytic coagulation process that utilized hydrated aluminum ions from the aluminum anode to induce coagulation (Figure 19). Hydrogen bubbles formed at the cathode aided removal of the coagulated material by flotation. Tests were run on chlorination and extraction stage effluents from a kraft bleach plant. Color removal was shown to be pH dependent, with best results occurring between pH 4.0 and 6.0. Color removal also increased with the concentration of aluminum ions. The maximum observed removal efficiencies were 92% and 99% for the chlorination and extraction stages, respectively.

Oehr(1978) described a system which uses an effluent with high chloride content as the electrolyte. An inexpensive source of chloride such as sea water can be added if the effluent to be treated does not contain the required amount. The electrical current causes formation of chlorine, hypochlorite, and chlorate ions. The chlorine and hypochlorite oxidize organic compounds and are reduced to chlorides to begin the cycle again. It was found that the decolorization rate increased with chloride content. Also, it was noted that temperature had no significant effect on the process; therefore, no pretreatment for temperature adjustment would be needed.

Electrochemical processes have not been utilized due, in part, to inefficiencies in reactor design. Gupta (1979) discussed the advantages of a

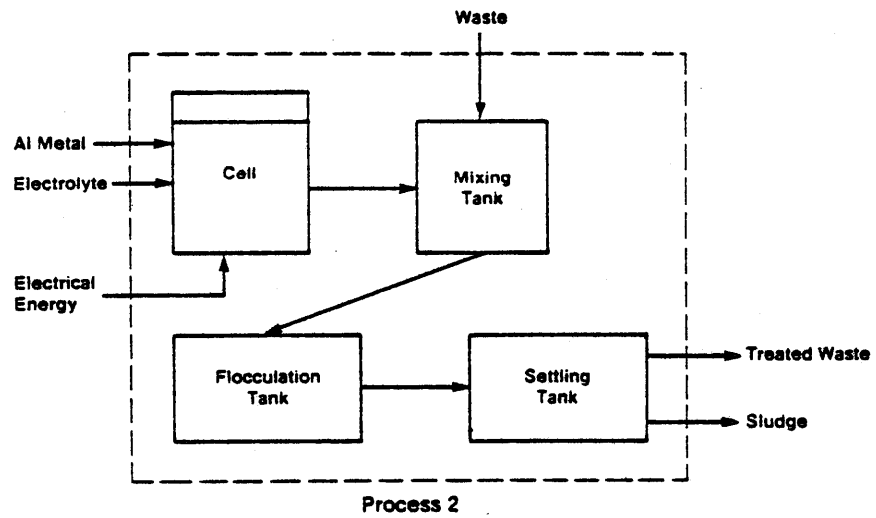
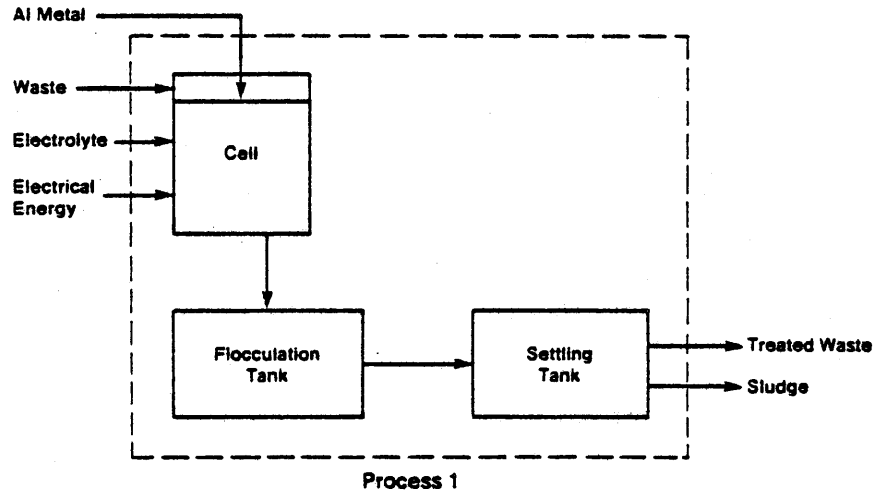


Figure 18. Electrolytic Treatment Processes [after (Herer and Woodard, 1976)]

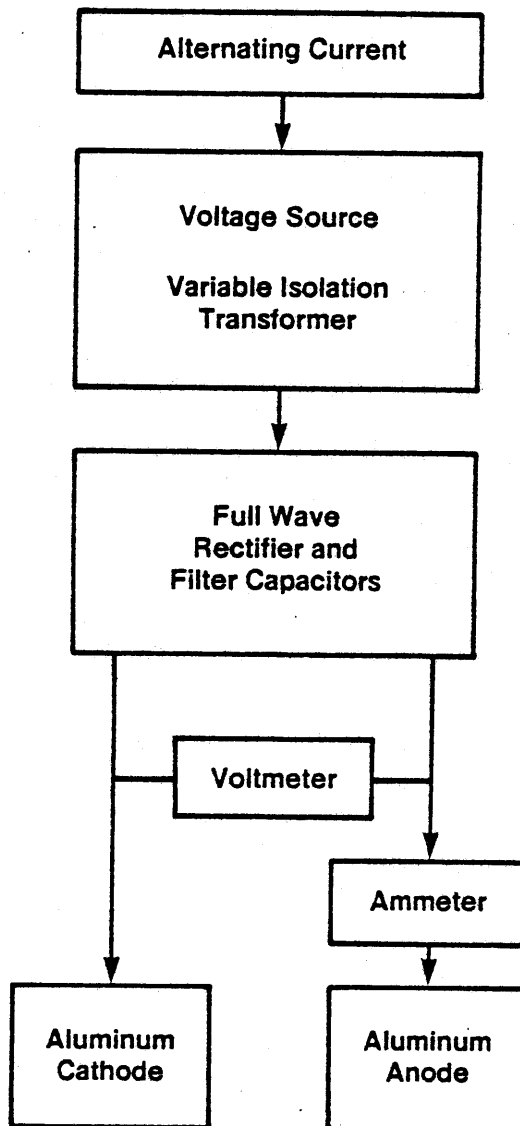


Figure 19. Production of Metal Ion Coagulant by Electrolytic Means [after (Herer and Woodard, 1976)]

new carbon-fiber reactor. Results from trials treating alkaline bleach extract from a kraft mill yielded 92% reduction in color, 72% reduction in COD and elimination of toxicity, as defined by Canadian standards. Other advantages of the process were reported to include low operating costs and a very small treatment area.

Activated Carbon

Activated carbon has been utilized in water treatment for many years. Organics responsible for color, taste, and odor can be adsorbed into the surface pores of the carbon particles. Once the capacity of the carbon's adsorptive properties is reached, the carbon can be regenerated by a variety of means. Regeneration removes the adsorbed organics, thus freeing the pores for additional adsorption.

Two general forms of carbon are available for treatment systems, powdered activated carbon (PAC) and granular activated carbon (GAC). These terms refer to the particle size of the carbon in question. The adsorptive capacity is dependent on the surface area of the particles and the size of the surface pores. Although powdered carbon offers more surface area per unit volume than the granular form, GAC has been used most extensively in treatment systems.

The general design of a GAC system involves a tower, either in an upward or downward flow configuration. This design necessitates the pretreatment of the water to remove any substances which could become entrapped between the carbon particles and result in clogging of the system. PAC allows the carbon to be added directly to the effluent to be treated without any pretreatment. The carbon is then settled out along with the other substances which comprise the sludge. Reclamation and regeneration are practiced on both forms of activated carbon. This step enables this type of treatment to be economically

competitive with alternative treatment processes. Possibilities also exists for the on-site generation of activated carbon using wood residues such as charcoal.

In relation to the performance of an activated carbon being dependent on pore size, Huang and Garrett (1975) made a study on capillary blockage. Adsorptive capacities were based on phenol adsorption. They reported no reduction of capacity when the carbon was exposed to polyelectrolytes and clay minerals in a slurry-type treatment system. However, humic acids did reduce capacity due to competitive adsorption. It was also noted that, although they had no effect in the treatment slurry, the clay materials could cause blockage in a tower system.

Activated carbon is not sufficient by itself for treatment of wastewater. Therefore, it is used in conjunction with other processes to obtain an acceptable effluent. Callahan and Pincine (1977) discussed the operation of a municipal treatment plant that treats mainly a papermill wastewater. The facility utilized an activated carbon tower after physical - chemical processes to improve the overall performance of the facility. Reductions in color, BOD and COD, along with an improvement in sludge handling characteristics were realized.

A new treatment system (Figure 20) has been developed by Wong, et al (1977). This system, which uses a combination of proven processes, was employed to decolorize and detoxify bleached kraft wastes. PAC was used in conjunction with air, alum, and polyelectrolyte treatments. The system was tested on bleach plant effluent and total mill effluent. Along with 70-85% reduction in color and efficient detoxification, reductions of BOD and COD by 20-40% and excellent handling characteristics for the resulting sludge were

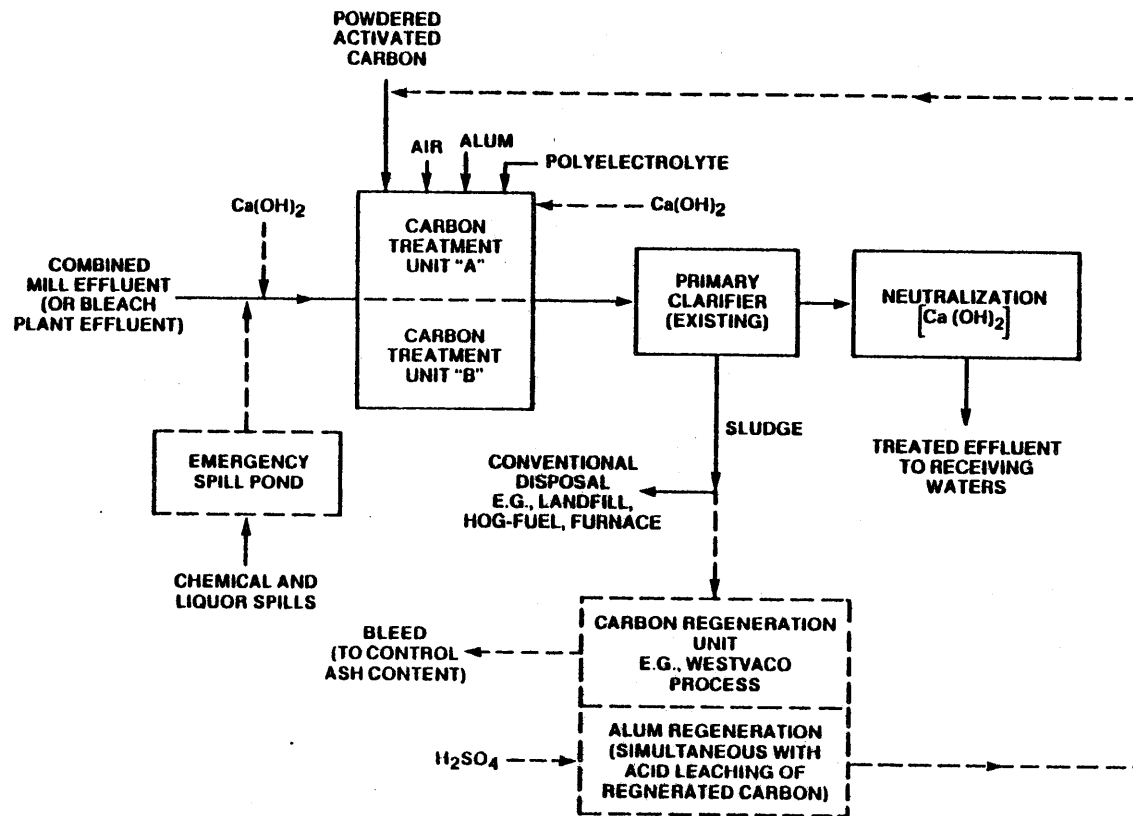


Figure 20. Activated Carbon System [after (Wong, et al, 1977)]

reported. The amount of decolorization and detoxification by the system in relation to that predicted by addition of individual treatment steps indicated synergistic effects.

Land Treatment

Treatment of wastewater by applying it to the land is a well-developed treatment method (Figure 21). The soil acts as a filter, trapping contaminants as they pass through it. The microorganisms in the soil use the trapped material as a substrate and the purified water eventually seeps down to the groundwater. The most effective systems use intermittent dosing of the treatment area. This technique maintains aerobic conditions in the soil which provides a much better environment for the degradation of the waste constituents. It is also necessary to pretreat the waste stream to remove any solid that could clog the soil and result in anaerobic conditions. Land treatment is a site specific operation depending on soil type, microbial community, and waste characteristics. Skopintsev (1981) discussed the natural decolorization of organic runoff in detail.

All waste constituents are not assimilated at the same rate. This results in the build up of some substances in the soil over a period of time. When the accumulation of a material in the soil causes the condition of the soil to drop below acceptable standards, the material is referred to as the land-limiting constituent (LLC). A larger land area would be required to accept the given concentration of the LLC if treatment was continued at the same rate. Overcash and Pal (1979) provide a very thorough discussion regarding land disposal and determination of LLC's.

