POLLUTION OF STREAMS FROM
PULP AND PAPER MILLS

No. 1207

Revised December 1956
POLLUTION OF STREAMS FROM PULP AND PAPER MILLS

By

E. R. SCHAFFER, Chemical Engineer

Forest Products Laboratory, 1 Forest Service
U. S. Department of Agriculture

Fiber and chemical wastes from pulp and paper mills may cause stream pollution if not properly controlled. Fiber wastes are contained in the so-called "white waters," which are fiber-bearing effluents resulting from the washing and screening of pulp or from the operation of the paper machines. Chemical wastes are present in the spent digestion liquors that are drained or washed from chemical pulps during production.

Although water containing these wastes does not present a health hazard to persons or land animals, it may be harmful to aquatic life. It may also become a nuisance because of odor, color, and creation of unsightly conditions. White-water wastes are objectionable because they contain insoluble components subject to a certain amount of decomposition. Under certain conditions, the materials in the white water may be deposited on the stream bed, and they may inhibit the normal growth of aquatic plant and animal life. In addition to fibers, white waters contain varying quantities of clay or other filler, organic dyestuffs, alum, and other chemical compounds.

The fiber in white water has a reuse value that is fully recognized by the pulp and paper industry, and extensive progress has been made in controlling this source of pollution. Save-all equipment has been developed to a high degree of efficiency, and white water is reused in place of fresh water for stock dilution and for machine showers in closed systems of operation. This reuse has been effective in reducing the pollution of streams from the fiber.

In mechanical pulping, the same methods of recovery of fiber and reuse of water can be employed as for recovery of white water from the paper mills.

The alkaline pulping processes, such as the sulfate process used for the manufacture of strong kraft wrapping papers and boards and the soda process used for the production of book and magazine papers, do not cause the serious pollution problems that acid processes do. Most of the spent liquors from the

1 Maintained at Madison, Wis., in cooperation with the University of Wisconsin.
alkaline pulping processes are concentrated and burned, and the alkali recovered
is reused in the process. A certain amount of the wash water goes into the
streams. This effluent consists of the tailings and very dilute spent liquors
containing so little chemical that recovery is unprofitable. Ordinarily, this
waste water causes no serious trouble if the recovery operation is functioning
properly. However, the large volume of effluent from a big mill may cause
pollution, particularly if the receiving stream does not have enough volume
and flow to dilute and aerate the waste. Some large sulfate pulp mills pond
the effluent in an oxidation lagoon from which the waste is discharged in regu-
lated amounts. Other mills use oxidation treatments similar to the activated
sludge sewage disposal systems, and some combine lagooning with treatment.

Other compounds, called mercaptans, are produced in sulfate pulping operations
and occasionally get into the waste waters. Mercaptans are sulphur ethers or
alcohols that are formed in the cooking process. They have a very disagreeable
odor and are poisonous to fish life if present in the water in any appreciable
amount. Concentrations greater than about one part per million are serious.
Beyond this concentration, the nervous system of the fish is seriously impaired,
and death eventually results. The quantity of mercaptans formed is small, and
only under exceptional conditions does their effect seem to be serious.

Another source of pollution from both sulfate and soda pulp mills is a sludge
produced in the causticizing of the recovered chemicals. The sodium carbonate
in this liquor is converted to caustic soda by treatment with calcium hydroxide
(hydrated lime) with a precipitation of calcium carbonate. This precipitate
is filtered off and must be properly eliminated. If it is washed into the
stream, it forms a calcareous deposit for some miles down the stream bed. How-
ever, the pulp mills have recognized this potential pollution, and most of
them either "burn" the carbonate sludge and recover the lime for reuse in the
process, or they dump the sludge at some point where only small quantities at
a time will get into the stream. This residue can be used for fertilizer,
and it is frequently either sold or given away to farmers for agricultural use.
In 1 or 2 mills, it is converted into whiting.

