Industrial Waste Treatment Practice

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CHAPTER I

STREAM POLLUTION

The conservation of natural resources is one of the most important problems at present before this country. Some of the most serious phases of this problem are connected with waterway development and utilization. Stream-pollution control is an important part of the waterway-conservation program.

The idea of streams of pristine purity has long been abandoned. It is readily apparent that, even with more than reasonable protection, streams in populous areas will become polluted much beyond the point at which they may be used as a water supply without treatment. On the other hand, uncontrolled pollution may soon result in an economic and aesthetic loss to a community.

Some middle ground must be established in each case, where economy, utilization, and aesthetics may reach a proper equilibrium. This requires a delicate balancing of conditions and is not often easily accomplished.

The results of pollution and the self-purification of a stream that follows it are biological phenomena. The many factors involved, most of which concern processes of nature, make definite and precise control almost impossible. Standards imposed for one set of conditions may be impossible under another.

The control of stream pollution, therefore, requires a knowledge of the physical and biological processes involved. This knowledge is also invaluable to those concerned with industrial-waste treatment, since, as will be shown later, the sole object of the treatment processes is to relieve the stream of some of the burden of self-purification.

ORGANIC POLLUTION

The most common type of pollution is caused by the discharge of wastes that contain organic compounds either in suspension or in solution. This type of material predominates in domestic

sewage and most industrial wastes. Pollution from organic matter is caused by the decomposition of the organic compounds by the action of certain types of bacteria and other organisms. These organisms consume the organic solids and combine them with oxygen to produce the energy for their life processes. The reaction by which the organisms break down and utilize organic matter is known as "biological decomposition."

Anaerobic and Aerobic Decomposition.—Biological decomposition is commonly considered as being divided into two processes known as "anaerobic" and "aerobic." Actually the division is far from being definite and is a matter of degree or extent of decomposition rather than of distinct processes. Anaerobic decomposition is said to take place in the absence of elementary oxygen. Since the organisms causing the reaction require oxygen in the same way as do others, the oxygen is taken from the organic compounds. Organic matter is composed of carbon, hydrogen, oxygen, nitrogen, sulphur, and a few other elements. The removal of oxygen from these compounds leaves combinations of the remaining elements forming compounds, such as methane, hydrogen sulphide, ammonia, and others, having little or no oxygen.

Many of these products of anaerobic decomposition have distinct odors and are the usual cause of odor nuisances in polluted streams. The condition caused by a predominance of anaerobic decomposition products is said to be "septic." The active natural life of a stream is impaired and often destroyed by the toxic nature of the compounds produced by this type of decomposition.

Aerobic decomposition is said to take place in the presence of elementary oxygen, the aerobic process being largely a continuation of the anaerobic process. When oxygen is available, these two processes take place simultaneously; the products of the anaerobic process are immediately oxidized and are, therefore, not noticeable.

The final products of the aerobic process are stable compounds such as carbon dioxide, water, nitrates, and sulphates. These compounds have no further demand for oxygen. They have no odors and do not cause septic conditions. Their effect on the plant and animal life of a stream is exhilarating rather than inhibiting.

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These reactions are similar to the oxidation and destruction of organic matter in the soil. For their occurrence, it is necessary to bring together oxidizable organic matter, oxygen, and the oxidizing bacteria and other organisms. The organic matter and organisms are necessarily present in polluted waters. The elementary oxygen is the variable factor.

Oxygen, the Vital Element.—Oxygen, therefore, is the vital element for biological decomposition of an organic waste. When these wastes are discharged into stream water, the decomposition by the organisms starts immediately. If the oxygen in the water is sufficient for complete aerobic oxidation of the organic matter, stable final products will result. In this case no septic conditions will be apparent. If the oxygen is not sufficient, it will first be entirely depleted, after which the stream will become septic because of the formation of the products of anaerobic decomposition.

A very small amount of oxygen is required to produce a saturated condition in water. The saturation value depends on the temperature of the water, since more oxygen will dissolve in cold than in warm water. Table 2 shows the solubility of oxygen in water at various temperatures.

The rate at which oxygen will dissolve in water after it is partially or wholly depleted depends on the amount of oxygen present and on the area of the surface exposed to the atmosphere. The intensity of reaeration is a direct function of the lowering of the oxygen content—that is, the lower the oxygen content the more rapidly will reaeration take place. It is therefore most intense in badly polluted streams, for there the oxygen content may be almost entirely depleted by the action of the organisms.

Table 3 gives the rate at which oxygen will dissolve in water at various percentage of saturation. The rate is given in grams per square foot of surface per day and is best applied to water in a more or less quiet condition. Percentage saturation may be calculated by the following formula:

$$\text{Percentage saturation} = \frac{\text{dissolved oxygen in p.p.m.} \times 100}{\text{saturation value at given temperature}}$$

Although the rate of reaeration is greatest when the oxygen content is entirely depleted, yet it is obvious that a condition of depletion is undesirable. However, the lower the permissible

oxygen concentration the greater the proportion of the initial dissolved oxygen available for the oxidation reaction and the greater the capacity of the stream to absorb oxygen from the

TABLE 2.—SATURATION VALUE OF OXYGEN IN WATER

Temperature		Dissolved oxygen	
Deg. C.	Deg. F.	P. p. m.	Lb. per million gal.
0	32	14.62	122.3
1	33.8	14.23	119.0
2	35.6	13.84	115.8
3	37.4	13.48	112.5
4	39.2	13.13	109.5
5	41.0	12.80	106.9
6	42.8	12.48	104.0
7	44.6	12.17	101.5
8	46.4	11.87	98.9
9	48.2	11.59	96.5
10	50.0	11.33	94.5
11	51.8	11.08	92.4
12	53.6	10.83	90.4
13	55.4	10.60	88.4
14	57.2	10.37	86.4
15	59.0	10.15	84.6
16	60.8	9.95	83.0
17	62.6	9.74	81.1
18	64.4	9.54	79.5
19	66.2	9.35	78.0
20	68.0	9.17	76.5
21	69.8	8.99	75.0
22	71.6	8.83	73.7
23	73.4	8.68	72.5
24	75.2	8.53	71.2
25	77.0	8.38	70.0
26	78.8	8.22	68.6
27	80.6	8.07	67.4
28	82.4	7.92	66.2
29	84.2	7.77	65.0
30	86.0	7.63	63.7

atmosphere. It becomes important, therefore, to determine the minimum permissible oxygen content. This content practically fixes the capacity of the stream for self-purification and establishes the allowable pollution. The minimum oxygen content

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11.87	98.9
11.59	96.5
11.33	94.5
11.08	92.4
10.83	90.4
10.60	88.4
10.37	86.4
10.15	84.6
9.95	83.0
9.74	81.1
9.54	79.5
9.35	78.0
9.17	76.5
8.99	75.0
8.83	73.7
8.68	72.5
8.53	71.2
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7.77	65.0
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will vary in different streams or parts of the same stream, depending on the desired use to be made of the stream water.

The amount of oxygen necessary to prevent odors and nuisances is said to be about 2 p.p.m. That required for the support of slow-moving, bottom-feeding fish life is 4 p.p.m. For game fish, from 6 to 10 p.p.m. is required. The latter concentration is possible only in cold-water streams.

TABLE 3.—RATE AT WHICH OXYGEN DISSOLVES IN WATER

Percentage saturation	Oxygen dissolved, g. per sq. ft. per day	Percentage saturation	Oxygen dissolved, g. per sq. ft. per day
0	1.00	45	0.15
5	0.83	50	0.12
10	0.58	55	0.10
15	0.47	60	0.08
20	0.38	65	0.06
25	0.31	70	0.05
30	0.27	80	0.03
35	0.23	90	0.01
40	0.18	100	0.00

Another important factor in reaeration is the degree of agitation of the stream water. The rate at which oxygen is absorbed depends not only on the initial concentration but on the rate of vertical distribution. Oxygen absorbed on the surface will diffuse downward, and in time a condition is established in which the concentration varies from almost saturation on the surface to the initial content at some point below. The more quiet the water, the slower is this rate of diffusion, until in quiescent water an equilibrium is established, even at low oxygen concentration, at which the diffusion almost ceases. Mixing of the water after this period of quiescence causes an even distribution of the oxygen and allows absorption to proceed to a new equilibrium. It is apparent, therefore, that as the water becomes more turbulent the rate of reaeration increases, and the equilibrium of the oxygen concentration is established at a higher level.

The amount of oxygen available from the reaeration of a stream water is extremely variable and cannot be determined without extensive study. This resource must be taken into account,

however, in a determination of the self-purification capacity of a stream and requires an assumption based on known or determined factors.

SELF-PURIFICATION

The purification process in a stream takes place in a series of overlapping steps. These steps, more or less in the order of their happening, are as follows: (*a*) Wastes discharged into a stream may have an immediate oxygen demand because of the presence of compounds, such as hydrogen sulphide, calcium sulphite, etc., which unite chemically with oxygen. This reaction takes place within a short distance below the point of discharge. (*b*) Suspended material is deposited on the bed of the stream, causing the formation of sludge beds. (*c*) Colloidal and soluble material is precipitated biologically by the action of the stream organisms. Much of this material also settles on the stream bed and adds to the sludge deposits. (*d*) Anaerobic and aerobic decomposition of both precipitated and soluble material takes place with the depletion of oxygen. The organic matter is liquefied or gasified by the reducing and oxidizing action of the organisms.

Environmental Factors.—There are numerous factors affecting the self-purification of a stream. Since the process is largely biological, factors affecting the life of the organisms are most important. Each type of organism has a set of environmental conditions that are optimum for its growth and development. The kind of food, the amount of light, the temperature, and the quantity of oxygen are some of the controlling factors. These conditions are continually fluctuating.

Since the environmental conditions affect the organisms, the presence of any particular organism in unusual abundance is evidence of the existence of certain conditions that favor this organism. Thus, in an unpolluted stream, clean-water organisms predominate. Gross pollution caused by the discharge of waste materials results in the growth of gray fungus, bottom-feeding organisms of the scavenger type, and a large number of bacteria. As self-purification progresses, these give place to forms of blue-green algae, some diatoms, and certain chlorophyll-bearing organisms. Finally, as the stream approaches its normal condition, green algae appear along with a large variety of plankton, insect larvae, mussels, snails, and other clean-water organisms.

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This changing flora reflects the variations in food supply and oxygen content. To the student of biology these forms are indicative of the condition of the stream.

Sunshine and temperature affect the activity of the plant and animal life of a stream. Again, each organism has a condition of light and temperature to which it is best adapted. For instance, the activity of chlorophyll-bearing plants and animals is greatly

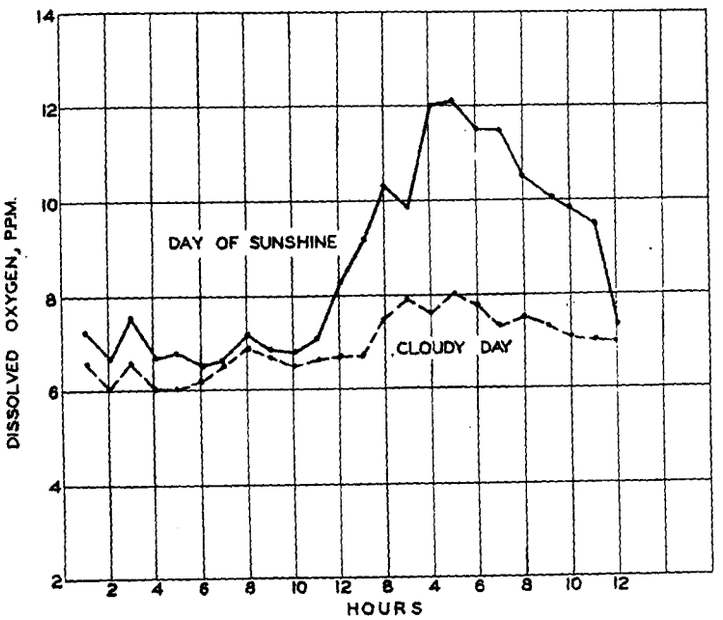

FIG. 1.—The effect of photosynthesis on the dissolved-oxygen content of stream water.

exhilarated by sunlight. The green algae are active producers of oxygen during daylight hours and help considerably in providing this agent of self-purification.

The effect of photosynthesis on the dissolved-oxygen content of stream water is shown by Fig. 1. These curves were prepared from the results of surveys made on the Illinois River by the Sanitary District of Chicago.

Temperature has a profound effect on most organisms. Usually the advent of cold weather results in a large decrease in number, although some thrive best during the cooler weather of

spring and fall. Very few withstand the cold prevalent during the winter in the northern streams.

During this cold weather, waste materials deposited in streams remain almost unchanged. These deposits accumulate until the warmer conditions of spring. Increased activity during this time places a considerable demand on the purification resources of a stream, although this condition is often relieved by high water. High temperatures and low water during the summer months result in an increase in the number and activity of the stream organisms and are largely responsible for the condition of polluted streams at that time.

Rate of Oxidation.—As has been previously stated, the rate of biological oxidation depends on time, temperature, and the activity of organisms. This process is not rapid even under optimum conditions. Table 4 shows the rate as the percentage of the total oxygen demand satisfied each day at 20°C., other conditions being favorable. The rate is comparatively high during the first 5 to 6 days but gradually decreases. From about 20 to 30 days is required for complete oxidation. The table was developed from Phelps's formula and applies to a specific set of conditions.

TABLE 4.—RATE OF BIOCHEMICAL OXIDATION

Days	Percentage of total demand	Days	Percentage of total demand
1	21	8	84
2	37	9	87
3	50	10	90
4	60	12	94
5	68	14	96
6	75	16	97
7	80	20	99

Figure 2 shows the effect of temperature on the rate of biochemical oxidation for various periods of time. Complete oxidation at 20°C. occurs in about 20 days. At 26°C. complete oxidation occurs in about 10 days, and at 28°C. in about 5 days. Temperatures higher than 28 to 30°C. are seldom obtained under natural stream conditions. Other factors that have a con-

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siderable influence on the rate of oxidation will be discussed later.

Sludge Deposits.—The solids deposited on the bed of a stream play an all-important part in the conditions caused by organic pollution. The critical zone in a polluted stream is usually

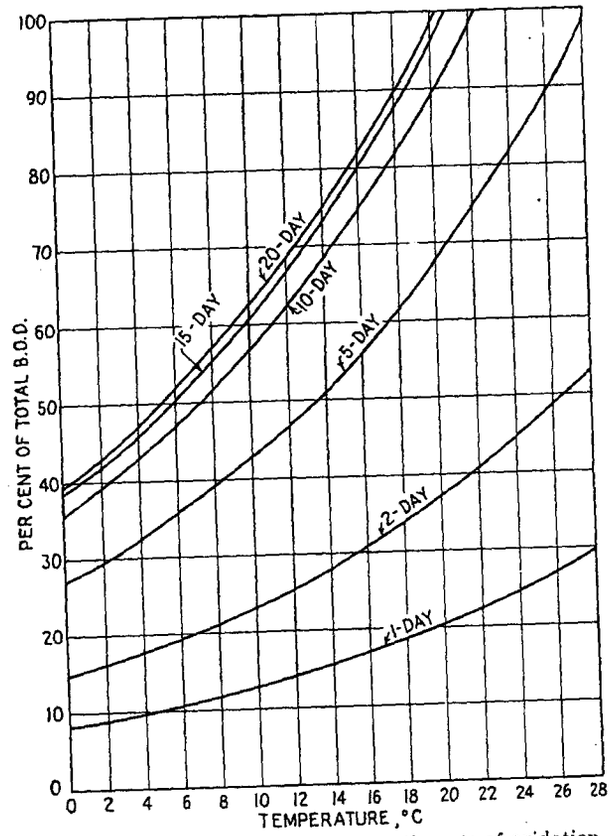

FIG. 2.—The effect of temperature on the rate of oxidation.

within a comparatively short distance below the source of the pollution. Suppose, as is usually the case, that this zone was located within 1 day's flow from the point of discharge of the waste. From Table 4 it is seen that only about 21 per cent of the total oxidation takes place in 1 day. If the materials discharged were soluble and moved at the same rate as the stream water, it would be necessary to supply oxygen in this zone for only 21 per

cent of the total demand. This is not the case, however, since much of the solid matter is deposited within this critical zone and undergoes almost complete oxidation there. Thus, in a free-flowing stream, the deposited solids exert from four to five times the effect on the oxygen resources within the critical zone as do the soluble solids.

Time Required for Self-purification.—The time required for the self-purification of a stream is variable and often indeterminate. Contrary to the layman opinion, there is no definite time or distance within which it can be said that a stream will purify itself. Some of the influencing factors have been mentioned, such as temperature and environment. Other factors are (*a*) the character of the waste causing pollution, (*b*) the dilution available, (*c*) the condition of the stream above the source of pollution, (*d*) rate of stream flow, and (*e*) obstructions in the stream bed, such as dams.

Some wastes cause conditions in a stream that are unfavorable to the activity of organisms even when oxygen, temperature, and other conditions are optimum. Acid or alkaline conditions inhibit organism development, and toxic materials may even destroy the organisms. Until these conditions are corrected by dilution or natural neutralization, the rate of active self-purification will be decreased.

If a large dilution with stream water is available, the intensity of self-purification processes is increased, other factors being favorable. More oxygen is supplied, a larger number of organisms are available in proportion to the food, and inhibiting compounds are less concentrated. The time required for self-purification is, therefore, decreased.

Stream water that is unpolluted prior to the entrance of the waste usually has a larger reserve of oxygen than stream water already carrying a considerable load of polluting material. However, a stream which is not grossly polluted but which carries some pollution develops a large number of active organisms that act rapidly on the newly discharged waste. Thus, the speed of self-purification may be greater in a stream that is slightly polluted above the point of the discharge of a particular waste than in one that has no pollution. Gross pollution, of course, is not favorable to self-purification and will lengthen the time required for the stream to return to normal.

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Obstructions in a stream bed favor the deposition of sludge and decrease the rate of reaeration. In general, such obstructions are not favorable to self-purification.

THE STREAM SURVEY

The stream survey, so far as the industrial-waste-treatment problem is concerned, is usually confined to the making of chemical, biological, and hydraulic observations to show the condition of the stream caused by the discharge of the waste. It is not usually expected that the results of such a survey serve as a basis for calculating oxygen balance, reaeration, and other technical factors.

Since oxygen is the vital element in self-purification, the first item in such a survey usually involves a determination of the oxygen resources of the stream. This comprises a measurement of stream flow, a test for the quantity of oxygen dissolved in the stream water (dissolved oxygen), and a determination of the amount of oxygen required to oxidize the organic matter (oxygen demand) in the stream above the point of waste discharge. For this purpose a sampling point should be selected at some convenient location above the entrance of the waste but below the source of other pollution.

Next, several other points should be selected below that at which the waste discharges. The selection of these points should be such as to show the effect of the pollution in question. In some cases it may be impossible to segregate the one source from other pollution that may enter the stream in the same vicinity.

Sampling points downstream should extend below the critical zone, which is usually the zone of lowest oxygen content. The location of this zone will vary with the temperature and stream flow.

The survey should be made during the season of the year when the conditions caused by pollution are at their worst. This is usually at a time when stream flow is at its minimum and temperature conditions are favorable for biological activity. Industries having seasonal operation should take this factor into consideration when selecting the survey period.

Stream conditions vary considerably during a 24-hr. period. The industry may operate only 8 hr. a day, and the waste may be discharged only during this time. However, the effect of the

waste continues over the entire day. For this reason samples should be taken at regular intervals over the 24 hr. A much more complete picture of actual conditions may be obtained from a few such 24-hr. surveys than from a large number of catch samples. Intervals of 2 hr. are usually selected for the survey unless conditions warrant shorter ones.

The samples should be taken at a point in the cross section of the stream that appears to be representative of the stream water. The point selected should be in the current and at about two-thirds of the depth of the stream at that point. This may not be possible if the stream is shallow. If the stream is large, it may be necessary to select more than one point in the cross section in order to obtain a true representation of the stream conditions. The selection of the sampling points is largely a matter of trial and judgment.

Usually two samples are taken, one for the dissolved-oxygen (D.O.) test and the other for the biochemical-oxygen-demand (B.O.D.) determination. The samples should be collected by means of the special sampling can shown on Fig. 77. Tests for dissolved oxygen must be made immediately upon collection of the sample. The sample for the B.O.D. test should be incubated for 5 days at 20°C., after which a D.O. test should be made on the incubated sample. If the stream is badly polluted, it may be necessary to dilute this sample prior to incubation. Methods for making these tests are given on pages 376 to 380. Temperature and stream-flow measurements should be made at the same time. In most cases one stream-flow measurement at each point during the day of the survey will suffice.

Visual observations sometimes are of value in such a survey. The records should include an estimation of the extent and depth of sludge beds; stream growths such as gray fungus, green algae, etc.; turbidity of stream water; odors; and any other condition typical of the type of pollution.

MEASUREMENT OF STREAM FLOW

The stream flow may be estimated or measured accurately according to the requirements of the particular survey and the equipment available. Usually an estimation is sufficient for the purpose since the flow of the stream is one variable that

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The stream flow is obtained by a determination of the area of a section of a stream and the average velocity of the water passing that section. The cross-sectional area is obtained by measuring or estimating the width and the average depth of the stream. It is usually calculated in square feet.

The velocity of flow may be estimated by timing the travel of floats over a short portion of the stream or, if a more accurate measurement is desired, it may be measured by use of a current meter. This value is obtained in feet per second. The two values are multiplied and the flow reported in cubic feet per second (c.f.s.). Cubic feet per second may be converted to gallons per time interval as shown in Table 5.

TABLE 5.—CONVERSION OF CUBIC FEET PER SECOND TO GALLONS

Gallons per second	= c.f.s. × 7.48
Gallons per minute	= c.f.s. × 449
Gallons per hour	= c.f.s. × 26,930
Gallons per day	= c.f.s. × 646,300

RESULTS OF POLLUTION SURVEY

Figure 3 shows the results of a typical pollution survey. This survey was made by the Michigan Stream Control Commission on the Grand River at Jackson, Mich., prior to the installation of the municipal sewage-treatment plant at that city.

The first sampling point was selected above the city and several miles above the entrance of the municipal sewage. At this point oxygen conditions were satisfactory (high D.O. and low B.O.D.). The second point was just below the city. The results at this point show the effect of the organic pollution from a population equivalent of more than 60,000. The B.O.D. is suddenly increased while the D.O. drops almost to depletion. These curves are plotted from the averages of a large number of analyses. At times the dissolved oxygen at point 2 was entirely depleted.

The drop in the B.O.D. from the second to the third point is due primarily to sedimentation: Sludge beds are formed over this section of the stream.

After a distance of about 20 miles, through which the stream flow increases considerably, the oxygen conditions start to

improve. Here the two curves again cross. Almost complete recovery is shown at a point from 30 to 35 miles below the city. Another source of pollution is indicated near the end of the curves by a drop in the D.O. and a slight increase in the B.O.D. This pollution results from the discharge of sewage from a city of about 3,000 population. The conditions caused by this pollution are not pronounced because of the large stream flow at this point.

The results of the Jackson survey are typical of those of streams polluted by an organic waste. These surveys show the

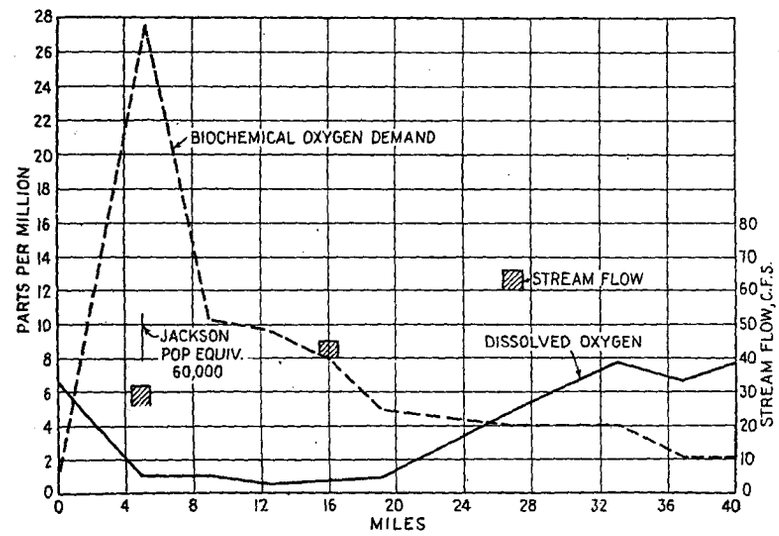

FIG. 3.—A typical pollution-survey curve.

degree of pollution and indicate the amount of treatment required. In the case of Jackson, it was necessary to install complete treatment facilities for the municipal sewage before stream conditions were satisfactory.

The object of any treatment plant in which an organic waste is treated is to relieve the stream of the burden of oxidation of the organic matter in the waste. This may be accomplished in a number of ways. One of the primary treatment processes is the removal of settleable material by sedimentation. The process may be assisted by the addition of some chemical to coagulate and carry down a larger portion of the suspended solids. In many

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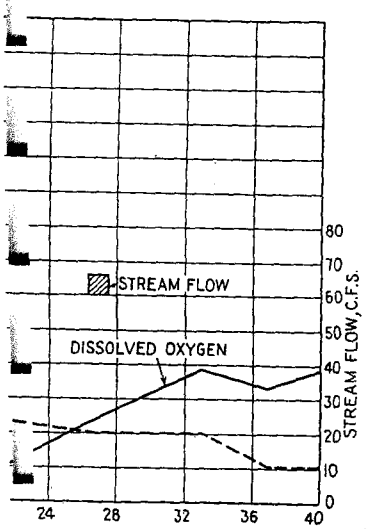

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Oxidation of finely divided suspended matter and soluble organic compounds constitutes a secondary method of treatment. Natural processes are employed in the treatment plant by the development of active organisms in specially designed treatment units. Treatment processes and the structures employed will be discussed in detail in Chap. III.

CHAPTER II

CHARACTERISTICS OF INDUSTRIAL WASTES

The composition of industrial wastes varies not only with the type of industry but with the processes used within the same industry. Even in the same factory both the composition and volume of waste may vary widely within a period of a few minutes. Some industries, notably the tanning industry, employ the batch process, by which the periodic dumping of vats and tanks causes extreme variations in the composition of the wastes.

A discussion of industrial-waste characteristics must therefore be more or less general. For true values, each factory must be made the object of a careful study, sometimes extending over long periods in order to take into account seasonal variations and other factors that may affect the composition of the waste.

CLASSIFICATION OF INDUSTRIAL WASTES

Industrial wastes have been classified in many ways, usually according to their composition. One of the more general arrangements classifies them into two groups: (*a*) those which show promise of utilization for profit and (*b*) those for which there is no apparent use.

Wastes That May Be Utilized.—The wastes of the first group, those which may be utilized, are becoming fewer in number as industry gradually comes to the conclusion that "waste is extravagance." In the past, industries have thrived in spite of waste. Many of the same manufacturing processes remain, and any means of stopping waste is disparaged as theoretical because it did not enter into the practice of earlier generations of the industry. The importance of recognizing unnecessary waste is growing as competition cuts profits and, in order to live, an industry must save and make use of all available resources.

The following are some of the wastes that may be included in this group.

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1. Sulphite liquor from wood-pulp mills
2. White water from paper mills
3. Tan liquor from vegetable tanneries
4. Blood wastes from packing plants and slaughter houses
5. Steffens wastes from beet-sugar factories
6. Certain wastes, from chemical plants, that contain valuable materials
7. Oil wastes from some industries
8. Acid pickling liquors
9. Those wastes that contain an appreciable amount of fertilizer ingredients
10. Skim milk, buttermilk, and whey from milk-products factories

One of the specifications for wastes of this group is that they be utilized for profit. There is a considerable difference of opinion as to what constitutes profit in the utilization of a waste. This determination would be rather simple if it were a matter of adding up the costs of processing and comparing them with the market value of the products obtained and if the waste could be discarded, should the costs exceed the final value. Another consideration, however, enters into such a determination. Some of these wastes cannot be discarded without the creation of the problem of stream pollution or the production of a nuisance. Into the calculation of profit from utilization, therefore, must enter the cost of waste disposal, and this must be added to the value of the product obtained by the recovery processes. If the value of the product plus the cost of disposal exceeds the cost of processing the waste, this excess must be considered profit, although no actual gain in dollars and cents is shown.

Wastes That Require Treatment.—It is the second group of wastes which should have more of the attention of industry and for which standardized economical treatment methods are desired. These wastes are usually liquids containing waste materials in a more or less dilute condition of solution or suspension. It is by this dilute condition that they are classified in this group, since any materials of value are present in such small quantities that they cannot be economically recovered by known processes. Some of the members of this group have not been definitely placed, since pressure imposed on industry

for a reduction of waste often results in the development of processes whereby wastes that are normally of no value may be recovered for profit.

The second group may be further divided into at least three classes of wastes as follows: (*a*) those wastes in which organic compounds predominate and constitute the undesirable components; (*b*) those wastes which contain poisonous substances; and (*c*) those wastes which contain certain inert materials in such concentrations as to have undesirable features.

Some of the wastes may be placed in more than one of these classes, although in most cases one of the characteristics predominates and the waste is placed in that class. The following are the more important wastes of the three classes:

1. Organic wastes
   - *a*. Washings from condenseries, powdered-milk plants, dairies, creameries, and cheese factories
   - *b*. Wastes waters from beet-sugar factories (flume water and process water)
   - *c*. Tan-yard and beamhouse wastes from tanneries
   - *d*. Wash waters from canning factories of all kinds
   - *e*. Wash waters from killing floor and other sources from slaughter houses and meat-packing plants
   - *f*. Wastes from breweries and distilleries
   - *g*. Wash and process waters from pulp and paper mills
   - *h*. Liquid wastes from strawboard mills
   - *i*. Wash waters from laundries
   - *j*. Liquid wastes from textile and dye works
   - *k*. Wastes from cane-sugar mills
   - *l*. Waste waters from corn-products manufacture
2. Toxic wastes
   - *a*. Wash waters from metal plating
   - *b*. Pickling liquors and washings from metal-parts manufacture
   - *c*. Scrubber liquors and wash waters from gas-plant and coke ovens
   - *d*. Wastes from chemical-manufacturing plants
   - *e*. Drainage from coal and other mines
   - *f*. Brines and phenolic wastes from oil wells and refineries

3. Inert wastes
   a. Lime sludge from water-softening plants, beet-sugar factories, chemical-manufacturing plants, and other sources
   b. Oils and tars from oil wells and oil refineries
   c. Sawdust from saw mills
   d. Washings from gravel pits
   e. Stamp-sand washings from copper mines

Organic wastes contain varying quantities of carbonaceous, nitrogenous, and fatty materials. Each waste may contain one of these classes of compounds or a mixture of them, but usually certain definite compounds predominate. For instance, grease predominates in the wastes from certain meat-packing operations and in the washings from the treatment of wool and silk; highly carbonaceous material predominates in the wastes from starch and glucose factories, pulp and paper mills, and sugar factories; whereas nitrogenous compounds predominate in certain tannery wastes and slaughter-house killing-floor washings.

The poisonous nature of the toxic wastes is also due to specific compounds or mixtures that are characteristic of the particular waste. Cyanides and copper from plating-room operations, phenols and cyanides from gas plants, and acids from metal pickling are typical.

The predominating compounds in a waste determine in a large measure the treatment processes adapted to that waste. Each waste may require a different method of treatment, the object in each case being to reduce the objectionable characteristics. The general methods of treatment that are adapted to these characteristics of composition will be discussed later in this chapter.

VOLUME DETERMINATIONS

One of the most important characteristics affecting the treatment process and structures is the volume of the waste to be treated. The volume of waste governs to a considerable extent the size of units and hence the cost of the treatment plant.

Volume measurements are one of the first considerations when treatment of a waste is contemplated. These measurements are made at a time when the factory operations are at the peak; otherwise the treatment structures may not be sufficient to take

peak loads. Seasonal variation as well as daily and weekly variation must be considered.

Some industries have greatly increased operations during certain seasons of the year. These seasons often come during summer or fall, when pollution has its greatest effect. If this is the case, volume measurements are made at this time. Others, such as laundries, have periods during the week when the waste volume is greatest. Since treatment facilities are usually based on the maximum flow of waste, the volume at the peak periods is determined.

The method of measuring the volume of a waste must be adapted to the particular waste. Sewer and pipe lines at industrial plants are laid in every conceivable condition and position. It is often difficult to find a method that is adaptable. The methods that follow are preferred and are used whenever possible. They are adapted to different flows and have a wide range. These methods are used for temporary measurements. If permanent flow records are desired, commercial equipment is available for that purpose.