A municipal waste treatment facility in the state of New York began operating a plant which utilized land treatment as the final step in it's

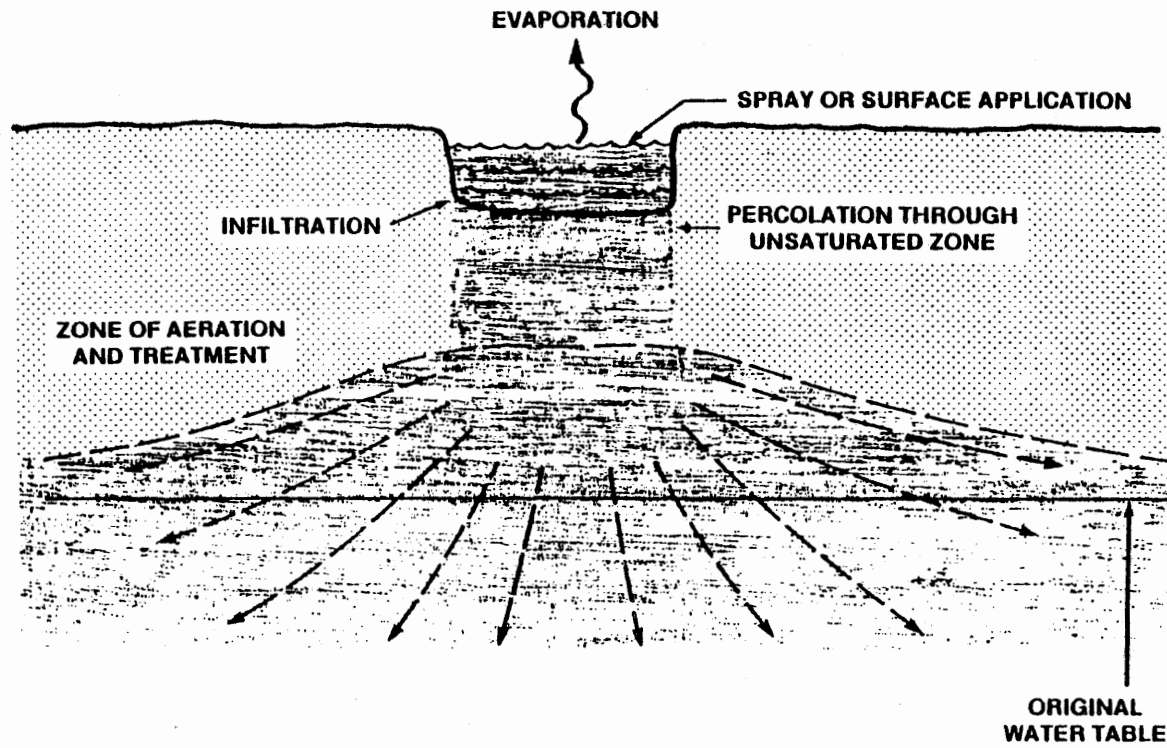


Figure 21. Rapid Infiltration System [after (Culp, et al, 1980)]

treatment scheme in 1936. Aulenbach, et al (1975) described the system from its inception and the modifications made over the years. After settling, the wastewater is passed through a trickling filter. Secondary sedimentation is followed by application to a sand bed. These beds are flooded several times before they are allowed to thoroughly dry; they are then reconditioned by removing the surface mat which forms during treatment. Recent tests showed no signs of pollution seeping into the water sources in the area.

Olsen, et al (1976) described the operation of the first full-scale rapid infiltration treatment system for pulp and paper wastes in North America. This plant also employed a percolation system in which waste water was first ponded and then allowed to seep through the soil under anaerobic conditions. In a comparison of the two systems it was found that the rapid infiltration system provided more efficient wastewater disposal per acre. After clarification and secondary treatment by aeration, the waste was sent to the infiltration basins. During operation, it was discovered that, after a period of treatment, anaerobic conditions tended to form. By plowing the basins and allowing them to dry completely, aerobic conditions could be returned. Factors affecting the infiltration rate were discussed; an average color reduction of 60% was reported for the unbleached kraft waste.

Another full-scale rapid infiltration system has begun operating in North America. A Canadian bleached kraft mill began pilot studies in 1977 and were so pleased with the results that they began a full-scale operation in 1981. Keenan (1981) described the operation and proposed pollutant removal mechanism of this treatment system. The soil at the site had a high content of limestone. After conventional treatment the effluent was pumped to one of seven infiltration basins. One basin was provided for each day of the week to

provide adequate drying and aeration of the soil between applications. Ion precipitation is credited with the high degree of success realized at this site. During periods of high natural runoff in the spring, the basins will be allowed to adequately dry out to maintain their color removal properties. Color removal efficiencies of 90% have been reported (Anonymous, 1982).

Amine Processes

Amine extraction involves treating the effluent with an organic amine and a water immiscible solvent. The colored organic compounds are extracted by the amines and form a precipitate. Centrifuging is used for separation; then, the amines are reclaimed by dissolution in alkali. The development of this process has been hampered by the loss of amine due to the formation of an emulsion throughout the treatment process and by residual odors from organic solvents. In an attempt to alleviate these problems, Svarz (1977) developed an amine process which uses relatively small amounts of alkylated and acylated amines. The wastewater must be at a pH between 2.0 and 5.0. The addition of small amounts of the amine compounds complex with the color bodies to form insoluble compounds. Settling or filtration can be used to remove the solids. This is not an extraction process, thus there is no recovery of the amines. Color reductions ranging from 80% to 96% were reported using varying concentrations of different alkylated and acylated amine compounds. Concentrations and removal efficiencies depend on the chemical composition of the waste stream.

Ozone

Ozone treatment (Figure 22) has been used for many years in municipal wastewater treatment systems. Ozone has found numerous applications as a disinfectant, and more recently as a deodorizer. Industrial wastewater

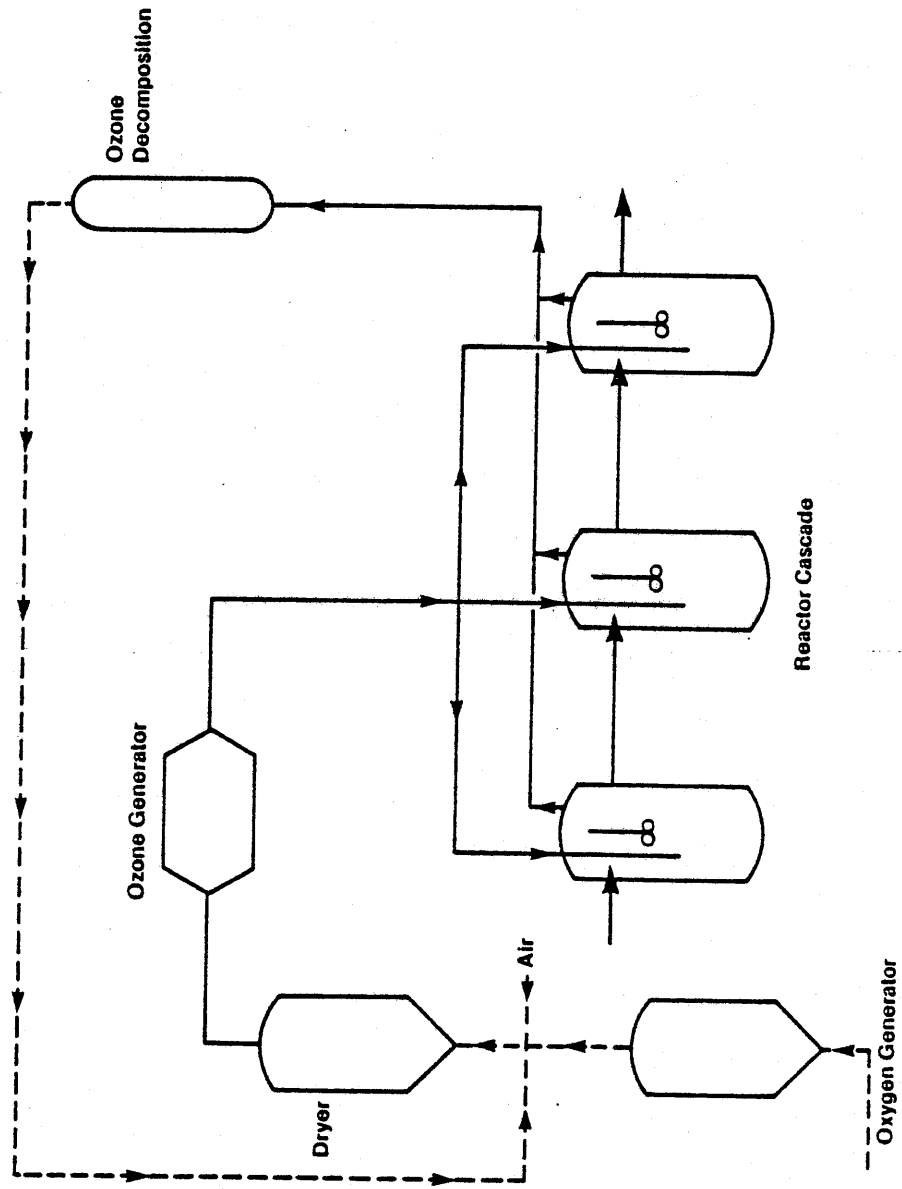


Figure 22. Ozone Decolorization System [after (Melnyk, et al, 1977)]

systems have utilized ozone treatment as well. Being a very powerful oxidant, ozone is capable of oxidizing most organic compounds found in wastewater. The treatment process consists of bubbling ozone through the wastewater to maximize the liquid-gas interface for better mass transfer. The effects of ozone occur rapidly and short retention times are usually adequate.

Ozone is an unstable compound and therefore must be manufactured on-site. It has not been a highly favored treatment option in the United States because ozone, unlike chlorine, has no residual disinfecting power. Once the effluent has been treated, it is once again susceptible to contamination. The process does, however, increase the dissolved oxygen level in the effluent and is effective over a wide temperature and pH range.

Oxidation methods to decolorize an effluent rely on the alteration of the chemical structure of the color forming bodies. These alterations must cause the light absorbance of the bodies to shift out of the visible range. Nebel, et al (1974) reviewed the basic considerations of ozone generation and its applications for color removal. Bauman and Lutz (1974) reported on the operation of an ozone pilot plant for the color removal from an integrated bleached kraft mill. The total mill effluent was treated after primary and secondary wastewater treatment had been completed. Applications of 30 to 40 ppm of ozone to the wastewater resulted in color reductions of 60 to 70%. Increases in the application concentration did not improve the color reduction significantly. A 100% increase in BOD was caused by ozonation, but the dissolved oxygen content that also resulted from the treatment was high enough to offset the BOD increase. It was also found that the color removal was dependent on the quantity of ozone applied, initial color, and COD, and on the suspended solids concentration.

Experimental studies led Melnyk et al (1977) to develop a process to remove color from kraft bleach plant effluents. An ozone reactor was designed based on experimental data which related color removal rates to the concentration of lignin. The data obtained from the experiment showed an increase in BOD when less than 50% of the color was removed, but an approximate 40% decrease in both BOD and COD was observed when the color removal approached 90%. Experimental data yielded not only a strong dependence of color removal on chromophoric lignin concentration, but also a relationship between ozone concentration, mass transfer, chemical reaction rate, and a slight correlation to reactor temperature.

Process Modifications

Oxygen Pulping and Anthraquinone

One method of reducing the effluent flow to the wastewater treatment plant is to reduce the flow of waste streams in which recycling to the recovery system is either not possible or not feasible. With respect to color removal technology, the main streams in this classification are the chloride containing bleach plant effluents. Without making changes in the bleach plant itself, a technique that would decrease the discharge of color would involve supplying the bleach plant with a lower lignin content pulp to bleach. This would result in fewer compounds which needed to be removed and correspond to less color discharge into the effluents. Pulping systems using either anthraquinone or a method of oxygen pulping are capable of accomplishing the necessary pulp delignification.

Oxygen involvement in the pulping process may take several forms. McKean (1976) gives a complete description of the basic principles involved in

single- and multiple-stage oxygen pulping and delignification processes. Delignification by oxygen proceeds by different mechanisms and results in different pulp qualities than conventional pulping processes. Gadda (1982a) used ultraviolet microscopic studies to identify some of the delignification differences. Tests involving the use of selected additives in conjunction with soda-oxygen pulping were reported by Gadda (1982b). These tests also utilized UV-microscopic methods in the determination of specific delignification results. Oxygen pulps may exhibit easier beating characteristics, higher sheet density and carboxyl content, and lower tear strength in relation to kraft pulps. Chang, et al (1974), in reporting these results, also noted that the delignification of soda-oxygen pulps was mostly dependent on the alkali charge and the reaction temperature. However, to prevent unnecessarily low pulp yield and strength properties the temperature should be maintained less than 120°C and the alkali charge maintained less than 5%.