From a stream-pollution standpoint, the principal offender is the acid sulfite
process. In this process, sulphurous acid and a bisulfite are employed. The
principal bisulfite used is calcium bisulfite (lime base). Other bisulfites
used are magnesium bisulfite (magnesia base), ammonium bisulfite (ammonia base),
and sodium bisulfite (soda base). Fifty percent or more of the wood is dis-
solved in the cooking process, and the spent liquor produced contains a large
amount of carbohydrate material (sugars). When discharged into a stream,
these sugars increase the supply of food for bacteria, yeasts, and molds. The
rapid and enormous multiplication of these organisms quickly reduces the nor-
mal content of dissolved oxygen in the water adjacent to the mill until not
only the organisms but fish and other animal forms also perish. The spent
liquor will also impart to such waters an acidic condition and possibly intro-
duce poisonous compounds which can be harmful to aquatic life.
The injurious effects of waste sulfite liquor have long been recognized by the industry, and a determined effort has been made to solve this problem. In the early days, the efforts were directed principally toward development of useful byproducts that might offset recovery costs, and many such products have been produced. Spent sulfite liquor can be used in adhesives suitable for many purposes, in fertilizer, as a source of sugar from which alcohol and yeast can be manufactured, as the base of certain dyestuffs, in tanning compounds, and as an initial substance for the production of various other organic chemicals. Not many of these products, however, can be absorbed industrially in very large amount, and in many instances, their production from spent sulfite liquor is not economical because of other cheaper sources.

Some years ago, the West Virginia Pulp and Paper Co. perfected the Robeson process in which the liquors are neutralized with lime and concentrated in evaporators. This concentrate is used mainly for making adhesives. A large quantity of evaporated spent liquor is so used.

Nearly 75 million gallons of unconcentrated spent sulfite liquor are used annually in the United States for road binder. The use of the spent liquor in the manufacture of ethyl alcohol for motor fuel is common practice in Europe, but fuel alcohol cannot compete with gasoline in the United States. Although some alcohol is produced in Canada and the United States, the most practicable fermentation product to make in this country seems to be yeast for use in stock and poultry feeds. Two mills in the United States produce yeast. In the production of tanning agents, dyestuffs, and organic chemical compounds, the output from any one mill will often saturate the market.

Attention has been directed in recent years toward some means of utilizing the spent liquor within the mill, either as fuel or in the recovery of chemicals for reuse in the production process. Excellent progress has been made in this direction, especially at the Marathon Paper Co. mill in Rothschild, Wis., where the Howard process of spent sulfite liquor recovery was developed. This process is one of precipitation. The waste liquors from the blow pits are treated with a precipitant, which results in a deposition of calcium sulfite. This product is used in the preparation of bisulfite of lime and reused in cooking. The filtrate from the first step is treated with lime, which precipitates a large percentage of the lignin, presumably as lignin sulphonic acid residues. This material can be dried and used as boiler fuel in the plant, but it is more valuable in the production of vanillin and lignin derivatives. A third treatment of the filtrate provides the material used as a precipitant in the first step. At the present time, the only apparent disadvantage of the Howard process is the fact that some tailings with a biochemical oxygen demand still remain from the final precipitation. This demand is only about one-sixth of the original value, but it still can be objectionable in some instances. There is no question, however, that the Howard process is an excellent forward step toward the goal of spent sulfite liquor recovery and use.
Recently, improvements have been made in equipment for evaporating and burning spent sulfite liquor, although for many years, this was a difficult and apparently uneconomical means of disposal. The advantage of the evaporation and burning processes is that no waste other than very dilute wash waters from the blow pits gets into the stream. All of the oxygen-consuming components are destroyed. These processes have become practical because of the development of acid-resistant steels and high-velocity, reverse flow, evaporation equipment, which eliminate scale formation. The return is in the form of heat energy, which can be used for both process steam and operation of machinery.

The difficulties encountered in the evaporation of ordinary lime-base spent liquor have given impetus to the development of processes using the more soluble bases, such as soda, magnesia, and ammonia. These can be evaporated with a minimum danger of scale. However, the higher operating costs are likely to put these processes at a disadvantage with the ordinary lime-cook operation. For this reason, the soda-base process has not become established in this country. The magnesium- and ammonium-base processes are used to a limited extent. The economical use of the magnesium-base process requires that magnesium oxide be recovered. It has not been found practicable to recover the chemicals in ammonia-base spent liquor for reuse in pulping, although some other uses have been suggested for the recovered product.