Timing Method.—The first method, which might be called the "timing" method, is adapted to very small flows (under 20 g.p.m.). It requires a condition in which the waste may be discharged into a pail or drum of known capacity. The method is outlined as follows:

1. Procure a drum of from 5 to 10 gal. capacity. If the capacity is not known, calibrate by using a gallon jug or some other suitable measure.
2. Time the filling of this drum by means of a stop watch or the second hand of an ordinary watch.
3. Fill at least three times, and take the average reading of the watch.
4. Make this measurement at least once each hour (preferably every 30 min.) over a period of time sufficient to establish the flow during peak production.
5. Calculate the hourly flow by means of the following formula:

$$\frac{\text{Capacity of drum, gallons} \times 3{,}600}{\text{Seconds to fill}} = \text{gallons per hour}$$

V-notch Weir.—The second method is adapted for flows from about 20 to 400 g.p.m. It consists of a weir box constructed

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at some convenient location in the sewer line. A suggested design for this box is shown in Fig. 4. The size of the box depends to some extent on the flow of waste. A convenient size is about 3 by 5 ft., with the weir placed about 18 in. from the outlet end. The weir may be made of 18-gauge galvanized iron, fastened to a plank partition. A 90-deg. notch is usually

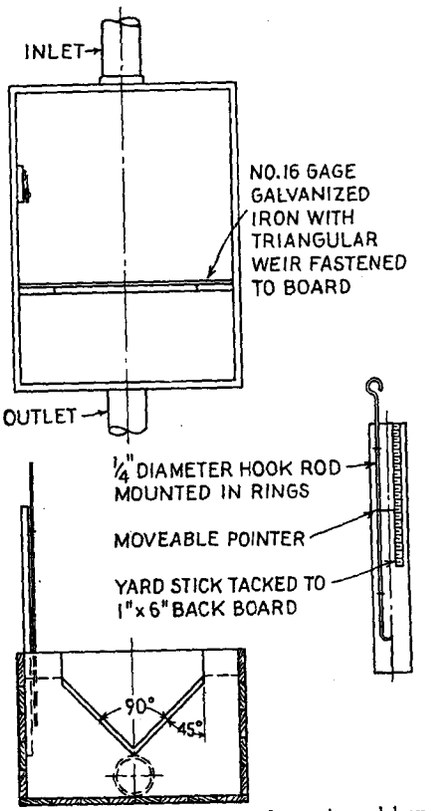

FIG. 4.—Design of a triangular weir and box.

used. In setting the weir, the notch should be higher than the outlet so as to give a free drop over the weir at all times.

The hook gauge shown in Fig. 4 provides a convenient way of measuring the head of water over the weir. The pointer on the hook is set to read zero when the water is just level with the apex of the notch. Measurements are taken by raising the hook until the point just breaks the surface of the water. The head

is indicated by the pointer. Table 6 gives the flow in gallons per minute for the head of water over the weir.

Care is taken to avoid a high velocity of approach from the inlet sewer. A dam or baffle in the box is often necessary to slow the velocity. If a water-level recorder is available, it is used to measure the head of water over the weir. If not, measurements are taken at regular intervals (30 min.) during daily operations and for a period of several days during peak factory operations.

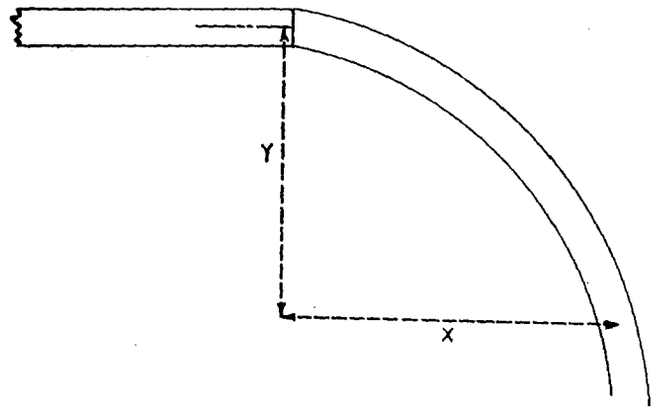

FIG. 5.—Sketch of coordinate measurement.

Coordinate Method.—The coordinate method is used to estimate the flow of waste from the end of a pipe. The measurements for x and y shown in Fig. 5 are made in the center and in the smooth portion of the stream leaving the pipe. The values are determined in feet or decimals thereof. If the flow is not constant, the measurements are made at intervals, as previously suggested for the weir readings. Greater accuracy is obtained if the x and y distances are large. The velocity of flow V_H is calculated by use of the formula

$$V_H = 4\frac{x}{\sqrt{y}}$$

In order to obtain the rate of flow, the section S of the pipe covered by the waste must be determined. If the pipe is running full, the section is constant. If not, it is determined by measuring the depth of water in the pipe and calculating the wetted section in terms of square feet or decimal thereof.

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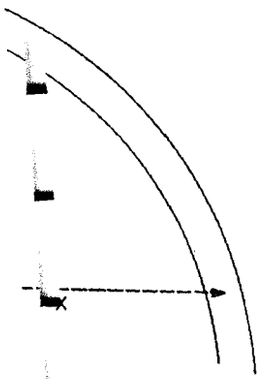

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Q (flow in cubic feet per second) $= V_H S$
F (flow in gallons per minute) $= 450 V_H S$

The complete formula for obtaining the flow in gallons per minute is

$$F = 1{,}800 \frac{xS}{\sqrt{y}}$$

TABLE 6.—RATE OF FLOW OVER 90-DEG. V-NOTCH WEIR

Head over weir, in.	Volume, g.p.m.	Size of sample, cc.
2	13	13
2½	24	24
3	37	37
3¼	45	45
3½	54	54
3¾	64	64
4	75	75
4¼	85	85
4½	101	100
4¾	115	115
5	131	130
5¼	147	150
5½	165	165
5¾	188	190
6	215	215
6¼	237	240
6½	250	250
6¾	274	275
7	300	300
7¼	326	325
7½	354	350
7¾	386	390
8	418	420

Rectangular Weir.—The third method of measurement is adapted to flows from about 100 to 4,000 g.p.m. It makes use of a rectangular weir of various widths set in a weir box similar to that just previously described for the V-notch weir.

The design of the box and the setting of the weir are shown in Fig. 6. The size of the box must be adapted to the flow, as is also the length of the weir. Table 7 shows the flow over rectangular weirs having no end constrictions. For weirs with end

constrictions, a correction must be applied to the length of the weir. This correction is $L - 0.2H$, where L is the weir length in feet and H is the water head in feet. In applying this correction, the values given in Table 7 for a 1-ft. weir are multiplied by the corrected length. For example, if the head of water over a 2-ft. constricted weir is 9 in. (0.75 ft.), the correction for

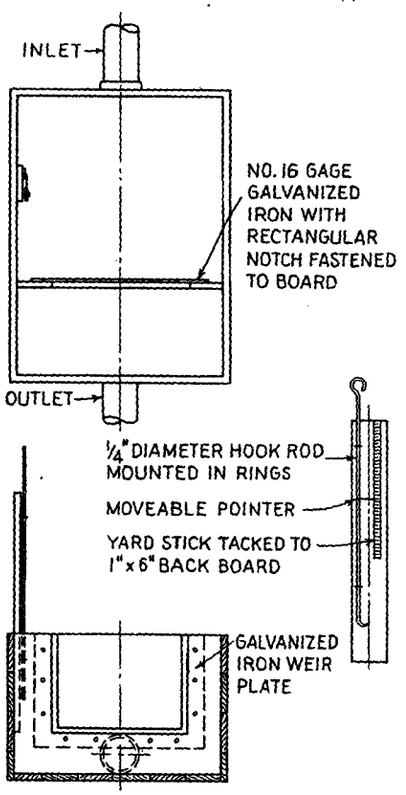

FIG. 6.—Design of rectangular weir and box.

length is $2.0 - (0.2 \times 0.75) = 1.84$ ft. The flow over a 1-ft. weir under a 9-in. head is 972 g.p.m. Then the flow over the above weir is $972 \times 1.84 = 1{,}788$ g.p.m.

The head of water over the weir is measured by means of a hook gauge, as previously described. Sometimes the reading of the gauge is difficult because of the turbulence of the water in the box. In such cases, the hook is set in a well or protected

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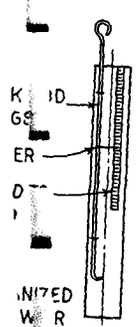

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by means of a baffle. The measurement is made in the manner previously described for the V-notch weir.

A clock gauge or water-level recorder may be used to record the head of water and is preferred to manual periodic readings, since it provides a continuous record. It may be used with either the V-notch or rectangular weirs.

TESTING WASTES FOR COMPOSITION

The testing of an industrial waste for composition may be divided into two distinct steps: (*a*) the collection of the samples; (*b*) the analysis. Each is of equal importance, and the same care must be taken in the collection of the samples as is used in following the analytical procedures.

Collection of Samples.—The sampling operation must be executed with proper precautions to secure representative samples, since they must contain all the characteristics of the larger volume of waste. Too often the error in sampling is inconsistent with the accuracy of the determinations made in the laboratory. It is seldom sufficient to rely on the results of a single ("grab") sample unless the waste to be sampled is in a container or tank and can be uniformly mixed. It is more often necessary to use a composite sample made up of a number of individual or composite samples. Good judgment must be used in any case in selecting the sampling methods, the selection of the method often being influenced by the laboratory facilities available. It is evident that the results of a laboratory analysis, however accurate that analysis may be, cannot represent an accuracy for the material sampled of a greater degree than the accuracy with which the sample was taken.

In the collection of representative samples, the following points must be taken into consideration:

1. The laboratory examinations to be made. These influence the size of sample to be collected, since some tests require larger samples than others. Also, some tests, like those for dissolved gases, must be made immediately following the taking of the sample and cannot be made on samples that have been composited over a long period of time.
2. The use to be made of the results of the analysis.
3. The character of the material sampled and the variation in character over the period of sampling. Some wastes, such as

TABLE 7.—RATE OF FLOW OVER RECTANGULAR WEIRS
(Gallons per minute)

Head over weir, in.	Width of weir				Size of sample, c.c.
	1 ft.	2 ft.	3 ft.	4 ft.	
1	48	96	144	192	24
1¼	50	100	150	200	25
1½	66	132	198	264	35
1¾	83	166	249	332	40
2	101	202	303	404	50
2¼	121	242	363	484	60
2½	143	286	429	572	70
2¾	165	330	495	660	80
3	187	374	561	748	95
3¼	212	424	636	848	105
3½	227	454	681	908	115
3¾	263	526	789	1,052	130
4	288	576	864	1,152	145
4¼	317	634	915	1,268	160
4½	344	688	1,032	1,376	170
4¾	374	748	1,122	1,496	185
5	398	796	1,194	1,592	200
5¼	434	868	1,202	1,776	215
5½	465	930	1,395	1,860	230
5¾	496	992	1,488	1,984	245
6	530	1,060	1,590	2,120	265
6¼	563	1,126	1,689	2,252	280
6½	596	1,192	1,788	2,384	300
6¾	631	1,262	1,893	2,524	315
7	667	1,334	2,001	2,668	335
7¼	705	1,410	2,115	2,820	350
7½	740	1,480	2,220	2,960	370
7¾	778	1,556	2,334	3,112	390
8	816	1,632	2,448	3,264	410
8¼	850	1,700	2,550	3,400	425
8½	890	1,780	2,670	3,560	445
8¾	930	1,860	2,790	3,720	465
9	972	1,944	2,916	3,888	485
9¼	1,014	2,028	3,042	4,056	505
9½	1,055	2,110	3,165	4,220	525
9¾	1,098	2,196	3,294	4,392	550
10	1,140	2,280	3,420	4,560	570

ECTANGULAR WEIRS

)

	Size of sample, c.c.
4 ft.	
192	24
200	25
264	35
332	40
404	50
484	60
572	70
660	80
748	95
848	105
908	115
1,052	130
1,152	145
1,268	160
1,376	170
1,496	185
1,592	200
1,776	215
1,860	230
1,984	245
2,120	265
2,252	280
2,384	300
2,524	315
2,668	335
2,820	350
2,960	370
3,112	390
3,264	410
3,400	425
3,560	445
3,720	465
3,888	485
4,056	505
4,220	525
4,392	550
4,560	570

those from the beet-sugar industry, are fairly constant in the amount and character, even over long periods. Others, such as those from the tanning industry, vary widely and rapidly because of periodic dumping of vats of concentrated materials. In the former case the individual samples of a composite need not be taken so often as is necessary in the latter case. Other waste characteristics will influence the manner of sampling.

4. The variation in the rate of flow over the period of sampling. If the flow varies rapidly, samples must be taken much more frequently than is necessary when the flow is more constant. This variation also influences the size of the individual samples to be taken. If the composite sample is to be representative of the entire flow over a definite period of time, the individual samples must vary in size according to the relative flows at the time they are taken.

General directions for the collection of industrial-waste samples cannot be given, since the method must be adapted to the particular waste. The following suggestions will assist in establishing the method best adapted.

Samples are collected by means of dippers or cans with a wide opening. Narrow-mouthed samplers may prevent the entrance of suspended material. The samplers may be made of various capacities to conform to the flows from which the individual samples are taken. If a sampler of a definite size is used, the individual samples are measured before they are combined.

The last column on each of Tables 6 and 7 gives the suggested size of sample to be collected according to the flow over the respective weirs at the time of collection. Usually it is convenient to take these samples when the readings of the water head are made.

The samples are taken at a point in the flow of waste that is likely to be most representative of the entire waste volume at the time of collection. For instance, in a deep-flowing channel, samples are not taken by skimming the top or scraping the bottom. In such a case, a point about one-third of the way from the bottom is usually selected.

Each individual sample is deposited in a receptacle of sufficient size to hold the entire composite. If the nature of the waste is such as to decompose rapidly, the composite is kept at a low

temperature to inhibit bacterial action and prevent as much change in character as possible. A smaller sample for analysis may be taken from the composite after thoroughly mixing to keep the solids in suspension.

Individual samples are collected at least at hourly intervals over the daily operation period of the factory. If the flow and character of the waste varies to a considerable extent, the sampling periods must be more frequent.

Special methods of collecting samples are necessary for some tests, notably that for dissolved oxygen. These will be discussed later in Chap. XVII.

Organic-waste Testing.—The compounds present in organic industrial wastes are too numerous to mention, and in most cases making tests for specific compounds is impracticable. Usually the type of industry and the products used or manufactured will give some indication of the class of compounds to be expected in the waste. Where this is not the case, it may be necessary to examine the waste to determine the general character of these compounds before treatment methods can be adapted to them.

Organic compounds have one thing in common—they are capable of being decomposed biologically. As has been shown in Chap. I, this characteristic is responsible for the conditions produced when the waste is discharged into a stream. Many of the treatment processes adapted to organic wastes are biological in nature and take advantage of this common property of organic material.

Biochemical Oxygen Demand.—The B.O.D. test has been shown in the previous chapter to be a measure of the quantity of putrescible organic matter in a waste. This is the most important test made in organic-industrial-waste analysis. It is used for many purposes, among which are the following: (*a*) it determines the probable effect of the discharge of the waste to a stream, since it is a measure of the demand on the oxygen resources of the stream water; (*b*) it determines to a great extent the type of treatment to be applied to a waste; (*c*) it is used to establish the capacities of certain of the treatment units; (*d*) it is used to control the treatment processes and to measure the efficiency of the treatment.

The B.O.D. test is outlined and discussed on page 376.

Population Equivalent.—In order to compare the strength of an organic industrial waste with that of domestic sewage, use is made of the "population equivalent." This value is based upon a determination of volume and 5-day B.O.D.

The B.O.D. contributed by domestic sewage per capita of population has been found to average 0.167 lb. per day. The population equivalent is determined by calculating the pounds of 5-day B.O.D. per day contributed by an industrial waste and dividing by 0.167. The following formula may be used:

$$\text{Volume (gallons per day)} \times \text{p.p.m. 5-day B.O.D.} \times 0.00005 = \text{population equivalent of waste}$$

Solid Tests.—Most of the organic wastes contain matter in suspension. This material forms sludge beds in streams and exerts a continuing demand on the oxygen resources. The removal of the suspended solids from a waste is of primary importance. The suspended-solids test is, therefore, next in importance to the B.O.D. test in the analysis of a waste. The results of this determination also govern, to some extent, the type of treatment adapted to the waste, the capacities of certain treatment units, and the effectiveness of the treatment processes. The suspended-solids test is outlined on page 375.

The total-solids test, together with the suspended-solids test, shows the quantity of dissolved solids in a waste. This value is of importance, since it determines to some extent the necessity for treatment beyond the sedimentation of the suspended matter.

Both the suspended-solids and total-solids values include the quantities of inorganic as well as of organic material. Ignition of these solids at the proper temperature gives some indication of the amount of organic matter. The dissolved material usually contains the mineral matter from the water supply. The solids and loss on ignition tests are given on pages 375 and 376.

Other Tests.—The B.O.D. and solids tests are easily made and do not require a large outlay of laboratory equipment. They usually constitute the extent of the tests required for a waste analysis unless the waste is a new one and it is desired to know more of its characteristics.

The total- and organic-nitrogen tests are a measure of the nitrogenous material present in a waste, such as the proteins and intermediate decomposition products of proteins. Ammonia,

nitrite, and nitrate nitrogen tests are used to determine the degree of oxidation of nitrogenous compounds by certain biological-treatment processes. The nitrogen in the form of nitrates indicates complete oxidation. Ammonia nitrogen is an end product of anaerobic decomposition, and the nitrite nitrogen is intermediate between ammonia and nitrate. The ratio of the three values indicates the completeness of the oxidation process.

Fats are determined by extraction from the waste with ether. This test is of importance in determining the necessity for grease traps or skimming tanks as a part of the treatment process.

The oxygen-consumed test was used to a great extent prior to the introduction of the B.O.D. determination. This test is much less time-consuming, and the results are obtained in a much shorter time than is possible with the B.O.D. test. However, it does not give the total demand, since the chemical oxidizing agent (potassium permanganate) will oxidize carbonaceous but not nitrogenous material. It is used occasionally in conjunction with the B.O.D. test where an immediate indication of treatment-plant efficiencies is desired.

Other special tests are sometimes used in an organic-waste analysis but are of only special significance and will not be mentioned here.

Toxicity Tests.—The toxicity of an industrial waste is usually due to specific compounds or classes of compounds, and specific tests must be made rather than tests for the general characteristics of the compounds, such as is possible with organic wastes. The most common toxic compounds found in wastes from industrial plants are phenols, cresols and like compounds, cyanides, copper, acids, alkalies, sulphides, sulphites, arsenic, chromic acid, and chlorine. Outlines for the analysis of toxic wastes for the specific compounds or groups are given on pages 384 and 385.

PREDOMINATING CHARACTERISTICS

Although industrial wastes vary considerably in composition, as has been mentioned, each waste has some predominating characteristic. A detailed description of each of the wastes will be given in the chapters that follow as each industry is treated specifically. While dealing with waste characteristics, however, an enumeration of the predominating characteristic of some of the more important wastes may be of interest.

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1. The wastes from the milk industry are typically organic. They contain, in varying proportions, casein and other proteins, milk sugars, and fats. Such compounds indicate biological processes as means of treatment. Since the solids are mostly in true solution or colloidal suspension, sedimentation is not an important consideration. Some anaerobic or aerobic oxidation process is best adapted to such wastes.

2. The wastes from the straight-house beet-sugar factory are not typically organic, since they contain large quantities of inert soil and sand in suspension. The process waters contain some carbohydrates (sugars) in solution, but a major portion of the organic material is in suspension. This material may be either carbonaceous or nitrogenous. Because of the large suspended-matter content, sedimentation and sludge disposal are major problems. The Steffens process used in some beet-sugar factories produces a waste which is high in nitrogenous and carbonaceous compounds and which is very alkaline in reaction. This waste contains valuable by-products, a fact that indicates some type of recovery process.

3. Tannery wastes contain large amounts of inert inorganic material and nitrogenous organic compounds in suspension and some organic matter (tannins, etc.) in solution. The wastes contain both acid and alkaline properties, depending on the source. These characteristics indicate that neutralization and sedimentation must be primary methods of treatment with probable oxidation processes for the soluble material.

4. Cannery wastes probably vary more in typical characteristics than any of the other wastes. Each product canned has its characteristic waste. Many classes of organic compounds as well as both suspended and soluble materials are to be found. Biological processes are indicated as means of treatment but because of the short season may or may not be practical.

5. Slaughter-house and meat-packing-plant wastes are typically nitrogenous and fatty. Some of the material is in true suspension, but most of it is colloidal. These characteristics call for skimming devices and some method for coagulating and settling the colloids.

6. The wastes from breweries and distilleries are for the most part carbonaceous, although proteins are present in considerable amounts. Some of this material is in suspension, but the major

portion is in solution. Biological treatment by oxidation processes is indicated for this waste. Screening or sedimentation may be required as preliminary treatment for suspended-solids removal.

7. Paper-mill wastes contain, predominantly, cellulose and inert filler compounds in suspension. These characteristics indicate recovery where possible, followed by coagulation and sedimentation to remove the remaining suspended material.

8. The wastes from the pulp mills contain a large variety of compounds. Recovery processes may be applied to many of these wastes, especially those from the sulphate and sulphite processes.

9. Corn-products wastes contain starchy compounds, a major portion of which are in true or colloidal suspension. Recovery processes have been applied to these wastes in the past. Treatment processes consist of some type of coagulation and sedimentation as indicated by the predominating characteristics of the waste.

10. Metal-plating wastes contain toxic substances, the most important of which are cyanides, copper compounds, and acids. Metal-pickling liquors contain acids and iron compounds. Gas plants contain phenols and like compounds. These specific compounds have no general characteristics that give indications of the type of treatment adapted to them.

From the foregoing discussion of the effect of predominating characteristics on the type of treatment, it will be seen that, in general, biological treatment is indicated for organic wastes. However, other factors may have sufficient influence to cause a change in the treatment selected for any specific waste.

Solids in suspension call for sedimentation and sludge disposal. Solids in colloidal suspension require some type of coagulation, either biological or chemical, followed by sedimentation. Organic solids in solution may be treated by some form of biological oxidation.

Although the predominating characteristics of individual wastes influence the type of treatment, these are not the only factors governing such a selection. Other factors will be discussed in later chapters.

Industrial Waste Treatment Practice

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Michigan State College

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1942

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CHAPTER VII

TANNERY WASTES

Factories engaged in the tanning of leather are not so plentiful and are much more widely scattered than are those of some of the other industries. These factories are usually located in urban communities and in many cases have access to municipal sewer systems. However, the wastes produced during the process of tanning make necessary certain variations in the treatment processes adapted to the usual municipal sewage. In cases where the effect of these wastes is considerable, it is often necessary for the tannery to pretreat their wastes to some degree prior to discharge into the municipal system. If the tannery wastes predominate, it is usually necessary to provide separate treatment facilities.

Most tanneries are engaged in the tanning of hides from which the hair has been removed. The wastes from these operations are not so rapidly putrescible as are those from some other industries. Considerable solid material is discharged in the form of spent limes. These cause a precipitation of the material contained in the tan liquors which, when it settles in a stream, causes extensive sludge-bed formation. These beds do not ferment rapidly, and for that reason their effect on oxygen resources is not pronounced. However, because of the large amount of settleable material, the stream bed is soon filled, and aquatic life is driven from the vicinity.

There are a few tanneries, notably those processing sheepskins, in which the hair is not removed prior to the tanning operations. The wastes from such tanneries contain large amounts of grease and certain nitrogenous compounds and require a somewhat different treatment from operations in which lime is used for dehairing the hides. In the discussion that follows, the sheepskin tannery will be treated separately.

THE TANNING PROCESS

The object of the tanning process is to render the animal skin imputrescible and pliable. In most cases it is first necessary to

remove the hair from the skin, although some leather is tanned with the hair on.

The skins are received at the tannery in a dried and salted condition. They are soaked in water to remove the salt and to restore the skin to its original soft and permeable condition.

The hides are then soaked for some days in a milk-of-lime solution, to which alkaline sulphides may be added. The solution not only loosens the hair but also causes a swelling of the hide tissue so that it will more readily absorb the tan liquors. This process requires from 3 to 6 days.

The hair that has been loosened is scraped off by means of a dehairing machine. The dehairing process is often preceded by the removal of fleshings. After the hair is removed, it is generally necessary to follow with a defleshing operation to remove the remaining flesh, fat, and loose tissue.

For sole leather, the hides, after some washing in soft water or weak acid solution to remove the lime, are ready for the tanning process. Softer leathers require more thorough treatment to remove the lime and to soften the skin further. This is accomplished by treatment with certain chemicals and is known as the process of "bating." After dehairing and bating, the hides are ready for tanning and are kept in clear-water pools.

The tanning process consists of soaking the hides in extracts or solutions of various vegetable products containing tannins. These liquors are composed of infusions of hemlock or oak bark, chestnut wood, or quebracho wood. The compounds contained in these liquors have the power to combine with the skin fiber and convert it into leather. If strong solutions are first used, they act too violently and cause the skin to harden and become drawn and wrinkled. New skins are first treated with partly spent liquors that have been previously used for hides in a more advanced stage of tanning. As the process proceeds, they are transferred to the stronger solutions.

In the case of sole leather, the processes of dehairing and tanning may require from 6 weeks to 12 months for completion. The leather is then dried, smoothed, and pressed between rolls. Calfskins receive a much shorter tannage, after which they are treated with fats and oils to render them pliable and, to some extent, waterproof.

Many skins for the manufacture of special goods, such as shoe tops, gloves, etc., are tanned with solutions of chromium or aluminum salts. These metallic salts produce a more permanent and durable leather.

The tanning process is often followed by the application of dyes and other special treatment to produce the leather desired for certain types of goods. Figure 47 shows a flow diagram of a typical tannery using the vegetable-tan process. Figure 47*a* is a

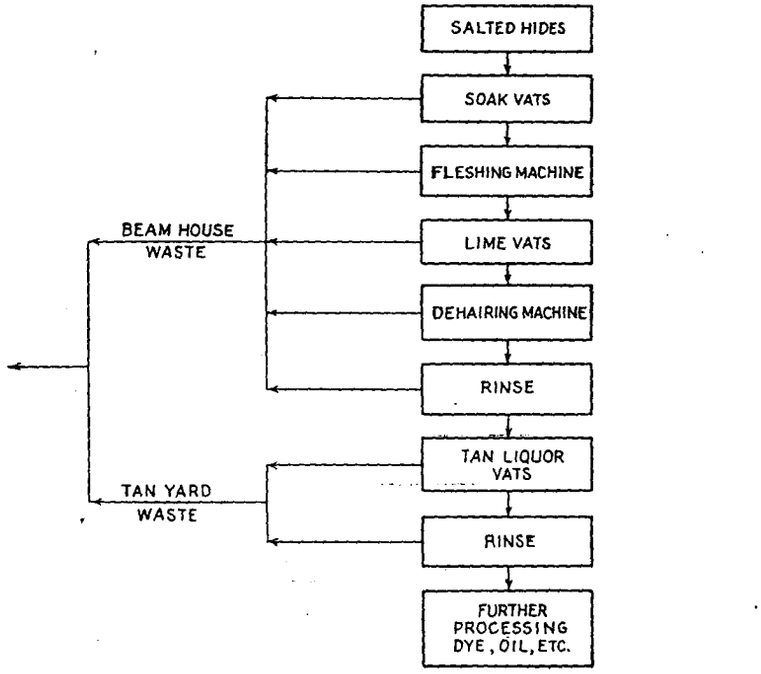

FIG. 47.—Flow diagram of a tannery using the vegetable-tan process.

flow diagram of a sheepskin tannery. The processes shown are subject to considerable variation for the production of special types of leather.

Most of the tanning processes are carried out in vats arranged in series. The hides are first placed in vats containing partly spent lime, from which they are moved progressively into stronger solutions. When the lime becomes too weak for further use the vat is emptied, and a new batch is made up. This vat then becomes the last in line, taking the hides that have been pre-

viously treated with the partially spent lime solutions. Operations having to do with the preparation of the hides for tanning are carried out in the beamhouse.

The vats in the tan yard contain the tanning liquors. These vats may be of the rocker or paddle type. The rockers are frames over which the hides are suspended. They move with a dipping motion up and down into the vat of liquor. The

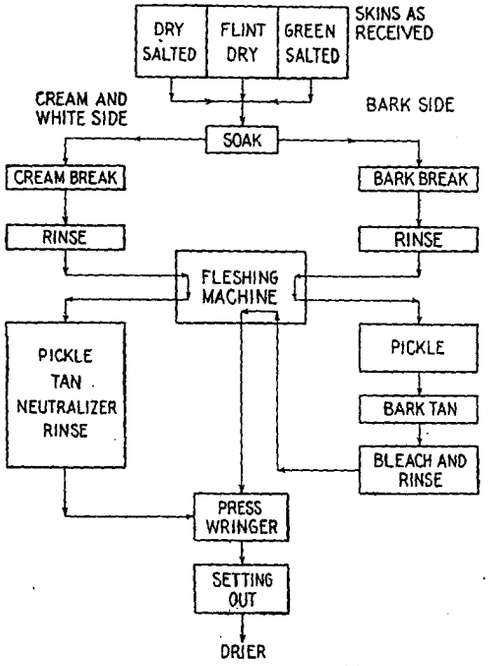

FIG. 47a.—Flow sheet of a sheepskin tannery.

paddles are rotating blades that continually move the hides about in the tan liquor.

SOURCES AND COMPOSITION OF WASTES

Since many of the tanning operations are batch processes, the wastes are produced intermittently by the dumping of the vats containing the various mixtures. Figure 47 shows the major sources of liquid wastes.

The first source of waste in the beamhouse is from the soaks. This waste is discharged intermittently and contains salt, dirt, dung, blood, and hair washed from the dried and salted hides.

The dumping of the lime vats produces a waste that in many cases contains up to 8 per cent solids. This material consists of spent lime (calcium carbonate and other calcium salts), some unspent lime (calcium hydroxide), calcium sulphide, hair, dirt, and the dissolved organic substances from the outer hide layers.

The warm-water wash is also discharged intermittently and is similar in content to the limes except that the waste material is in a much less concentrated form. The dehairing machine, fleshing machine, and washer have continuous discharges of wastes containing some lime, hair, fat, and fleshings. The clear-water pools also have a continuous discharge of wastes. These wastes are slightly milky in appearance because of lime but contain very little other material.

The worst single waste comes from the intermittent discharge of vats of spent tan liquor from the vegetable-tan process. This waste is dark brown in color, has an acid reaction, and contains a large amount of soluble organic material.

When chromium and aluminum salts are used for tanning, these wastes contain very little organic material but do contain a small amount of the metallic salts. They are usually turbid and will produce a floc of the metal hydroxides when mixed with the limes or with water containing some natural alkalinity.

"Finishing" in some cases produces a waste containing small amounts of sodium hypochlorite, sulphuric acid, and dyes. This waste is discharged intermittently. In addition to the wastes mentioned are the usual floor washings, which may contain any of the characteristics of the other wastes.

VOLUME AND STRENGTH OF WASTES

The volume of waste varies widely in the different tanneries. A survey of some 50 plants[1] showed the quantity to range from 230 to 1,790 gal. per 100 lb. of salted hides. The average is about 600 gal. per 100 lb. of hides. Howalt and Cavett[1] give the following distribution of wastes from the tannery at Instanter, Pa. (see Table 40): The average weight of a cow hide is about 60 lb., in which case the average volume of waste per hide is about 360 gal. The volume from a calfskin tannery has been reported at 75 gal. per skin and from a sheepskin tannery, at 4 gal. per skin.[2] From Table 40, it is apparent

that the major volume of waste (88.7 per cent) is produced in the beamhouse.

Table 41 shows the results of the analysis of wastes from 13 tanneries, most of which are located in Pennsylvania. The first 8 tanneries produce heavy leathers, such as soles and belting. The next 3 produce light leathers, such as shoe tops and sporting goods. These first 11 tanneries employ primarily the vegetable-tan process, although some mineral tan may be used. The last two are strictly chrome- or alum-tan processes.

The average 5-day B.O.D. of tannery waste is usually considered to be about 1,200 p.p.m. and the average suspended solids, about 3,000 p.p.m. The daily B.O.D. may vary from as low as 800 to over 2,500 p.p.m., and the suspended solids may range from 2,000 to 6,000 p.p.m. There is a considerable quantity of dissolved solids present in these wastes, as is shown by the difference between the total- and suspended-solids values given in Table 41. A major portion of this soluble matter is contributed by the vegetable-tan liquors.