Oxygen delignification is a more yield-selective process than kraft delignification. When an oxygen delignification stage is applied after a conventional pulping process, it is most effective when the conventional pulp is discharged at a higher than normal kappa number. Markham and Magnotta (1981) reported that this practice gave higher pulp yields and resulted in a much easier pulp to bleach, requiring less chemical and fewer stages. This reduced the effluent load in comparison to a conventional kraft pulp bleached to the same brightness. They also reported equal or better bleached pulp-strength properties for their kraft-oxygen system than those of conventional kraft bleached pulp.

Lund and Cook (1980) discussed the integration and operation of a full-scale oxygen delignification stage in a Canadian mill. This installation has

resulted in improved bleach plant pollution levels while simultaneously increasing pulp quality and brightness at reduced chemical costs. Worster and Pudek (1973) also reported improved effluents due to oxygen pulping applications. The color and toxicity of white water from these processes were found to be reduced or eliminated in relation to conventional kraft levels. Yield increases were also reported without suffering strength losses at comparable kappa numbers.

The transformation from mill-scale trials to a commercial installation of a medium consistency oxygen/alkali delignification system was reported by Kleppe, et al (1981). The initial pilot plant utilized an abandoned batch digester for the oxygen reactor. The system was designed to handle 150 tons of pulp per day. The polysulfide pulp had a kappa number in the 55-60 range and it was desired to reduce this to a range of 30-35. The system initially used an abandoned refiner to mix the oxygen and alkali with the pulp prior to the reactor. Further studies found that, using a two-stage system, a kappa number of 14 to 15 could be reached with relatively short retention times. Since the application only required a pulp in the 30-35 kappa number range, a single stage system was eventually installed. A small diffuser was installed prior to the oxygen/alkali mixer to displace the unoxidized liquor in the pulp with oxidized liquor recycled from the wash unit. This resulted in lower oxygen consumption and improved the energy balance around the reactor. Since mechanical treatment of pulp containing alkali was detrimental to strength properties, it was necessary to add the alkali near the outlet of the mixer after the addition of the oxygen.

The effects and mechanisms of anthraquinone (AQ) and similar pulping additives are well known. Werthemann (1982) discussed the mechanisms of

anthraquinone and sulfide catalysts in alkaline pulping. Reactions and condensation products due to AQ are reviewed by Cassidy, et al (1981), and Fullerton and Fleming (1980). Crude tall oil recovered from a soda/AQ process may have less odor and have more end uses than a kraft crude tall oil according to Dimmell, et al (1982). It was reported that the extractives are not significantly involved in the AQ delignification process. Although tall oil yields were approximately the same, the soda/AQ tall oil was a more versatile end product due to the absence of significant sulfur impurities and the resulting higher acid number.

Zanella, et al (1979) showed that the addition of AQ to a pulping system did not increase the toxicity of the effluent. No significant difference were reported in the color from the bleach plant because the kraft/AQ and conventional kraft pulps were pulped to the same kappa number. Zanella, et al (1979) also reported on a similar experiment using AQ and soda based pulping schemes. AQ has been documented as having favorable effects on pulping operations, such as increased yield and decreased chemical consumption. Nomura (1980), Blain (1979), and Holton and Chapman (1977) all reported the advantages of AQ pulping. To realize the beneficial effects with regard to color removal, the pulp must be pulped to a lower than normal kappa number. This technique will allow the same considerations for bleaching operations as employed for oxygen delignification to low kappa numbers.

Bleachability of AQ pulps has been shown to be similar to that of conventional pulps by McDonough and Herro (1982), although it was reported that AQ addition caused a small decrease in pulp brightness. On studies pulping several wood species with and without AQ, MacLeod, et al (1982) recorded slight yield advantages on bleached kraft pulps using AQ. Although

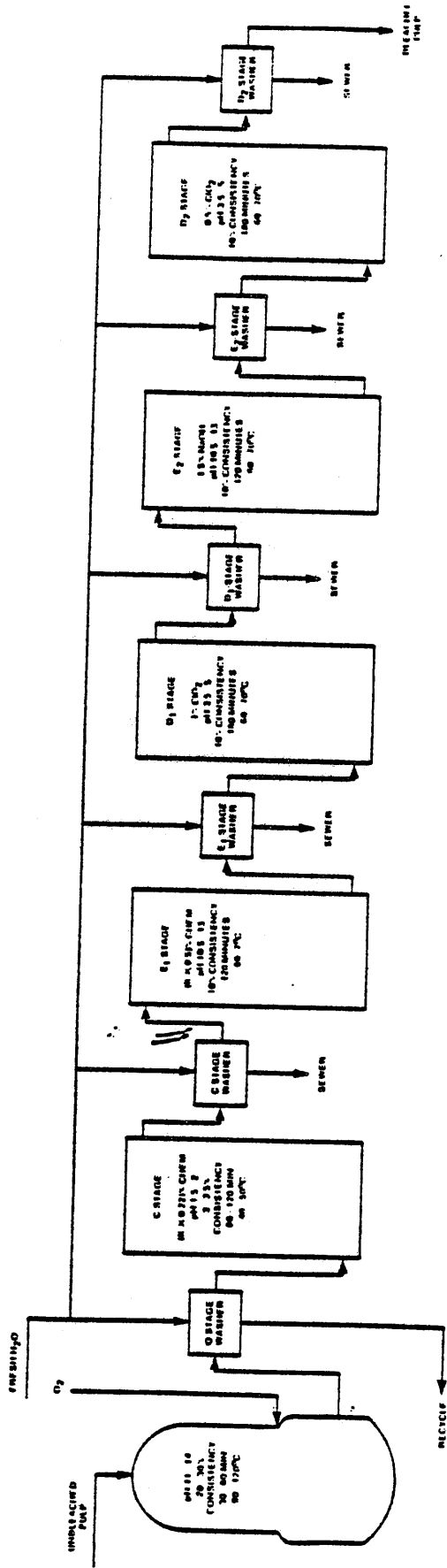
the unbleached kraft-AQ pulps did not have the strength properties of the unbleached kraft pulp, the resulting bleached pulps were equivalent. All systems will not benefit from the use of AQ. An analysis of four different cases was given by Virkola (1981) on the feasibility of AQ addition. Each application must be considered on an individual basis.

Bleach Plant Modifications

Bleach plant effluents are notorious for the pollution load that they contribute to the total mill effluent. Many systems and techniques have been developed to try to improve the quality of the effluents without adversely affecting the pulp strength properties. Bodenheimer and Enloe (1976a and 1976b) presented a thorough discussion of the technology of bleaching and the principles involved. They also included operating conditions and effects of the different stages employed in most modern bleach plants. The majority of the pollutants come from the first two stages of a conventional bleaching sequence. Much work has been done to determine the constituents of these flows. Hardell and de Sousa (1977) have even classified such characteristics as color and TOC according to molecular weight. Most of the work involving reduction in bleach plant effluent loading has been done with regard to the chlorination and first alkali extraction stages.

Oxygen Bleaching

Oxygen bleaching (Figure 23) has recently received the most attention of all of the bleaching alternatives. A substantial amount of research has been carried out concerning the bleaching technology of oxygen systems. Jarrehult and Samuelson (1978) concluded that oxygen selectivity decreased and oxygen consumption increased as the pulp consistency was reduced to very low values in the oxygen bleach stage. These results were attributed to interference by



K x 0.22 = CHEMICAL CHARGE REQUIRED, g/g KAPPA No. x 30.
 THEN CHEMICAL CHARGE REQUIRED = 30 / 0.22
 = 60 lbs Cl₂/100 lbs pulp O.D.

K = KAPPA NUMBER OF UNBLEACHED PULP

Figure 23. Oxygen Bleach Plant

the large volume of spent cooking liquor. In a related study, Elton, et al (1980) determined that consumption and selectivity of oxygen was optimal at medium consistencies (10-15%). Higher consistencies gave no additional benefits in the operation of the oxygen reactor. Nasman and Annergren (1980) reported results of similar testing which support these conclusions.

Pfister and Sjoström (1978) compared the effluents of O-C-E, O-D-E, and C-E-H bleaching sequences. Molecular fractionation was performed on each stage for organic solids, BOD, TOC, permanganate number, and color. The oxygen sequences, although consisting of different results, both yielded impressive improvements in the color loading of the effluent compared to the conventional chlorination sequence. The O-D-E sequence resulted in the most impressive reduction in color. Experimentation by Carpenter, et al (1976) showed that effluent loading can be cut drastically for all of the pollution considerations by introducing an oxygen stage prior to a conventional bleaching sequence. The oxygen effluent does not contain the compounds which prohibit the recovery of conventional bleaching effluents. By recovering just the oxygen effluent, a softwood kraft bleach plant can realize reductions in color of 85%, BOD of 31%, COD of 61%, and chlorides of 40%. The reduction in chlorides is due to a decreased chemical demand for the original conventional sequence.

Many full-scale operations, using some form of oxygen bleaching, are now on-line. Jamieson and Smedman (1973) reported on the operation of a 150 ton per day pilot plant using a O-C-E-D-E-D bleaching sequence. A 92% brightness pulp was produced while pollution was reduced and substantial chemical savings were realized. A Swedish mill has incorporated an oxygen-extraction (OE) stage in their bleaching system. Nasman (1981) described the advantages of

oxygen-extraction. It was reported that an OE stage can make a three stage bleach plant as effective as a conventional five stage system. Using a D/C-O/E-D sequence, it is possible to bleach pulp to a 90 to 91% GE brightness while saving a substantial amount of bleaching chemical.

Studies are already underway to develop other new bleaching methods utilizing oxygen. Abrahamsson (1981) used nitrogen dioxide and oxygen to pretreat pulp before oxygen bleaching. Retardation of cellulose depolymerization and lower lignin content in the final bleached pulp were reported. Changes in the composition of the spent oxygen liquor were also discussed. In corresponding research, Abrahamsson and Samuelson (1982) reported on the effect of oxygen/hydrogen carbonate bleaching after the pulp was pretreated with nitrogen dioxide and oxygen.

Chlorine Dioxide

Chlorine dioxide has become a very popular bleaching chemical as more attention is being paid to bleach plant pollution loads. It has historically been applied in one or more polishing stages to bring the pulp up to required brightness levels. Interest has also developed in the utilization of chlorine dioxide as a substitute for chlorine in the initial bleaching stage. Methods employing partial or complete substitution of chlorine have been developed in hopes of improving the quality of both the pulp and the resulting effluent.

Chlorine has a tendency to form a variety of undesirable organic compounds via chlorine substitution. Chlorine dioxide acts to cause more delignification and less substitution by chlorine. The total replacement with chlorine dioxide is generally more expensive than the improved pulp and effluent considerations would warrant. Rapson and Anderson (1978) discussed the pH effects on the chlorination stage in relation to chlorine dioxide

substitution (Figure 24). As less chlorine was applied, the formation of hydrochloric acid was reduced. This in turn resulted in a higher pH. It was found that above a pH of 1.4, viscosity decreased linearly to a pH of 2.7 using chlorine alone. The introduction of chlorine dioxide increased the viscosity over the entire pH range, but the viscosity also began to decline after a pH of about 1.8. Improved color values were reported for increases in chlorine dioxide substitution. Reeve (1981) reviewed the results obtained by various researchers on substitution rates ranging from 0% to 100%.

In extensive experimentation by Belt, et al (1981), the advantages of various bleaching alternatives were investigated. Conventional bleaching sequences were compared to sequences involving oxygen pre-bleaching and various levels of chlorine dioxide substitution (Figure 25). Results for several different pollution parameters were discussed. Substantial reductions were reported for color due to increasing chlorine dioxide substitution, but, contrary to other research, no significant decreases in BOD levels could be claimed.

Hypochlorite

Hypochlorite acts, through oxidation reactions, to decolorize and solubilize lignin and other impurities in pulp. The pH of the hypochlorite stage is usually kept above 8 to prevent undesirable reactions. Some degree of cellulose degradation will usually accompany this process regardless of the pH. Hypochlorite is available in both sodium and calcium forms. Bleaching characteristics were shown to be dependent upon which form was used in the process by Akiyama, et al (1980). Pulp properties were not reported as significantly different, but calcium hypochlorite was reported to offer increased pulp yield, lower pH, and reduced effluent pollution.