Three semichemical pulping processes employ either solutions of sodium sulfite and sodium bicarbonate (neutral sulfite semichemical), sodium hydroxide and sodium sulfide (kraft semichemical), or sodium hydroxide only (cold soda semichemical). The chemical concentrations are lower and pulping conditions less severe than in chemical pulping. A smaller proportion of the wood is dissolved and the biochemical oxygen demand of the spent liquors is much less than in the chemical processes. Kraft semichemical and cold soda spent liquors can be combined with kraft and soda chemical pulping spent liquors and recovered in the usual systems. Neutral sulfite spent liquor can also be combined with kraft chemical pulping spent liquor up to about one-fourth of the recovery plant capacity. Semichemical plants not integrated with chemical pulping plants are confronted with more difficult problems in recovery.

In recent years, at least six processes have been developed for the recovery of sodium compounds from sodium acid sulfite and neutral sodium sulfite spent liquors. Some of these processes are in operation in a few mills, and additional installations are being made where the economics are favorable. Ponding of lime-base acid sulfite liquor has been employed for several years, but the practice has not proven successful in all cases. Soil filtration and pond seepage methods now being studied promise to be practicable where soil conditions are suitable.

The waste materials in the sewer waters of paper deinking plants also constitute a pollution problem. These materials consisting of the fillers, sizes,
coatings, and dyes may amount to as much as 40 percent of the weight of waste paper processed. The biochemical oxygen demand of deinking waste is a little lower than that of semichemical spent liquor. The principal offending materials are the suspended solids, which settle out on the stream bed if not removed beforehand. Several methods of removal are employed. The usual ones are sedimentation systems using various combinations of lagoons, settling tanks and basins, and vacuum filtration. The effluent is sometimes treated with coagulants before settling or filtering. From 40 to 80 percent of the suspended solids and from 25 to 50 percent of the oxygen demand are removed in these systems. The problem of disposing of the settled solids is often difficult. No reuse value has been found for the material, and the only present use is as low-grade land fill.

Streams and lakes are self-purifying, and their capacity to recover from oxygen depletion depends on the volume and rate of flow. The lowest amount of dissolved oxygen in a stream that will support fish life is about 3 parts per million in the Middle and Eastern States, and about 5 parts per million for cold-water fish in the streams of the Western States. To avoid development of critical conditions, the flow in a stream receiving the effluent from a sulfite pulp mill that produces 100 tons a day and has no spent liquor recovery should be at least as follows in Wisconsin:

<table>
<thead>
<tr>
<th>Temperature (°F.)</th>
<th>Flow (Cubic feet per second)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1,200</td>
</tr>
<tr>
<td>70</td>
<td>2,000</td>
</tr>
<tr>
<td>80</td>
<td>2,900</td>
</tr>
</tbody>
</table>

In most instances, stream flows well above these minimum values should be available. In addition, the use of methods to reduce the amounts of pollutional material discharged is generally highly desirable and perhaps a necessity. The minimum flow of streams receiving the effluent from other kinds of mills may be estimated by comparing the strength of the waste from that mill with the strength of the waste from a sulfite mill. The relative strengths of pulp and paper mill wastes are indicated by the B.O.D. values.

The 5-day biochemical oxygen demand test (B.O.D.) is a measure of the consumption of oxygen in the stream by a waste effluent. The following B.O.D. values expressed in terms of pounds of oxygen per ton of pulp produced give the relative polluting capacities of effluents from different processes:

<table>
<thead>
<tr>
<th>Process</th>
<th>B.O.D. (approximate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwood pulping</td>
<td>3-8</td>
</tr>
<tr>
<td>Kraft (sulfate) pulping</td>
<td>55-70</td>
</tr>
<tr>
<td>Deinking plant wastes¹</td>
<td>260-100</td>
</tr>
<tr>
<td>Sulfite pulping²</td>
<td>400-600</td>
</tr>
<tr>
<td>Semichemical (neutral sulfite) pulping²</td>
<td>125-275</td>
</tr>
</tbody>
</table>

¹Without recovery or treatment.
²Per ton of waste paper processed.

Rept. No. 1207
For comparison, the B. O. D. of municipal sewage is about 167 pounds per 1,000 persons. Acknowledgment is made to the Office of the Wisconsin Sanitary Engineer for supplying the stream flow and B. O. D. data. The review of this report by Theodore F. Wisniewski, Director, Wisconsin Committee on Waste Pollution, is greatly appreciated.