Table 40 shows the distribution of strength, as measured by the B.O.D. test, through the various operations. Although the major volume of wastes comes from the beamhouse, these wastes contribute only 41.7 per cent of the B.O.D. The spent tan

TABLE 40.—DISTRIBUTION OF VOLUME AND STRENGTH OF TANNERY WASTES

Waste	Volume, per cent of total	B.O.D., per cent of total
Beamhouse:		
Soaks	7.4	4.3
Limes	2.2	8.3
Hot water	2.2	4.8
Dehairing machine	2.4	0.5
Wash	19.9	14.4
Fleshing machine	5.6	4.9
Clear-water pools	37.1	0.3
Hair wash	11.9	4.2
Total beamhouse	88.7	41.7
Spent tan	6.0	46.4
Bleaches	3.9	11.9
Floor wash	1.4	
Total	100.0	100.0

TABLE 41.—ANALYSIS OF COMBINED TANNERY WASTES

Number	Hides per day, lb.	Volume of waste, gal.	5-day B.O.D., p.p.m.	Suspended solids, p.p.m.	Total solids, p.p.m.	Color
1	.....	204,000	1,245	3,485	8,812	
2	36,000	283,000	1,281	4,131	9,827	3,400
3	20,000	92,800	1,672	4,230	13,980	8,000
4	18,000	69,100	603	1,449	5,236	1,150
5	19,500	85,700	1,221	4,574	9,557	7,250
6	21,000	110,000	1,490	2,030	10,970	5,900
7	25,000	126,000	1,523	3,238	7,467	4,180
8	22,500	82,650	2,082	5,297	14,702	3,950
Average*	23,100	131,660	1,390	3,554	10,070	4,830
9	.....	216,000	1,376	2,606	6,820	
10	15,000	160,000	1,460	2,292	4,714	5,000
11	4,700	32,765	1,223	1,619	3,238	5,550
Average†	9,850	136,280	1,353	2,172	4,924	5,250
Average‡	20,200	142,000	1,380	3,176	8,666	4,930
12	.....	600,000	612	1,887	5,876	
13	10,500	130,000	300	5,635	10,846	200
Average§	10,500	365,000	456	3,761	8,360	200

* Average of tanneries producing heavy leather (soles and belting).
† Average of tanneries producing light-weight leather (shoe tops and sporting goods).
‡ Average of all tanneries using vegetable-tan process.
§ Average of tanneries using chrome or alum tan.

liquors contribute 46.4 per cent of the B.O.D. from but 6 per cent of the volume. Beamhouse wastes contain over 90 per cent of the suspended material, the major portion of which is lime.

SEGREGATION OF WASTES

Segregation of wastes not requiring treatment from those that do is an important consideration in the treatment of most industrial wastes. It is often possible to reduce the volume to an appreciable extent and in this way decrease the cost of treatment units. Segregation of wastes in the tannery depends primarily upon the degree of treatment required, since all the wastes contain some polluting materials. If the stream receiving the tannery discharge is such as to require a high degree of removal of this material, all the wastes must be treated. If, however, some lesser degree is the requirement, such as the

removal of the major portion of the suspended matter by sedimentation, then some of the wastes may be segregated.

Table 40 shows that in the tannery from which these results were taken the clear-water pools represent 37.1 per cent of the total volume of waste but contain only 0.3 per cent of the material having an oxygen demand. In most cases this waste could be segregated unless it was required for dilution of the more concentrated wastes to facilitate the treatment processes selected.

It has been found that the wastes from some tanneries can best be treated by the segregation of all the weaker wastes and treatment of the more concentrated ones. At the Holland, Mich., tannery, the waste volume was reduced from 204,000 to about 70,000 gal. by selecting only the concentrated wastes for treatment. The desired degree of treatment in this case was the removal of suspended material. About 80 per cent of the suspended material in the total was contained in the 70,000 gal. of concentrated wastes. Another segregation at Holland that materially aided in the removal of solids was the ponding of the heavy limes. These limes contained about 7 per cent solids, which represents one-third the total weight of solids in the combined wastes. Since this is as thick a sludge as may be expected from the best sedimentation, there seemed to be no reason for mixing the limes with the other wastes.

An attempt to duplicate this plan at another tannery in Michigan was not so easily accomplished. At this factory the processes within the tannery were such that segregation was not feasible. Wastes that were low in solids represented but a small proportion of the total volume. The difficulties encountered in a change of the sewer system to effect the segregation more than offset the advantages gained by the reduction in volume.

These cases indicate that segregation is a matter of individual tannery conditions. A study must be made in each tannery to determine the feasibility of such a plan, both from the standpoint of the advantage gained in the treatment of the waste and from the standpoint of the economies resulting.

WASTE TREATMENT PROCESSES

There are a number of methods in use at the present time for the treatment of tannery wastes. The differences in the methods employed are largely due to an attempt to adapt the treatment

to the individual tannery. The following steps are accepted as generally applicable to most tanneries and especially to those using the vegetable-tanning processes.

For the removal of solids:

1. Segregation of clear-water pools if found to be practical from the standpoint of sewer arrangement
2. Ponding the discharge from the lime vats when the solids exceed 3 to 4 per cent
3. Screening of other beamhouse wastes
4. Storage and gradual discharge of vegetable-tan liquor
5. Mixture of the wastes in proportions that give optimum flocculation
6. Coagulation and sedimentation of the mixture
7. The drying and disposal of sludge

For further B.O.D. reduction:

8. Biofiltration of settling-tank effluent
9. Secondary sedimentation unless it is desirable to proceed to step 10
10. Chemical coagulation and sedimentation

SCREENING OF BEAMHOUSE WASTES

The wastes from the beamhouse contain a considerable amount of hair and fleshings. In addition to being troublesome in the operation of other treatment units, this material has some value and should be removed at some point prior to the sedimentation structures.

A fine screen of the rotary type has been used successfully for this purpose. This screen is covered with a perforated brass plate having $\frac{3}{32}$- to $\frac{1}{4}$-in. slots and is cleaned with jets of water under pressure. Provision is made for the draining and disposal of the material removed by the screen.

TAN-LIQUOR STORAGE

The spent tan liquors are usually discharged from the rocker pits during the early hours of the morning. These liquors are acid in reaction. Since this is the strongest of the concentrated wastes, it is sometimes evaporated when stream conditions do not permit its discharge even after passing through treatment processes. When this liquor is mixed with the alkaline beamhouse wastes in proportions equivalent to the daily flow from

each process, a precipitation of a considerable amount of the soluble organic material results. In cases where this waste is treated along with the other wastes, it is necessary to store the tan liquor and to discharge it slowly and evenly over the entire working day.

The storage tank may consist of a wood-stave tank of a capacity sufficient to hold the maximum daily volume of tan liquor. This waste is pumped into the tank from the pits. The rate of discharge is controlled by means of a weir box with a float-controlled valve arranged to maintain a constant head over the weir. The head is adjusted so as to empty the tank completely during the day. A slight excess capacity is desirable in order to provide for emergencies such as occur when a valve sticks or the weir becomes plugged. The line from the weir box leads to the mixing tank or trough into which the beamhouse wastes are discharged.

COAGULATION AND SEDIMENTATION

The high alkalinity and the nature of the organic matter in this waste is such that it does not decompose rapidly. The rate of oxygen utilization is slow as compared with that of many other organic wastes. For this reason the removal of suspended material and the consequent elimination of sludge beds from the streams into which the wastes are discharged is in many cases sufficient treatment to meet the oxygen requirements of the stream. In the discussion that follows, two methods for the removal of this suspended matter are given. This will be followed by suggestions for the secondary treatment of the settled effluents.

The first method involves continuous-flow coagulation and sedimentation. This principle is adapted to most tannery wastes but is not so easily controlled as is the second principle. The second makes use of fill-and-draw coagulation and sedimentation and is especially adapted to the treatment of the concentrated wastes from sole-leather tanneries. It is also used for the treatment of sheepskin tannery wastes, as will be described later.

Continuous-flow Sedimentation.—Figure 48 gives a suggested plan for a primary coagulation and sedimentation plant for tannery wastes using the continuous-flow principle. In this plan the beamhouse wastes flow into a screen chamber, where the

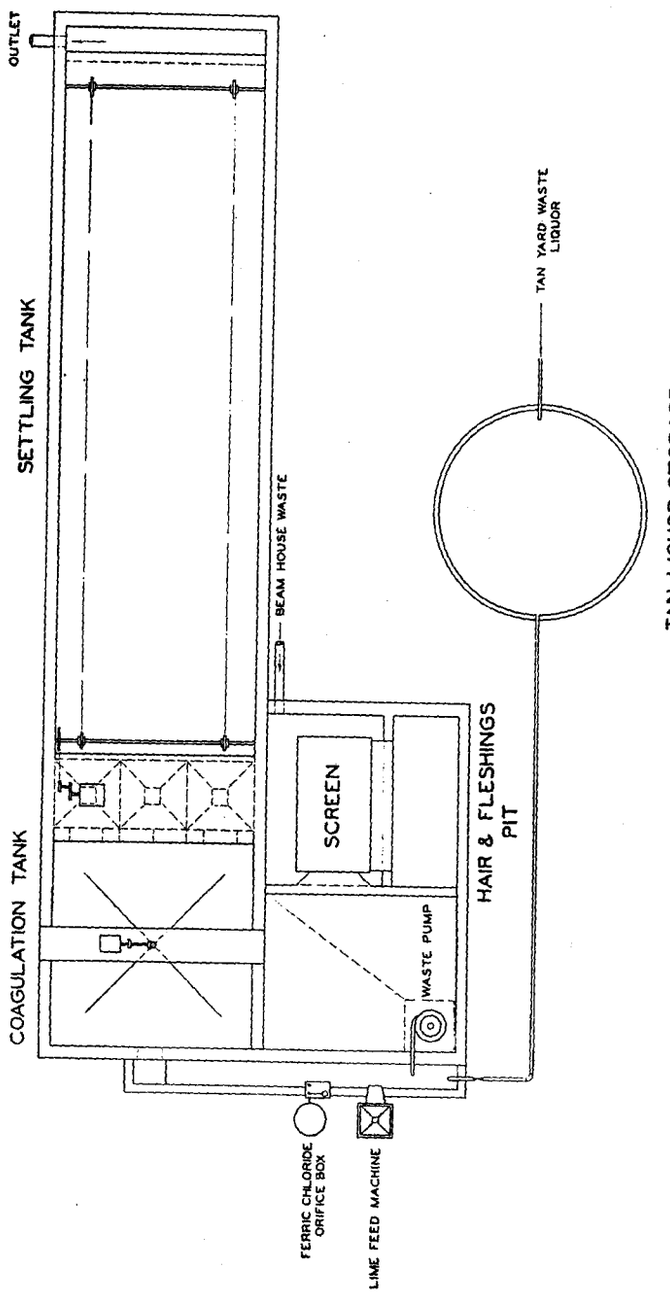

FIG. 48.—Plan for continuous-flow sedimentation of tannery wastes.

hair and fleshings are removed. The screened waste passes into a pump well, from which it is lifted by means of a vertical-type, nonclog centrifugal pump to a mixing box or flume.

Tan liquors are pumped to the tan-liquor storage tank, from which they flow by gravity to the upper end of the mixing flume and are mixed with the beamhouse wastes. Auxiliary chemical-feeding equipment is installed so as to discharge into the mixed wastes in the trough. This equipment is not necessary for all types of tannery wastes. It may be necessary in tanneries where the alkalinity of the beamhouse waste is not sufficient to neutralize the tan liquors completely, as, for example, in the sheepskin tannery, where the dehairing operations are not used.

The mixed liquors flow from the mixing trough into the coagulation tank. The purpose of this tank is to build up the size of the floc formed by the mixture of wastes or by the addition of the chemicals, as the case may be. The coagulation mechanism may consist of either the vertical- or the horizontal-type paddles. The horizontal type is shown in the drawing. The capacity of the coagulation tank is such as to give a 30-min. detention period for the maximum flow.

TABLE 42.—TANNERY WASTE-TREATMENT PLANT CAPACITIES
(Continuous-flow Sedimentation)

Maximum volume, gal. per hr.	Coagulation tank				Settling tank			
	Capacity, gal.	Length, ft.*	Width, ft.*	Depth, ft.*	Capacity, gal.	Length, ft.*	Width, ft.*	Depth, ft.*
25,000	12,500	16	16	7.5	50,000	64	16	7.5
30,000	15,000	17	17	8.5	60,000	68	17	8.5
35,000	17,500	18	18	8.5	70,000	72	18	8.5
40,000	20,000	18	18	9.5	80,000	72	18	9.5
45,000	22,500	19	19	9.5	90,000	76	19	9.5
50,000	25,000	20	20	9.5	100,000	80	20	9.5

* Dimensions are inside dimensions, including 18-in. freeboard above water line.

The sedimentation tank shown is the conventional rectangular type. Square or circular tanks may be used with equal success. A 2-hr. sedimentation period is provided. The capacity and dimensions of the coagulation and settling tanks are given in Table 42 and are based on various maximum hourly flows of

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ation)

	Settling tank		
[illegible]	Length, ft.*	Width, ft.*	Depth, ft.*
00	64	16	7.5
00	68	17	8.5
00	72	18	8.5
00	72	18	9.5
00	76	19	9.5
00	80	20	9.5

[illegible] above water line.

ventional rectangular
with equal success.
The capacity and
tanks are given in
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combined wastes. The settling tanks are equipped with a mechanism for the continuous removal of sludge.

The connection between the coagulation tanks is of such a size that the velocity of flow of waste does not exceed 60 to 80 ft. per minute. If smaller connections are used, the increased velocity tends to break up the floc which is formed in the coagulation tank and lowers the efficiency of settling. The connection in the plan is by way of large ports in the dividing wall between the two tanks.

The volume of sludge produced varies from 5 to 9 per cent of the waste volume. The average is about 7 per cent. This sludge is drawn from the settling-tank hoppers by gravity, if the elevations are favorable. When necessary, it may be pumped. The sludge pump is of the open-impeller, nonclog centrifugal type. It is set in a pit outside the wall of the settling tank in such a manner as to have a suction head of at least 3 ft. A pump with a capacity of 50 gal. per minute is satisfactory for all installations regardless of size. The rate of sludge pumping should not be greater than 50 gal. per minute, since a higher rate results in a thin sludge. Because of the presence of considerable hair and some fleshings that pass the screen, difficulties are encountered with clogging if the pump is too small. Much more satisfactory results are obtained by adjusting the speed of a large pump than by operating a smaller one at full capacity. The suction and discharge of the pump should be less than 3 in. and preferably should be 4 in. All sludge lines are constructed of 4-in. pipe.

The solid content of the sludge from continuous-flow sedimentation varies from 1 to 3 per cent. These solids are viscous and are inclined to be sticky. This characteristic is the cause of a difficult sludge-drying and -disposal problem, as will be discussed later.

Fill-and-draw Sedimentation.—The floc produced as a result of the mixing of the beamhouse and tan-yard wastes is very light, and much of it is held in suspension by the slight currents that may develop in the continuous-flow tanks. Fill-and-draw sedimentation results in a somewhat more concentrated sludge. The process, however, requires greater capacities and somewhat more operating attention. It is especially important that as much as possible of the clearer water be segregated when the

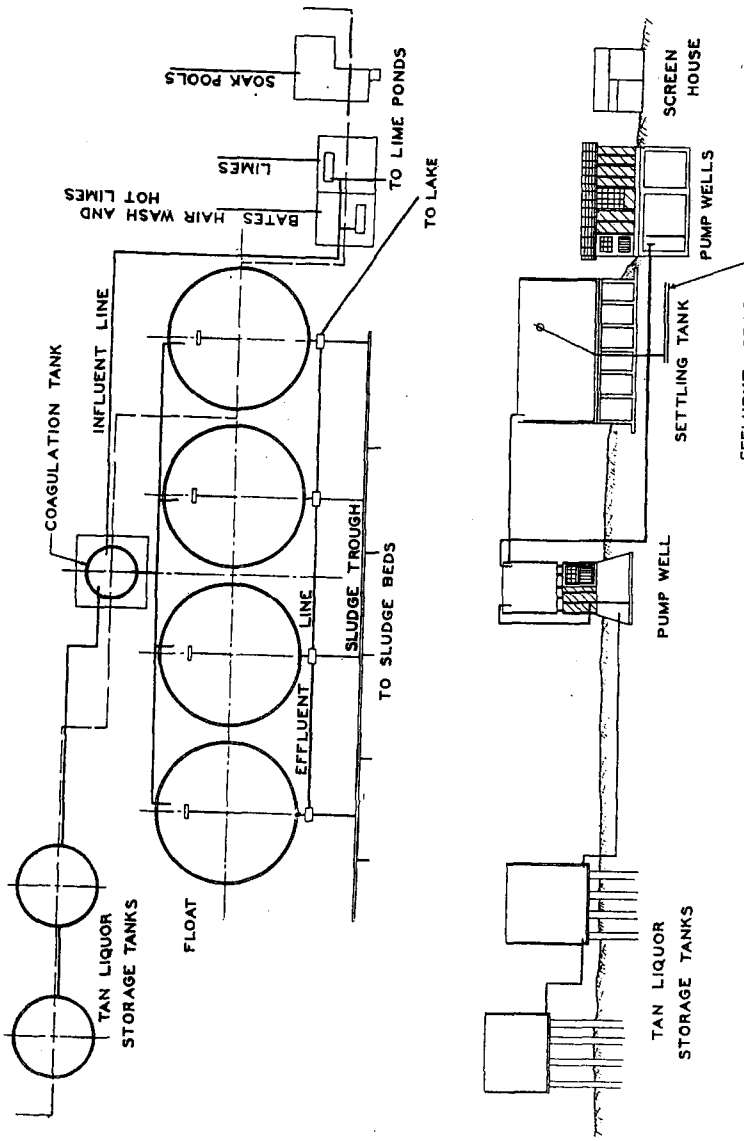

FIG. 49.—Fill-and-draw sedimentation plant for tannery wastes, Holland, Mich.

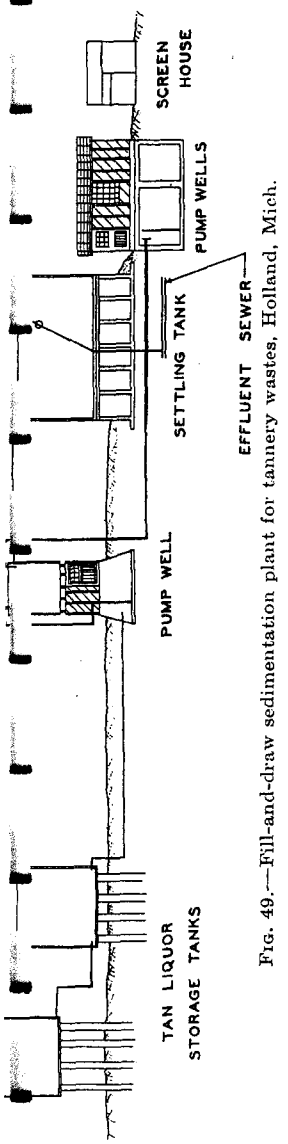

FIG. 49.—Fill-and-draw sedimentation plant for tannery wastes, Holland, Mich.

fill-and-draw principle is used, in order to decrease the required capacities.

Figure 49 shows the general arrangement of the units of the fill-and-draw coagulation and settling plant at the tannery in Holland, Mich. This plant is designed to handle 80,000 gal. daily of concentrated wastes consisting of soaks, acid and alkali-bleach liquors, hair wash, hot lime washes, and tan liquors. The spent limes are pumped to a lime pond.

Beamhouse wastes at Holland are segregated and then pumped to a continuous-flow coagulation tank, where they are mixed with the liquor from the tan-liquor storage tanks. These storage tanks are of wood-stave construction and have a combined capacity of about 40,000 gal. The wood-stave coagulation tank has a capacity of 5,000 gal. and a detention period of about 30 min. The coagulation mechanism consists of horizontal paddles operated on a vertical shaft.

From the coagulation tank the waste flows to any one of four wood-stave tanks through 10-in. cast-iron pipe lines. Each tank has a capacity of about 1 day's flow of waste. They are equipped with sludge draw-off lines leading from the bottom of the tank to sludge beds. The supernatant liquor is drawn by means of a skimming pipe attached to a swivel joint and is held in position by a float. This allows the withdrawing of the clarified wastes without disturbing the sludge.

Each tank is filled alternately and allowed to settle until the remaining tanks are almost filled. The clarified waste is then drawn to the lake. It was found that a more concentrated sludge was obtained if the sludge was allowed to remain in the tanks for several fillings. This decreased the detention period and caused some changes to be made in the operation schedule. However, since the sludge-disposal problem is a major item in plant operation, this method of decreasing the volume of sludge had a decided advantage. The same advantage could be had by designating one of the tanks as a sludge-concentration tank into which all the sludge would be pumped. Such an arrangement would allow a better control of the process, since the lower heavier sludge could be drawn as space was required. This would give a longer period for the lighter sludge to settle.

The settling tanks in this installation are constructed with flat bottoms, and considerable difficulty is experienced in the

FIG. 50.—Arrangement of units for the fill-and-draw sedimentation of tannery wastes.

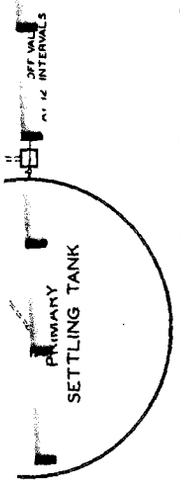

FIG. 50.—Arrangement of units for the fill-and-draw sedimentation of tannery wastes.

removal of sludge. Sloping-bottom tanks, although decreasing the capacity, would materially simplify the operation.

Figure 50 shows the general arrangement of units required for the treatment of tannery wastes by the fill-and-draw process. The main requirements for a plant of this type are as follows:

1. Segregation of wastes not containing an appreciable amount of suspended matter. These wastes may be added to the settled effluent for secondary treatment, if necessary, to meet B.O.D. requirements.

2. Screening of beamhouse wastes except the heavy limes. These may be ponded if they are high in suspended matter. There is usually sufficient alkalinity in the warm waters and other wastes to neutralize the tan liquors.

3. Storage of tan liquors and regulated discharge over the entire day.

4. A 30-min. coagulation period. This may be accomplished in a separate unit, as shown in Fig. 49, or the coagulation mechanism may be located in the settling tanks.

5. Two or more hopper-bottom settling tanks having a combined capacity of from one and one-half to two times the daily flow. These are connected to the coagulation tank by large-diameter pipe lines so that the floc is not broken up in passing between the tanks. Each tank has a sludge withdrawal line and a flexible floating effluent line.

6. A sludge-concentration tank having a capacity for about 4 days' sludge. This tank also has a sloping bottom. The sludge line leads from the bottom of the tank to the sludge beds or other sludge-drying media.

SLUDGE DRYING AND DISPOSAL

Sludge drying and disposal are two of the major problems, if not the two major problems, in connection with tannery-waste treatment. A high degree of suspended-solids removal can be obtained quite easily by the coagulating and settling units previously described. The main problem is the disposal of the large quantity of fairly thin sludge that is obtained.

There are various ways by which the sludge may be handled. Each of these has disadvantages.

Probably the most commonly used method is that of ponding the sludge in a series of large storage lagoons, where it will

eventually decrease in volume and become fairly dry. It is then removed by means of shovels and trucked away to some final disposal site.

In some cases the wet sludge is drawn directly into a tank truck and hauled immediately to the dump. This is an expensive method of handling, but, where land is not available for ponds or beds, it may be a necessity.

The sludge dries slowly on sand beds. Such beds may or may not be underdrained. The underdrainage system is of little value, since the sludge soon plugs the sand and very little water escapes by seepage. Skimming pipes are provided for the removal of the clear water that collects on top of the sludge. The pipes are swiveled and are controlled entirely by hand. The water drawn from the beds by the skimming pipes is returned to the raw waste.

The sludge-bed area is such as to provide 100 sq. ft. per 100 lb. of dried and salted hides. Sludge is drawn to a depth of not over 18 in. to 2 ft. New sludge should not be drawn onto a bed containing partly dried sludge. A sludge dried to about 75 to 80 per cent moisture is usually obtained. This is removed from the beds and used for fill.

Sludge produced at some tanneries can be dried on the vacuum filter or by means of specially constructed centrifuges. Usually, however, the sludge is sticky and will not allow the passage of the water. Even with preconditioning by the usual coagulating agents, ferric chloride and lime, this sludge will not filter well on the vacuum. A very thin mat is produced that cannot be removed and that entirely fills the openings in the filter cloth.

SECONDARY FILTRATION

Whenever it is necessary to reduce further the B.O.D. of the settled wastes beyond that possible by coagulation and sedimentation, biological filtration is used. It is unfortunate that this process has a tendency to darken the color of the waste. Although this color is not in itself harmful, it is usually the cause of complaints. Some types of filter medium cause greater increase in color than do others. Slag produces a dark color almost as black as ink, due undoubtedly to the formation of tannates of iron. Coke or gravel filters, although increasing the color to some extent, do not produce this black effluent.

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Figure 51 shows a plan for a biological filter for B.O.D. reduction. If the settling tanks are at an elevation that will allow gravity flow to the filter, the settled waste is discharged into a control box. This box contains a float-controlled valve for maintaining a constant flow of waste as the head in the settling tanks is lowered. The discharge line from the box is connected to the rotary distribution.

If the elevation is such as to necessitate pumping, the effluent from the settling tanks is discharged into a pump sump. A float-controlled centrifugal pump lifts the waste to the distributor. This pump may be connected directly to the distributor, or the waste may be applied through a siphon box. The siphon has two purposes: (*a*) It allows an intermittent application of waste to the filter, which, because of the high B.O.D. and the slow reaction, is a distinct advantage. (*b*) It maintains sufficient head to turn the distributor at all times, provided that the mechanism does not have a power drive.

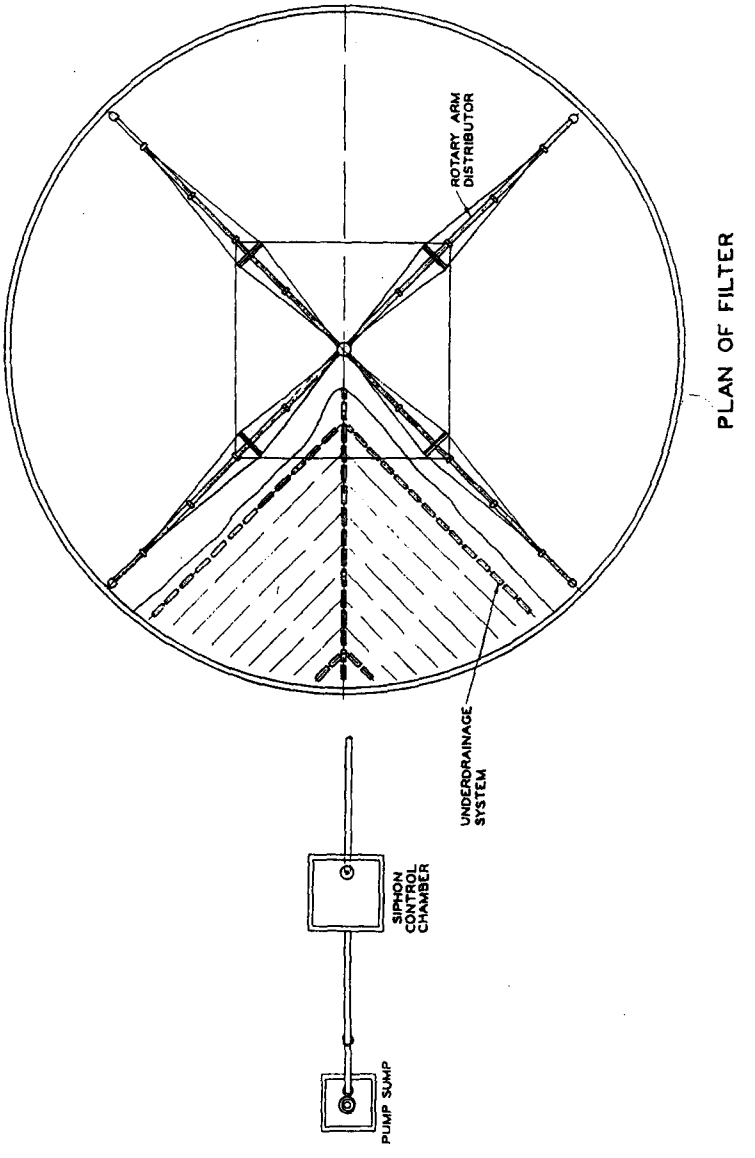
The siphon box has a capacity of about 10 per cent of the maximum hourly flow. It is set at an elevation to maintain a minimum of 18 in. of head over the distributor.

The capacity of the filter is based on the B.O.D. load to be applied. The B.O.D. of the settled mixed wastes is determined by preliminary laboratory or pilot-plant studies. The problem is of sufficient importance to warrant the operation of a pilot plant in every case prior to design of the treatment structures. The wastes from the various tanneries vary over such a wide range that no accurate prediction of the strength of the settled effluent can be made.

Filter design is based on maximum B.O.D. load. The capacity of the filter is such as to provide at least 60 cu. ft. of medium per pound of 5-day B.O.D. The filter depth is 6 ft. The area is 10 sq. ft. at 6-ft. filter per pound of B.O.D. per day.

The average B.O.D. of settled effluent on the basis of the treatment of the total flow of waste is about 750 p.p.m., and the average volume of waste is 600 gal. per 100 lb. of hides. The average B.O.D. per 100 lb. of hides is, therefore, 3.75 lb. The filter area required per 100 lb. of hides averages about 37.5 sq. ft.

The best filter medium from the standpoint of efficiency in B.O.D. reduction is coke or hard clinkers. This medium gives some trouble from clogging. A smooth hard stone will give less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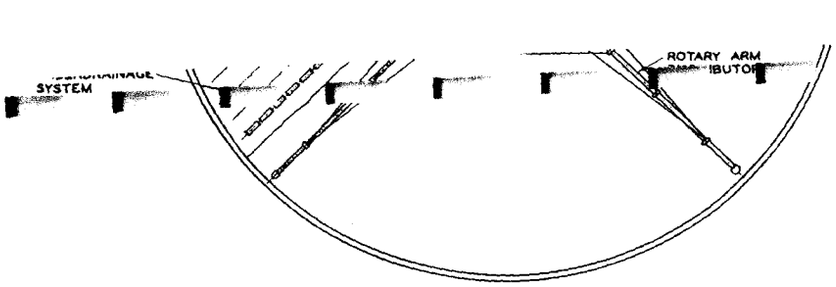
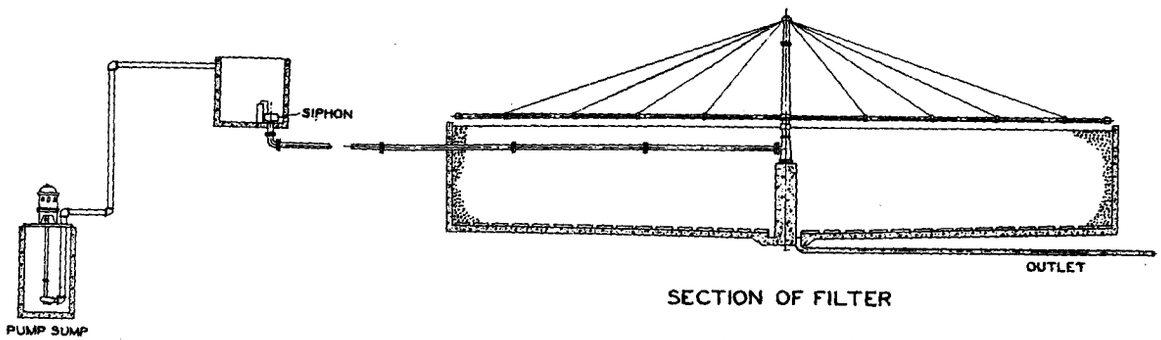


PLAN OF FILTER



SECTION OF FILTER

FIG. 51.—Filter for the secondary treatment of tannery wastes.

trouble from this standpoint, since the filter growth is not so firmly held on the smooth surface. The efficiency of the stone is not so great as that of the coke filter. This medium is clean and hard and entirely free from small material. It is graded to sizes ranging between 2½ and 3½ in.

The underdrainage system is constructed of a grid of ceramic tile carefully layed on the filter floor. This system is so constructed as to allow a free movement of air through the tile and upward or downward through the filter stones. This is accomplished by leaving openings in the filter wall at the elevation of the underdrains. The filter effluent is collected in the center well and conducted to a secondary settling tank.

FINAL COAGULATION AND SETTLING

In order to remove the material that continuously breaks loose from the filter medium, it is necessary to follow the filtration process with a secondary-sedimentation tank. This tank has a detention period of from 1 to 1½ hr. for the maximum rate of flow. The conventional tank equipped for continuous sludge removal is used. This may be of the rectangular type shown in Fig. 48 or may be of any of the conventional types previously mentioned.

In rare cases it becomes necessary to provide for further reduction in color and B.O.D., particularly the former. In these cases chemical treatment and coagulation precedes secondary sedimentation. The effluent from the filter is discharged into a mixing box equipped with a high-speed stirring mechanism or into a mixing trough, as shown in Fig. 48. The chemicals are added to the waste, which is then passed through a coagulation and settling unit. Lime is the usual coagulant and may be augmented by alum in some cases. Iron salts tend to increase the color due to the formation of iron tannates. A coagulation period of 20 min. is provided.

Very rarely is treatment carried beyond this point. Secondary filtration following the above chemical treatment will result in the removal of almost all the color and a total of from 85 to 90 per cent of the B.O.D.

EFFICIENCY OF THE VARIOUS UNITS

The efficiencies to be expected of the processes listed has been determined by the work at Emporium, Pa.[3] These values are given in Table 43.