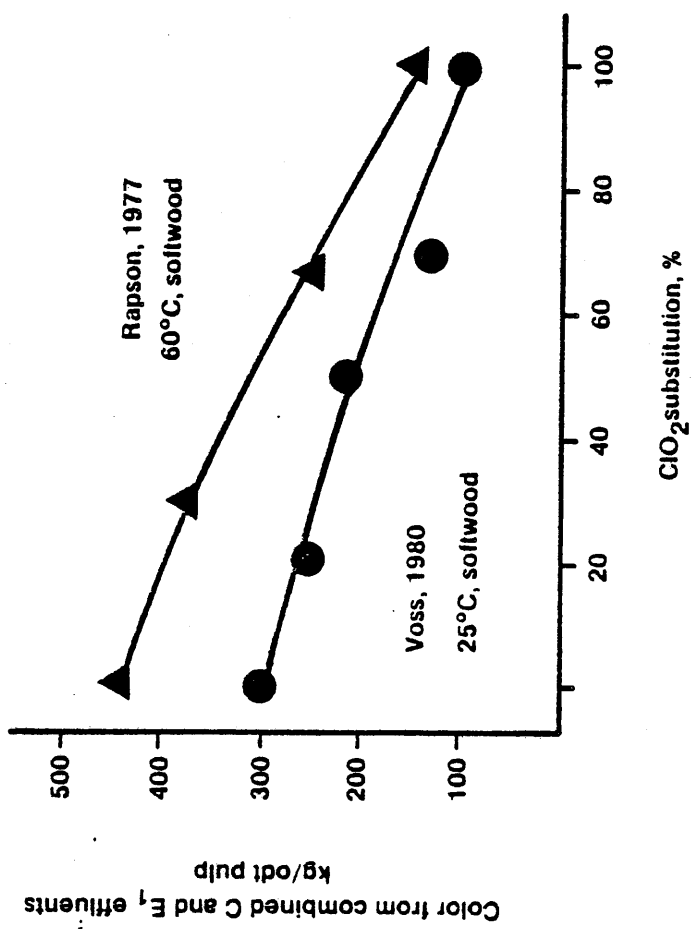


Figure 24. Reduction in Color Discharge by ClO₂ Substitution

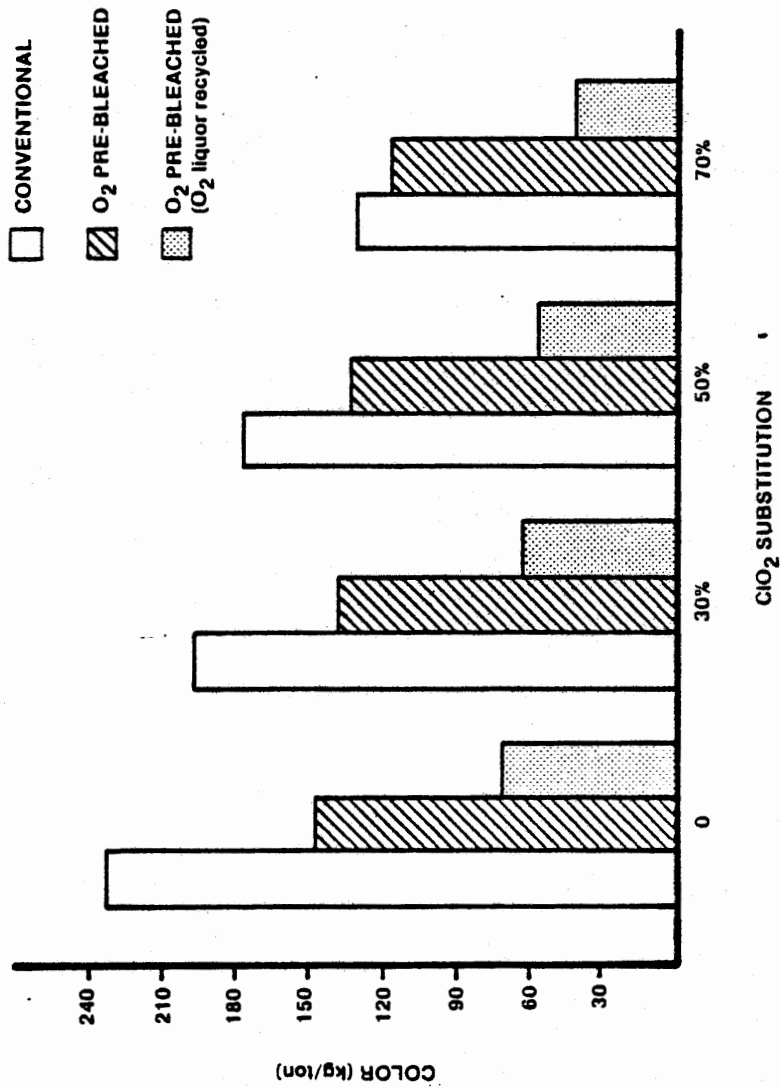


Figure 25. Effect of ClO₂ Substitution on Color Discharge [after (Belt, et al, 1981)]

Despite its tendency to cause degradation of strength properties, hypochlorite processes have found many uses in the bleach plant. Milne (1981) described the development and installation of a hot-hypochlorite stage in an 1100 ton per day bleached kraft mill. Brightness stability was increased with the C_D -E-HE-D bleach sequence. The incorporation of the hypochlorite stage with the extraction stage resulted in a decrease in fresh water requirements due to the reduction of washers required from five to four. A process aimed at the reduction of color from the bleach plant was developed by Gall and Thompson (1978). This process involves the utilization of a sequential chlorine dioxide-chlorine treatment followed by a buffered hypochlorite stage and subsequent chlorine dioxide treatment. Additional bleaching stages could be incorporated into the sequences. From comparisons between a C-E-H-D sequence and the D_C - H_S -D sequence, color reductions of 70% to 90% and a yield increase of 0.5% were reported for softwood. Effluent color was reduced by 50% to 70% with a corresponding yield increase of 1.0% for hardwood pulps.

Peroxide

Bleaching with peroxides has been performed since the 1940's. According to Kindron (1978), hydrogen peroxide is one of the most versatile bleaching chemicals in use today and also the most popular peroxide. Among its noted advantages are no introduction of chlorides or chlorinated organics to the bleachery effluent. Another advantage includes operation at a wide range of pulp consistencies. Replacement or substitution of chlorine dioxide or hypochlorite can result in chemical and energy savings and a potential for improved pulp properties. As pointed out by McDonough (1977), different applications can yield improved strength characteristics over certain conventional processes, particularly in the treatment of high-yield pulps.

Although traditionally used as an intermediate or final step in the bleaching process, peroxide has been considered as an alternative to chlorination in regard to its environmental attributes. Ruhanen and Dugal (1982) have reported encouraging results using peroxide in place of chlorine in the first bleaching stage. Pulp having strength properties comparable to conventional bleaching was obtained by peroxide bleaching. Acid pretreatment followed by peroxide treatment was used to replace C-E-H and C-E stages in conventional sequences. Recycle of effluent from the substituted peroxide stages could result in significant color reductions as compared to a C-E-D-E-D bleachery effluent. The possibility of over 90% color reduction concurrent with 40% BOD and 64% TOC reductions was raised. Decreases in corrosivity, toxicity, and dissolved solids were also mentioned.

Ozone

Recently ozone has gained prominence as a successor to chlorine in pulp bleaching. Singh (1982) stated that the degradation of cellulose has been generally associated with ozone bleaching. A high pulp consistency process under optimum conditions could produce a pulp with most strength properties being comparable to pulps from C-E-H-D and C-E-H-E-D systems. The retention time for the system was less than six minutes, but slight departures from the optimum conditions could result in fiber degradation. Brightness levels up to 60-70 could be obtained by ozone alone, without resulting in severe yield and strength losses.

Kubo, et al (1977) reported lignin levels in bleachery wastewater were reduced due to the destruction of lignin which occurs in ozone bleaching. Takagi and Kayama (1980) and Kamishima, et al (1976) reported similar results regarding pulp quality and characteristics of ozone-bleached pulps. Pulps

bleached at 50% consistency had improved beating properties, but the strength properties were inferior to those of unbleached and conventionally bleached pulps.

Multistage ozone bleaching also offers promise. Kobayashi, et al (1982) tested pulps bleached by single-stage and multi-stage ozone treatment. The multiple stage process was washed with water between applications. Ozone consumption was greatly diminished in the multi-stage process due to the removal of ozone oxidation products by washing. Rothenberg, et al (1975) also conducted studies involving single and multiple stage ozonation. In comparison with conventional white birch, bleached kraft pulp, ozone bleached oxygen pulp resulted in better strength properties. High brightnesses were also noted for the environmentally superior oxygen-ozone systems.

Gas-Phase Bleaching

Bleaching with compounds in their gaseous form is not new to bleaching technology. Oxygen and ozone are both gaseous bleaching chemicals and chlorine vapor was used until the low-consistency technology was developed. Gas phase systems are characterized by short retention times and reduced effluent volumes. Carlsmith, et al (1977) presented a description of the principles involved and the equipment necessary for the operation of gaseous treatment stages. Instead of replacing the conventional chlorination stage, it was reported that it may be possible to meet potential environmental conditions by utilizing a gas-phase system. Annergren, et al (1977) proposed a chlorination stage (Figure 26) that would fit into a closed system perspective. A chlorine reactor is described that uses chlorine vapor to bleach high-consistency pulp. Unbleached pulp waiting to be admitted to the reactor absorbs residual chlorine which may be vented from the system.

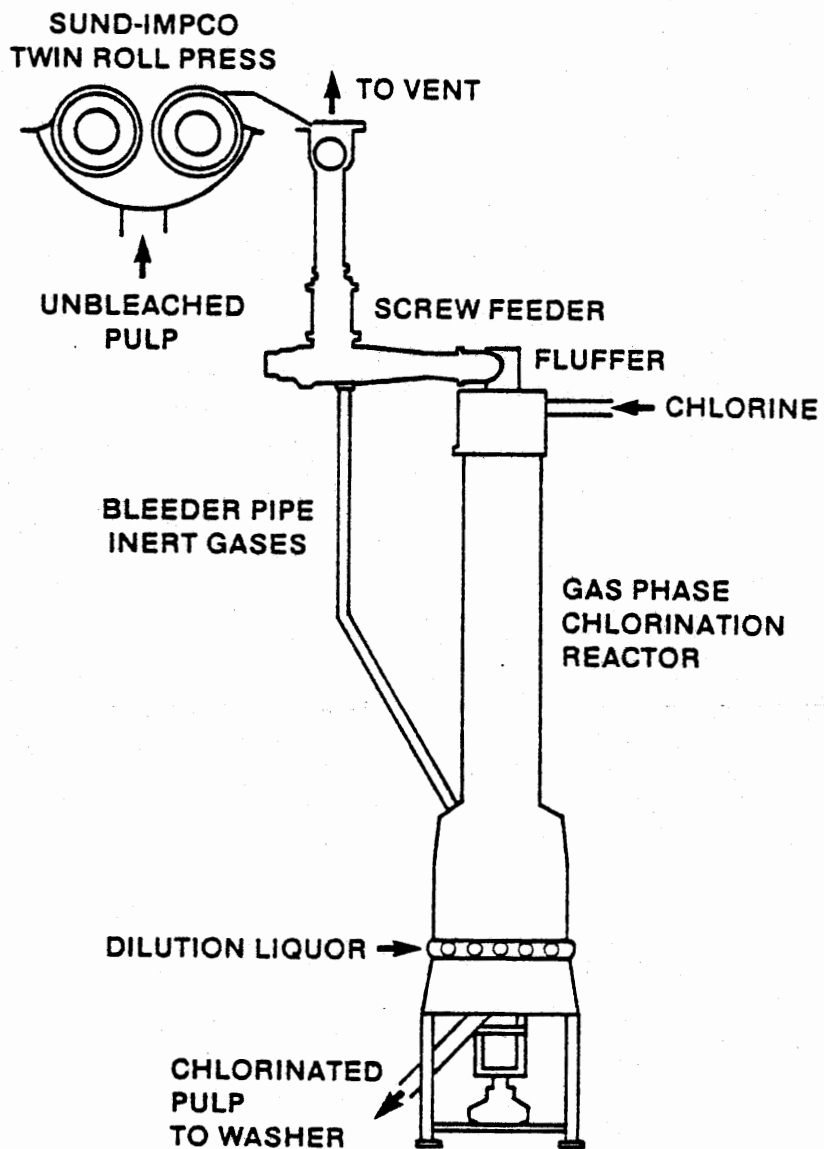


Figure 26. Gas Phase Chlorinator
 [after (Annergren, et al, 1977)]

Favorable results are predicted for water consumption and pollutant reductions.

The general operation of a gas-phase system involves fluffing high-consistency pulp in the top of a reactor and allowing it to fall through an upward flow of the vaporized chemical. Wong, et al (1978) described several novel bleaching processes in which gaseous compounds were employed. The sequences tested were $C_g-E_x-D_g$, $O-C_g-E_x$, D_g-P-D_g , $O-D_g-E_x$, and $O-C-E$. The subscript "g" refers to application of the chemical in its gaseous form and E_x refers to a rapid-press caustic extraction. The results indicated that the $O-D_g-E_x$ sequence produced the least amount of color, BOD, COD and toxicity. It should be noted, however, that these results are based on the complete recycle of the oxygen stage effluent. The D_g-P-D_g sequence also resulted in excellent color reductions without the benefit of effluent recycling. Additional advantages of gas-phase systems include compact plant size, excellent bleaching control, and reduced chemical usage.

Displacement Bleaching

A displacement bleaching system (Figure 27) consists of a single bleaching tower which is occupied by several bleaching stages. Bleaching liquor from one stage is displaced by the incoming liquor from the next stage. The displaced liquor is recycled and, in turn, displaces the liquor from a previous stage. Considerable savings in bleaching time and capital requirements are realized by the lack of need for washers between each stage. The turbulence created by the continuous flow of chemicals through the fiber allows for faster reaction rates. Space and equipment savings are an important consideration in a displacement bleaching operation.

The first commercial displacement bleach plant was began in 1975

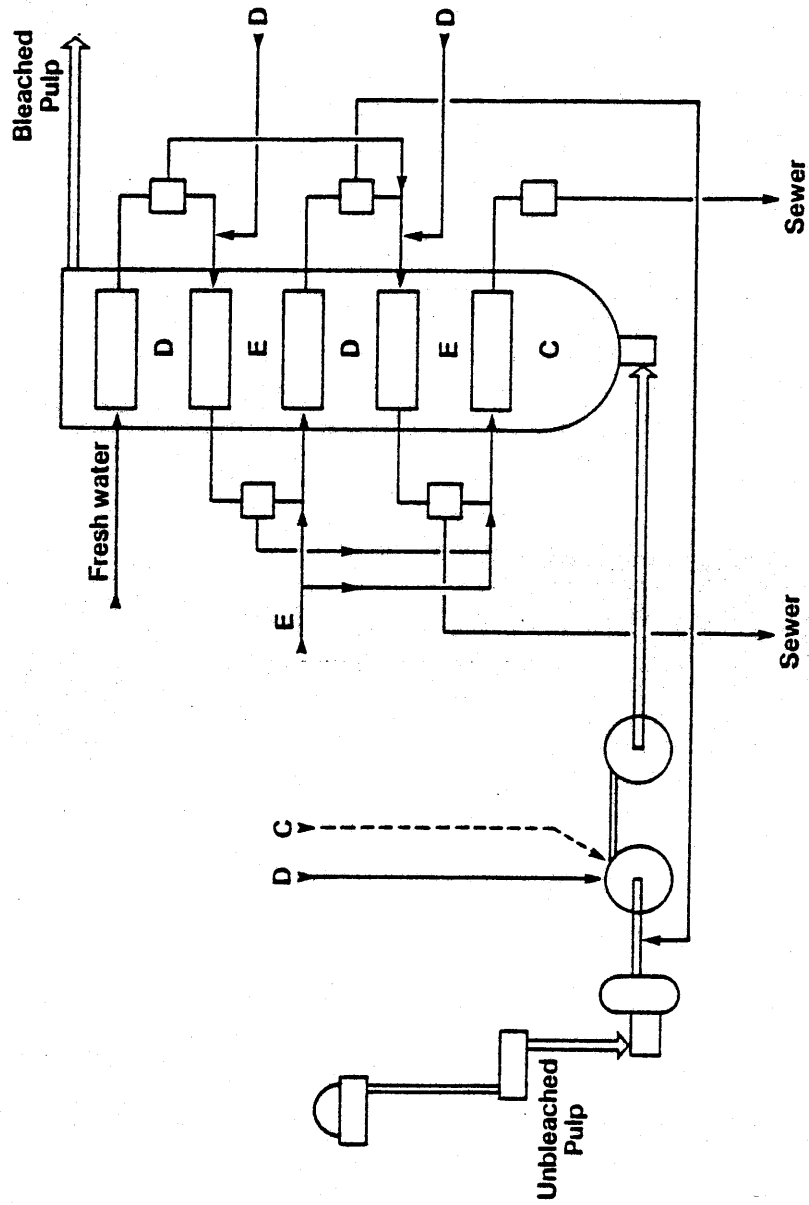


Figure 27. Displacement Bleach Plant [after (Singh, 1979)]

according to a review of the operation (Anonymous, 1976). The pulp quality and chemical usage were reported to be the same as for a conventional system. Effluent pollutant discharge was the same also, but reductions in water usage, power, and steam were pointed out. Haas (1978) described a prototype plant in Finland which was bleaching to over 90° G.E. brightness. It was of the same design as the plant started by Eastex in 1975. Reductions in chemical consumption were reported for a similar Weyerhaeuser displacement bleach plant as compared to a conventional system. The system's developers also reported substantial reduction in heat, energy, space, and water requirements. The reduced volume of effluent resulted in a higher concentration of the pollutants.

The Rapson-Reeve Closed Bleach Plant

As was pointed out previously, the accumulation of chloride ion which would result if bleach plant liquors were recycled would promote austenitic corrosion of stainless steel equipment in the mill. Thus, most mills are very reluctant to consider such process effluent recycling.

At the Thunder Bay, Ontario, mill of Great Lakes Forest Products Ltd., the Rapson-Reeve closed-cycle bleach plant has been installed (Anonymous, 1977; Reeve, et al 1982). Several process modifications have been made to the conventional C-E-D-E-D bleach sequence. These modifications include:

1. substantial replacement of chlorine with chlorine dioxide in the first bleach stage,
2. high temperature chlorination in the first bleach stage,
3. countercurrent washing from the bleached decker through the brown stock diffuser using recycled white water,
4. minimization of fresh water make-up, and,

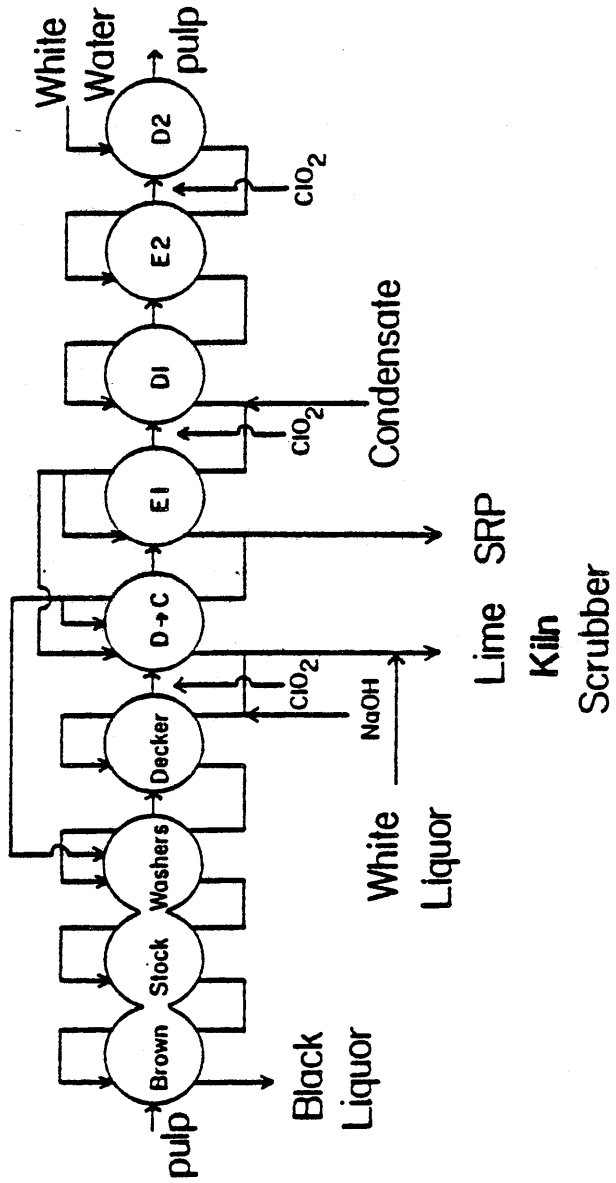
5. installation of the salt recovery process (SRP) for sodium chloride purging.

A process flow sheet for the filtrate recovery mill is presented in Figure 28, while the SRP is shown in Figure 29.

The key unit operation of the Rapson-Reeve scheme is the SRP. In this operation, sodium chloride is removed from the white liquor. This is accomplished by precipitating sodium chloride, sodium carbonate, and sodium sulfate from the white liquor after it has been concentrated by evaporation. The recovered NaCl subsequently becomes the feed stock for the manufacture of chlorine dioxide or chlorine, or is used as make-up saltcake for the R-3 process.

Although the Rapson-Reeve process continues to be tested at Great Lakes Paper, several operational problems have surfaced. One of the major problems was that there has been an increase in corrosion in the superheater tubes in the recovery boiler. At one time, the mill had to be shut down to replace the tubes. Attempts to develop a workable system continue.

Figure 28. The closed-cycle mill bleach plant filtrate recovery



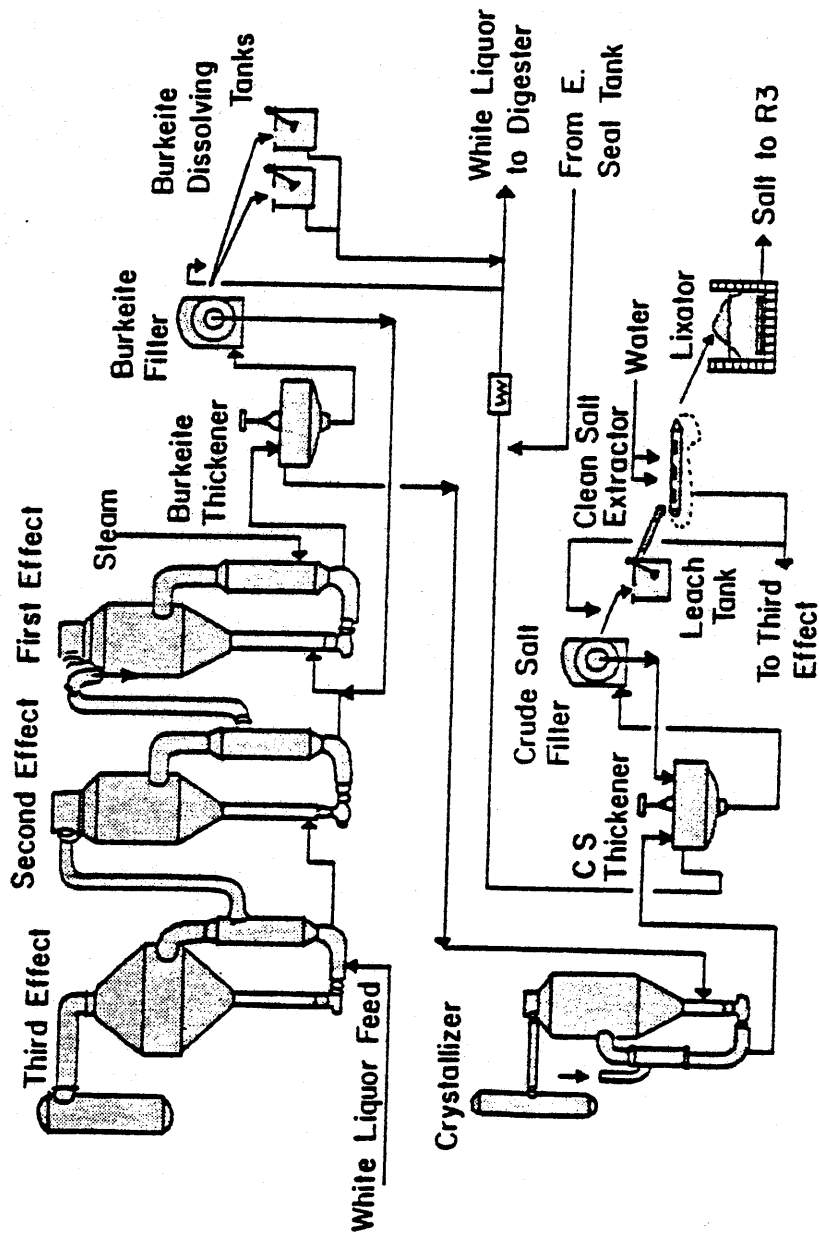


Figure 29. The Salt Recovery Process

ECONOMICS

Because the costs of color removal are dependent on the specific unit processes used in a mill, it is not possible to estimate an "average" cost for color removal. However, costs of some color removal technologies are shown in Tables 8 and 9. Some investigators have chosen to treat only the first caustic extraction stage because it contains a relatively high proportion of the color in a relatively small volume. Decolorization of the first caustic extraction stage may reduce total color discharged to the environment by two-thirds.

If present decolorization costs are estimated to be on the order of \$10-20/ton pulp, then decolorization regulations may require a significant increase in the selling price of bleached pulp, currently about \$350-400/ton pulp (Anonymous, 1983).

Even these costs may be somewhat dubious since it is assumed that there will be no effect on mill operations and there will be no problems with retrofit. For example, Wright, et al (1974) report the following problems with a proposed massive lime precipitation process:

- a. increase in white liquor clarification capacity required,
- b. larger lime kiln needed,
- c. increased fuel consumption in lime kiln,
- d. increase in multiple effect evaporator capacity required, and,
- e. increase in recovery furnace capacity required.

These are just some of the problems involved in the retrofit. It must be remembered that a pulp and paper mill is a large, complex, highly interactive operation. Perturbations in one area may have a larger than expected impact in another area.