TABLE 43.—EFFICIENCIES OF TREATMENT-PLANT PROCESSES, TANNERY WASTES

Treatment	Percentage reductions		
	Suspended solids	Color	5-day B.O.D.
1. Coagulation and settling	85	6	41
2. Coagulation with chemicals and settling	97	50	50
3. Step 1 plus filtration and secondary settling	93	15	68
4. Step 1 plus filtration, chemical treatment, and settling	95	35	80
5. Step 3 plus secondary filtration and settling	98	8	85
6. Step 5 plus chemical coagulation following filtration	98	45	88

WASTES FROM SHEEPSKIN TANNERY

There are few sheepskin tanneries in this country. The general operations of these tanneries and the wastes produced are similar to those of plants processing hides without the removal of the hair or wool. The main difference is in the preparation of the dried or salted hides for the tanning process. The following is a description of the process used in a typical sheepskin tannery (see Fig. 47*a*).

The skins are received either dry-salted, flint-dry (sun-dried), or green-salted. They are first placed in the soak, where dirt, salt, and other foreign matter are removed. From here they go to either the "bark side" or the "cream-and-white side" of the tannery, depending on the type of tan desired. Tanning is accomplished on the bark side by means of bark extract (vegetable tan) and on the cream-and-white side by metallic salts such as chrome and alum.

The first operation on either side is the "break." The purpose of the break is to remove the major portion of the fat and grease from the skins. This is accomplished by the saponification of the fats in vats ("paddles") of alkaline mixtures, principally sodium carbonate. The skins are then washed with water and passed on to the fleshing machine, where the remaining fat and flesh are cut from the hides.

They are then placed in pickling vats, where chemicals are added to prepare the skins for the tanning process. The skins

on the cream-and-white side do not leave the pickle vat; nor is the pickle solution removed. Chrome or alum salts are added, converting the pickle to a tan. After the tanning process is complete, the mixture is neutralized, and emulsified oils are added.

On the bark side, the skins are removed from the bark pickle and placed in paddles containing the bark-extract tan liquors. When tanning is complete they are removed to other paddles for rinsing and bleaching. These skins again go to the fleshing machine, where the wool side is raked and washed by the cylinder.

All skins then pass through the press wringer and are dried. Some of these skins go to the dye room, where they are placed in paddles containing various chemicals and dyes.

TABLE 44.—ANALYSIS OF CONCENTRATED WASTES FROM A SHEEPSKIN TANNERY

Waste	Suspended solids, p.p.m.	Total solids, p.p.m.	B.O.D., p.p.m.	Fat, p.p.m.
Bark tan	43,000	180,000	18,000	
Cream tan	180	80,000	700	
Bark break	7,500	40,000	13,000	8,200
Cream break	2,200	27,000	3,000	1,300
Bark rinse	900	47,000	1,100	
Cream wash	900	5,000	2,000	
Pickle	450	67,000	300	
Fleshing machine	4,200	28,000	.....	2,600

The wastes from the tannery are contributed from a number of distinct operations. As in the case of the other tanneries discussed previously, many of the wastes are discharged intermittently by the dumping of vats. The average volume of waste per skin is between 4 and 5 gal. About one-third of this is made up of the concentrated wastes from the various vats. The remaining two-thirds is composed of wash waters from floors and equipment and the continuous flow of water from soaks. The average suspended solids and B.O.D. of the combined wastes is 1,300 and 1,060 p.p.m., respectively. These wastes are slightly acid, having an average pH of 6.6.

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STES FROM A SHEEPSKIN

Total solids, p.p.m.	B.O.D., p.p.m.	Fat, p.p.m.
180,000	18,000	
80,000	700	
40,000	13,000	8,200
27,000	3,000	1,300
47,000	1,100	
5,000	2,000	
67,000	300	
28,000	.....	2,600

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The major concentrated wastes are bark tan, cream tan, bark break, cream break, bark rinse, cream wash, pickle, and fleshing machine. Table 44 gives the average analysis of these wastes.

A large quantity of salt is used in the various processes, which accounts for the high total solids. The bark-tan liquors are the strongest of the wastes. However, the volume of this waste is small (not over 2,000 to 5,000 gal. per week). Of the other wastes, the breaks and the fleshing-machine waste contain the major portion of the suspended material. Most of this suspended material is saponified fat.

TREATMENT OF SHEEPSKIN-TANNERY WASTES

For the removal of suspended material and the partial reduction of B.O.D., coagulation and sedimentation using the fill-and-draw principle give the greatest efficiency. Lime is used as the coagulant. Other chemicals such as alum and ferric salts give only slightly better removals. The use of the fill-and-draw process allows a much better control than is possible by the continuous-flow, since preliminary tests can be made for lime requirements prior to the treatment of the batch. The average quantity of lime necessary has been found to be about 14 lb. per 1,000 gal.

The treatment units are shown in Fig. 50. The first unit is an adequate screen for removing wool and fleshings. This is a self-cleaning rotary screen covered with sections of perforated brass plates with $\frac{3}{32}$- to $\frac{1}{4}$-in. slots. The waste from the screen is pumped to a coagulation tank, from which it flows to one of several wood-stave settling tanks. These tanks and the sludge-storage tank have been previously described for the treatment of tannery wastes (page 189). The coagulating mechanism may be installed in each of the settling tanks and the coagulation tank eliminated. The lime is added by means of a vibrating lime-feed machine mounted on a platform so as to discharge into the line to the coagulation tank. Lime may be added by hand if desired.

A considerable quantity of sludge is obtained. This sludge is concentrated in the sludge tank, and the bottom sludge is drawn to sand beds, where it dries rapidly and can be removed from the site by truck. The concentrating tank and sludge

beds have also been described earlier in this chapter (pages 189 and 190).

If a further reduction of B.O.D. is desired, the settled waste is treated on the biological filter. This filter is shown in Fig. 51 and described on page 190.

FAT RECOVERY FROM SHEEPSKIN-TANNERY WASTES

As has been stated, the major portion of the suspended matter in this waste consists of fats removed from the skins in the breaks and the fleshing machines. This fat may be removed from the concentrated breaks and machine waste first by screening to remove wool and fleshings and then by treatment with sulphuric acid. The screened concentrated wastes make up about 10 per cent of the total waste volume. This waste is pumped to degreasing tanks consisting of several wood-stave tanks having a combined capacity of about 2 days' flow. These tanks are equipped with air diffusers and air compressors. Sulphuric acid is added in sufficient quantity to separate the fat. Air is applied to mix the acid with the waste and to assist in floating the grease. The latter is allowed to collect on the surface and is then skimmed into barrels. The waste from which the fat has been removed is mixed with the other waste from the tannery.

About 1.25 gal. of technical acid is required on the average for each 1,000 gal. of concentrated waste. A study made at one sheepskin tannery indicated that from 500 to 600 lb. of fat may be recovered daily. This fat has a commercial value.

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Industrial Waste Treatment Practice

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Michigan State College

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ENT PRACTICE

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TANNERY WASTES

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CHAPTER VIII

PULP- AND PAPER-MILL WASTES

Paper is described as "a fabric composed mainly of minute vegetable fibers which have been deposited on to a sievelike structure from their suspension in water and commingled and fitted together in such a manner as to form a homogeneous sheet or web."

Cellulose is the basis of all paper. The sources of cellulose are the tissues from a large variety of plants. Since plant tissues are composed of cells and cellulose fibers, it becomes necessary to remove these cells from the fibers subsequent to the manufacture of the paper. This process of preparing the fibers for paper manufacture is known as "pulping."

Paper production is, therefore, divided into two distinct operations: (*a*) the preparation of the fiber in the *pulp mill* and (*b*) the actual manufacture of the paper in the *paper mill*. These mills may be entirely separate, in which case the pulp mill is concerned only in the production of pulp that is sold to the paper mills. In many cases the two mills are combined, the papermaking following the production of pulp in more or less continuous and related operations. In this discussion the two mills will be considered as two distinct operations, although in some cases wastes may be combined for treatment.

TYPES OF PULP

Pulp is made from a large number of raw products, of which some of the more important are wood, straw, rags, wastepaper, threads, textile cuttings, bagging, esparto, flax, hemp, bamboo, and sugar cane. Cotton is almost pure cellulose and is ideal for papermaking. Wood is a lignocellulose, and flax is representative of the so-called "pectocelluloses." Each of these raw products requires a somewhat different process for the removal of foreign material and the release of the cellulose in a form that is usable for the manufacture of the different grades of

paper. The more important processes consist of those used for the preparation of pulp from wood, rags, wastepaper, and straw. These will be briefly discussed here mainly for the purpose of pointing out the sources of the major wastes.

PRODUCTION OF WOOD PULP

There are four processes used for the manufacture of pulp from wood. Each process produces a pulp with characteristics desirable for certain grades of paper. The processes are (*a*) mechanical or groundwood, (*b*) sulphite process, (*c*) soda process, and (*d*) sulphate process.

Mechanical Process.—Mechanical or groundwood pulp is produced for the manufacture of the cheaper grades of paper, such as newsprint, cheap Manila, wrapping paper, and building papers.

Spruce, balsam, and poplar are the types of wood generally used. The logs are cut into 2-ft. lengths and debarked, and as many as possible of the knots are removed. The grinding machine consists of an emery or sandstone cylinder, the face of which is grooved and serrated. Hydraulic pressure is used to maintain a constant contact with the revolving stone. A constant flow of water cools the stone and prevents the burning of the fiber. The hot or cold process is employed, depending on the amount of water used. The former is in general use in this country.

The fibers produced by the stone are coarse and irregular. In order to produce a more uniform pulp the ground material is run through a series of coarse vibrating strainer plates that separate the fibers into respective sizes. The large pieces are subjected to further disintegration. The finer material is run into refiners that squeeze and grind the fibers between revolving stones and finally produce a consistent pulp.

There is only a limited amount of liquid waste from this process. This waste is the "white water" containing pulp as it comes from the grinders and refining machines. Much of this water can be reused, effecting a considerable saving in pulp.

Sulphite (Acid) Process.—Figure 52 is a flow diagram showing the major units of a sulphite pulp mill. The process depends on the action of bisulphites of calcium and magnesium on the foreign materials in the wood. The cooking liquor is produced by burning sulphur or pyrites in special ovens under a carefully

controlled supply of air so as to produce sulphur dioxide. This gas is rapidly cooled to prevent further oxidation to sulphur trioxide. It is then conveyed into the bottom of a tower containing lime. Water is constantly sprayed in at the top and aids in the reaction by producing sulphurous acid. The acid and lime react to form the calcium and magnesium bisulphites, which dissolve in the water and pass to storage tanks. An

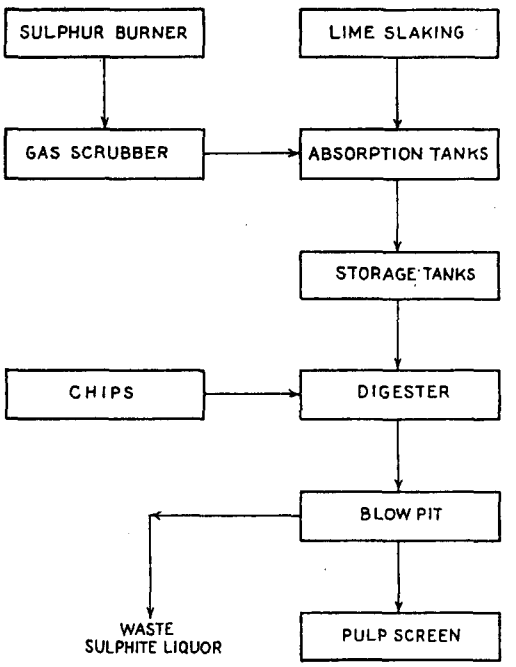

FIG. 52.—Flow diagram of a sulphite pulp mill.

average of 200 lb. of lime and 300 lb. of sulphur are required per ton of dry pulp produced.

The wood chips and cooking liquors are mixed in large, specially lined steel digester tanks. They are cooked under from 80 to 100 lb. pressure with live steam for a period of about 10 hr. The contents of the digester are dumped into a blow-pit having a perforated floor through which the liquor passes. The mass is washed to remove the strongest of the remaining liquor and is passed to the screens. Here knots and larger particles are removed, after which the pulp is passed to stove chests.

In some cases calcium carbonate (limestone) is used in the production of the cooking liquors in place of lime. There may also be some variation in the cooking process. The Mitscherlich process employs much longer cooking periods (48 hr.) and lower temperatures and pressure. In this case, the pressure does not exceed 15 lb., and heat is produced through heating coils rather than by live steam. Pulp of greater strength is said to result from this process.

The sulphite waste from the blow-pits constitutes one of the strongest of industrial wastes. Many attempts have been made to utilize the ingredients of this waste with varying success. Some of these methods will be discussed in some detail later. The noncellulose compounds that have been dissolved by the liquor represent more than 50 per cent of the weight of the wood. They are comprised of lignins, carbohydrates, and resins. The exact chemical composition of these ingredients is not known, although certain substances have been isolated. About 1.2 tons of solids are produced from the manufacture of 1 ton of pulp. This is contained in about 9 tons of waste sulphite liquor.

The pulp from the process is washed and converted into "half stuff" in a thickener. If a bleached stock is required, the pulp is subjected to the action of bleaching powder or liquid chlorine and lime, after which the excess chemical is removed by washing. If the pulp mill is not combined with a paper mill, this sulphite "half stuff" is converted into boards and packed in bales for shipment.

Other sources of liquid waste from a sulphite pulp mill are the water from the screens, thickeners, and wet machine and the excess bleach liquor and washings from the bleached pulp. These wastes contain some dilute sulphite liquor, fine pulp, and the chemicals used in the bleach.

Soda and Sulphate Processes.—The soda and sulphate processes constitute the two principal methods for the production of alkaline pulp. Both processes make use of caustic soda for the removal of nonfibrous material. The essential feature of the processes is the recovery of the chemicals from the waste cooking liquors.

The soda process is used primarily for the pulping of wood from deciduous trees. Coniferous woods, such as pine, spruce, and tamarack, are pulped by the sulphate process. The soda

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process produces a soft paper used mainly in books and magazines. Sulphate pulp is known as "kraft" and produces a paper of high strength but of poor color. This pulp is used largely for wrapping paper, bags, etc.

The process of producing pulp by these two methods is similar in essential features. The wood chips are introduced into large iron digesters along with the cooking liquor. The cooking is accomplished under about 115 lb. pressure and 344°F. temperature over a period of from 8 to 10 hr. The material is dumped on to the perforated floor of a blow-pit, where the liquors drain from the pulp. Much of the liquor that remains in the pulp is removed by washing with hot water. These washings, together with the liquor that has drained from the pulp, is known as "black liquor" and is passed to storage tanks. The pulp is screened, washed, thickened, and sometimes bleached. It is then converted into boards that are baled for shipment.

Caustic soda is the active ingredient in the cooking liquors of both processes. In the soda process the liquor is made up by adding soda ash and lime or caustic soda. Sodium sulphate and caustic soda are used in the sulphate process. In the recovery of the chemical from the latter, a considerable amount of sodium sulphide is produced along with other sulphur compounds. These are the source of considerable odor at the mill, and these odors are carried to some extent by the pulp.

The black liquor contains the chemicals in a rather dilute condition. The liquor is evaporated and the solids burned, producing a *black ash*. The black ash from the soda process is mostly crude soda ash. This is made up with fresh soda ash, producing what is known as "green liquor." The carbonate is converted to caustic soda by treating the green liquor with quick lime. This mixture is settled and filtered, producing "white liquor," which is then ready for cooking.

Carbon and calcium carbonate are the chief by-products of chemical recovery in the soda and sulphate processes. The carbon is activated and used commercially as a decolorizing agent. Lime is burned and reused or may be marketed as agricultural lime.

When the black liquor from the sulphate process is evaporated and burned, the carbon of the organic compounds reduces some of the sulphate to sulphide. The black ash therefore contains

sodium carbonate, sodium sulphide, and sodium sulphate. This is made up with sodium sulphate forming the green liquor that is converted to white liquor by causticizing with lime.

Although there is no black-liquor waste from the soda or sulphate mills, some of the chemicals and organic substances are contained in the wash waters. The sources of these wastes are the washers, screens, thickeners, and, in some cases, the bleach. The wastes contain fiber, bleach chemicals, and the compounds from black-liquor washings. Sulphate-mill wastes have very strong "rotten-cabbage" odor due to sulphur compounds (mercaptans).

OLD PAPER STOCK

The use of "old paper stock" has developed in this country to the point where it exceeds almost all other sources of pulp for the manufacture of certain grades of paper. This stock is used for making boxboard, wallboard, roofing paper, wrapping paper, and printing paper. Some of the finer grades of paper, such as book and printing paper and the cheaper grades of writing, drawing, blotting, parchment, catalogue, tissue, etc., use varying amounts of the old paper stock together with pulp from other sources.

In working over the old paper stock there is a certain amount of shortening of the fibers. Thus the stock cannot be used where long fibers and high strength is desired.

In mills where the color of the final product is of no consequence, mechanical processes are used entirely for producing the pulp from the paper stock. Where it is necessary to remove ink and other coloring matter from the stock, a combination of chemical and mechanical processes is used. Alkalies, such as caustic soda, soda ash, ammonia, or sodium silicate are used for releasing the ink or dye. These chemicals react with the adhesive that holds the ink, clay, and other materials in the paper, thus freeing them so that they may be removed by washing.

Figure 53 shows the major operation for converting old paper stock to half stuff. Papers are sorted by hand in grades, depending on the desired product. They are dusted, shredded, and placed in cookers for the removal of ink, dye, and other foreign matter. Following the deinking process, the stock is defibered, washed, thickened, bleached, and stored for use in the paper mill.

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There are several types of cooking tank used for deinking old paper stock, for example, the open tank (now in use in only a very few of the older mills), the cylindrical or globe rotary boiler, and the horizontal circulating cooker.

In the open-tank process the papers are packed in a stationary cylindrical tank. The cooking liquor is poured over the mass.

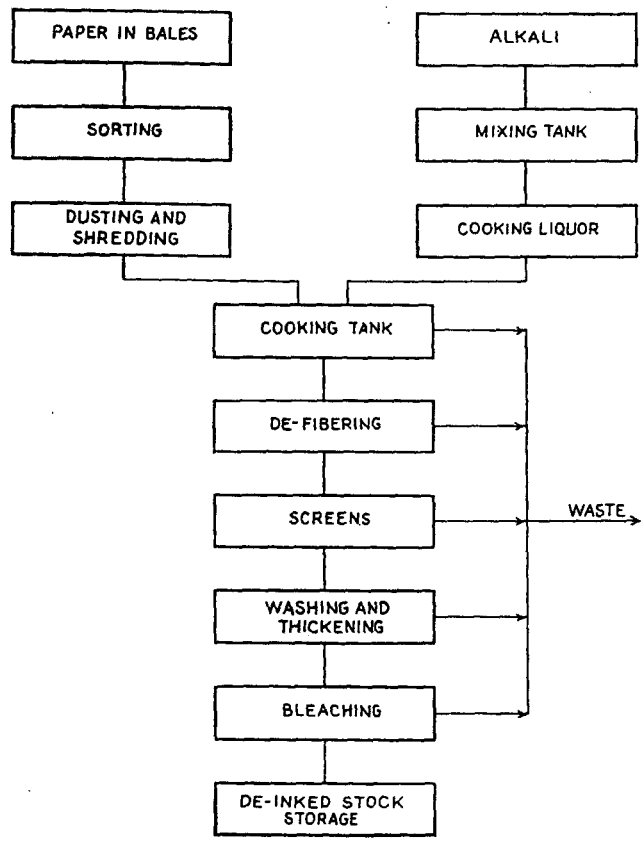

FIG. 53.—Flow diagram of conversion mill for old paper stock.

The cooking solution used in this type of cooker is usually composed of about 45.4 lb. of soda ash or its equivalent of caustic soda per 100 gal. of liquor. About 400 lb. of chemical is required per ton of paper treated. This mixture is heated with steam and allowed to cook for 5 to 15 hr., depending on the type of stock. The chemical dissolves the material that holds the ink

to the paper. The ink is then easily washed from the pulp in the washer. Some attempt is made to reuse the cooking liquor, since there is an apparent advantage of old liquor over new. About one-third of the liquor is lost during cooking and washing. Much of this could be recovered by careful operation and by using a portion of the wash for making up the fresh solution.

The rotary cylindrical or globe cookers deink and defiber at the same time. This is accomplished in rotating boilers under from 40 to 50 lb. pressure for periods varying from 6 to 10 hr. The papers are reduced to a pulpy mass that takes up most of the liquor. Only a small amount of this liquor is recovered; the remainder is lost through the washer. Usually the recovery of chemicals is lost sight of in this process, although it is possible to recover much of this material by batch washing using small amounts of water for the first washings. This water will contain the major portion of the chemicals and can be collected and used for the preparation of fresh liquors. The quantity of soda ash required for this type of cooker varies from 3 to 10 per cent of the weight of the paper. The tendency in modern mills is to reduce the quantity of chemical, and 3 per cent soda ash is now most frequently used.

The horizontal-circulating cooking engines are similar in design to beaters used in paper mills except that they are tightly covered. Ten per cent soda ash based on the weight of the paper is commonly used. The papers are defibered, deinked, and washed in the same process. No attempt is made to recover the cooking liquors, since they are in dilute solution in the washings.

Bleaching of the pulp from the cooking process is usually necessary following the washer. The bleach liquor has a concentration of about ½ lb. of bleaching powder per gallon of water. About 40 to 50 lb. of powder is required per ton of paper.

The liquid wastes from the production of pulp from old paper stock consist of wash water from the washers and thickeners and the bleach liquors and washings. These wastes contain most of the spent chemical from the cooking and bleach, fine fibers, and the sizing, casein, clay, ink, dyes, and other compounds removed from the paper stock. The weight of these materials is from 20 to 24 per cent of the weight of the old paper.

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RAG STOCK

Rag stock is said to constitute the ideal material for the manufacture of high-grade paper. Clean cotton and linen cloth go into a class of paper known as "fine writing." Low-grade rags, burlap, and hemp rope are used in making roofing and wrapping paper.

On arrival at the mill, the rags are sorted and cut into small pieces, and all buttons, rubber, and other material are removed. The rags are then dusted in machines that remove loose dirt and partly rend the cloth. Some of the better grades are washed before proceeding to the cookers. The purpose of the cooking operation is to remove starch, dirt, grease, and other impurities and to start the dyes on colored rags. Three different cooking liquors are in general use: one made with lime, the second with caustic soda, and a third of a combination of lime and soda ash. The one chief objection to the lime and the combined lime-soda liquor is that the calcium soaps that are produced are insoluble and difficult to remove during washing. Caustic soda is a much stronger reagent and is usually employed for the production of high-grade papers. Lime is especially adapted to the removal of dyes and imparts a much better color to the pulp. Lime also is a weak alkali and does not attach cellulose as does caustic soda under the same conditions.

About 125 lb. of lime is used per ton of rags. Cooking is accomplished under 30 to 40 lb. pressure for 10 to 12 hr. The lime-soda combination requires 200 lb. of lime and about 80 lb. of soda ash. The pressure required is about the same as for lime, and the period is slightly longer. The caustic-soda liquor requires about 100 lb. of chemical per ton of rags. The quantities vary widely with specific mill practice.

Cylindrical or spherical boilers are used for cooking. Following this operation, the rags are washed and rended in a hollander. This material is now known as "half stuff" and is ready for bleaching. Chloride of lime or chlorine and lime is used for this purpose. The bleached "half stuff" is pulped and partly dewatered and is then ready for the paper mill. The weight of the "half stuff" produced varies from 60 to 80 per cent of the weight of rags.

The wastes from the processing of rags consist of the spent cooking liquors that are drained and washed from the cooked rags, bleach liquors, and the washing from the bleached pulp. The quantity of cooking liquor has been found to average about 500 gal. per ton of pulp. This material as it is drained from the pulp has a 5-day B.O.D. of about 7,200 p.p.m. and a suspended-solids content of about 1,200 p.p.m. The cooking liquor is washed from the pulp with about 65,000 gal. of water per ton of rags treated. The bleach-washer wastes have a B.O.D. from 300 to 400 p.p.m. and a suspended-solids content between the same ranges. The general sources of these wastes are the cookers, hollanders, screens, and bleach. They contain the cooking and bleaching chemical, dirt, dyes, starch, waxes, grease, oils, and other impurities and some fiber.

STRAW STOCK

Yellow-straw pulp is used for the manufacture of strawboard, corrugated paper, and a large number of different types of containers. Bleached-straw cellulose is used for the making of fine writing papers.

Wheat, rye, and oat straw are used for the production of yellow-straw pulp. The straw is placed in rotary spherical digesters without preliminary treatment and is subjected to the action of alkali cooking liquors under pressures from 15 to 60 lb. Lime was the only chemical used for cooking straw for many years. Recently lime-and-soda ash has been adopted for stock that is to be used for corrugated-board manufacture. The quantity of chemical required varies with mill conditions and the use to be made of the pulp. About 4.5 per cent caustic soda equivalent is considered the average minimum requirement.

After the cooking is complete, the contents of the rotaries is discharged into a pit, where a small amount of the cooking liquor drains through the perforated floor. The stock is transferred to breaker beaters and finally to finishing beaters, where the pulp is formed and the chemicals and impurities removed by washing. It is then pumped through Jordans, where the fibers are made uniform by refining, and then goes to the machine chests of the paper mill.

The waste from the pulping of straw consists of the cooking liquor drained or washed from the stock in the beaters. This

waste contains, besides the cooking chemicals, about 30 per cent of the weight of the straw as solubles removed by the cooking liquor. A large proportion of these solubles are organic and undergo rapid decomposition with the production of odors.

PULP-MILL WASTES

In general, the pulp-mill wastes are of two distinct groups that may be distinguished by the terms "chemical" wastes and "fiber" wastes. There is some overlapping of the composition of the two groups, since some fiber is always present in the chemical wastes and there may be a small amount of the cooking chemical and soluble impurities present in the so-called "fiber" wastes.

Wood and Bark Wastes.—In the preparation of wood for cooking in the wood-pulp mill, a waste is produced that contains suspended bark and other woody matter. This material is effectively removed by screening and may be burned in the boilers. The water from the screen is either discharged direct to the stream or used in other parts of the mill. It has little, if any, material of a polluting character.

Cooking Liquors and Washings.—The chemical wastes consist of the cooking liquors and the washings from the blow-pit, wash tank, and washers. The composition of the cooking liquors used for the pulping of the various raw products has already been discussed. Spent cooking liquors contain, in addition to the excess chemicals, the reaction products from the process. These cover a wide range of organic and inorganic impurities.

Spent cooking liquors from wood-pulp production are treated for the recovery or utilization of products they contain. These are the black liquors from the soda, sulphate, and sulphite processes. The chemicals employed in the first two are of sufficient value to pay for their recovery. In fact, the recovery of these chemicals is usually essential for the economical application of the process. The chemical wastes from the sulphite mill may be treated for the utilization of certain of its characteristics or chemical compounds. Recovery processes applied to sulphite wastes may or may not pay economically but are usually effective in reducing the pollution load from the mill. Some of these processes will be discussed later.

Wash waters used for washing the wood pulp after it has drained in the pit have the same characteristics as the strong cooking liquors, except that they are much more dilute. These wastes may be stored in equalizing tanks to provide a supply as needed and reused for the preliminary stages of countercurrent washing. Fresh water is used for the last stages. When the wash water becomes sufficiently concentrated it is passed to the recovery process. In this way a closed system is possible. Because of the presence of the chemicals, difficulties with slime as are experienced in "white-water" closed systems are not encountered. Such an arrangement for the reuse of chemical washings is far superior to waste-treatment methods. Some return in chemicals saved is possible and assists in partially paying for the additional equipment and labor necessary.

The quantity of waste water from wood-pulp mills varies over a wide range. These ranges and the average in each case are as follows:

	Gal. per ton of dry pulp	
	Range	Average
Groundwood pulp	3,000 to 50,000	17,000
Soda pulp	.....	110,000
Sulphite pulp	10,000 to 160,000	75,000

It is possible to reduce these volumes materially without interfering seriously with mill practice. A major portion of this reduction is accomplished by reuse of wash water in the preliminary washing of pulp and in making up fresh cooking liquors. Such a reduction campaign carried on in Wisconsin[1] reduced the average groundwood-mill waste to 4,300 gal. and the average sulphite-mill waste to 58,700 gal.

Pulp mills utilizing rags, old paper stock, and other raw products except wood seldom make any attempt to recover or reuse cooking liquors or the washings of the pulp. When the open-tank cookers were in use with old paper stock, recovery of chemicals from cooking liquors was more or less standard practice. Similar arrangements are possible to a limited extent with the rotary cookers now in use, although the advantage of such a

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recovery process is questionable. Most of the cooking liquor is contained in the pulp as it is dropped from the cookers. In order to recover the chemicals, arrangements must be made to wash the pulp in the pit with a small amount of water and collect the solution that drains from the pit. A comparatively small portion of the chemicals is recovered by this procedure.

The washing of the cooked old paper stock is accomplished either by the batch process in hollander washers or by the continuous process in cylinder or "deckle" washers. The wastes from the batch process vary widely in composition from a very concentrated condition at the beginning of the washing to a fairly dilute waste at the end. Those from the continuous washer are much more constant in composition, although even these wastes vary to some extent.

A survey of the waste from the cooking of old paper stock was made in six mills in Michigan in 1940 and 1941 (results not published as yet). This survey showed that the volume of washer waste per ton of paper produced by the mills varied from 10,000 to 18,000 gal. The suspended-solids content varied from 2,200 to 3,200 p.p.m. and the B.O.D. from 190 to 380 p.p.m.

This waste is very turbid and contains considerable colloidal material in a condition that is extremely difficult to coagulate. Only about 50 per cent of the suspended matter settles after prolonged standing. The solids are composed of some fiber, considerable clay, ink, starch, casein, and alum. The casein acts as a protective colloid preventing the coagulation of the clay and other finely divided solids.

The method of treatment adapted to this waste consists of coagulation with lime, using an optimum dose that ranges between 4 and 8 lb. of lime per 1,000 gal. This process works effectively when the raw paper stock contains only a small proportion of coated paper. However, when large amounts of coated paper are worked, the casein content of the waste is increased to a point at which coagulation is difficult. In these cases dilution of the waste with an equal amount of white water from the paper mill prior to the application of the lime is apparently necessary. A coagulation period of 20 min. and a settling period of 1 hr. are required for the effective removal of the suspended solids. The structures required for the process will be discussed later under the treatment of white water from paper mills.

Certain portions of the wastes from the strawboard mill may be considered among the chemical wastes. These consist of the cooking liquors and the wash waters from the beaters and washing machines. Methods have not been established for the reuse of these wastes. They are high in organic solubles as well as in suspended solids. At present these liquors are ponded in large diked areas where seepage and evaporation is expected to keep the volume of water fairly constant. This is usually not accomplished, and it is often necessary to discharge large amounts of the ponded waste to the stream during high water. Because of the fermentation of the organic matter in the ponds, odors are produced that cause a nuisance for a considerable area in the vicinity of the mill.

Biological-treatment processes for this waste have been developed[12] as will be discussed later. These processes appear to be expensive if not impractical under many conditions. The most feasible attack on the problem seems to be from the standpoint of recovery, using processes similar to those used in the recovery of chemicals from wood-pulp mills.

Fiber Wastes.—The fiber wastes from the various types of pulp mills have their source in screens, rifflers, knotters, and thickeners. These wastes contain undisintegrated material, sand and other insoluble impurities, and fiber. Much of this fiber may be removed by the use of save-alls, as will be discussed later when "white water" from the paper mill is considered. In addition to the fiber, these wastes contain a considerable amount of material for which there is at present no apparent use.

Bleach Wastes.—Bleach liquors and washings from bleached pulp contain considerable fiber as well as the excess bleaching agent (calcium hypochlorite) and foreign material removed from the pulp. This waste is usually considered as a part of the fiber wastes, and no attempt to recover chemicals is practical, since they are present in such small amounts. The waste is alkaline and has an oxygen demand somewhat higher than the usual fiber wastes.

SULPHITE LIQUOR

The acid cooking liquor from the sulphite pulp mill has the highest polluting value of any of the pulp-mill wastes. The

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average analysis of sulphite wastes taken from four Wisconsin mills[1] follows.

	P.p.m.
Total solids	106,400
Dissolved solids	106,300
Total volatile	94,900
5-day B.O.D.	11,100
Chemical-oxygen demand	2,500
pH	5.7

In Table 45, Kobe[2] gives results that show the general character of the compounds contained in this waste. The volume of this liquor is about 2,000 gal. per ton of pulp produced. It contains solids amounting to more than half of the weight of the wood processed. These solids are composed of a variety of chemical substances and may sometime be the source of raw materials for other types of products. Already a number of by-products have been produced with varying success, as will be discussed briefly below.