Table 8. Costs of Decolorization Alternatives for the First Caustic Extraction Stage Effluent

| Type | Scale | Costs (1980 \$ Basis) | | | |
|---------------------|--------------------|-----------------------|-----------------------|-------------------------|---------------------|
| | | Percent Color Removal | Capital Cost (\$/ton) | Operating Cost (\$/ton) | Total Cost (\$/ton) |
| Ion Exchange | Mill (300 tpd) | 90 | 2.8 | 3.7 | 6.5 |
| Ultrafiltration | Mill (54.7 tpd) | 87 | 1.7 | 3.8 | 5.5 |
| Mini-lime | Mill (625 tpd) | 90 | 0.7 | 2.7 | 3.4 |
| Massive-lime | Pilot Plant | 93 | 3.1 | 3.2 | 6.3 |
| Polymeric Adsorbent | Pilot Plant | 85 | 0.6 | 1.3 | 1.9 |

Table 9. Costs of Decolorization Alternatives for the Total Mill Effluent

| Type | Scale | Costs (1980 \$ Basis) | | | |
|---|-------------|-----------------------|-----------------------|-------------------------|---------------------|
| | | Percent Color Removal | Capital Cost (\$/ton) | Operating Cost (\$/ton) | Total Cost (\$/ton) |
| Ozone | Pilot Plant | 85 | 1.0 | 4.0 | 5.0 |
| Dispersed Air Flotation | Laboratory | 90 | NR | 6.9 | NR |
| Fe ₂ (SO ₄) ₃ | Laboratory | 91 | 2.3 | 10.8 | 13.1 |
| Alum | Laboratory | 93 | 2.3 | 10.3 | 12.6 |
| Activated Carbon Adsorption | Pilot Plant | 80 | 2.2 | 7.8 | 10.0 |

NR = not reported

LITERATURE REVIEWED

- Abrahamsson, K., Pretreatment of Kraft Pulp with Nitrogen Dioxide before Oxygen Bleaching, Svensk Papperstidning, Vol. 84, No. 18, p. R152, 1981.
- Abrahamsson, K., Samuelson, D., The Influence of Oxygen Pressure During Oxygen Bleaching of Kraft Pulp Pretreated with Nitrogen Dioxide/Oxygen, Svensk Papperstidning, Vol. 85, No. 3, p. R27, 1982.
- Abrahamsson, K., Samuelson, O., Oxygen/Hydrogen Carbonate Bleaching After Pretreatment With Nitrogen Dioxide, Svensk Papperstidning, Vol. 85, No. 18, p. R156, 1982.
- Adams, R. M., Inapplicability of Batch Kinetic Data to Analysis of Soil Treatment Systems, Journal Water Pollution Control Federation, Vol. 50, No. 2, p. 386, 1978.
- Akiyama, T., Murashige, K., Veno, T., Studies on Bleaching of Pulps. Part 2. Comparison of Calcium Hypochlorite and Sodium Hypochlorite in Hypochlorite Bleaching Stages, Japan Tappi, Vol. 34, No. 10, p. 706, 1980.
- Anderson, K. A., The Non-Polluting Bleaching Plant, Tappi, Vol. 60, No. 3, p. 95, 1977.
- Annergren, G. E., Linblad, P. O., Pettersson, B., Gas-Phase Chlorination in Closed Systems, Pulp & Paper Canada, Vol. 78, No. 7, p. 25, 1977.
- Anonymous, Acadia Starts Up Two-Stage Bleach Plant, Southern Pulp and Paper Manufacturerer, Vol. 39, No. 7, p. 12, 1976.
- Anonymous, Eastex Starts Up First Commercial Displacement Bleach Plant In World, Paper Trade Journal, Vol. 160, No. 11, p. 36, 1976.
- Anonymous, Effluent-Free Bleached Kraft Mill Is Pioneered At Great Lakes Paper, Pulp and Paper, Vol. 51, No. 3, p. 94, 1977.
- Anonymous, Skookumchuck Decolorization System Meets High Expectations, Pulp and Paper Journal, Vol. 35, No. 5, p. 12, 1982.
- Anonymous, Marketing Trends, Paper Trade Journal, Vol. 167, No. 15, p. 4, 1983.
- Armentrout, D. N., Liquid Chromatographic Determination of Anthraquinone in Soda and Kraft Pulping Liquor, Pulp, Air Filters, and Wastewater, Tappi, Vol. 64, No. 9, p. 165, 1981.
- Aulenbach, D. G., Clesceri, N. L., Beyer, S., Hajas, L., Tofflemire, T. J., Water Renovation Using Deep Natural Sand Beds, Proceedings of the 30th Industrial Waste Conference, 1975 May 6-8; W. Lafayette, Indiana, Purdue University. c1977:345-357.

- Backlund, A., Anthonisen, K., Kamyir Medium-Consistency Oxygen Delignification, Japan Tappi, Vol. 36, No. 1, p. 51, 1982.
- Bauman, H. D., Lutz, L. R., Ozonation of a Kraft Mill Effluent, Tappi, Vol. 57, No. 5, p. 116, 1974.
- Belt, P. B., Joyce, T. W., Chang, H.-m., Environmental Aspects of Some Alternative Pulp Bleaching Techniques, Report No. 175 to the Water Resources Research Institute of The University North Carolina, May, 1981.
- Bennett, D. J., Dence, C. W., Kung, F.-L., Luner, P., Ota, M., The Mechanism of Color Removal in the Treatment of Spent Bleaching Liquors with Lime, Tappi, Vol. 54, No. 12, p. 2019, 1971.
- Bhattacharyya, D., Garrison, K. A., The, P. J. W., Grives, R. B., Membrane Ultrafiltration: Waste Treatment Application for Water Reuse, Proceedings of the 30th Industrial Waste Conference; 1975 May 6-8; W. Lafayette, Indiana. Purdue University. c1977: 120-131.
- Blain, T. J., Low-Sulfidity Pulping with Anthraquinone, Tappi, Vol. 62, No. 6, p. 53, 1979.
- Bodenheimer, V. B., Enloe, J. O., Principles of Pulp Bleaching, Southern Pulp and Paper Manufacturer, Vol. 39, No. 3, p. 29, 1976a.
- Bodenheimer, V. B., Enloe, J. O., Principles of Pulp Bleaching, Southern Pulp and Paper Manufacturer, Vol. 39, No. 4, p. 30, 1976b.
- Bordelon, B. R., Environmental Factors Affecting the Properties and Precipitation of Coloring Colloids in Aquatic Habitats, M. S. Thesis, Louisiana State University, Baton Rouge, LA, 1973.
- Borjeson, H. B., Lindberg, S., Field Report on a Nonpolluting Bleach Plant, Tappi, Vol. 64, No. 10, p. 89, 1981.
- Bouveng, H. O., Solyom, P., Long Term Stability of Waste Lignins in Aquatic Systems, Svensk Papperstidning, Vol. 76, p. 26, 1972.
- Broddevall, B. G., Purification of Waste Water from Sulphate Pulp Bleaching Plants, U.S. Patent No. 3990969, 1976.
- Brodén, A., Simonson, R., Oxygen Cooking of Birch Chips with Addition of Hydrogen Peroxide, Paperi Puu, Vol. 63, No. 12, p. 787, 1981.
- Bureau of the Census, U. S. Department of Commerce, Current Industrial Report Series M262A, Pulp, Paper, and Board, 1979.
- Callahan, W. F., Pincine, A. B., An Activated Carbon Wastewater Treatment System at Fitchburg, Mass., Tappi, Vol. 60, No. 11, p. 146, 1977.

- Campbell, A., A Bench Scale Evaluation of a Process for Decolorization of Bleach Plant Effluent Using the White Rot Fungus Phanerochaete Chrysosporium, Ph.D. Thesis, Dept. of Wood and Paper Science, North Carolina State University, 1983.
- Campbell, J. and Joyce, T., Enzymatic Pretreatment of Pulp Mill Effluents Prior to Decolorization by Lime Precipitation, Report No. 197 to the Water Resources Research Institute of The University of North Carolina, 1983.
- Carlsmith, L. A., Schleinkofer, R. W., Hoag, R. W., Commercial Gaseous Bleaching Equipment, Tappi, Vol. 60, No. 5, p. 106, 1977.
- Carpenter, W. L., McKean, W. T., Berger, H. F., Gellman, I., Characteristics of Effluents from Conventional and Oxygen Bleaching Sequences, Tappi, Vol. 59, No. 11, p. 81, 1976
- Cassidy, R. F., Falk, L. E., Dence, C. W., The Reactions of Radiolabelled Anthraquinone with Wood Constituents in Soda Pulping, Svensk Papperstidning, Vol. 84, No. 12, p. R94, 1981.
- Chang, H.-m., Kleppe, P. J., Delignification of High-Yield Pulp with Oxygen and Alkali, Tappi, Vol. 56, No. 1, p. 97, 1973.
- Chang, H.-m., Gratzl, J. S., McKean, W. T., Delignification of High-Yield Pulps with Oxygen and Alkali, Tappi, Vol. 57, No. 5, p. 123, 1974.
- Chapell, W. R., Sievers, R. E., Shapiro, R. H., Effects of Ozonation of Organics in Waste Water, U. S. EPA Report, EPA 600/1-18-005, 1981.
- Christman, R. F., Ghassemi, M., Chemical Nature of Organic Color in Water, Journal of the American Water Works Association, Vol. 58, p. 723, 1966.
- Claussen, P., Membrane Filtration of SSL for By-Product Recovery and Pollution Control, Pulp & Paper Canada, Vol. 79, No. 3, p. 41, 1978.
- Collins, J. W., Webb, A. A., Detection and Gel Chromatography of Carbohydrates in Pulp Mill Effluents, Tappi, Vol. 55, No. 9, p. 1335, 1972.
- Collins, J. W., Webb, A. A., Boggs, L. A., Characterization of Lignin and Carbohydrate Residues Found in Bleach Effluents, Tappi, Vol. 54, No. 1, p. 105, 1971.
- Collins, J. W., Webb, A. A., Didwania, H. P., Lueck, B. F., Components of Wood Pulp Bleach Effluents, Environmental Science and Technology, Vol. 3, No. 4, p. 371, 1969.
- Crawford, R. L., Lignin Biodegradation and Transformation, New York: Wiley-Interscience, 1981.
- Croon, I., Technical-Economic Aspects of Some Future Bleach Plant Technology, Paperi Puu, Vol. 64, No. 4, p. 139, 1982.

- Croon, I., Andrews, D. G., Advances in Oxygen Bleaching, Tappi, Vol. 54, No. 11, p. 1893, 1971.
- Culp, G., Wesner, G., Williams, R., Hughes, M. V., Wastewater Reuse and Recycling Technology, Noyes Data Corporation, Park Ridge, New Jersey, 1980.
- Davis, C. L., Jr., Lime Precipitation for Color Removal in Tertiary Treatment of Kraft Mill Effluent at the Interstate Paper Corp., Riceboro, Ga., Chemical Engineering Progress Symposium Series, Vol. 67, p. 458, 1971.
- Dimmell, D. R., Thireault, D. D., Curti, P. D., Seefelt, R. G., The Interaction of Anthraquinone with Tall Oil Components, Tappi, Vol. 65, No. 6, p. 123, 1982.
- Dogherty, E., Mutant Bacteria Undergo Field Evaluation, Pulp and Paper Canada, Vol. 83, No. 4, p. 32, 1982.
- Dugal H. S., Swanson, J. W., Dickey, E. E., Buchanan, M. A., Effect of Lime Treatment on Molecular Weight Distribution of Color Linerboard Decker Effluents, Tappi, Vol. 58, p. 132, 1975.
- Eaton, D., Chang, H., Joyce, T., Jeffries, T., and Kirk, K., Method to Obtain Fungal Reduction of Color of Extraction-Stage Kraft Bleach Effluents, Tappi, Vol. 65, No. 6, p. 89, 1982.
- Eaton, D. C., Chang, H.-m., Kirk, T. K., Kraft Bleaching Plant Effluent Can Be Decolorized Using the Synergistic Effects of Cations Solubilized by Acidification of Waste Sludge, Tappi, Vol. 65, No. 5, p. 167, 1982.
- Elton, E. F., Magnotta, V. L., Markham, L. D., Courchene, C. E., New Technology for Medium-Consistency Oxygen Bleaching, Tappi, Vol. 63, No. 11, p. 79, 1980.
- EPA Development Document for in Interim Final and Proposed Effluent Limitations, and Proposed New Source Performance Standards, Vol. 1, EPA 440/10-76/047- a, 1976.
- Evans, J. E., Venkatesh, V., Gratzl, J. S., Chang, H.-m., The Kinetics of Low-Consistency Oxygen Delignification, Kraft and Soda-Anthraquinone Pulps, Tappi, Vol. 62, No. 6, p. 37, 1979.
- Fremont, H. A., Color Removal from Paper and Pulp Mill Aqueous Effluents, U.S. Patent No. 4226673, 1980.
- Fuller, R. R., Effluent Treatment Processes, U.S. Patent No. 374-363, 1973.
- Fullerton, T. J., Fleming, B. I., Anthraquinone Condensation Products Formed During Pulping, Svensk Papperstidning, Vol. 83, No. 14, p. 396, 1980.

- Gadda, L., UV-microscopic Study of Delignification During a Two-Stage Soda-Oxygen Pulping of Pine, Svensk Papperstidning, Vol. 85, No. 9, p. R57, 1982a.
- Gadda, L., Soda-Oxygen Pulping with Additives, Svensk Papperstidning, Vol. 85, No. 12, p. R87, 1982b.
- Gall, R. J. Thompson, F. H., The Anti-Pollution Sequence--A New Route to Reduced Pollutants in Bleach Plant Effluent, Tappi, Vol. 56, No. 11, p. 72, 1973.
- Gall, R. J., Thompson, F. H., Process for the Reduction of Effluent Color from a Cellulosic Pulp Bleaching Sequence, U.S. Patent No. 4081317, 1978.
- Gallay, W., In-Depth Assessment of the Present Status of the Problems of Pollution Abatement in the Pulp and Paper Industry, Report to the Canadian Pollution Abatement Research Program, 1973.
- Ganczarczyk, J., Obiaga, T., Mechanism of Lignin Removal in Activated Sludge Treatment of Pulp Mill Effluents, University of Toronto, Civil Engineering Publication 74-08, April, 1974.
- Gehm, H., State-of-the-Art Review of Pulp and Paper Waste Treatment, Environmental Protection Technology Series, EPA-R2-73-184, 1973.
- Gellman, I., Berger, H., Current Status of the Effluent Decolorization Problem, Tappi, Vol. 57, No. 9, p. 69, 1974.
- Gerrard, E., Some Factors Affecting Fungal Decolorization of Pulp and Paper Mill Effluents in the MyCoR Process, M.S. Thesis, Dept. of Wood and Paper Science, North Carolina State University, 1983.
- Gillespie, W. J., Berger, H. F., Chemical-Physical Renovations of Pulp Mill Effluents, Proceedings of the 15th Annual Pulp and Paper Conference; Jan. 1971; Kalamazoo, Michigan, p. 118-138.
- Gould, M., Color Removal from Kraft Mill Effluent by an Improved Lime Process, Tappi, Vol. 56, p. 79, 1973.
- Gupta, S. D., A Novel Electrochemical Process for Effluent Treatment in Kraft Mill Effluents, Pulp & Paper Canada, Vol. 80, No. 4, p. 68, 1979.
- Haas, L., Finnish Displacement Bleaching Line Achieves over 90° Final Brightness, Pulp & Paper, Vol. 52, No. 7, p. 137, 1978.
- Hardell, H-L., de Sousa, F., Characterization of Spent Bleaching Liquors. Part 1. Spent Liquors from the Chlorine and Alkali Extraction Stages in the Prebleaching of Pine Kraft Pulp, Svensk Papperstidning, Vol. 80, No. 4, p. 110, 1977.

- Herer, D. O., Woodard, F. E., Electrolytic Coagulation of Lignin from Kraft Mill Bleach Plant Wastewaters, Tappi, Vol. 59, No. 1, p. 134, 1976.
- Hofreiter, B. T., Fecht, R. G., Irradiation of Wastewaters, Tappi, Vol. 62, No. 4, p. 53, 1979.
- Holton, H. H., Chapman, F. L., Kraft Pulping with Anthraquinone, Tappi, Vol. 60, No. 11, p. 121, 1977.
- Hosokawa, J., Kobayashi, T., Kubo, T., Kimura, Y., Studies on Color Reversion of Ozone-Bleached K(raft) P(ulp). (1). Properties of Ozone-Bleached KP in Color Reversions, Journal Japan Wood Research Society, Vol. 22, No. 12, p. 683, 1976.
- Hosoya, S., Seike, K., Nakano, J., Bleaching of High-Yield Pulp, Journal of Japan Wood Research Society, Vol. 22, No. 6, p. 314, 1976.
- Hwang, C. P., Carbon and Color Distribution in Various Size Fractions of Treated Pulp Mill and Board Mill Waste Effluent, Tappi, Vol. 57, No. 12, p. 148, 1974.
- Huang, J.-C., Garrett, J. T., Effects of Colloidal Material and Polyelectrolytes on Carbon Adsorption in Aqueous Solution, Proceedings of the 30th Industrial Waste Conference; 1975 May 6-8, Lafayette, Indiana. Purdue University. c1977. p. 1111-1121.
- Ishikawa, H., Iida, N., Okubo, K., Oki, T., Bleaching of High-Yield Pulp with NaOCl/Peroxide, Japan Tappi, Vol. 35, No. 3, p. 270, 1981.
- Ishikawa, H., Iida, N., Okubo, K., Oki, T., Bleaching of Pulps with Sodium Hypochlorite/Hydrogen Peroxide, Japan Tappi, Vol. 36, No. 6, p. 642, 1982.
- Jamieson, A., Smedman, L., Oxygen Bleaching--A Mill-Tested Approach to Pollution Abatement, Tappi, Vol. 56, No. 6, p. 107, 1973.
- Jarrehult, B., Samuelson, O., Oxygen Bleaching of Kraft Pulps at Low Consistency, Svensk Papperstidning, Vol. 81, No. 17, p. 533, 1978.
- Joyce, T. W., Studies on Filamentous Bacteria in Pulp and Paper Mill Activated Sludge Plants, Proceedings of the 1979 Tappi Annual Meeting, New York, March, 1979.
- Joyce, T., and Beshire, A., unpublished data, North Carolina State University, 1981.
- Joyce, T., Chang, H.-m., Campbell, A., Eaton, D., and Kirk, K., Removal of Kraft Bleach Plant Color by a Ligninolytic Fungus, Proceedings of the 1981 Tappi Environmental Conference, New Orleans, LA, April 27-29, 1981.
- Joyce, T. W., Dubey, G. A., Webb, A. A., The Effect of Biological Treatment on the Lime Precipitation Color Removal Process, Tappi, Vol. 62, No. 12, p. 107, 1979.

- Joyce, T. W., and Tesmer, M., Effect of Color on Primary Productivity of an Alga Test Species, Tappi, Vol. 63, No. 9, p. 105, 1980.
- Kamishima, H., Fujii, T., Akamatsu, I., Bleachability of Softwood and Hardwood Kraft Pulps in Ozone Bleaching, Japan Tappi, Vol. 30, No. 7, 1976.
- Kamishima, H., Fujii, T., Akamatsu, I., Nakayama, S., Effect of Organic Acids on Carbohydrate Protection During Ozone Bleaching of Kraft Pulp, Journal Japan Wood Research Society, Vol. 28, No. 6, p. 370, 1982.
- Kamishima, H., Fujii, T., Akamatsu, I., Verification of Effectiveness of Methanol and Oxalic Acid for Carbohydrate Protection during Ozone Bleaching, Journal Japan Wood Research Society, Vol. 28, No. 7, p. 480, 1982.
- Kanneko, H., Nakano, J., Ozonation of Lignin: Dispersing Power of Ozonized Thioglignin, Journal Japan Wood Research Society, Vol. 28, No. 9, p. 577, 1982.
- Kanneko, H., Hosoya, S., Nakano, J., Degradation of Lignin with Ozone: Reaction of Biphenol and Alpha-Carbonyl Type Model Compounds with Ozone, Journal Japan Wood Research Society, Vol. 27, No. 9, p. 678, 1981.
- Keenan, W., Crestbrook Forest Industries Treats Mill Effluent with a 'Rapid Infiltration' System, Paper Trade Journal, Vol. 165, No. 7, p. 63, 1981.
- Kindron, R. R., Hydrogen Peroxide: It Carries a Heavier Production Work Load in Today's Pulp Mill, Paper Trade Journal, Vol. 162, No. 11, p. 32, 1978.
- Kleppe, P. J., Knutsen, P. C., Jacobsen, F., Oxygen/Alkali Delignification at Medium Consistency, Mill-Scale Trials to Commercial Installation, Tappi, Vol. 64, No. 6, p.87, 1981.
- Kobayashi, T., Hosokawa, J., Kubo, T., Kimura, Y., Effects of Multistage Ozone Bleaching Process of Pulp, Japan Tappi, Vol. 36, No. 6, p. 330, 1982.
- Kubo, T., Hosokawa, J., Kobayashi, T., Kimura, Y., On the Properties of Wastewater Produced in Ozone-Bleaching Kraft Pulp, Japan Tappi, Vol. 31, No. 2, p. 104, 1977.
- Kuenzler, E., Stone, K., and Albert, D., Phytoplankton Uptake and Sediment Release of Nitrogen and Phosphorus in the Chowan River, North Carolina, Report No. 186 to the Water Resources Research Institute of The University of North Carolina, September, 1982.
- Lang, E. W., Miller, R. L., Color Increase of Treated Kraft Mill Effluents, Proceedings of the 1977 Tappi Environmental Conference, Tappi Press, Atlanta, Georgia, pp. 117-124, 1977.
- Lathia, S. and Joyce, T., Dewatering Characteristics of a Sludge Derived from a Color Removal Process, Indian Pulp and Paper, Vol. 33, No. 4, p. 13, Dec. 1978-Jan. 1979.

- Lent, D. S., Treatment of Power Laundry Wastewater Utilizing Powdered Activated Carbon and Cationic Polyelectrolyte, Proceedings of the 30th Industrial Waste Conference; 1978 May 6-8; Lafayette, Indiana. Purdue University. c1977. p. 751-759.
- Libby, E. C., Editor, Pulp & Paper Science and Technology, Vol. I Pulp, McGraw-Hill, New York, 1962.
- Lindberg, S., Lund, L.-B., A "Nonpolluting" Bleach Plant, Tappi, Vol. 63, No. 3, p. 65, 1980.
- Lindholm, C.-A., Ozone Treatment of Mechanical Pulps. (1). Treatment at Low Consistency (1-3%), Paperi Puu, Vol. 59, No. 1, p. 17, 1977.
- Lowe, K. E., Chesapeake Launches Oxygen Bleaching, Pulp & Paper, Vol. 47, No. 10, p. 48, 1973.
- Lund, J. H., Cook, C. R., O₂ Delignification System is Successful at Eddy, Pulp & Paper Canada, Vol. 81, No. 1, p. 49, 1980.
- Lundahl, H., Mansson, I., Ett Milsonvardssystem for Blekerier, Svensk Papperstidning, Vol. 82, No. 5, p. 119, 1979.
- Lundahl, H., Mansson, I., Ultrafiltration for Removing Color from Bleach Plant Effluent, Tappi, Vol. 63, No. 4, p. 97, 1980.
- MacLeod, M., Evolution and Revolution in Pulp Bleaching--A Current Perspective, Pulp & Paper, Vol. 50, No. 5, p. 88, 1976.
- MacLeod, J. M., van Lierop, B., Fleming, B. I., Kubes, G. J., Bolker, H. I., The Bleachability of Kraft-AQ and Soda-AQ Pulps, Tappi, Vol. 65, No. 6, p. 113, 1982.
- Markham, L. D., Magnotta, V. L., O₂ Delignification at Medium Consistency Can Raise Yield, Cut BOD, Pulp & Paper, Vol. 55, No. 10, p. 139, 1981.
- McDonough, T. J., Simultaneous Brightening and Strengthening of GW, TMP, and High-Yield Bisulphite Pulp, Pulp & Paper Canada, Vol. 78, No. 12, p. 63, 1977.
- McDonough, T. J., Herro, J. L., The Influence of Low-Lignin Pulping Conditions on Bleachability, Tappi Journal, Vol. 65, No. 9, p. 117, 1982.
- McKean, W. T., Potential Pollution Loads from Oxygen Pulping, Proceeding of the Tappi Environmental Conference; 1976 April 26-29; Atlanta, GA, p. 17-21.
- Mechenich, C., Shaw, B. W., Roeder, T. S., Sources and Effects of Color in the Wisconsin River, Wisconsin, Technical Report, Wisconsin Water Research Center No. 80-09, 1980.