TABLE 45.—COMPOSITION OF SULPHITE-WASTE LIQUOR

Component	P.p.m.	Percentage of dry solids
Total solids	118,000	
Ash	19,000	16.2
Volatile organic acids	5,300	4.5
Sulphur (as S)	10,300	8.7
Liquor	61,500	52.2
Total sugars	20,100	17.0

Concentration of Sulphite Waste.—The concentration of this waste may be accomplished by several methods. Multiple-effect tube evaporators made of corrosion-resisting material have been used.[3] Many difficulties are encountered with this method because of foaming, scale formation, and the sirupy condition of the concentrate. The concentrate contains about 50 per cent solids.

The waste has been spray-dried with reasonable success. The Rainer Pulp and Paper Company of Shelton, Wash., produces a concentrate known as Raylig by spraying sulphite

liquor downward into a 120-ft. stack. The hot gases from the boiler plant provide sufficient heat to evaporate the waste to about 50 per cent solids. The principal use of this concentrated material is as an adhesive. It is used in most linoleum cements, as a binder in briqueting coal, and as a road binder. The latter probably represents the most extensive market for the material.

The 50 per cent concentrate may be burned without the aid of fuels. Once the process is started there is sufficient heat produced to evaporate the waste liquor. Although there is no return from this method of disposal, it is used as a means of stream-pollution prevention.

Production of Chemicals.—The polluting effect of the waste sulphite liquors is due to a considerable extent to sugars. Fermentation of the sugars to alcohol is accomplished on a commercial scale in some countries in Europe. About 0.8 per cent of the weight of the liquor is recovered as alcohol. Baker's yeast is produced by inoculating the neutralized liquor with yeast. Alcohol may be recovered from the waste after the removal of the yeast. Because of the low cost of alcohol from molasses in this country, alcohol from this source does not pay the cost of production.

Oxalic acid may be produced by adding concentrated nitric acid in about three times the weight of the dry solids to the concentrated sulphite liquor.[4] The reaction is allowed to proceed under its own heat. About 25 per cent of the weight of dry solids is recovered as oxalic acid.

The Howard Process.—The Howard process of sulphite-waste utilization[5] is probably the most promising of all methods attempted. This process is designed to handle both the strong liquor and the more dilute washings from the blow-pits. It consists of a "fractional precipitation" treatment with lime, and the following three primary products are segregated: (*a*) an inorganic product consisting largely of calcium sulphite for use in making fresh cooking liquor, (*b*) an organic product consisting of the lignin components for use as a boiler fuel, and (*c*) a tail-liquor effluent that carries most of the carbohydrates. Figure 54 shows a flow diagram of this process.

The first addition of lime to the waste is made in a "reaction tank" where calcium sulphite is precipitated. The quantity is regulated to give a desired pH. The mixture is settled in a

settling tank from which the sludge is removed, refined, and used for fresh cooking liquor.

The waste then passes to a second reaction tank, where sufficient lime is added to precipitate the lignins. This material is removed by a second settling tank and dried on a vacuum filter. This product is used for the manufacture of tanning extract, plastics, phenols, and vanillin. The unused portions are used as a solid fuel.

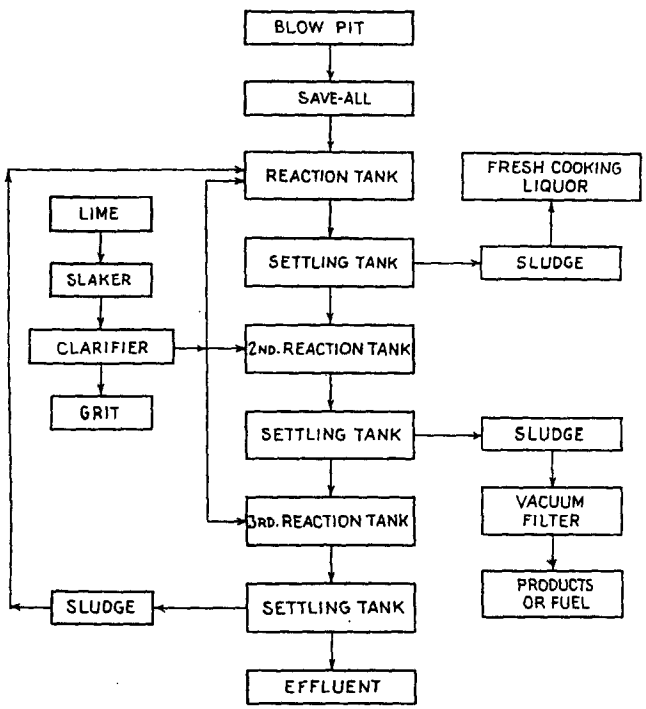

FIG. 54. Flow diagram of the Howard process.

Following the second settling tank, the waste is given a further treatment of lime to assure the complete removal of the lignins. The sludge in this case contains the precipitated organic material and an excess of lime. This is used as a reacting chemical in the first tank.

The effluent from this recovery process contains the carbohydrates in solution. These, it is claimed, are stabilized against biological oxidation. A total reduction in B.O.D. of 75 to 85

per cent is said to result from the application of the process.

Considerable work has been reported[6],[7] during the last 2 years on the recovery of certain chemicals from sulphite liquors. These methods are not as yet on a commercial or practical basis.

PROCESS OF PAPER MANUFACTURE

Half stuff or pulp manufactured in the pulp mill is the basic material used by the paper mill in the manufacture of paper.

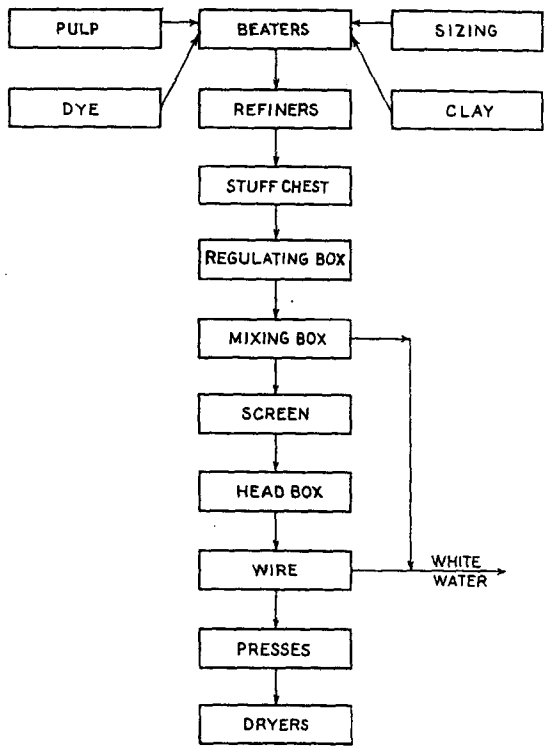

FIG. 55.—Flow diagram of a paper mill.

This half stuff has been washed, bleached, and partly defibered, as the case requires, but lacks regularity. The purpose of the paper mill is to refine this material and work it into the desired type of paper. Figure 55 is a flow diagram that shows the major operation of a typical paper mill.

The pulp or half stuff or any desired combination of these basic materials is loaded into beaters. Clays or other loading material, sizing, dyes, and other additional products, depending on the

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UFACTURE

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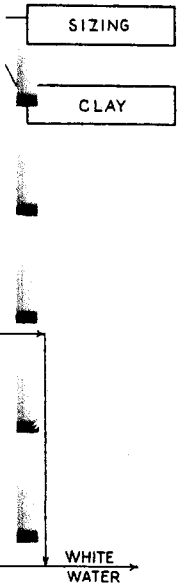

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type of paper, are added to the pulp in the beaters. In these machines the materials are passed under a rotating cylinder equipped with dull knives that beat and break up the bunched fibers. The operation in the beaters has two objectives: (*a*) to mix and blend the various materials and (*b*) to reduce the fibers to a uniform size and to a size best fitted for the production of the type of paper desired.

After the beating operation the stuff may be refined in the beaters or passed to separate machines for the refining operation. The refiners or Jordans consist of a tapered knife-equipped cone rotating in a close-fitting casing in which knives are embedded. This operation brushes out the fibers and reduces them to uniform length.

The chief loading materials added to the pulp consist of China clay, calcium sulphate, agalite, barytes, and titanium oxide. Each of these imparts specific properties to the paper. Certain dyes are used to impart whiteness to paper. The chief ones for this purpose are ultramarine, cochineal, and some aniline dyes. Colored papers are produced by the addition of organic dyes or inorganic pigments. Rosin and alum, casein, glue, starch, and other materials are added for sizing.

From the beaters or refiners the stuff is discharged into a stuff chest, which is used for the purpose of storage so that the paper machines may receive a uniform flow. Stuff chests consist of tanks capable of holding upward of 1,000 lb. of pulp. They are provided with horizontal paddles that keep the material mixed.

There is no continuous waste from the beaters, refiners, or chest. Some beaters are provided with a sand trap that collects heavy foreign material. The dumping of this trap and the washing of the beaters and refiners contribute some small amount of waste. This waste contains considerable fiber but is small in volume.

From the stuff chest the material goes to a regulating or mixing box, where the stuff is diluted to the proper consistency for application to the machine. To avoid the possibility of sand, knotted fibers, or other foreign material reaching the machine, the stuff is passed over rifflers or sand traps and from there to the screens. These screens remove materials of improper size and impart an evenness and regularity to the finished paper. Screens may be of the vibrating or revolving type.

The stuff then passes direct to the paper-machine wires or to a head box at the upper end of the machine, from which it is fed to the wires. The pulp, as it reaches the wires, contains from 97 to 99 per cent water. The wires form an endless belt, moving rapidly from the "breast" roll to the first "couch" roll and return again under the web to the breast roll. They are of fine mesh, varying from 60 to 70 strands to the inch, and are from 30 to 50 ft. long. As the stuff is fed onto the wire, most of the water passes through, leaving the fibers spread in a uniform mat on the wire.

It is essential that most of the water be removed from the web before it reaches the felts, since it must support itself for a short distance in the transfer from wire to felt. To accomplish this two or more suction boxes and a suction roll are placed near the end of the wire. Showers of clean water are directed against the web as it forms.

After transfer to endless felts, the web passes between suction rolls or couch rolls and wet presses to remove excess moisture. It is then passed in a sheet between drying cylinders and eventually between calenders, where it is given the desired smoothness. The paper is then cut and rolled.

In the production of some grades of paper, particularly writing paper, sizing is applied in the paper machine. In this case the web, after passing the first drying rolls, enters a vat of sizing material. Upon emerging from the vat it is squeezed through a set of rolls to remove the excess size and then passes on to the second set of drying cylinders and calenders.

Some of the principal types of papers are described[8] as follows:

Printing papers are made largely of wood and contain large amounts of loading materials.

Newspapers are made chiefly from groundwood pulp mixed with unbleached sulphite pulp.

Wrapping papers are made from straw, jute, hemp, old rope, and colored rags. Sulphate (kraft) pulp gives a particularly strong wrapping paper. The paper is sized and calendered but seldom bleached.

Writing papers are made from high-grade wood pulp with or without rag pulp. They contain considerable size and are carefully calendered.

Blotting and tissue papers are unsized and are not loaded. Tissue is made from long fibers, usually from hemp and cotton.

Parchment paper is made by treating unsized paper with sulphuric acid and glycerine. The acid is neutralized with ammonia.

Impervious wrapping paper for confectionery, butter, etc., is produced by a long heating of pulp or rags, during which time the fibers are broken down into a gelatinous mass and take on a considerable amount of water. This mass produces a thin transparent paper.

WASTE FROM PAPER MILL

The principal liquid waste from the paper mill consists of the water that passes through the wires, showers, and felts of the paper machine. This waste is known as "white water" and contains varying amounts of fiber, size, dye, and loading material. Other sources of waste in the mill may be from the beaters, regulating and mixing tanks, and screens.

TABLE 46.—WISCONSIN PAPER-MILL SURVEY

Volume and content	1932	1937
Waste, gal. per ton:		
Maximum	102,000	104,000
Minimum	1,300	6,100
Average	24,400	23,900
Fiber, percentage of production:		
Maximum	9.5	4.7
Minimum	0.1	0.4
Average	2.3	1.3

The volume of waste and fiber losses from the paper mills of Wisconsin was determined by a survey made of 21 mills by the Wisconsin Department of Health[1] in 1932 and again in 1937. Table 46 gives the maximum, minimum, and average values obtained by these surveys. A similar survey was made in Michigan in 1937 by the Michigan Stream Control Commission.[9] Table 47 shows the results of this survey.

From the 44 mills surveyed in Wisconsin and Michigan during 1937, the average volume of waste was 33,000 gal. per ton of paper produced. The fiber loss in Wisconsin was considerably less than in Michigan because of a campaign conducted between

1932 and 1937 to reduce those losses. Average Wisconsin losses were 1.3 per cent and Michigan, 4.81 per cent on paper production.

The major portion of the oxygen demand of a paper-mill waste is due to dissolved organic substances removed from the pulp. Cellulose fiber is oxidized biologically but slowly. Population equivalents have been shown to be between 25 and 30 per ton of paper processed.

TABLE 47.—MICHIGAN PAPER-MILL SURVEY

Mill number	Paper production, tons per day	Waste flow, gal. per ton	Fiber loss, percentage of production	Type of paper
1	21	77,000	20.40	Book
2	22	58,500	4.05	Book
3	24	53,000	12.50	Board
4	31	93,300	6.30	Book
5	32	68,800	5.15	Writing
6	33	42,500	0.30	Parchment
7	35	26,500	2.58	Book
8	49	36,000	4.68	Book
9	49	210,000*	9.98	Book
10	50	43,100	2.84	Book
11	59	59,400	13.10	Book
12	81	18,200	1.81	Board
13	99	21,300	1.46	Board
14	100	19,290	0.43	Coating
15	106	41,000	2.48	Book
16	127	34,400	7.20	Book
17	145	23,700	1.76	Board
18	157	55,200	2.04	Board
19	161	41,100	7.40	Book
20	182	17,900	0.75	Board
21	217	19,290	2.10	Board
22	251	25,300	2.18	Board
23	318	25,300	2.43	Board
24	329	19,800	1.56	Board
Average	...	40,000	4.81	

* Includes condenser water and is not considered in average.

RECOVERY AND UTILIZATION

Recovery processes in the paper mill involve the use of "save-alls," either in closed or partly closed systems. In a completely closed system no white-water waste is discharged, and all the

water is reused in the mill. This ensures a 100 per cent recovery of stock. Such systems have been developed in mills without the use of save-alls, as will be shown later. Where partly closed systems are in use, save-alls are necessary for the recovery of stock from the discharged white water. In mills using old paper stock, white water is used for washing the cooked stock and for washing the pulp after it is bleached.

The chief objection to the reuse of white water on the paper machine is the growth of slime which develops in pipe lines and on equipment and which shows up as objectionable spots in the finished paper. This slime is successfully controlled by the chlorination of the white water prior to its reuse.

In general, recovery systems have been used only to the point at which they are profitable to the mill. Where it becomes necessary to correct a condition of pollution, these processes may be expanded beyond the point of profit. Recovery—to a certain degree, at least,—provides a much less expensive means of pollution reduction than treatment of the white water following its discharge.

The Closed System.—The basic principle of the closed system is the pumping back of white water to take the place of fresh water in the paper mill. This may be accomplished without the use of save-alls, in which case the paper machine itself becomes the save-all. The more concentrated white water is returned either to the beaters and is used for dilution of the stock in dropping the beaters or to the regulating box or machine chest. The less concentrated waters are used for the showers. In most cases it is necessary to pass the shower water through a save-all to remove the fine pulp, which has a tendency to clog the shower openings. One of the chief needs in white-water reuse at the present time is the development of a shower-head that will not clog. A change from an open system to a typical closed system has been described in detail by C. M. Baker.[10] The following discussion of this system was taken from this reference:

Original method.—The original method of operation for this mill was as follows: The pulp was placed in beaters and diluted with fresh water to a consistency of about 6 per cent. It was refined by beating with a rotating drum and then dropped into the beater chest. Here it was diluted to a consistency of 3 per cent with fresh water or white water from a paper machine.

From the beater chest it was pumped to the machine chest and from there to the stuff chest. There was no dilution in either of these chests. The stuff then flowed by gravity to Jordans for refining. More fresh water was added in these machines. After it was properly refined it flowed to the mixing box, where it was further diluted with white water. It was pumped to a sand table, where heavy particles were removed, and then was flowed to the screens. Here it was washed with fresh-water showers and dropped into the head box of the paper machine.

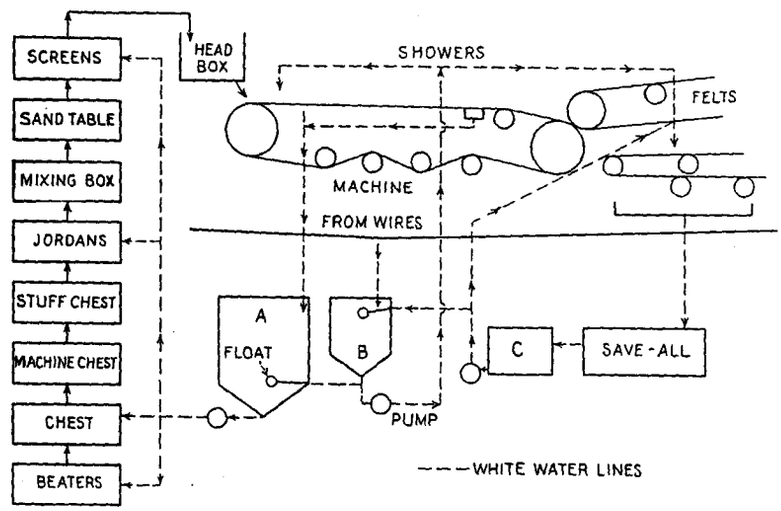

FIG. 56.—Flow diagram of white-water reuse.

Fresh-water-spray showers were used in the head box. Six fresh-water showers were used to wash the wires and three to wash the felts of the paper machine. About 750,000 gal. of water daily was required for this purpose.

From the paper machine a portion of the white water was passed through the save-all. The capacity of the save-all was not sufficient for the entire volume. Practically all the water used for diluting the stock to a consistency of about 6 per cent in the beaters and finally to about ½ per cent at the machine was removed between the head box and the felt end of the machine. A small amount of this white water was used in the mixing box, but the major portion was discharged to the sewers.

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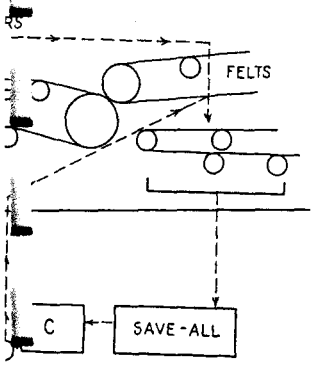

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Revised method.—The revised method of reuse is shown in Fig. 56. It is described as follows:

1. The white water is collected from the upper stretch of wire between the head box and felts in an equalizing tank *A*, from which it is pumped back for dilution at the beaters, beater chest, Jordans and for the screen showers. The tank *A* has a capacity of about 5,000 gal.

2. The white water from the wire showers is collected into a tank *B*, from which it is returned directly to the showers. Make-up is supplied through a float-controlled inlet from *B* to *A*, so adjusted that it opens only when tank *A* is nearly empty.

3. The felt-shower white water is collected in a tray and passed through the save-all to remove threads and ravelings into a sump *C*, from which it returns to the felt showers and also supplies a make-up through the float-controlled valve on the inlet to tank *B*. Clean, fresh water is taken into the system through sump *C*.

Fresh water is taken in only in the felt-shower system and from there bleeds into the wire-shower system (tank *B*) and from this system to the dilution system (tank *A*). The only loss of water in the closed system results from evaporation. Not only is fiber recovered by the system but heat losses are greatly reduced, which is often an important consideration.

As has been previously mentioned, the principal difficulty in the reuse of white water is due to the accumulation of slime. In the mill employing the foregoing system, slime is controlled by the application of ammonia and chlorine.

Colored Stock.—The application of the closed system is somewhat more difficult when changes in color or other characteristics of the paper occur at frequent intervals. These losses due to color changes, breaks, or shutdowns may be largely eliminated by a system proposed by the Bird Machine Co.[11] White water from the wire pit, squirt trim, wire showers, and couch pit is retained in the system. From the bottom of the wire pit, some of the water flows to the inlet of the fan pump, where it is mixed with stock and pumped to the screens. The couch pit is dumped directly to the machine chest after a break.

White water flows to the return water tank in the basement, from which it is pumped to a save-all. Fiber and filler from the save-all are collected and returned to the beaters or machine

chest, depending on the type of save-all used. The line to the save-all is partly closed during normal operation to keep the reserve in the return-water tank. The pump from this tank is considerably overcapacity. Before a color change, this line is opened so that the tank is about empty when the machine is ready to shut down. In this way the entire system, including tanks and save-alls, is washed up at once without the loss of the tankful of return water with its fiber.

The filtered water from the save-all flows to a filtered-water tank, from the bottom of which a sump supplies water to the beaters, shredders, pulp mill, or other points. Excess water from this tank flows to a third tank (shower-supply tank), where fresh water is also supplied for the showers. This is the only point at which fresh water enters the system.

Partial Closing of System.—There are many methods by which a system may be partially closed. The method used is adapted to the individual mill and depends to a great extent on the type of paper produced and the mill process. Mills operating in connection with pulp mills may divert the white water back to the pulp mill without passing it through save-alls. Here it is used for make-up of cooking liquor, washing the wood or old-paper pulp, and for the make-up of bleach liquor. Save-alls are installed on the pulp-mill waste to recover the fiber contained in the water required for washing.

In many cases, save-alls are installed on the more concentrated white water. Stock is returned to the system and the water discharged to the sewer or reused. Shower water and the less concentrated white water are returned without passing through the save-all.

USE OF SAVE-ALLS

The term "save-all" in the paper industry is applied to fine screens, vacuum filters, settling tanks, or tray clarifiers that are used for the recovery of fiber and other valuable materials from white water. There are numerous makes of these different types of save-alls, and only a general discussion of the types will be attempted.

Figure 57 shows a general layout for the installation of a save-all in the white-water system of a paper machine. The white water is pumped to the save-all. If the save-all is of the con-

tinuous-vacuum type, a small amount of 3 per cent stuff (furnish) is borrowed from the machine chest to assist in forming the mat. The recovered stock is returned to the machine chest or beaters. The water from the save-all may be used for the showers or discharged to the sewer. White water is also recirculated to the fan pump to dilute the 3 per cent stock from the Jordans to the screens.

Chlorination for Slime Control.—The slime that often accumulates in white-water systems is the result of bacterial growth and is most prevalent when a dirty, polluted water is used. Little trouble is experienced in mills in which the water supply is clean

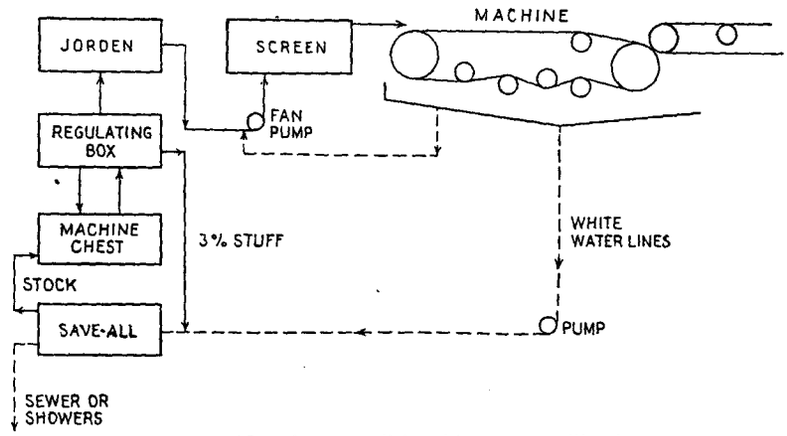

FIG. 57.—Use of a save-all in white-water utilization.

and fresh. Chlorine eliminates odors, reduces shrinkage due to fermentation, and destroys slime-producing organisms.

Chlorine is applied either to the mill supply or to the return white water. When the entire water supply is chlorinated, the requirement for clean stock is between 1 and 2 lb. per ton of finished paper. Recirculated white water under the same conditions has much the same requirements. If the water supply is polluted and the stock dirty, as much as 4 to 5 lb. per ton may be necessary.

Continuous Vacuum Filter.—The continuous vacuum filter of the drum type has been described in a previous chapter (page 59). These filters are adapted to use as save-alls for the removal of fiber and filler from white water. Another type frequently

used is known as the "disk filter." Both types are primarily the same in principle, the difference being in the shape of the structure on which the filter wire and cloth are mounted. In the drum type these are mounted on a cylinder that revolves in a vat containing the white water. Vacuum is applied to the sections of the cylinder. The disk type consists of a series of circular disks attached to a shaft. These disks revolve with the shaft and are also partly submerged in a vat containing the white water. The filter wire and cloth are stretched on both sides of the disk. Vacuum is applied through the shaft to the space between the two layers of wire and inside the disk. About 50 to 60 per cent of the disk is submerged in the white water. As the disk leaves the water, air is drawn through the filter and the stock is peeled off by high-pressure showers or other means. The disk type has the advantage of a larger filtering area per unit of space.

The amount of fiber in white water is usually too small to form a satisfactory mat or sheet on the filter. To make up for this deficiency, long-fibered stock is borrowed from the machine chest. This stock is almost entirely returned to the machine chest along with the recovered fiber from the white water. The borrowed stock has a consistency of 3 per cent. About 18 lb. of this stock is required for each 1,000 gal. of white water.

The continuous vacuum filters have several advantages over other types of save-alls. They are very high in efficiency, removing from 90 to 95 per cent of the suspended fiber in news-machine white water and from 95 to 98 per cent in the case of machines making chemical-fiber paper. They produce a clear filtrate that may be used as shower water without the difficulty of clogging of shower openings. Because of the small capacity of the filter vat, orders can be readily changed on the machine with the loss of only a small quantity of fiber.

Wire-cylinder-type Save-all.—The wire-cylinder type of save-all consists of a cylinder covered with a bronze or brass wire cloth. This cylinder revolves, partially submerged, in a vat containing the white water. The water passes through the wire and leaves at the end of the cylinder. Fiber is caught on the wire and lifted as the cylinder leaves the water. It is removed by a jet of water striking the inner side of the wire and is caught in a compartment from which it is pumped back to the

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beaters or machine chest. Sometimes a brush is used to assist in lifting the fiber from the wire.

The speed of the cylinder is controlled by a float located in the vat outside the cylinder and connected to a variable-speed drive. If the volume or consistency of the water increases, the head is raised outside the cylinder, and the speed is increased to meet the new demand.

Felt-type Save-all.—This type of save-all is particularly adapted to white water from certain fine grades of stock. It removes a large percentage of the filler and fine fiber but has a considerably lower capacity than the wire-cylinder type. This capacity varies with the type of white water filtered between the limits of about 20 to 100 g.p.m. per square foot of surface.

It consists of a polygonal drum revolving partly submerged in a vat of white water. The drum is covered for about five-sixths of its surface with brass wire covered with an endless felt. As the drum revolves, the felt travels with it, passing upward out of the vat over several rolls and finally between two press rolls and back to the drum. Water from the vat passes through, leaving the fiber on the felt. As the fiber passes between the press rolls it is picked off by the upper roll, from which a "doctor" scrapes it into a container for transfer to beaters or machine chest. After the felt passes through the press rolls it is cleaned by a shower and pressed between "squeeze" rolls before it again enters the vat.

Incline-wire Save-alls.—There are several forms of incline-wire save-alls in use, many of which are homemade. The power requirements of this type are low; it requires little attention and has the advantage of a low initial cost. However, these save-alls are not nearly so efficient in the removal of fiber as are many of the other types. They consist of a wire screen placed on an incline and sometimes given a slight motion. The fibers are collected in the form of a light slurry and are pumped back into the system.

One of the simplest forms of incline save-all consists of a vibrating screen set at an angle above a collecting tank. White water is discharged at the top of the screen and flows through the wire into the tank. Fiber is retained on the wire and is washed into a container by showers directed against the underside of the screen.

Two other forms are shown in Fig. 58. The Whitman save-all consists of a cone screen revolving inside a conical tank. The white water enters at the top and is distributed over the surface of the cone. The water passes through, and fibers retained are washed off by showers and removed at the apex. This screen must be of 120-mesh wire to be efficient in the removal of fiber. The cone revolves about 6 r.p.m. For a machine producing 50 tons of paper per day, the diameter of the cone at the top is about 11 ft. The opening at the bottom is 2 ft. and the height, 10 ft. A cone of these dimensions handles about 400 g.p.m. of white water.

The Shevlin save-all is not truly an incline type. It consists of a cylinder of fine wire revolving above a collecting tank. The white water enters one end and flows through the wire into the

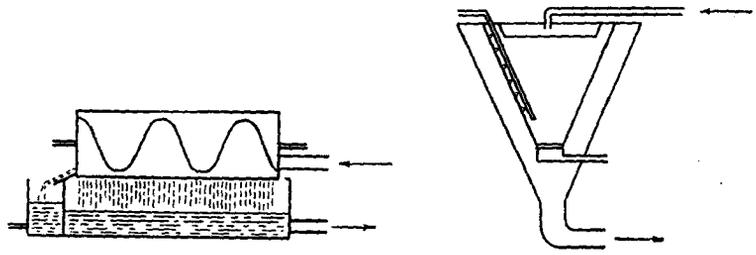

FIG. 58.—Whitman- and Shevlin-type save-alls.

tank. A revolving worm acting inside the cylinder gradually pushes the fibers to the end of the screen, where they are collected and returned to the system.

Settling-tank Save-alls.—Settling-tank save-alls consist of tanks of various forms and materials, into which the white water is distributed. The fibers and loading materials are removed by sedimentation and are pumped in the form of a light slurry from the bottom of the tanks. This type of save-all is inexpensive to operate and keep in repair, since in most cases there are no moving parts. Its first cost may be somewhat greater than that of some of the other types. It is largely used in book and other mills in which the white water contains considerable loading material.

The tanks are cone-shaped or at least have a conical bottom into which the sludge collects by gravity. In some cases a mechanism is provided for concentrating the fibers in the center

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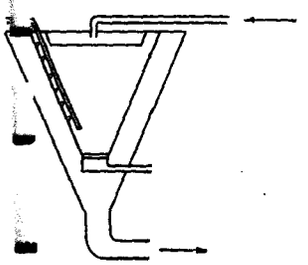

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of the cone. The capacity of the tanks is such as to provide sufficient time for efficient settling, usually about 60 to 80 min. In case only the larger fibers are to be removed, the detention period is shortened considerably.

The water enters the tank at the center, where it is distributed evenly to avoid short-circuiting. The clarified effluent is collected on the perimeter of the tank by weirs or other arrangements that cause an even removal around the tank. Tanks are usually about 20 ft. deep. The fibers are drawn as a thin sludge from the apex of the cone and are pumped to the system. The drawing of the fiber may be intermittent, but much better operation in the mill results from a continuous removal of the settled material to the machine chest.

Tray-type Save-all.—This is a type of sedimentation save-all also adapted to white water containing considerable loading material. It has been developed for use in limited areas and has proved very efficient. It consists of a wooden or metal circular tank divided horizontally into four or five compartments by means of metal trays. A central opening in each tray connects all compartments. Each tray is provided with a scraper operated from a center shaft. The white water is distributed equally to the center of each compartment and flows over the trays to the outside wall, where it is taken off. The fibers and other suspended matter settle on the trays and are scraped to the center, where they fall to the lower compartment and are removed and returned to the mill.

The advantage of the tray-type tank is in the increased capacity, since each compartment has almost the same settling capacity as a single tank of equal area. The detention period required for these tanks is about 45 min. The initial cost of construction of the tray save-all and the space required for its use are much less than for the other types of settling tanks mentioned. Figure 59 shows the general arrangement of a save-all of this type.

Flotation Save-all.—The flotation save-all is a Swedish invention that makes use of the buoyancy of air bubbles in the separation of suspended filter and fiber from the water. The ADKA save-all of The Dorr Company, Inc., is an example of this type.