- Meguro, S., Sameshima, K., Sumimoto, M., Kondo, T., On Spent Liquor of Semichemical Pulping (V) Improvement of the Color Removal Efficiency by the Photochemical Treatment, Japan Tappi, Vol. 30, No. 8, p. 44, 1976.
- Melnyk, P. B., Judkins, D., Netzer, A., An Ozone Reactor for Color Removal from Pulp Bleachery Wastes, Tappi, Vol. 60, No. 3, p. 97, 1977.
- Milne, P. T., High-Temperature, Short-Retention Hypo Stage Cuts Chemical, Water Use, Pulp & Paper, Vol. 5, No. 3, p. 72, 1981.
- Moggio, W. A., Color Removal from Kraft Mill Effluent, Tappi, Vol. 38, p. 564, 1955.
- Moll, R., Centrifuge Plus Limits Lignin in Waste Water, Southern Pulp and Paper Manufacturer, Vol. 39, p. 14, 1976.
- Mortimore, R. D., Fleming, B. I., The Analysis of Anthraquinone in Pulping Liquors and Pulp Products by HPLC and TLC, Tappi, Vol. 64, No. 11, p. 114, 1981.
- Mutamore, E., Pichon, M., Monzie, P., Color Removal from Kraft Effluent by Ultrafiltration with New Polymeric Membranes, Svensk Papperstidning, Vol. 7, No. 16, p. 573, 1975.
- Naish, V. A., Sandilands, L. M., "Lime Treatment of Bleached Softwood Kraft Mill Effluents," Cooperative Pollution Abatement Research (CPAR) Project Report 475-1, March, 1977.
- Nasman, L. E. A. System Using Medium-Consistency Oxygen Bleaching Works In Sweden, Pulp & Paper, Vol. 55, No. 10, p. 137, 1981.
- Nasman, L., Annergren, G., Medium-Consistency Oxygen Bleaching, Tappi, Vol. 63, No. 4, p. 105, 1980.
- National Council of the Paper Industry for Air and Stream Improvement, An Investigation of Improved Procedures for Measurement of Mill Effluent and Receiving Water Color, Technical Bulletin No. 253, December, 1971.
- Nebel, C., Gottschling, R. D., O'Neill, H. J., Ozone Decolorization of Effluents from Secondary Treatment, Paper Trade Journal, Vol. 158, No. 3, p. 24, 1974.
- Nelson, P. J., Irvine, G. M., Puri, V. P., Higgins, H. G., Effect of Mild Oxidative Treatments on Eucalyptus Regnans Wood and on Derived CMP and CTMP, Tappi, Vol. 65, No. 8, p. 84, 1982.
- Ng, K. S., Mueller, J. C., Walden, C. C., Ozone Treatment of Kraft Mill Wastes, Journal Water Pollution Control Federation, Vol. 50, No. 7, p. 17402, 1978.
- Nicolle, F. M. A., Histed, J. A., Nayak, K. V., Removal of Color and Organic Matter from Kraft Process Bleach Effluents, U.S. Patent No. 4000033, 1976.

Nomura, Y., Quinone Additive Cooking, Japan Tappi, Vol. 34, No. 1, p. 50, 1980.

Nörrstrom, H., Chemical Pulping, Pure & Applied Chemistry Vol. 45, p. 181, 1976.

Obiaga, T., Ganczarzyk, J., Biological Removal of Lignin from Kraft Mill Effluents - Changes in Molecular Size Distribution, Tappi, Vol. 57, p. 137, 1974.

Oehr, K., Electrochemical Decolorization of Kraft Mill Effluents, Journal Water Pollution Control Federation, Vol. 50, No. 2, p. 286, 1978.

Okubo, K., Oki, T., Ishikawa, H., Bleaching of Thermomechanical Pulp by NaOCl/Ozone System and the Characteristic Properties of Bleached Pulp, Japan Tappi, Vol. 36, No. 8, p. 807, 1982.

Olsen, M., Luoma, D., Wallace, A. T., Grimestad, G., Percolating Effluent into Ground Reduces Color at Missoula Mill, Pulp & Paper, Vol. 50, No. 10, p. 142, 1976.

Overcash, M. R., Pal, D., Design of Land Treatment Systems for Industrial Wastes - Theory and Practice, Ann Arbor, MI: Ann Arbor Science, c1979.

Paerl, H., Environmental Factors Promoting and Regulating N₂ Fixing Blue-Green Algae Blooms in the Chowan River, North Carolina, Report No. 176 to the Water Resources Research Institute of The University of North Carolina, January, 1982.

Pfister, K., Sjöström, E., Characterization of Spent Bleaching Liquors. Part 1. Ultrafiltration of Effluents from Conventional and Oxygen Bleaching Sequences, Svensk Papperstidning, Vol. 81, No. 6, p. 195, 1978.

Pfister, K., Sjöström, E., Characterization of Spent Bleaching Liquors. (4). Composition of Material Dissolved During Hypochlorite Bleaching (CEH Sequence), Paperi Puu, Vol. 61, No. 6/7, p. 449, 1979.

Plummer, A. W., South, W. D., Minimizing the Pollution Impact of Kraft Pulping through Oxygen Bleaching, U.S. EPA Report, EPA 600/2 - 80 - 189, 1980.

Poots, V. J. P., McKay, G. Healy, J. J., Removal of Basic Dye from Effluent Using Wood as an Adsorbent, Journal Water Pollution Control Federation, Vol. 50, No. 5, p. 926, 1978.

Porter, J. J., Edwards, J. L., A Study of Comparisons of Three Membrane Separation Systems Relative to Discharge Water from Kraft Pulp and Paper Mill Process Streams, Southern Pulp and Paper Manufacturer, Vol. 40, No. 12, p. 24, 1977.

Rapson, W. H., Anderson, C. B., Kraft Pulp Bleaching with Chlorine and Chlorine Dioxide, Tappi, Vol. 61, No. 10, p. 97, 1978.

- Rapson, H., Anderson, C. B., Reeve, D., The Effluent Free Bleached Kraft Mill, Pulp & Paper Canada, Vol. 78, No. 6, p. 111, 1977.
- Reeve, D. W., The Effect of Chlorine Dioxide Substitution in the First Stage of Pulp Bleaching on Bleach Plant Effluent BOD, Pulp & Paper Canada, Vol. 82, No. 10, p.78, 1981.
- Reeve, D., Rowlandson, G., Kramer, J., and Rapson, H., The Closed-Cycle Bleached Kraft Pulp Mill - 1978, Tappi, Vol. 68, No. 8, p. 51, 1979.
- Renard, J. J., Phillips, R. B., Jameel, H., Rudie, A. W., New Opportunities for In-Plant Reduction of Pollutants through Process Changes, Tappi, Vol. 64, No. 8, p. 51, 1981.
- Rock, S. L., Bruner, A., Kennedy, D. C., Decolorization of Kraft Mill Effluents with Polymeric Adsorbents, Tappi, Vol. 57, No. 9, p. 87, 1974.
- Rothenberg, S., Robinson, D. H., Johnsonbaugh, D. K., Bleaching of Oxygen Pulps with Ozone, Tappi, Vol. 58, No. 8, p. 182, 1975.
- Rowlandson, G., Review of Oxygen Bleaching after 17 Months of Operation, Pulp and Paper Magazine of Canada, Vol. 74, No. 3, p. 74, 1973.
- Ruhanen, M., Dugal, H. S., First-Stage Bleaching of Softwood Kraft Pulp with Peroxide Instead of Chlorine, Tappi, Vol. 65, No. 9, p. 107, 1982.
- Rush, R. J., Shannon, E. E., Review of Color Removal Technology in the Pulp and Paper Industry, Environmental Canada Report No. EPS 3-WP-76-5, 1976.
- Samuelson, O., Wennergren, B., Purification of Bleach Plant Effluents by Adsorption on Crosslinked Polymers, Svensk Papperstidning, Vol. 80, No. 15, p. 477, 1977.
- Sameshima, K., Sumimoto, M., Kondo, T., The Color of Waste Liquor from Pulp Industry. VII. Color Reduction by Ultraviolet Irradiation Treatment, Journal of Japan Wood Research Society, Vol. 21, No. 3, p. 188, 1975.
- Sarkanen, K. V., Ludwig, C. G., Editors, Lignins: Occurrence, Formation, Structure and Reactions, New York, Wiley-Interscience, 1971.
- Schmidt, R. L., Joyce, T. W., An Enzymatic Pretreatment to Enhance the Lime Precipitability of Pulp Mill Effluents, Tappi, Vol. 63, p. 63, 1980.
- Serafin, J., Jamieson, A., Oxygen Bleaching at Husum, Sweden, Pulp and Paper Magazine of Canada, Vol. 73, No. 10, p. 81, 1972.
- Sethuraman, V. V., Raymahashay, B. C., Color Removal by Clays, Environmental Science & Technology, Vol. 9, No. 13, p. 1139, 1975.
- Seymour, G. W., How to Plan a Bleach Plant Control Strategy for Reducing Costs, Tappi, Vol. 63, No. 1, p. 23, 1980.

- Singh, R. P., Editor, The Bleaching of Pulp, Atlanta, GA: Tappi Press, 1979.
- Singh, R. P., Ozone Replaces Chlorine in the First Bleaching Stage, Tappi, Vol. 65, No. 2, p. 45, 1982.
- Sjöström, Eero, Wood Chemistry - Fundamentals and Applications, Academic Press: New York, 1981.
- Skopintsev, B. A., Decolorization of Infiltration Water under Natural Conditions, Water Resources, Vol. 8, No. 5, p. 558, 1981.
- Smith, K., Oxygen Bleaching System is One of Many Innovations at Mill in Norway, Pulp & Paper, Vol. 55, No. 10, p. 133, 1981.
- Smith, O. L., Soil Microbiology: A Model of Decomposition and Nutrient Cycling, Boca Raton, FL.: CRC Press, 1982.
- Spruill, E. L., Color Removal and Sludge Recovery from Total Mill Effluent, Tappi, Vol. 56, p. 98, 1973.
- Stensby, D. G., Harkin, J. M., Chemical Nature and Toxicity of Chlorophenol Derivatives Related to Pulp Bleaching, Wisconsin Water Research Center Technical Report No. 77-10, 1977.
- Svarz, J. J., Removal of Color from Paper Mill Waste Waters, U.S. Patent No. 4058458, 1977.
- Takagi, H., Kayama, T., Alkali-Dioxane Pulping (Part II). Bleaching with Ozone and Hydrogen Peroxide, Japan Tappi, Vol. 34, No. 2, p. 204, 1980.
- The Kline Guide to the Paper Industry, 4th edition, Fairfield, N. J., Charles H. Kline and Company Inc., 1980.
- Thomas, R. J., Wood Anatomy and Ultrastructure, Wangaard, F. F. Editor, Wood: Its Structure and Properties, University Park, penn., Penn State Univ. EMMSE Coordinator, 1981, p. 101-146.
- Timpe, W. G., Lang, E., Miller, R. L., Kraft Pulping Effluent Treatment and Reuse: State-of-the-Art, Environmental Protection Technology Series, EPA-R2-73-164, 1973.
- Tyler, M. A., Fitzgerald, A. D., A Review of Color Reduction Technology in Pulp and Paper Mill Effluents, Presented at 58th Annual Meeting, Technical Section, Canadian Pulp and Paper Association, 1972.
- Ullrich, H., Purification of Pulp-Bleaching Waste Water with Aluminium Oxide, Progress in Water Technology, Vol. 10, No. 5/6, p.89, 1978.
- Vincent, D. L., Colour Removal from Biologically Treated Pulp and Paper Mill Effluents, Canadian Cooperative Pollution Abatement Research Program, Project No. 210, Final Report, 1974.

- Virkola, N.-E., Would Anthraquinone be Economical in Your Pulp Mill?, Tappi, Vol. 64, No. 6, p. 51, 1981.
- Voss, R., Wearing, J. T., Wong, A., Pulp Chlorination in Relation to Bleaching Effluents, Pulp & Paper Canada, Vol. 81, No. 12, p. 133, 1980.
- Werthemann, D. P., Sulfide and Anthraquinone-like Catalysts Delignify Wood Via Different Chemical Mechanisms in Alkaline Pulping, Tappi, Vol. 65, No. 7, p. 98, 1982.
- Witherspoon, A., and Pearce, R., Nutrient and Multi-Species Criteria Standard for the Chowan River, North Carolina, Report No. 187 to The Water Resources Research Institute of the University of North Carolina, December 1982.
- Wong, A., Tenn, T., Dorica, J., Prahacs, S., Detoxification and Decolorization of Kraft Pulp Mill Effluents Using Activated Carbon, Pulp & Paper Canada, Vol. 78, No. 4, p. 37, 1977.
- Wong, A., LeBourhis, M., Wostradowski, R., Prahacs, S., Toxicity, BOD and Color of Effluents from Novel Bleaching Processes, Pulp & Paper Canada, Vol. 79, No. 7, p. 41, 1978.
- Worster, H. E., Pudek, M. F., The Effects of Oxygen Pulping on Toxicity and Colour of Effluent, Pulp and Paper Magazine of Canada, Vol. 74, No. 3, p. 95, 1973.
- Wright, R. S., Oswalt, J. L., Land, J. G., Color Removal from Kraft Pulp Mill Effluents by Massive Lime Treatment, Tappi, Vol. 57, p. 126, 1974.
- Yonekura, K., Operating Experience of Displacement Bleaching, Japan Tappi, Vol. 33, No. 1, p. 32, 1979.
- Zanella, E. F., McKelvey, R. D., Joyce, T. W., Effect of Anthraquinone on Toxicity and Treatability of Bleached Kraft Pulp Mill Effluents, Tappi, Vol. 62, No. 2, p. 65, 1979.
- Zanella, E. F., Joyce, T. W., McDonough, T. J., Acute Toxicity of Simulated Soda, Soda-Anthraquinone, and Soda-Anthraquinone-Borate Pulping Effluents, Tappi, Vol. 62, No. 10, p. 71, 1979.