White water is first treated with the conditioning chemical, which in most cases is alum. Resin or caustic soda may be used. Air is introduced into the mixture and the chemicals and solids

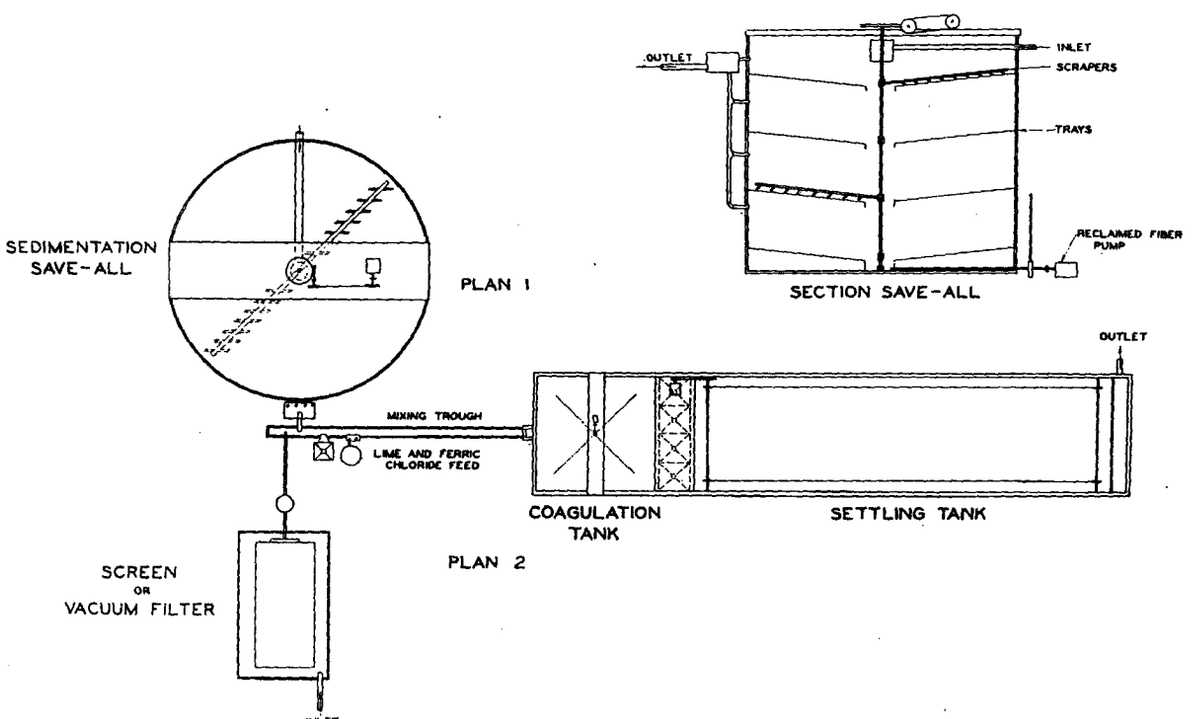

FIG. 59.—Paper-mill save-alls and final settling tank.

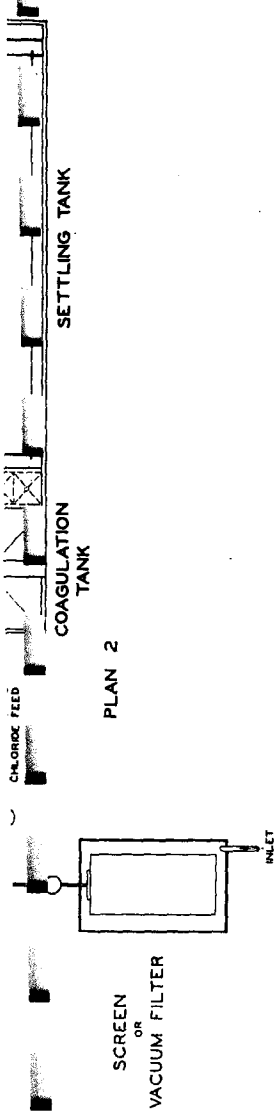

FIG. 59.—Paper-mill save-alls and final settling tank.

flocculated in the "conditioning" box. The waste then enters the lower end of a draft tube, from which it discharges into a tank. The air bubbles cause the suspended material to rise to the top of the tank, where it is removed by a rotating-suction mechanism.

The Dorr Company, Inc., lists the following advantages of this type of save-all:

1. "The recovered stock is returned direct to the feed end of the machine and consequently has the same value as the sheet."
2. "The stock is returned to the machine direct without causing variations in the basic weight of the sheet. Fiber length is not lost."
3. "Color and furnish may be changed without emptying and cleaning the save-all."
4. "Over-all stock recoveries up to 95.99 per cent are obtained. . . . The clarified water can be used almost anywhere in place of fresh water."
5. "The use of stock for sweetening to promote clarification is unnecessary."

TREATMENT OF WASTES

The usual methods adapted to the recovery and reuse of the materials contained in the liquid wastes from pulp and paper mills have been considered. The general trend at the present time is toward the conservation of pulp and the reuse of white water and some of the cooking chemicals. The recovery of chemicals in the soda and sulphate processes has been shown to be necessary for the successful use of the process. Some reuse of sulphite liquors has been shown to be practical, although there is still much to be done in this connection. The practical reuse of certain cooking liquors from the pulping of other raw materials has also been discussed. The recovery of fiber and the substitution of white water for fresh water in closed or partly closed systems generally should prove of financial advantage to the paper mills. This form of disposal should pay its own way. The recovery of fiber from pulp-mill wastes by the use of save-alls is also a practical procedure under most conditions.

Following the reuse and recovery methods, there will usually remain wastes for which treatment processes must be devised. These wastes have their source in the pulp mill, although there

are conditions under which white water may require further purification than can be effected by recovery methods. Such wastes as those from deinking processes; washings from rag, old paper stock, and other similar raw products; wash water from wood-pulp production by any of the four processes previously mentioned; straw-pulp-waste waters; and other lesser wastes are among the group requiring treatment.

In general, the treatment process should consist at least of primary sedimentation and sludge disposal. In many cases the sedimentation process must be assisted by chemical coagulation. This may be accomplished by the use of the conventional coagulation and sedimentation tank discussed in Chap. III.

Figure 59 shows a typical layout for such a plant. The use of some type of save-all for fiber recovery may precede the treatment process. The plant consists of (*a*) a mixing trough or tank into which the coagulating chemicals are discharged by constant-feed machines; (*b*) a coagulating tank and mechanism; (*c*) a settling tank provided with sludge-removal mechanism; and (*d*) sludge-disposal facilities.

The mixing tank has a capacity of about 1 min. maximum flow of waste. It may consist of a trough with "around-the-end" baffles or may be a tank equipped with a "flash" mixer. The chemical feeders are of either the dry- or solution-feed type.

The coagulating chemicals may be alum or lime or a combination of the two. Lime is often required to assist in the formation of the metal hydroxide where the quantity of coagulant is greater than its equivalent of natural alkalinity of the waste. If the precipitated material or the clarified water is to be reused in the plant, alum is preferred as the coagulant, since iron compounds are not a desirable component of most types of paper products. The iron salts, such as ferric chloride and sulphate, however, usually produce a heavier floc than alum and one that settles rapidly. They may be used in cases where the sludge and water are not to be utilized in the mill.

Iron salts, when applied in solution form, require rubber-lined solution tanks, pipe lines, and orifice box, since iron salts are very corrosive. The quantity of ferric or alum salts required for white-water coagulation usually varies between 25 and 50 p.p.m. or 0.2 and 0.4 lb. per 1,000 gal. The dosage must be determined by trial methods for the particular waste to be treated. The

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coagulation period is 20 min. and the settling period, 2 hr. In cases where deinking wash water is to be treated, lime is used as a coagulant. Some wastes may not require the addition of chemicals, since effective settling is obtained without this aid. In this case mixing and coagulating tanks are omitted.

The coagulation tank is provided with a mechanism for slow mixing of the waste and chemicals. Either the horizontal or vertical type of mechanism is used. These types have been discussed in Chap. III. The settling tank is provided with sludge-collecting mechanism. Conventional settling tanks are also shown in Chap. III.

In some cases the sludge or water from the settling tank is used back in the mill. Sludge disposal depends to some extent on local conditions. If space permits, the sludge may be lagooned in a series of ponds or may be dried on sand-drying beds. In the latter case, the use of lime with the coagulant improves the drying qualities of the sludge. The chief objections to sludge-drying beds are their weather limitations. These beds can be used only during the dry summer season. The design of the beds is discussed in Chap. III. If lagoons are used, they should be constructed in series so as to allow them to be drained and cleaned during favorable weather.

In limited space, sludge drying is accomplished on the vacuum filter. Some of the sludges, especially those containing clay, are difficult to dry and require preconditioning prior to their application to the filter. Lime is usually used as a preconditioning agent.

The quantity of sludge varies with the waste treated. It averages between 1 and 5 per cent of the volume of waste. It is usually light, containing from 97 to 99 per cent moisture.

STRAWBOARD-WASTE TREATMENT

The treatment of strawboard wastes was considered by Homman[12] in 1922. The method suggested as a result of these studies consists of primary sedimentation followed by biological filtration. Although this process involves considerable expense, it may present a feasible method of treatment in cases where no other process of waste reduction is possible.

The wastes are from two distinct sources: (*a*) the cooking liquor and washings from the pulp mill and (*b*) the white water

from the paper machines. Those two wastes are of about the same volume but vary considerably in composition. The quantity of water from the pulp mill averages 18,000 gal. per ton of product and from the paper mill, about 20,000 gal., making a total of about 38,000 gal. Table 48 shows the limits in the composition of these wastes and the mixed-mill waste, as determined from a survey of eight mills.

The waste treatment plant suggested for the mixed strawboard-mill wastes consists of sedimentation units of the conventional type, followed by biological filters composed of washed cinders. The sedimentation period is 2 hr., during which time about 50 per cent of the solids is removed. The average mill is said to use about 50 tons of straw daily, of which about 20 tons is lost during the process.' On the basis of 30 tons of production, the volume of waste discharged from the mill daily is 1,140,000 gal., or an average of 47,500 gal. per hour. The capacity of the sedimentation tank would therefore be 95,000 gal., or 12,700 cu. ft. This capacity requires a tank 80 by 20 by 8 ft. (circular clarifier 8 ft. deep and 45 ft. in diameter).

The sedimentation tank is equipped with sludge-collecting mechanism. Sludge is dried on beds of the conventional design. The sludge-bed area required is 875 sq. ft. per daily ton of product, or, on the basis of 30 tons daily, the bed area is 26,000 sq. ft. (about 0.6 acre).

TABLE 48.—STRAWBOARD-MILL WASTES

Waste	Suspended solids, p.p.m.	Organic nitrogen, p.p.m.	5-day B.O.D., p.p.m.
Pulp-mill washings	3,100 to 6,900	47 to 105	1,250 to 2,400
Paper-mill waste	545 to 1,440	11.6 to 20.8	115 to 640
Combined wastes	1,030 to 4,090	34 to 72	420 to 707

The biological filters are composed of 5 ft. of cinders washed to remove all particles below ¼ in. The area of the filters is such as to allow the recommended rate of application of 400,000 gal. per acre per day. The 30-ton mill will require about 2.8 acres of filters.

There are numerous difficulties involved in the design of a filter following the recommendation of Homman. Because of

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WASTES

Organic nitrogen, p.p.m.	5-day B.O.D., p.p.m.
47 to 105	1,250 to 2,400
to 20.8	115 to 640
to 72	420 to 707

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the large area required, the conventional type of filter described in Chap. III is entirely too expensive for use in this connection. It is suggested that the filter be built without floor or walls. An area of ground is graded to slope slightly toward a collecting trough. Tile underdrains, consisting of 4-in. farm tile or 6-in. half tile, are laid in lines with 2-ft. centers, each connecting with this trough. Stone is placed over the underdrains to support the cinders. The outer edge of the cinders is allowed to assume its own slope.

The distribution system consists of a dosing tank and sprinkler system. Some clogging difficulties will be encountered because of the solids still contained in the waste and the bacterial slime that develops in the dosing tank and pipe lines.

Homman states that beds of this material will last many years but should be flushed with clear water once each year to clear them of deposited materials.

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CHAPTER IX

TEXTILE WASTES

The problem of textile-waste treatment is one of the most complicated of industrial-waste problems, mainly because of the extreme variation in textile manufacturing processes. Not only is the combined waste from a mill different from the waste from other mills but the waste continually changes with changes in orders and the introduction of new processes and products. Textile wastes are as varied as the kinds and colors of goods produced by the mill.

During recent years considerable information has been gathered by various agencies relating to the utilization or treatment of textile wastes. These investigations have shown that, although few textile wastes can be utilized at a profit, yet the consideration of recovery or utilization is important, since in many cases it is possible to pay at least a portion of the cost of treatment by the returns obtained from recovered materials. The solution to most of the problems of recovery and treatment are dependent on the processes in the individual mill. Each of these problems involves independent studies to fit general-treatment methods to the specific cases.

The Textile Foundation, Inc., through the cooperation of the University of North Carolina and an advisory committee, undertook to compile the information available on textile-waste treatment. This compilation was published in 1936 as a bulletin of the foundation.[1]

Because of the wide variety of products and processes, flow diagrams of mill processes, as shown in previous chapters, become impractical in this case. The wastes will be considered from each of four general sources: (*a*) from deterging (cleaning) operations, (*b*) from bleaching, (*c*) from certain miscellaneous operations, and (*d*) from the dyeing and printing operations.

THE MANUFACTURING PROCESSES AND SOURCES OF WASTE

The following is a general classification of textile operations from which liquid wastes are produced:

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SOURCES OF WASTE

textile operations

1. Deterging
   a. Wool scouring
   b. Cotton kiering
   c. Silk degumming
   d. Flax retting
2. Bleach
   a. Chlorine or hypochlorite bleach
   b. Peroxide bleach
3. Miscellaneous operations
   a. Desizing
   b. Mercerizing
   c. Weighting
   d. Carbonizing
4. Dye-and-print operations
   a. Direct acid or basic dyes
   b. Sulphur dyes
   c. Vat dyes
   d. Printing
   e. Finishing

The deterging processes are those in which dirt, fat, and other foreign materials are removed from the raw fibers. The wastes produced from these processes are the strongest of all wastes from textile manufacture, since they contain a large amount of putrescible organic matter.

Wool Scouring.—The foreign matter in wool may be classified under four headings:

1. Mineral matter such as sand and earth mechanically attached to the fibers

2. Vegetable matter, straw, burrs, seed pods, and other similar substances

3. Wool perspiration or sweat in the form of dried excretion from the sweat glands of the skin, consisting largely of potash salts and organic acids that are easily soluble in water

4. Wool fat or yolk, which is an impure lanolin, insoluble in water but soluble in certain organic solvents

The impurities in wool vary from 30 to 80 per cent of the weight of the raw product. When the impurities are high, the wool is given a dusting and burring operation to remove the major portion of the mechanically held foreign matter. Three processes

are used for removing the grease and dirt remaining on the fibers: (*a*) The "frosted"-wool process, (*b*) the solvent process, and (*c*) the scouring process.

The "frosted"-wool process consists of passing the wool through a freezing compartment maintained at −35°F. The fat is solidified at this temperature and is removed by a duster. From 60 to 94 per cent of the vegetable matter and 30 to 70 per cent of the grease is removed by this process. The method has not been used on a large scale. The wool is subjected to scouring liquors following the freezing chamber. The waste from the scouring in this case is much lower in polluting matter than when the scouring process alone is used.

The solvent process consists of treating the wool with naphtha, carbon tetrachloride, or carbon disulphide. The extracted material and solvent are recovered by distillation. Some use is made of the recovered grease. This process is also followed by scouring, but the waste is greatly reduced by the pretreatment.

The wool-scouring process is used either following the two processes mentioned above or alone. The wool is first steeped in warm water to remove the soluble impurities. If this water is used for successive batches of wool, the potash salts may become of sufficient concentration to permit their recovery, which is accomplished by evaporation and crystallization from a slightly acid medium.

Following the water soaks, the wool is treated in scouring "bowls" with scouring liquor consisting of soda ash and soap. After the wool is sufficiently treated with the liquor it is raked or lifted from the bowl, forced through squeeze rolls to remove the major portion of the solution, and passed into a series of bowls containing wash water. The soapy liquor is reused until it becomes saturated with dirt and grease. It is then discharged and a new solution prepared.

The waste liquor from wool scouring constitutes one of the strongest wastes produced by the textile industry. Table 49 shows the variation in the strength of this waste as collected from a large number of mills.[2] These liquors are highly alkaline, high in organic and suspended matter, and easily putrescible. About 75 per cent of the solid matter in the waste is in suspension. The wash water from the process has the same characteristics as the waste liquor but is much more dilute. Although treat-

ment methods are possible with these wash waters, recovery processes are usually applied to the concentrated liquors. A considerable reduction in the strength results from the use of either the "frosted" wool or extraction process prior to scouring. Recovery and treatment will be discussed later in this chapter.

TABLE 49.—WOOL-SCOURING LIQUOR

Item	Maximum p.p.m.	Minimum p.p.m.	Average p.p.m.
Grease	25,800	3,000	8,650
Suspended solids	30,300	2,400	11,520
Alkalinity	29,400	3,430	6,780
Oxygen consumed (4 hr.)	7,400	398	1,830
B.O.D.*	22,000	1,200	5,500

* B.O.D. results calculated. Approximately three times oxygen-consumed values.

Cotton-cloth Kiering.—Cotton cloth is cleaned to remove grease, waxes, natural fats, and pieces of the boll that may later interfere with bleaching and dyeing. The goods are placed in kiers containing a solution of 1 to 3 per cent caustic soda. Soda ash, sodium silicate, and other chemicals may also be used in the kiering bath. The material is boiled for several hours in this liquor. Two methods are employed and are known as the "one-boil method" and the "two-boil method." Following each boil, the solution is drawn and the material washed in the kier. Usually about 1 hr. is required for washing.

The kiering liquor is very strong and is highly alkaline. First washings are also high in polluting materials, since considerable of the liquor is retained on the cloth when the kier is drained. Subsequent washings become less concentrated until the final wash is almost clean. The amount of wash water varies considerably, depending on the mill process. The quantity as obtained from the average of a large number of mills is given in Table 50.

The wastes contain (*a*) the vegetable fats, waxes, and resins removed from the fiber; (*b*) particles of cotton boll and other organic material; (*c*) starch and other sizing material, if previously added to the cloth; (*d*) caustic soda, soda ash, sodium silicate, oils, and other chemicals used for making up the kiering liquors.

The strength of these wastes and the wash waters from the one-boil and two-boil methods is given in Table 50.

Kier and Bleach.—When used for white cloth or for delicate colors, cotton must be bleached. This may be done in connection with the kiering process or as a separate process.

Cotton in the loose state is seldom kiered or bleached. It is usually first worked into cloth, since the kiering removes the wax coating and harms the spinning qualities. Cotton used for yarn and knit goods is bleached in the loose state.

The kiering process has just been considered. When these processes are combined, the kiering and bleaching are accomplished in one machine, the operation being continuous, including the washings. The cloth is kiered and washed as described. Hypochlorite or peroxide solution is added as a bleach. The bleach is withdrawn and the excess alkali and chlorine are removed by treatment with calcium bisulphite and salt (scouring). Sometimes sulphuric acid is used in this process. Finally, the cotton is thoroughly washed.

TABLE 50.—WASTES FROM KIERING COTTON CLOTH

Waste	Volume, gal. per 100 lb. goods	B.O.D., p.p.m.	Population equivalent, 100 lb. goods
One-boil method:			
Waste liquor	33	2,900	4.84
Wash water	83	1,140	4.72
Composite waste	116	1,660	9.56
Two-boil method:			
First waste liquor	31	2,700	4.19
First wash	86	1,110	4.78
Second-waste liquor	30	680	1.02
Second wash	85	420	1.80
Composite waste	232	1,060	11.79
Kier and bleach, combined waste	970	136	6.60

The combined wastes from the process have the characteristics shown in Table 50. Because of the large volume of wash water used, the strength of the combined wastes is comparatively low.

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	2,900	4.84
	1,140	4.72
	1,660	9.56
	2,700	4.19
	1,110	4.78
	680	1.02
	420	1.80
	1,060	11.79
	136	6.60

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Silk Degumming.—Silk is received either in "hanks," in which case it has been removed from the cocoons, or in compressed bales containing the more or less damaged cocoons and the dead worms. The impurities in this material consist of sericin or silk gum, which must be removed before the silk is bleached or dyed.

The degumming ("boiling off") is accomplished by boiling the silk in a solution of soap to which a small amount of soda ash may be added. Sodium silicate or sodium phosphate may be used with the soap. The solution usually contains about 30 lb. of soap and 220 gal. of water to each 100 lb. of silk. The length of boil and the strength of the soap solution determine the amount of gum removed. From 1 to 2 hr. and from 3 to 12 per cent soap are required for a complete degumming. About 22 to 28 per cent of the weight of the silk is lost by this operation. Sometimes only a portion of the gum is removed, which leaves the silk in a more workable condition for bleaching and dyeing. About 10 to 15 per cent of the weight is lost by this so-called "souping" operation. General practice in most mills is to follow the boil-off with two washes, although only one wash may be used. A few mills do not wash the silk after the boil-off.

TABLE 51.—WASTES FROM SILK DEGUMMING

Item	First mill	Second mill
Volume, gal. per 100 lb. goods	850	825
Total solids, p.p.m.	4,330	3,090
Volatile solids, p.p.m.	3,200	1,960
Suspended solids, p.p.m.	520	132
B.O.D., p.p.m.	985	820
Population equivalent per 100 lb.	44.2	33.8

The strength of the waste and its volume depend upon the number of washes given the silk. Table 51 shows the values obtained from the analysis of combined degumming wastes from two mills. These are reported by the North Carolina Department of Health.[1] The degumming liquor contains sericin or silk gum, parts of cocoons, dead worms, other organic matter, soap, and alkali. It has a thick jellylike consistency.

Flax Retting.—The manufacture of textiles from flax is not an important industry in the United States. Retting consists of separating the crude fibers from the plant by a process of biological fermentation. Bundles of flax are steeped in water for several weeks, during which time fermentation takes place in the organic cells holding the fibers together.

The waste drained and washed from the fibers is high in organic matter, has an acid reaction due to organic acids resulting from the fermentation process, and is extremely odorous. An analysis (Table 52) is given by Howard, Gleeson, and Merryfield[3] of a retting waste produced by the Salem Flax Retting Plant at Salem, Ore.

TABLE 52.—FLAX-RETTING WASTE

Volume, gal. per ton	5,300
5-day B.O.D., p.p.m.	2,200
20-day B.O.D., p.p.m.	4,900
Total solids, p.p.m.	4,200
pH	4.8

Bleaching.—The bleaching operation is most commonly applied to cotton. Wool and silk are bleached only when white or delicate shades of material are desired. Bleaching usually follows the cleaning processes. Compounds of chlorine and hydrogen peroxide are used for bleaching cotton and silk. Sulphurous acid is often used for the reduction of colored compounds on wool.

Chlorine, sodium hypochlorite, or calcium hypochlorite may be used for the chlorine bleach. This process and the wastes produced have been discussed in connection with cotton kiering. The wastes are strongly alkaline and contain the excess and spent chemical and the impurities removed from the fiber. The bleach is followed by a wash and then by souring to remove alkali and excess chlorine. Sodium bisulphite and sodium hydrosulphite are used in the souring baths. The goods are again washed after the souring liquor is removed and are finally soaped and tinted to soften and whiten the fibers. Recovery methods are not applied to the wastes from these processes, since the chemicals are not present in sufficient concentration. They may be treated along with the other mill wastes, especially those from the dye room, since they tend to decolorize the dyes.

The peroxide bleaching bath is prepared from mixtures of sodium peroxide, sulphuric acid, sodium silicate, and a soluble oil. Caustic soda is produced by the action of the peroxide and water. The acid is necessary to neutralize partly the resulting alkalinity. In some cases hydrogen peroxide is used in place of sodium peroxide and sulphuric acid. Oxidation of the coloring matter is accomplished by the nascent oxygen produced when the peroxide is decomposed. The reaction is best in an alkaline solution. Sodium silicate is a weak alkali and does not injure the fibers.

The one-boil method is used for bleaching silk. The two-boil method may be employed for cotton. Varying degrees of washing follow the bleaching operation.

The wastes from the peroxide bleach vary to a considerable extent, depending on the washing following deterging operation and the type of goods treated. Table 53 gives the average analysis of waste from the one- and two-boil methods.

TABLE 53.—PEROXIDE-BLEACH WASTES

One-boil method:	
Volume, gal. per 100 lb.	1,430
Alkalinity, p.p.m.	153
Total solids, p.p.m.	1,680
B.O.D., p.p.m.	195
Population equivalent per 100 lb.	13.9
Two-boil method:	
Volume, gal. per 100 lb.	1,670
Alkalinity, p.p.m.	250
Total solids, p.p.m.	1,520
B.O.D., p.p.m.	218
Population equivalent per 100 lb.	18.1

Desizing.—Desizing removes starch and other materials used to protect the cotton thread during weaving. The sizing may be removed in the kiering operations already described or may be removed prior to the kier. There are two methods of desizing cotton cloth: (*a*) the "gray sour," in which the cloth is first treated with diluted sulphuric acid and followed by the kier boil; (*b*) the cloth is steeped in a malt or other enzyme bath, followed by an acid treatment. The wastes from the desizing processes are not large in volume and are similar to those from cotton kiering.

Mercerizing.—The mercerizing process consists of passing long warps of cotton yarn through a machine, where it is treated in succession with caustic soda, wash water, acid, and final wash. A cold solution of caustic soda applied to the stretched cotton yarn imparts a high degree of luster to the fibers. The acid treatment is used to remove excess caustic. Cotton cloth may also be mercerized in a similar manner. The strong wastes from the process are usually treated for the recovery of the chemicals. Washings are treated with other mill wastes.

Weighting.—Silk is weighted by one of two general processes. If used for black cloth, the iron-tannin process is usually employed. This consists of first steeping the goods in tannin. The excess solution is squeezed out through rolls and the goods passed to a bath of basic iron sulphate to produce iron tannate. It is then treated with potassium prussiate, producing a precipitate of Prussian blue. The excess chemicals are removed by washing with weak alkali and soap.

If the silk is to be white or lightly colored, the stannic chloride method is used. Stannic chloride is absorbed by the cloth and precipitated as the hydrate or phosphate by subsequent treatment with lime or sodium phosphate.

The wastes from these processes vary to a considerable extent, depending on the degree of washing. The concentrated-tin solution is treated for the recovery of tin. Other wastes and washings are treated with the general mill wastes.

Dyeing.—Dyeing of textiles is not discussed in much detail here because of the large number of different dyes and the varying methods employed in the application of these dyes to the cloth. The dyes may be classified roughly as follows:

1. Direct acid dyes
2. Direct basic dyes
3. Sulphur dyes
4. Vat dyes
5. Developed dyes
6. Naphthol dyes
7. Catechu dyes

Direct dyeing is accomplished by the use of soluble dyes that may be applied to vegetable fibers without the use of mordants. Mordants are compounds used to render the dyestuff soluble and increase the absorption of the dye by the goods. The amount of

dye employed varies widely, depending on the color, the goods, and the method of dyeing. The same is true of the chemicals, salt and sodium sulphate, used to force the dye into the goods. Dyes may vary between 0.01 and 6.5 per cent of the weight of the goods. Chemicals vary from 5 to 100 per cent. Color produced by direct dyes is almost entirely destroyed by boiling with soda ash.

Basic dyes require a mordant. Tannin extract is commonly used. Cotton is dyed by the basic dyes by first treating with tannic acid, followed by a solution of antimony in the form of tartar emetic. The color of basic dyes is best destroyed by the addition of ferric sulphate. The following is a typical formula of basic-dyeing liquors:

First bath:
4 per cent S. C. oil
1½ per cent pine oil
Second bath:
1 to 6 per cent tannin
Third bath:
1 to 4 per cent tartar emetic
Fourth bath:
0.9 per cent dye
2.5 per cent acetic acid
Fifth bath:
1 per cent oil

Sulphur dyes consist of compounds containing sulphur and are applied in baths to which sodium sulphide has been added. They are applied without mordant. There are two types of machines used for dyeing with sulphur dyes. The first involves a continuous process whereby the spent dye liquor is made up and used over again. The wastes consist of a continuous flow of washings. The second is known as the "jigger machine." This machine produces a waste that contains the dyeing liquors. The average sulphur-dye formula is given as

	Per Cent
Dye	7.8
Sodium sulphide	11.1
Sodium carbonate	4.1
Sodium chloride	21.6

Vat dyes are so called because they are applied in a dye bath in which the dye is reduced to a soluble form by means of a strong reducing agent such as hydrosulphite. This class includes the indigo dyes. A typical formula per vat is

100 lb. of dyestuff
20 gal. of water
2 to 6 lb. of caustic-soda solution
10 to 40 lb. of hydrosulphite

Developed dyes are dyes developed on the fabric. Direct dyes are first applied. These are converted to unstable diazo compounds with sodium nitrite and a strong acid. The unstable compound is made stable by the application of beta-naphthol or some other developer. The operation, since three distinct steps are involved, produces a comparatively large volume of waste. The three main wastes are the spent dye liquor, the spent diazotizing bath, and the spent developing bath. Washings follow each bath treatment, and finally the fabric is given a salt or soap rinse. At least seven wastes are discharged from the developed dye operations.

Naphthol dyeing is practically the reverse of developed dyeing. The developer is added first, followed by the diazotizing solution, such as paranitraniline. Beta- and alpha-naphthol and resorcine are used as developers. The following formula gives a fair idea of the quantities used in making the various baths:

	Per Cent
Naphthol bath:	
Sodium hydroxide	0.25 to 2.0
Naphthols	0.25 to 2.0
Dye bath:	
Dye base	0.25 to 2.0
Hydrochloric acid	1.0 to 3
Sodium nitrite	1.5
Sodium acetate	1.0
Acetic acid	0.5 to 2.0
Salt	40
Rinse:	
Soap	1.0 to 3.0
Sodium carbonate	0.5 to 2.0
Sodium hydroxide	0.5

Cutch dyes are obtained from extracts of certain Indian trees. They are extensively used as a mordant and dye for silk in

e applied in a dye bath
rm by means of a strong
This class includes the
is

solution
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the fabric. Direct dyes
to unstable diazo com-
g acid. The unstable
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tively large volume of
e spent dye liquor, the
developing bath. Wash-
lly the fabric is given a
are discharged from the

se of developed dyeing.
he diazotizing solution,
a-naphthol and resorcine
r formula gives a fair
various baths:

	Per Cent
.....	0.25 to 2.0
.....	0.25 to 2.0
.....	0.25 to 2.0
.....	1.0 to 3
.....	1.5
.....	1.0
.....	0.5 to 2.0
.....	40
.....	1.0 to 3.0
.....	0.5 to 2.0
.....	0.5

f certain Indian trees.
nt and dye for silk in

combination with coal-tar dyes. They are applied in the same manner as the sulphur dyes. A typical formula for the dye bath and wash is

Dye bath:	
Cutch extract	20.0 per cent
Copper sulphate	1.15 per cent
Wash bath:	
Sodium bichromate	3.0 per cent

Table 54 shows the volume of waste, alkalinity, B.O.D., and population equivalents of the wastes from the various dyeing processes. The wastes produced by sulphur dyeing are the strongest of the dye-room wastes. Other processes produce wastes having B.O.D. values in general somewhat greater than sanitary sewage.

REUSE AND RECOVERY PROCESSES

One of the first problems that should be investigated in a study of textile-mill-waste disposal is the possibility of the reuse of water and materials and the recovery of valuable components of the various wastes. Treatment of these wastes is expensive, and any procedure that reduces the volume or strength of the wastes usually more than pays for itself by savings in treatment-plant construction and operation.

Conservation of materials and reduction in waste volume are accomplished in a number of ways. In certain cases, wash waters or wastes from some processes may be used for making up a cooking bath. Rinses from dyeing may be used in making up the dye bath. Strong wash waters from kiering may be used for making up the kier and chlorine bleach. It may be necessary in some cases to remove the suspended matter from the waste water before reuse. Filters or small settling tanks are used for that purpose. Reuse and recirculation of wash waters increase the concentration of chemicals and may make possible the application of profitable recovery or at least will reduce the volume of waste requiring treatment.

The counterflow process is also used for increasing the concentration and reducing the volume of wash waters. This process consists of using fresh water for materials from which most of the foreign matter and chemicals have been washed. This wash water is then used for washing material containing a

TABLE 54.—TEXTILE-DYEING WASTES

Type of dyeing	Volume, gal. per 100 lb.	Alkalinity, p.p.m.	B.O.D., p.p.m.	Population equivalent per 100 lb.
Direct dyeing:				
Cotton	360	685	512	9.2
Cotton hosiery	650	265	163	5.8
Basic dyeing, cotton	1,910	125	152	14.1
Sulphur dyeing:				
Continuous machine	545	1,511	1,300	35.7
Jigger machine	1,738	1,730	2,040	177.5
Vat dyeing	1,890	1,675	137	12.9
Indigo dyeing	234	4,870	615	7.2
Developed dyeing:				
Raw cotton	895	.....	220	10.0
Spool cotton	1,035	.....	230	11.9
Beamed warp	1,325	.....	193	12.8
Skein cotton	2,520	.....	104	13.1
Naphthol dyeing	560	.....	75	2.1
Catechu dyeing	1,070	.....	219	11.7

larger amount of foreign matter, etc., until a very concentrated waste liquor is obtained. The fresh water moves in the opposite direction from that of the material being washed. This highly concentrated waste is then treated for the recovery of chemicals or may be clarified and used for making up cooking liquor or dye baths.

Modern processes and equipment invariably result in a saving of chemicals and a reduction in waste materials. "The modern textile plant of today employs such principles as counterflow washing, systematic control of bleach baths, recirculation of wash and scouring waters, reuse of dye baths, and other similar schemes."[1]

Recovery from Wool Scouring.—Wool-scouring liquors are treated for the recovery of grease and potash. Several processes are in use, of which three are mentioned briefly here. Some of these methods involve changes in mill procedures and are patented processes. The methods are (*a*) the acid treatment, (*b*) evaporation, (*c*) use of centrifuges.

Acid Treatment.—The acid-treatment method[4] consists of first settling out the heavier suspended matter in a sedimentation

NG WASTES

Alkalinity, p.p.m.	B.O.D., p.p.m.	Population equivalent per 100 lb.
685	512	9.2
265	163	5.8
125	152	14.1
1,511	1,300	35.7
,730	2,040	177.5
,675	137	12.9
,870	615	7.2
...	220	10.0
...	230	11.9
...	193	12.8
.....	104	13.1
...	75	2.1
...	219	11.7

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briefly here. Some of
procedures and are
(*a*) the acid treatment,

method[4] consists of
atter in a sedimentation

tank with a detention period of about 1 hr. The waste is then stored in a tank, from which it is drawn to small grease-recovery tanks. After the wastes in the grease tanks have become cold, sufficient sulphuric acid is added to reduce the soap emulsion. The quantity of acid required may be determined by titration of a sample removed from the tank. The contents of the tanks are stirred continuously during the addition of the acid. They are then allowed to stand quiet for several hours, during which time the major portion of the fat settles as a sludge. The remainder rises to the surface of the tank.

After the fat has been separated, the center acid liquor is removed to a tank and subjected to further treatment, along with the other wastes from the mill. This liquor can be successfully treated by the chemical-precipitation and biological-filtration process, which will be described later for the treatment of general mill wastes.

The sludge remaining in the grease tanks is withdrawn and dewatered on filter beds. It is then heated with steam and filter-pressed to recover the grease, which is easily separated from the dirt and water. The grease remaining in the filter cake may be discarded or in some cases is recovered by extracting with naphtha. The grease recovered by this method is of very poor grade.

Evaporation or Smith-Leach Method.—This process involves the recovery of both grease and potash and is comparatively expensive. It was used to some extent during the First World War, when potash brought a good price. The scouring liquors are first settled for about 1 hr. to remove the heavy suspended matter. They are then discharged to an evaporator, where they are concentrated to about 3 per cent of their original volume. The distilled water is condensed and used for wool washing. The hot concentrate is treated in a separator centrifuge that separates the water from the grease. When the price of potash permits, the water is evaporated and the residue incinerated for the recovery of the potassium salts. The crude grease is fairly free from mineral matter and has a low fatty acid content. It is of a much higher grade and demands a higher price than that recovered by the acid process. This process has the additional advantage of not leaving a waste that requires further treatment.

The Sharpless Centrifuge Process.—The centrifuge process consists of an improved method of scouring combined with grease recovery. The scouring bowls are arranged in series and in such a manner that the liquor flows in a countercurrent direction from the clean bowls to the bowls into which the raw wool is first placed. The liquor from the last bowl, which has now become very concentrated, is passed to the grease-recovery plant.

Each bowl is equipped with a float valve that admits liquor from the preceding bowl and keeps the level at a predetermined height. The liquor from the first bowl is drawn at a point above the hoppers and does not contain the sand and dirt. The hoppers are flushed out periodically to remove this accumulation.

The waste scouring liquor is first passed through a bulk centrifuge to remove the larger suspended solids and is pumped to a storage tank. The contents of the tank are heated to 190°F. and fed by gravity to centrifuges, where the emulsified grease is separated from the bulk of the water. The grease from the centrifuges is purified by mixing with fresh water, heating to 200°F., and again passing through the centrifuge. This grease is equal in quality to that obtained by the evaporation process.

The waste water from the recovery process is highly polluted. It may be reused for making up fresh liquor for some time until the solubles build up to a point at which the liquor must be discarded. It is then discharged to the regular mill wastes for further treatment, as will be described later.

Recovery of Dyes.—The recovery of dyes in many cases is a possibility, but with present methods of dyeing the quantity of dye lost in the waste waters is so small that recovery is seldom a paying proposition. It is sometimes possible to filter the dye liquor and reuse it from day to day. The major portion of the dye that is lost is contained in the wash waters and is present in a very dilute condition.

A method for the recovery of indigo has been suggested from laboratory tests of M. S. Campbell.[5] The waste is collected in a tank equipped with air diffusers and a stirring mechanism. Air is passed through the waste for a period of several hours, after which sufficient sulphuric acid is added to neutralize or make the solution slightly acid. The indigo will be precipitated and will settle out after standing for several hours. Sedimenta-

tion is aided by returning a part of the sludge to the tank on subsequent batches of waste.

Recovery of Caustic.—Caustic soda used in mercerizing cotton and in the rayon industry is recovered from the concentrated-waste-cooking liquors by one of two methods: (*a*) dialysis and (*b*) centrifuging and evaporation. Dialysis produces a very pure product but one that is much more dilute than the original waste. About 90 per cent of the dissolved hemicellulose and almost all the mineral impurities are removed.

The dialyser[6] consists of a tank containing a large number of diaphragms or membranes in the form of flat bags. These bags are mounted in parallel and are independent of each other. They are made of "a specially treated cotton cloth produced by a carefully controlled process to ensure long life and high purity of product." Each diaphragm consists of a wire mattress inside the flat cloth bag, supported by two rigid wire frames on either side. These frames are set crosswise in a rectangular tank. The bottom of each bag is connected to a header by means of a pipe attached to the bag. This provides an outlet for the purified soda solution. An automatically regulated fresh-water supply is led to the connections at the top of each bag.

The waste soda liquors are fed into the tank outside the bags. Fresh water is slowly admitted to the diaphragms and the level inside the bags kept about ½ in. above the water outside. The caustic passes through the cloth, leaving the impurities in the waste, which is continuously drawn off. The impure waste before treatment usually contains about 16 to 17 per cent caustic. The concentration of the purified solution varies to some extent with the time of contact but will average about 8 per cent.

The waste from the process contains about 4 per cent carbonates and 2 per cent organic matter, much of which is hemicellulose. This waste is high in polluting value and must be discharged into the other mill wastes for further treatment.

When the evaporation process is used, the wastes are first centrifuged to remove the larger suspended material. The centrifuge removes most of the hemicellulose and other impurities. At this point the concentration of the caustic solution is about 6.5 per cent NaOH. From the centrifuge it passes to a tank that supplies the evaporators. The evaporators are of the

quadruple-effect vacuum type. The first evaporator increases the caustic concentration to about 7.5 per cent; the second, to 18 per cent; the third, to 24 per cent; and the last, to about 30 per cent. The concentrated solution is then passed through a cooling system to a storage tank, where it is ready for reuse in the mill. About 97 per cent of the caustic is recovered. The system and process is more expensive than the purification by dialysis. However, a concentrated liquor is obtained which is used to a better advantage in the mill, although this liquor is not so pure as that obtained by the previous method.

PREPARING THE WASTES FOR TREATMENT

In this discussion of treatment processes, the first consideration will be given to those processes adapted to the total mill wastes. However, it is often necessary or at least advantageous to pretreat certain of the more concentrated wastes prior to their combination with the other mill wastes for the final process. For instance, certain dye wastes may give trouble in the general-treatment process and must be bleached prior to their discharge. Also, deterging liquors must be treated for grease recovery before the final treatment is applied. The processes adapted to the pretreatment of certain of these concentrated wastes will be discussed later.

Segregation of Clean Water.—As much as 75 per cent of the total mill-waste flow is composed of comparatively clean water. This water is segregated from the more concentrated wastes and discharged direct to the stream. The selection of those wastes to be segregated is a matter for local study and depends on the dilution available in the stream and the desired condition of the stream. Wastes that might be considered too strong for direct discharge in one case may not cause difficulties in another. The degree of segregation in any mill depends also on the location of existing sewers and the difficulties and expense encountered in making the change.

Care must be taken not to place too much reliance on the millworker for the proper separation of concentrated and weak wastes—in cases, for example, where deterging and washing are carried on in the same container. The waste from the former operation is very concentrated and requires treatment. Per-

haps the same is true of the first washings. Subsequent washings become weaker and may not require treatment. In this case, the separation, if left entirely to the worker, usually results in an unsatisfactory condition. Much more satisfactory results are obtained by moving the material to another vat for the final wash, even if the additional labor involved is considered.

Acid or Alkaline Wastes.—Wastes that contain large amounts of either acid or alkali are often encountered. The unsatisfactory nature of these wastes is often remedied by dilution with other mill wastes. Small amounts of an acid waste may be neutralized by the natural alkalinity of the water or by the chemicals added in the treatment process. Excess alkali above that producing a pH of 9.0 to 9.5 is removed or neutralized prior to the treatment process, since the usual coagulant is dissolved by excessive caustic. In cases where the alkali is present in quantities that will impart a pH higher than 9.5 to the entire mill waste, caustic recovery from the concentrated wastes is desirable even if it is not profitable.

Bleaching of Dye Wastes.—Most dye wastes, particularly those from direct, basic, or sulphur dyeing, are decolorized prior to the application of the treatment process. In a few cases, the chemical coagulation and sedimentation processes greatly reduce the color of the dye, and preliminary bleaching is not necessary. This depends on the character of the dye used and must be given consideration when the local study is made.

Where bleaching processes are employed, the wastes from these processes may be used to decolorize the dye wastes. This necessitates the mixing of the two wastes prior to their entrance to the treatment plant proper. If the bleaching wastes are not sufficient to decolorize the dye entirely or if they are not available for that purpose, provision is made for adding chlorine, sodium hypochlorite, or chloride of lime to the dye wastes. This is accomplished in a small contact tank in which is installed a chlorine diffuser or other desirable dosing equipment. The amount of chlorine applied is best controlled manually. The contact time required is about 10 min.

Certain dyes are not decolorized by chlorine. Whether this type is used must be determined before the treatment process is installed.

TREATMENT METHODS

It is often necessary to vary the treatment to fit the individual mill wastes, yet in all cases the use of chemical precipitation is required to provide at least primary treatment. This may or may not be followed by biological processes, such as filtration, depending on the degree of treatment desired.

Primary Treatment.—Primary treatment of textile wastes consists of the equalization of the waste, coagulation with chemicals, sedimentation, sludge removal and drying, and final disposal of the sludge. The two principles of sedimentation, continuous flow and fill and draw, are applicable in most cases. If the former is used, a preliminary equalization or storage tank is required. Fill-and-draw sedimentation and equalization may be accomplished in the same set of tanks. At least two tanks operating in parallel are required for the fill-and-draw process. Whenever chemical precipitation is employed, effective results are obtained only when a period of slow mixing (flocculation) precedes sedimentation.

Continuous-flow Plant.—Figure 60 shows the suggested arrangements for the units for a continuous-flow treatment plant. This arrangement of the units is suggested for economy in construction. Any other arrangement that provides the same facilities and detention periods will do equally well.

The equalizing tank for the continuous flow has a capacity of at least 3 hr. maximum flow of waste. The tank is a concrete structure, built preferably in connection with the other units. The floor of the tank slopes slightly in the direction of a drainage line to provide for cleaning and flushing the tank. The drain line is connected to the sludge-pump line, or, if the sludge is drawn by gravity, the line may lead direct to the sludge beds. Table 55 shows the size and dimensions of equalizing tanks required on the basis of various maximum hourly flows of waste.

Nozzle or perforated-pipe aerators are installed in the equalization tank and are connected to an air compressor. The purpose of aeration in this tank is threefold: (*a*) it facilitates the mixing and equalization of the waste; (*b*) it prevents or decreases the accumulation of settled material in the tank; (*c*) it provides for the preliminary chemical oxidation of reducing

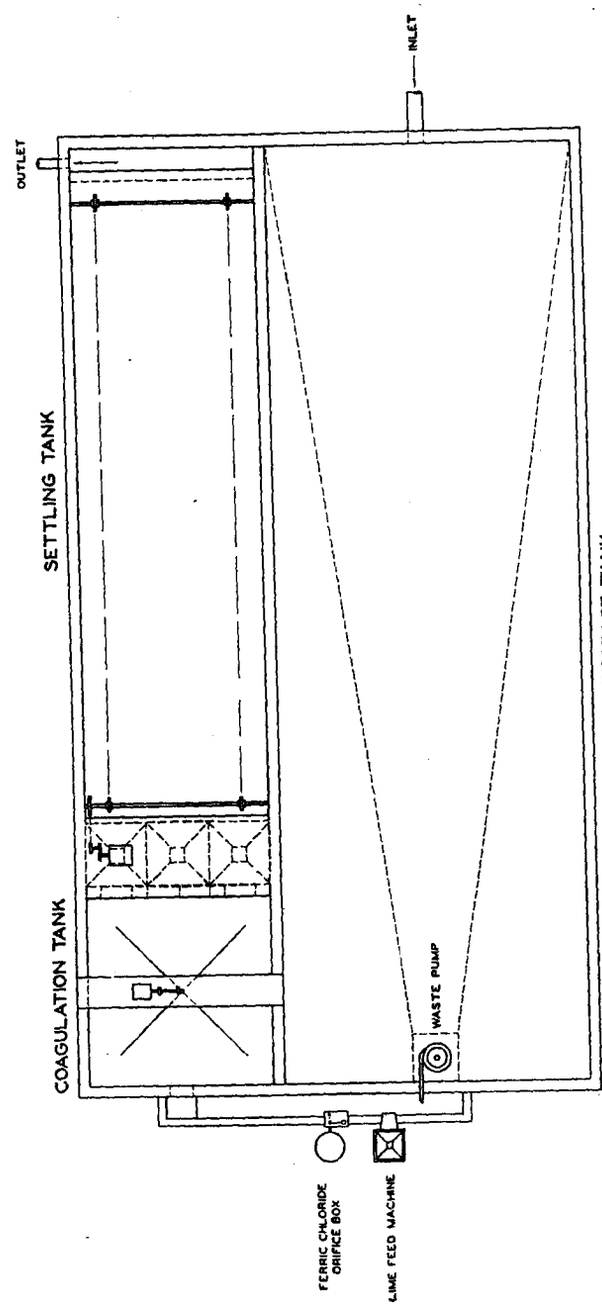

Fig. 60.—Plan for a continuous-flow treatment plant for textile wastes.

agents such as may be contributed by sulphur and other dye wastes. The air requirement for this purpose is about 0.5 cu. ft. per gallon of waste.

It is possible to use a portion of the equalizing tank for coagulation. To accomplish this purpose, aeration of the waste is confined to the first three-quarters of the tank. A coagulation mechanism is installed in the quarter nearest the sedimentation units. Chemicals are applied just prior to the coagulation portion. This plan provides a much longer coagulation period than is necessary and may result in a more rapid accumulation of sludge in the equalizing tank. A much better arrangement is shown in Fig. 60, in which the coagulation tank is a separate unit.

The waste is pumped from the equalizing tank into a mixing trough or tank where the chemicals are added. From the mixing trough the waste enters the bottom of a coagulation tank. This tank has a capacity detention period of from 15 to 20 min. for the maximum flow of waste. It is provided with coagulating equipment of either the horizontal- or vertical-paddle type, as described in Chap. III. Table 55 shows the required capacity of tanks for various rates of flow of waste.

From the coagulation tank the waste passes through large openings in the dividing wall between this tank and the settling tank. The sedimentation unit may be of either the rectangular

TABLE 55.—CAPACITY AND DIMENSIONS OF TANKS FOR CONTINUOUS-FLOW TREATMENT OF TEXTILE WASTES

Rate of flow of waste, gal. per hr.	Equalizing				Coagulation				Settling			
	Capacity, cu. ft.	Width, ft.*	Length, ft.*	Average water depth, ft.*	Capacity, cu. ft.	Width, ft.*	Length, ft.*	Average water depth, ft.*	Capacity, cu. ft.	Width, ft.*	Length, ft.*	Average water depth, ft.*
5,000	2,000	11	36	5	220	7	7	5	1,000	7	29	5
10,000	4,000	14	46	6	440	9	9	6	2,000	9	37	6
15,000	6,000	18	56	6	660	11	11	6	3,000	11	45	6
20,000	8,000	18	63	7	880	11	11	7	4,000	11	52	7
25,000	10,000	19	64	8	1,100	12	12	8	5,000	12	52	8
30,000	12,000	21	70	8	1,320	13	13	8	6,000	13	57	8

* Inside dimensions.

or the circular type, as discussed in Chap. III. It is equipped with a sludge-collecting mechanism. The capacity of this tank is such as to provide a 1½-hr. detention period for maximum flow. Table 55 also shows the size of tanks required for different rates of flow.

Sludge is drawn by gravity or pumped to sludge beds or sludge-drying equipment, depending on the respective elevation of the sedimentation and sludge-disposal units. The sludge pump is of the open-impeller, nonclog, centrifugal type. It has at least a 2-in. suction and discharge and a capacity of from 25 to 50 g.p.m. Sludge disposal will be discussed later.

Fill-and-draw Plant.—The fill-and-draw process is adapted for use in the smaller textile mills, where hourly waste flows do not exceed 10,000 to 12,000 gal. Since steel or wooden tanks may be used, the cost of the treatment units will be much less than the more permanent concrete structures required for the continuous-flow process. Because of the size and number of wooden tanks required for large volumes of waste and because the operation becomes more complicated as the number of units increases, the fill-and-draw process is not so well adapted to flows above the values given. The following is a brief description of the structures and equipment needed for the fill-and-draw process. Figure 61 shows a suggested plan for this plant.

The waste is collected in a sump having a capacity of about 5 to 10 min. flow. Here the waste is picked up by a float-controlled vertical-type centrifugal pump and discharged to a mixing trough. The pump has a capacity sufficient to discharge at the maximum rate of flow of waste from the mill.

The chemicals may be added in the mixing trough or direct to the waste in the tanks as they are filled. There are advantages in either method. The use of the mixing trough eliminates some of the labor of operation, since the chemicals are added continuously and are under automatic control. However, the amount of chemical added in this manner is more or less set and is not varied with the requirements of the specific waste. Since these wastes vary to a considerable extent, the quantity added may be too great or too little. In order to avoid undertreatment, the amount added is usually in excess of the requirements. When chemicals are added direct to the waste in the tank, the waste is

first mixed and tested to determine the amount required. This amount is then applied manually.

The mixing trough is constructed in such a manner that the mixed waste may be directed to either of the tanks as desired.

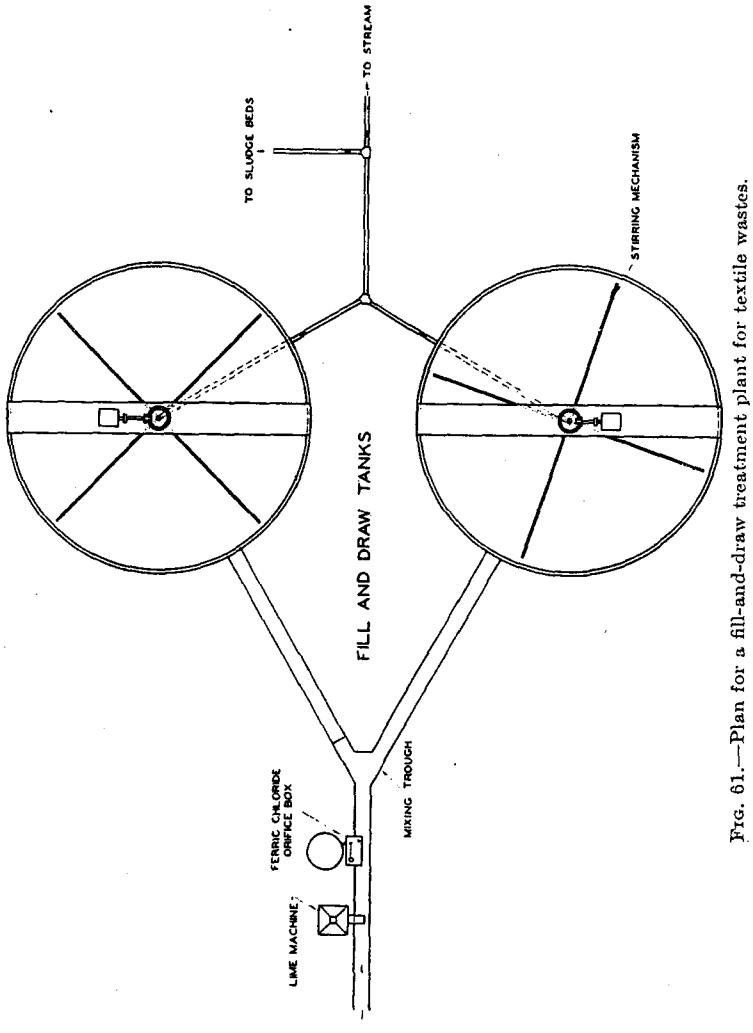

FIG. 61.—Plan for a fill-and-draw treatment plant for textile wastes.

Flash mixers may be used in place of the mixing troughs. At least two tanks are required for the fill-and-draw process. These tanks are set at an elevation that will allow the gravity with-

e amount required. This

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r of the tanks as desired.

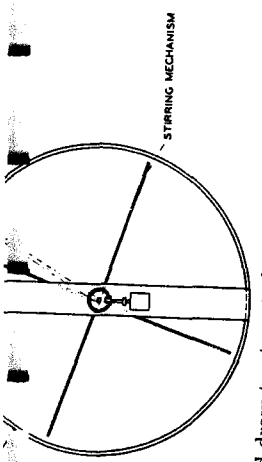

FIG. 61.—Plan for a fill-and-draw treatment plant for textile wastes.

he mixing troughs. At
d-draw process. These
ow the gravity with-

drawal of both sludge and supernatant liquor. They may be of wood-stave or steel construction with a hopper bottom of at least a 1-to-2 slope. Each tank is provided with a stirring mechanism for mixing and coagulating the waste. This mechanism consists of several horizontal paddles operated by a central shaft attached to a motor and reduction gear. The end velocity of these paddles is about 120 ft. per minute. Table 56 shows the capacity and dimensions of tanks required for various waste volumes and the detention periods provided. About 30 min. of this period is used for mixing and coagulation. The remainder is required for filling, settling, and drawing.

TABLE 56.—CAPACITIES AND DIMENSIONS OF FILL-AND-DRAW PLANT FOR TEXTILE WASTES

Flow, gal. per hr.	Number of tanks	Detention period, hr.	Capacity of tank, cu. ft.	Depth, ft.*	Diameter, ft.
2,000	2	5	1,330	10	13
4,000	2	5	2,650	10	18
6,000	2	5	4,000	12	20
8,000	2	5	5,350	12	24
10,000	2	5	6,650	14	25
12,000	3	4	6,400	14	24

* Water depth.

Sludge is removed by drawing from a line connected to the apex of the hopper. This line discharges into an inspection well which allows the operator to control the drawing of the sludge. The supernatant liquor is skimmed from the upper surface by means of a flexible hose or swivel pipe attached to a float. This line also discharges into an inspection well for convenience in operation. Both the sludge and supernatant lines are controlled by a manually operated valve.

Coagulants and Their Application.—Lime is one of the most common of the coagulants used for textile-waste treatment. In many cases it is possible to use lime without the addition of other chemicals. This is especially true if the mill wastes do not contain a large proportion of soapy detergent wastes. These wastes tend to make the precipitated floc light, and much of it will float rather than settle.

Lime is applied to the waste in the mixing tank or trough by means of either a wet- or dry-feed lime machine. The simplest dry-feed lime machine is of the vibrating type. This machine may discharge into a slaking tank and the milk of lime discharge into the waste, or the dry lime may be added direct to the waste in the trough. A high-calcium lime is most satisfactory for chemical precipitation.

Other coagulants may be necessary with certain types of wastes. The most commonly used coagulants are alum, ferrous sulphate, ferric chloride, and ferric sulphate. In general, iron salts are used in preference to alum because of the heavier floc formed. These chemicals are added in solution form by means of an automatically controlled orifice box or by a constant-head siphon. The chemicals are first weighed and then suspended in a solution tank containing the desired amount of water. This tank is equipped with a stirring mechanism. Iron compounds (ferric chloride and sulphate) are very corrosive in solution and must be kept in rubber-lined or wooden tanks. All dosing equipment must also be rubber-lined if it comes in contact with these solutions.

Sulphuric acid is sometimes used to neutralize strongly alkaline wastes and to precipitate certain of the sulphur and vat dyes that are soluble only in an alkaline medium. Acid is also used to break up emulsions of oils and soaps. The acid is applied in the same manner as are solutions of iron salts.

The quantity of chemicals required for coagulation varies over such a wide range that no definite limits can be given. The average amount of lime for the usual mill waste is about 4 lb. per 1,000 gal. When other coagulants are used, the average requirements are about 1 lb. of alum, ferric chloride, or ferrous sulphate per 1,000 gal. The selection of the coagulant and a determination of dosage requirements must be made by a study of the waste to be treated.

Sludge Drying and Disposal.—The sludge removed from the settling tank contains from 98 to 99 per cent water and has a volume from 3 to 5 per cent of that of the waste treated. The method used for the drying and disposal of this sludge depends somewhat on local conditions. There are several methods of sludge drying available, of which the most generally used is by application to sludge beds. The chief objection to the sand

drying bed is that it depends entirely on weather conditions and cannot be used during the rainy season or during the winter. Sludge-bed construction has been described in Chap. III. Each bed constructed is of such a size as will hold 1 day's supply of sludge when it is applied to a depth of about 12 in. Sludge is never applied over the top of partially dried sludge, since the water will not drain through the first application. The sludge is left on the beds until it is reduced to below 90 per cent water, in which condition it can be removed with a shovel. The sand is raked before a new batch is applied. During good drying weather, sludge may be removed in about 10 to 14 days. The sludge-bed area required per 1,000 gal. of waste treated varies between 4 and 6 sq. ft. for each day required for drying. The dried sludge is of no value whatever, and it can be used only as fill.

The simplest method of sludge disposal is by ponding. This method is used under certain local conditions. The ponds require large areas of land in such a location as not to be objectionable, if odors are produced. Decidedly unpleasant odors may arise from such ponds. These ponds are arranged in parallel so as to allow for periodic cleaning. They have a capacity of at least 6 to 8 months' production of sludge or from 4 to 6 cu. ft. for each 1,000 gal. of waste produced over that period.

The most dependable method of sludge drying and one that can be used over the entire year is vacuum filtration. This method, however, is not used generally, since considerable expense in equipment is involved. It is feasible when land areas are not available and when the volume of sludge is large. To use effectively a vacuum filter with textile wastes, the sludge is first pumped to a storage tank that has a capacity equal to the volume of sludge produced by 1 day's operation. This sludge is allowed to settle overnight and is filtered the following day. In most cases some concentration of the sludge is obtained by the prolonged period of settling. The clear upper layer is withdrawn to the fresh waste and passes through the treatment plant. Sludge from the tank is treated with ferric chloride, filtercel, or some satisfactory conditioning agent and applied to the vacuum filter. The quantity of conditioning chemical varies from 20 to 40 lb. per 1,000 gal. of sludge.

The area of the filter, in the case of small installations, is such as to allow for its operation for only a few hours daily. The rate of filtration is approximately 30 to 40 gal. of sludge per square foot of filter area per hour or, on the basis of the volume of waste, the filter area required is about 1 sq. ft. per 1,000 gal. of waste water.

Secondary Treatment.—Most textile wastes are amenable to biological treatment or can be made so, although this process is not often applied. This treatment is always secondary to sedimentation or chemical coagulation and sedimentation. It is used only when a higher degree of treatment is desired than is possible by the primary treatment previously described. Wastes containing scouring liquors and washings from deterging operations generally require secondary treatment.

The biological filter is best suited for the secondary treatment of these wastes, since it is not so easily upset by the varying character of the wastes as are other methods. Grease, oil, the major portion of the suspended solids, and any toxic materials present must be removed before the waste is applied to the filter. Methods for the removal of these substances have already been discussed.

The trickling filter of standard design, as shown on page 124, is used. This filter is composed of a circular bed of stones supported by a proper underdrainage system. The waste from the primary-sedimentation tank is applied to the filter by a rotary distributor. The depth of filter stones most commonly employed is 6 ft. The stones are of hard granite gravel or crushed rock having a size varying between 2½ and 3½ in. in diameter.

The area of filter required is based upon the B.O.D. load to be applied. The basis of design is 100 cu. ft. of medium per pound of B.O.D. or approximately 17 sq. ft. of filter surface per pound of B.O.D., if the filter is of standard depth (6 ft).

Biological filtration is followed by secondary sedimentation to remove solids that break loose from the filter medium. The secondary tank is of standard design, as shown for primary sedimentation in Fig. 60. The detention period is 1 hr.; average water depth, 6 ft.; width, about 25 per cent of length. The sludge from the secondary sedimentation is pumped back to the raw waste as it enters the mixing trough and is collected and

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treated along with the sludge from the primary process. This sludge decomposes readily and may cause disagreeable odors if applied direct to drying beds.

TREATMENT OF SPECIAL WASTES

Wool-scouring Liquors.—The recovery of grease and potash from wool-scouring liquors has already been discussed. Grease must be removed from this waste before any type of treatment is applied. Following the degreasing operations, the waste is then discharged into the general mill wastes and treated along with these other wastes by the chemical-precipitation process.

Cotton-kiering Wastes.—Usually cotton-kiering wastes may be treated along with the other mill wastes, provided their discharge is spread over the day. Some mills make a practice of dumping these kiering liquors at night or at some definite period during the day. Such an arrangement seriously affects the treatment-plant operation. The wastes should be stored in a tank and discharged uniformly over the entire day.

In cases where the alkalinity of these wastes is such as to increase that of the total waste above pH 9.0, it is necessary to neutralize partly the kier wastes in the storage tank. A commercial grade of sulphuric acid is used for this purpose. It may be applied to the waste as it leaves the tank or, better, to the tank contents before they are discharged.

Bleach Liquors.—Bleach wastes are usually purified along with the other mill wastes. Spent chlorine assists in the decolorization in the dyestuffs in the waste. As in the case of the kiering wastes, the alkalinity of the bleach liquors must sometimes be reduced by neutralization with acid. Usually the dilution afforded by mixing with the other mill wastes reduces both the alkalinity and chlorine content sufficiently so that no difficulties are encountered in either the chemical precipitation or the biological filtration of the mixed wastes.

Silk-degumming Wastes.—These wastes have a very high concentration of organic materials. If sufficiently diluted with other wastes, they may be treated by the chemical-precipitation and biological-filtration processes. In many, and perhaps most, cases it is better to treat these wastes for the recovery of oils and grease before mixing them with the mill wastes for final treatment. The method used for grease recovery is the acid

method previously discussed. The recovered material has a value in the manufacture of soaps that should be sufficient to pay the cost of acid treatment.

Dye Wastes.—Most of the dyes, especially the acid dyes used on wool and silk, are readily removed by chemical precipitation. A few, such as the basic and naphthol dyes, are somewhat difficult to decolorize. When the predominating dye used in the mill is of the type that resists removal, a special study is made to determine the required treatment.

Some of these dyes are decolorized by chlorine, hypochlorite, or waste bleach liquors. In cases where such dyes are used, the dye-room waste is first mixed with waste bleach liquors before they are discharged into the mill-waste line. It is often necessary to supply additional bleach to complete this reaction.

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Industrial Waste Treatment Practice

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CHAPTER XI

LAUNDRY WASTES

The laundry is a service rather than a manufacturing industry. The methods employed in the washing of clothes are quite well known. The wastes, however, have not received so much attention as have those from some other industries. Laundry wastes, although somewhat smaller in volume, are among the most objectionable from the standpoint of the pollution of streams and their effect on municipal-sewage-treatment facilities.

Laundries are usually located so as to discharge their wastes into municipal-sewer systems, where, in most cases, dilution is such that the presence of the waste is not noticeable. But in some small communities and especially in most institutions having sewage-treatment facilities, laundry wastes make up a large portion of the sewage flow. These wastes give rise to difficulties in the operation of certain of the treatment units, especially those designed for plain sedimentation. The soap and grease adhere to the sewage solids and rise to the surface of the water in the settling tanks. The scum formed in this manner is odorous and unsightly, cannot be made to settle, and eventually forms in such quantities as to impair the quality of the effluent. When such difficulties arise, it is usually advisable to provide separate treatment facilities for the laundry waste.

CHARACTER OF WASTE

The liquid wastes from a laundry are composed of the water used for washing, starching, and rinsing the clothes. This water contains the grease and dirt removed from the cloth, excess starch, a considerable amount of soap and soda ash, and, in some cases, dyes and bleach. It is turbid, highly alkaline, and readily putrescible.

The B.O.D. of this waste varies over a fairly wide range. The average is probably about 400 p.p.m. and the maximum about 1,000 p.p.m. No information is available as to the volume of

waste produced on the basis of the weight of the clothes washed. It is expected that this volume will also vary widely.

TREATMENT PROCESSES

Both chemical precipitation and biological filtration have been used for the treatment of this type of waste. Of the two, biological filtration appears to be the more effective, the less expensive, and the simpler from the standpoint of operation. There are conditions, however, under which the use of the chemical-precipitation process is more feasible. For instance, in Northern sections the winter conditions interfere with the filtration process. Chemical-treatment facilities are not so much affected by cold weather, and they do not require the space necessary for biological filtration. When used as pretreatment prior to the discharge of the waste to a sewage-treatment plant, the purification produced by the chemical process is sufficient to protect that plant. Because of their application to different conditions, both methods will be discussed here.

BIOLOGICAL FILTRATION

The biological-filtration process for laundry waste requires a holding tank, a filter, and a settling tank. The design of this plant is the same as that used for milk-waste treatment (standard filter) and is shown in Figs. 32 and 33.

Holding Tank.—Because of the wide variation in both the rate of flow and the strength of the waste, it becomes necessary to provide some equalizing period so that the waste applied to the filter may be more uniform. For this purpose, an equalizing tank having a capacity of about 2 to 3 hr. maximum flow is used. However, since most laundries operate only for 8 to 12 hr. daily, it is necessary that the filter be of a size that will allow the application of the entire daily volume during this working period. Less area of filter is required for the same volume of waste if the period of filter operation is extended. This may be accomplished by increasing the size of the holding tank. It is somewhat more costly to build the larger filter than it is to increase the size of the holding tank. Also, it is desirable to have more continuous filter operation. If possible, the filter should operate at least 20 hr. daily. This requires a holding tank with a capacity of about 65 to 70 per cent of the total

daily waste flow during maximum periods. The area of the filter in this case is decreased by about 50 per cent of that required for the short period of operation. Table 62 shows the required capacity and dimensions for various waste volumes.

Standard Filter.—The standard filter is used for the treatment of this waste. Possibly the recirculating principle may be applied in this case as it has been to other types of industrial wastes. No data, however, are available to substantiate the use of such a filter.

The design of the standard filter is shown in Fig. 33. The calculation to determine the volume of filter medium required is based on a loading that provides 80 cu. ft. of medium per pound of B.O.D. The standard depth of filter is 6 ft., so that the area required per pound of B.O.D. is 13.3 sq. ft. The area is calculated by use of the following formula:

P.p.m. of B.O.D. × gallon-day waste × 0.00011
= square feet filter

TABLE 62.—CAPACITY OF UNITS FOR THE BIOLOGICAL FILTRATION OF LAUNDRY WASTE

Volume, gal. per day	Holding tank, cu. ft.	Filter area, sq. ft.	Settling tank, cu. ft.
2,000	185	88	
4,000	370	175	
6,000	550	265	55
8,000	740	350	75
10,000	930	440	95
15,000	1,400	660	140
20,000	1,800	880	180
25,000	2,300	1,100	230

On the assumption that the B.O.D. of the waste is 400 p.p.m., Table 62 shows the area and diameter of filters required for various volumes of waste.

The details of the units and appurtenances for this filter are described on page 124.

Settling Tank.—The design of the settling tank is also shown in Fig. 32. This tank has a detention period of 2 hr. on the basis of the uniform-filtration rate established by pumping from the holding tank to the filter. Table 62 shows the capacity

required for various flows, if a 20-hr. operating period for the filter is assumed.

CHEMICAL PRECIPITATION

Chemical precipitation of laundry wastes is carried out in fill-and-draw tanks. This principle is superior to continuous flow, since the treatment is more easily controlled and is simpler to apply.

A detailed discussion of the fill-and-draw process may be found in the chapter on Textile-waste Treatment, pages 257 to 259. Figure 61 is a line drawing showing the arrangement of the required units. One or more tanks are used, having a combined capacity equal to the daily flow of waste. These tanks are filled with the waste, treated with the necessary amount of chemical, and coagulated for about 20 min. The coagulation mechanism is stopped, and the precipitated material is settled for a period of about 2 hr. The sludge is then drawn to a storage tank, lagoon, or sludge beds, according to which facility is provided.

Iron salts (ferric chloride or ferric sulphate) are the best coagulating chemicals for this purpose. The work of Boyer at the Agricultural and Mechanical College of Texas showed that considerable chemical may be saved by first adjusting the pH of the mixture to 6.4 before applying the chemical. Sulphuric acid is used for pH adjustment. The same condition of pH, however, is obtained by adding the additional coagulant. The price of the additional iron salt required is not much, if any, greater than that of the sulphuric acid, and pH adjustment complicates the operation.

The quantity of chemical is determined by the treatment of a sample taken from the batch of waste after thorough mixing. About 3.5 lb. of ferric chloride or ferric sulphate is usually required per 1,000 gal. of waste.

Boyer found that the quantity of sludge obtained was about 4 per cent of the volume of waste treated. The disposal of this sludge depends on local conditions. If room is available it may be lagooned. Two or more lagoons should be arranged to operate in parallel. One lagoon is used until filled. The upper liquor, which is usually clear, is decanted and the sludge allowed to dry, in which condition it can be removed. The size of

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lagoons required depends on the weather conditions. Sufficient capacity is provided to allow time for the cleaning of the lagoon before it is again placed in operation.

Sand beds may be used for sludge drying. The design of these beds is shown on page 58. Each sand bed has a capacity equal to the daily volume of sludge. The bed is filled to a depth of 1 ft. A sufficient number of beds are provided so that the sludge is dried and the bed cleaned before again being used. In good drying weather, about 5 to 7 days are required for sludge drying. Sludge may be stored in a tank during periods when the sludge beds are not available.

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CHAPTER XII

WASTES FROM THE METAL INDUSTRIES

The wastes from the metal industries discussed in this chapter are (*a*) acid and alkaline pickling liquors resulting from the cleaning of metal surfaces prior to plating or other processing; (*b*) the metallic-cyanide solutions and washings from plating processes; (*c*) waste cyanide from heat treating. Other wastes from these industries, such as those containing oil, will be discussed in a later chapter.

WASTE PICKLING LIQUORS

There are two general methods in use for cleaning metal, prior to the manufacture of metal parts, whereby a liquid is produced. Still pickling is used for the removal of red rust from iron. Electrolytic pickling is used for the removal of black magnetic oxide.

Still pickling usually consists of placing iron pipe, rods, or bars in a vat containing a 4 to 5 per cent solution of sulphuric acid. The solution is heated to 160 to 170°F. About 1½ hr. is required to clean pipe and a somewhat shorter time to clean rods and bars. The metal is then removed from the acid vat and placed in a vat through which clean water is constantly flowing. From the wash water it is placed in a solution consisting of ½ per cent caustic soda and ¾ per cent trisodium phosphate.

Black magnetic oxide is removed slowly by sulphuric acid. The electrolytic method is generally employed to clean metal covered with this oxide. The process is much the same as the still process except that the metal is made the anode of an electrolytic cell, a somewhat stronger solution of acid is used, and the process is much more rapid.

The Waste.—The waste, regardless of the process, consists of the partially spent acid and alkali solutions, when they are no longer usable, and the continuous washings. These wastes contain, in addition to the excess free acid and alkali, a large amount of soluble ferrous sulphate. Acid solutions are usually

discarded when the acid content is reduced to about 2 per cent. As the acid is neutralized, the ferrous sulphate is precipitated as a white or slightly green ferrous hydroxide, a jellylike material that turns brown on exposure to the air. In the hydrolysis of ferrous sulphate to ferrous hydroxide, sulphuric acid is produced. Thus, in addition to the free acid in the solution, there is the acid produced by hydrolysis. The washings contain a varying amount of the pickling solution that is carried over by the metal as it is transferred from the pickling to the washing vat.

When discharged into a stream, the waste has a very high initial oxygen demand because of the rapid oxidation of the ferrous hydroxide to the brown ferric oxide. The latter is insoluble and forms a covering over the stream bed. The free acid and alkali, unless neutralized, are extremely toxic to aquatic life.

Elimination or Reduction of Acid.—Processes for cleaning rust and grease from metal without the use of acid are available. These methods are expensive and often cannot be used because of interference with other processing operations. Whenever a new pickling room is contemplated, a study should be made of the relative costs of the acid and nonacid processes, keeping in mind the cost and difficulties of waste neutralization if the acid process is adopted.

Spent pickling liquors may be used for the production of commercial ferrous sulphate (copperas). The spent liquor is collected in a tank containing scrap iron and left until nearly all the free acid is removed. Heat is applied to speed up the reaction. The solution is then evaporated and the crystalline ferrous sulphate residue dried.

The acid liquor in the washings is greatly reduced by providing means for draining the liquor back into the pickling vat before the metal is transferred to the washing tank. If rods or strips are cleaned, the metal is suspended above the tank on a drainboard until the major portion of the solution drains back into the tank. Jets of air may be used to blow the acid solution from the metal. Tubes are held in a tilted position to allow the liquor to run from the inner surfaces.

Treatment of Acid Liquor.—The treatment of these wastes consists of neutralizing the excess acid and precipitating, oxidizing, and settling out the iron oxide. This is not easily

accomplished because of the thick jellylike character of the precipitated iron, especially from the more concentrated solutions. Alkali liquors used for neutralizing the excess acid on the metal parts and for removing grease are usually discharged with the acid wastes. The alkalinity of the wastes is not sufficient to neutralize the acid of the pickling liquors.

Lime is generally used as a neutralizing agent because of its low cost. However, caustic soda is a better reagent from the standpoint of operation, since it is more readily mixed with the waste and does not form such a heavy sludge. After the main portion of the sludge is removed, air is passed through the remaining liquid to oxidize and remove the excess iron oxide. Sufficient neutralizing reagent must be added to give a pink reaction with phenolphthalein.

When treatment of this waste is considered, a measurement of the maximum daily volume is first made. Usually the volume is comparatively small and may be measured by timing the filling of a 5- to 10-gal. receptacle. This is done at frequent intervals over several days and during a period when the factory is at its peak of production.

If the volume is not too great, the fill-and-draw principle of treatment can be used to best advantage. In this case, two tanks are provided, each having a capacity capable of holding the daily volume of waste. They may be wood-stave tanks. The first is equipped with a stirring mechanism consisting of a motor-driven vertical shaft, to which are attached several horizontal paddles. This tank has a hopper bottom, at the apex of which is a drainpipe.

The second tank is similar to the first, except that the paddles are omitted and air lines are installed for the aeration of the waste. The air lines are of perforated pipe and are connected to an air compressor. This tank is set at an elevation so that its water line is below the bottom drain of the first tank. The piping in each tank is arranged in such a manner as to allow the drawing of the sludge to a pit and the clear water to either the second tank or to the sewer.

The operating procedure is as follows: The waste is collected in a sump, from which it is lifted to the first tank by means of an air-lift pump. At the end of the working day, lime or caustic soda is added to the waste and the mixture stirred for about 1 hr.,

or until thoroughly mixed. The paddles are stopped and the mixture is allowed to settle overnight. Before the factory opens in the morning, the sludge is drawn to a pit and the liquor to the second tank. Here air is applied for most of the day. The contents of this tank are then allowed to settle, and the sludge is drawn to the pit and the waste discharged.

Thus, after the first day, both tanks are in operation, one filled with fresh waste to be neutralized and the second used for the aeration of the previous day's waste.

The quantity of lime required is determined on a sample of the mixed waste by a laboratory titration using a standard caustic soda solution. Sufficient lime is added to give a slight pink color with phenolphthalein.

A considerable quantity of sludge is obtained that consists of calcium sulphate and iron oxide. The disposal of this sludge depends on the size of the industry and local conditions. Where land is available, the sludge is pumped to lagoons, where it is allowed to dry. These lagoons are built to operate in parallel so that those filled with sludge may drain and be cleaned while the sludge is discharged into others. The sludge compacts in the lagoons, and much of the water may be withdrawn from the surface by a swivel pipe set in the bank of the lagoon. This water is discharged to the sewer or stream.

Where land is not available and the industry is large, the sludge is dried to about 55 per cent moisture on a vacuum filter. In this condition it is readily handled for final disposal. The dried material is usually used for fill. In at least one steel mill it is further dried and pressed into various types of construction boards.

PLATING-ROOM WASTES

Plating-room Process.—The raw material for the plating room usually consists of sheet steel. This steel is cleaned in the pickling department, as previously described, and passed to the stamping and punching room. Here it is punched and pressed into the desired shapes and sent to the plating room.

The usual plating room contains a series of vats in which are cleaning, plating, and washing solutions. The metal parts are moved from one vat to the other, either individually or on frames containing a number of parts. The movement of parts in the

more modern, large plating rooms is almost entirely automatic. In smaller or older establishments the parts are moved by hand. The operations in a typical plating room are much as follows:

The parts are first thoroughly cleaned, since even the smallest spot of grease or dirt will damage the final finish. The first bath consists of a strong solution of sodium carbonate and sodium silicate, in which the parts are boiled. They are then transferred to the electro cleaning bath, where they are alternately made the cathode and anode. The next vat contains hydrochloric acid, in which the parts are pickled, usually without the application of the electric current. From the acid bath they are lifted to a vat through which water is running continuously.

The next bath consists of a solution of copper cyanide. The parts are made the cathode, causing the plating of copper on the steel. They again pass into a washing tank, where the excess copper cyanide solution is removed. Following this bath, the parts may be buffed or may go direct to a nickel cyanide bath. If they are buffed between processes, they are again cleaned before being plated with nickel. After the nickel has been applied, the parts are again washed and buffed, after which they may go to a chromium bath. Each of the cyanide baths is usually followed by a wash in running water.

There is some variation in the composition of the cyanide baths. The following is a typical commercial formula for the copper solution:

	G. per l.
Copper cyanide	22.5
Sodium cyanide	34.0
Sodium carbonate	15.0

Wastes.—Cyanide wastes from the plating room arise from two sources: First, a continuous waste containing a small amount of cyanide is discharged from the washing tanks and from spillage or drippings that collect on the floors and is washed to the sewer. Even when the parts are suspended above the bath and allowed to drain, some of the solution is carried over into the wash tanks. Some parts retain more of the solution than others; consequently the strength of these washings varies considerably. Washings have been known to contain as high as 500 p.p.m. of cyanide as KCN. The average is somewhat below 100 p.p.m.

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The second source of cyanide waste is the "spoiled" cyanide solution. During the plating reaction, sodium carbonate is produced. The concentration of this compound eventually builds up to a point at which the bath cannot be used. The solution is then discarded. The volume of this waste usually averages about 5,000 gal., and the cyanide content may be as high as 15,000 to 20,000 p.p.m. Fortunately, the cyanide baths may be used for a considerable time before they become spoiled. A typical spoiled cyanide bath showed the following content:

	P.p.m.
Sodium cyanide	15,200
Sodium carbonate	60,000
Copper	26,300

THE TOXICITY OF THE CYANIDES

Dr. M. M. Ellis of the U. S. Bureau of Fisheries makes the following statement[4] about the toxic action of the cyanides on fish life: "The simple cyanides exert a toxic action on living organisms by reducing or eliminating the utilization of oxygen. As a result of this physiological action, cyanide compounds reduce oxygen consumption and develop symptoms simulating asphyxia." The action is very rapid, and a very small quantity of the chemical is required for the fatal dose.

Dr. Ellis and others have determined the quantity of cyanide required to kill certain animals and fish. About 0.5 to 2.0 p.p.m. of sodium cyanide will kill fish in a very few hours. Animals require about 4 mg. per pound of body weight, and about the same dose is fatal to man. Birds have about the same sensitiveness. The small aquatic life that is food for fish and the eggs of fish is destroyed by from 1 to 15 p.p.m. of the poison.

Upon acidification of the metal cyanides, an insoluble gas—hydrocyanic acid gas—is produced. This gas is also very poisonous, to about the same degree as the soluble cyanides.

PRESENT METHODS OF DISPOSAL

The discharge of cyanide into the public waters should be resorted to only when the volume of stream water is at all times sufficient to reduce the cyanide below the fatal dose for aquatic life, which is about 1 part in 2 or 3 million. Considerable care should be taken to disperse the waste throughout the entire

volume of stream water so as to prevent any local concentration of the cyanide. At best, this method of disposal is not satisfactory for this very toxic waste.

Many factories pond the cyanide containing wash waters from plating rooms. The ponds are usually enclosed by a strong fence and posted with signs stating the character of the waste in the area. This method, although it removes the menace from the streams, may become a menace in other ways. Wells in the vicinity of the ponds may become contaminated by seepage, or children may gain access to water in the ponds.

The cyanide content of wastes ponded in this manner will gradually decrease and will finally entirely disappear if no fresh waste is added. This gradual removal of cyanide is due to a number of factors, such as dilution by rain water, seepage, and the destruction of the cyanide by either oxidation, hydrolysis, or decomposition.

The time required for the complete decomposition of cyanides in ponded waste has not been definitely determined. It undoubtedly varies, depending on the initial concentration of the cyanide, temperature, wind conditions, and precipitation. Ponds arranged so as to be used in parallel are more satisfactory than the continuous use of one large pond. As each pond is filled, the waste is turned into the next. The waste is allowed to remain in the ponds until tests show it to be free from cyanide. It is then discharged. Seepage and the consequent contamination of ground waters may be prevented by laying a concrete bottom in each pond.

ACID TREATMENT

The removal of cyanide from plating-room wash waters, spoiled plating solutions, and other wastes containing cyanides may be accomplished by means of acid treatment followed by the volatilization of the hydrocyanic acid gas. All compounds of the cyanides are extremely toxic, and extreme care must be used in the application of the process.

The treatment process can best be applied to batches of waste wash water or cyanide solutions. In the case of the washings, the entire day's flow of cyanide-bearing wastes is collected. Figure 66 shows the general design of a plant for this purpose. Because of the poisonous character of the hydrocyanic acid gas

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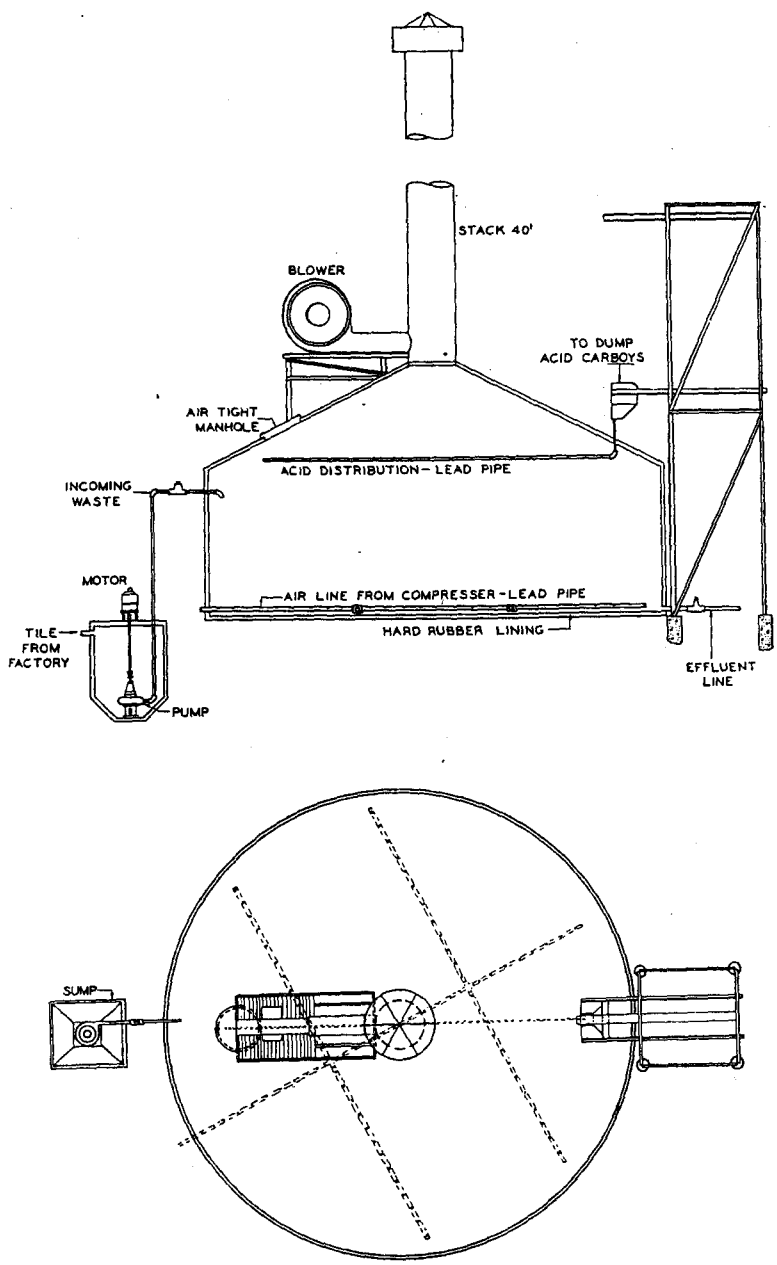

FIG. 66.—Cyanide-waste-treatment plant.

produced on the addition of acid to the waste, care must be taken in the location and design of the equipment to avoid possible danger from these fumes.

The plant consists of a rubber-lined tank of sufficient capacity to hold the daily volume of waste. This tank is tightly covered with a dome that is connected to a tall stack.

The wastes may either flow into the tank by gravity or be pumped from a sump connected to the factory drain. The acid (commercial sulphuric acid) is introduced from a carboy into the tank by means of a perforated lead pipe located above the solution surface of the tank. Care should be taken not to add the acid too rapidly, especially in the case of the concentrated cyanide solutions, since too great an evolution of the gas may cause trouble by not being sufficiently diluted with air.

Compressed air is introduced through perforated lead pipes laid on the floor of the tank. Diffusion plates may be used in place of the lead pipes. In order to dilute the gas further, a blower is located so as to blow a large volume of air into the side of the stack. The stack is at least 40 ft. high. In some cases existing boiler stacks may be used for the purpose of disseminating the gas into the atmosphere. Provision is made for drawing the treated waste to the stream after a test shows the desired reduction in cyanide content.

The amount of acid required for each batch may be roughly calculated as follows: (*a*) Determine the natural alkalinity of the water supply or the carbonate content of the spoiled plating solution, as the case may be. Calculate in terms of $CaCO_3$. (*b*) Determine the cyanide content in terms of KCN. (*c*) Apply the formula

$$(\text{P.p.m. of KCN} \times 0.0000068) + (\text{p.p.m. of } CaCO_3 \times 0.0000081) \times \text{gallons of waste} = \text{pounds of 100 per cent sulphuric acid required}$$

About 10 per cent more than the calculated amount is used.

The time of aeration required depends on the cyanide content of the waste. The initial period of aeration will remove the major portion of the cyanide. A total of about 16 hr. is usually sufficient. If the cyanide test shows that more than the desired amount of cyanide is present at the end of the aeration period, more acid is added and the aeration continued.

Figure 67 shows an acid-treatment plant for cyanide wastes at a large automobile factory. This plant is used exclusively for spoiled or waste cyanide solutions. The following is a report on the operation of the plant:

The cyanide copper-plating solution, of which there was 4,500 gal., was discharged into the tank and 10 carboys of sulphuric

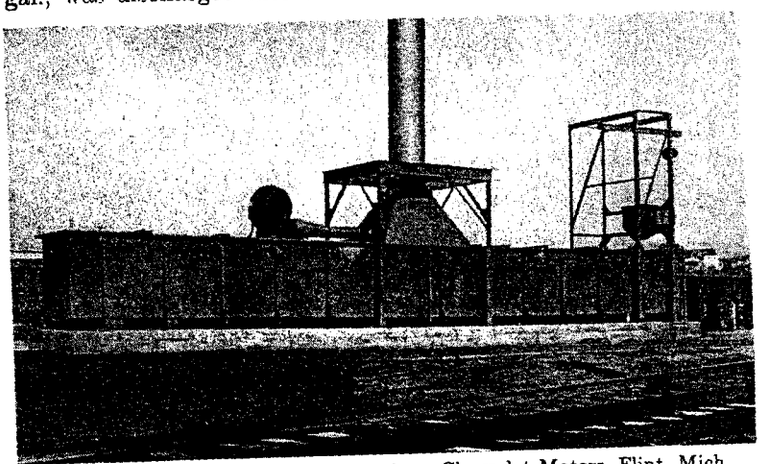

FIG. 67.—Cyanide-waste-treatment plant, Chevrolet Motors, Flint, Mich.

acid added while the solution was strongly agitated with air. A sample was taken for analysis and 10 more carboys of acid added. Another sample was taken and the final 3 carboys added. The solution was then thoroughly agitated by means of compressed air for a period of 16 hr., after which a final sample was taken. The analysis of these samples showed as follows:

Sample	Sodium cyanide, p.p.m.	Sodium carbonate, p.p.m.
Before treatment	15,200	60,000
After first 10 carboys of acid	3,400	3,380
After 23 carboys of acid	1.3	
After aeration	0.98	

The final analysis showed the solution to contain 0.98 p.p.m. sodium cyanide and some free acid. This solution was discharged to the stream.

WASTE CYANIDE FROM HEAT-TREATMENT PROCESSES

The process of heat treatment of metal parts produces a waste material containing a large proportion of sodium cyanide. This process consists of placing commercial sodium cyanide in pots that are inserted in an electric furnace. The temperature is raised until the cyanide is fused and takes on a bright red color. Parts are placed in baskets and submerged in the red-hot fusion for a definite length of time. They are then removed and quenched by dropping them in cold water or oil.

Occasionally during the treatment a scum is removed from the surface of the molten mass. On cooling, this scum forms a solid material similar in appearance to ash, containing considerable cyanide. When the pots containing the cyanide become cracked or thin, they are lifted from the furnace and discarded together with the solidified sodium cyanide they contain.

The disposal of the waste cyanide from the pots and that in the ash often present a difficult problem. Hauling to dumps, as is often the case, is a hazardous method of disposal, since the cyanide becomes accessible to humans or animals or may find its way into near-by streams or ground-water supplies.

The method of disposal used by one automobile manufacturing company appears to be the most satisfactory yet devised. This method involves the destruction of the toxic properties of the cyanide by changing it to the thiocyanate. Several hundred pounds of cyanide salts are disposed of at one time. The method used is as follows:

Waste cyanide is placed in an old steel tank located in an open yard in the factory grounds. No attempt is made to remove the cyanide from the pots. Pots and cyanide are placed in the tank and covered with a considerable amount of water. The tank contents are heated to about 140°F. by steam coils placed in the tank, and the cyanide rapidly goes into solution. Extreme care is taken to avoid contact of the operator with the cyanide or with the fumes arising from the tank.

Commercial lime-sulphur solution (spray material) is slowly added to the cyanide solution. An immediate yellow precipitate is produced. More lime-sulphur solution is added, with constant stirring until a permanent orange-red color is obtained.

This color indicates the end of the reaction. The precipitate settles rapidly to the bottom of the tank.

The supernatant liquor now contains sodium and calcium thiocyanate, sodium carbonate, sodium sulphate, and sulphur. This solution is allowed to leach into the ground in the vicinity of the tank. Preliminary tests have indicated that about 1 pint of lime-sulphur solution, (32°Bé.) is required to treat the cyanide contained in 1 lb. of 45 per cent sodium cyanide such as is used for heat-treating purposes. There is a definite possibility that this lime-sulphur method of treatment may sometime be applied to the treatment of spoiled plating-room solutions or washings from the plating process.

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CHAPTER XIII

GAS- AND COKE-PLANT WASTES, AND OTHER PHENOLIC WASTES

Wastes produced as a result of the manufacture of gas and coke from the destructive distillation of coal are representative of a group known as "phenolic" wastes. These wastes are of particular interest, because their discharge into the public waters is responsible for many cases of tastes and odors in public water supplies. Phenols and phenol-like substances are also toxic to aquatic life, although they are seldom present in stream water in sufficient quantity to exert this toxic action. A number of cases are recorded, however, in which these substances have seriously interfered with commercial and private fishing by imparting a taste to the fish caught for sale or private use.

Phenolic wastes are discharged by a number of other industries, although the by-product coke industry is perhaps the most common. Some of these are wood-distillation plants, certain chemical-manufacturing plants, and pentane-extraction plants. Much of the material given here in connection with the treatment of the gas-plant wastes may be applied to the wastes from these other industries.

THE MANUFACTURING PROCESS

The production of coke and coal gas consists of heating bituminous coal of a certain type at a high temperature until the coal is converted to coke. This is accomplished in a retort or oven from which the gas may escape but to which air does not have access. The products produced are coke, gas, tar, and ammonia liquor. Figure 68 is a flow diagram showing the major operations of a gas and coke plant.

The retort is usually composed of a silica brick tube set either horizontal, inclined, or vertical. Most of the plants in the United States have the horizontal type, although a number of the more modern plants have vertical retorts. The retorts are arranged in groups known as "benches." A typical bench is

made up of three horizontal rows with two or three retorts per row. The retort is equipped with iron doors, which are hinged and, during a run, are sealed with mud made of clay and water. Horizontal retorts are charged from one end and discharged at the other. The vertical retort is charged at the top. Each holds about 1,000 lb. of coal and requires about 8 hr. for carbonation. The gas is collected at either or both ends and is led through pipes to a common main. When the coking process is complete, the

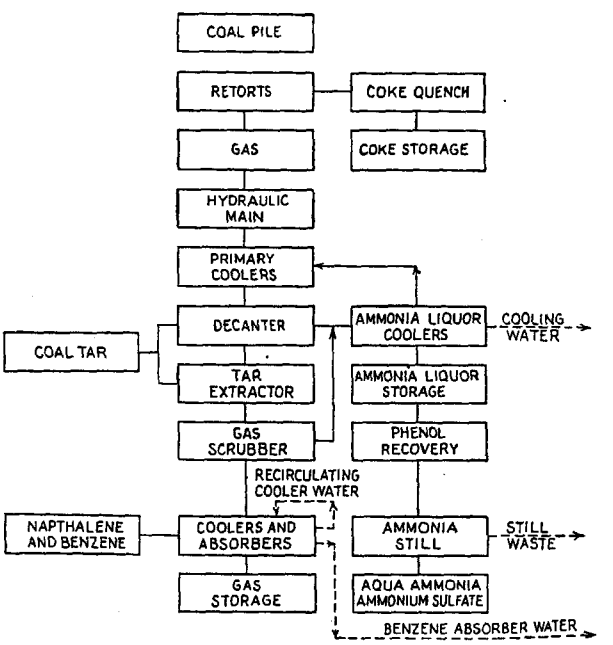

FIG. 68.—Flow diagram of coke and gas manufacture.

doors are opened and the hot coke is pushed out of the retort by means of a ram and drops into a conveyer, where it is quenched by water sprays.

The gas as it comes from the retorts is a mixture of gases, vapors, and finely divided liquid particles. This mixture is passed through water contained in a U-shaped "hydraulic main" or through individual wash boxes that operate like the hydraulic main. Much of the tar and a considerable portion of the water is collected in this main. The water contains ammonia and phenolic compounds. This water (called "ammonia liquor") is

cooled by means of cooling coils, and a portion is used for cooling the gases further in what are known as the "primary coolers." The balance is stored in an ammonia-liquor-storage tank.

Much of the tar is removed by decantation. The remainder is precipitated from the gases by a tar extractor using either mechanical or electrical methods.

There are now present in the gas small quantities of benzene, naphthalene, and like materials and other substances such as ammonia, hydrogen sulphide, hydrocyanic acid, and carbon disulphide. Ammonia is removed from the gas by two methods. One consists of "scrubbing" the gas with water, making a weak ammonia solution from which ammonia compounds are later manufactured. This weak solution also contains carbon dioxide, hydrogen sulphide, and phenols removed from the gas. The second involves the removing of the ammonia from the ammonical liquor, putting it back into the gas, heating with steam, and scrubbing the warm gas with sulphuric acid.

Naphthalene is removed by means of a fine spray of water in the final coolers. Benzol is scrubbed from the gas by a spray of "wash oil" in the benzol absorbers. Following the removal of benzol, the gas is discharged to a holder, from which it is distributed to the consumer.

The tar that is recovered from the various steps in the process is stored in tanks. This by-product is used for the manufacture of coal-tar products.

The ammonia liquor is used for the recovery of the ammonia and, in some cases, the phenol. When phenol is recovered, the recovery processes are applied to the weak ammonia liquor before it is passed to the ammonia still. Phenol recovery is rarely used and therefore is not considered a part of the by-product manufacturing processes. Methods adapted to its recovery will be discussed later.

The ammonia still has three sections: the preheating section, the volatile still, and the fixed still. In the volatile still, free ammonia is removed by distillation with steam. The liquid is then treated with lime and the ammonia thus liberated from its salts is distilled. The vapors are scrubbed with lime water, caustic soda, and oil; passed through activated carbon; and finally dissolved in distilled water or sulphuric acid. Aqua ammonia is made by the distilled water solution of ammonia.

Ammonium sulphate is produced by distilling the ammonia into sulphuric acid. The salt is crystallized and sold in the solid form.

The average yields of by-products from 1 ton of coal are:

Coke	1,400 lb.
Gas	11,000 to 13,000 cu. ft.
Tar	9 to 13 gal.
Ammonia	5 to 6 lb.
Ammonium sulphate	24 lb.
Light oils	3 to 4 gal.

Much of the phenol from the process is contained in the coal tar. About 2.2 per cent of the tar is phenol or phenol-like compounds. Because of the solubility of these compounds in water, some are found in the weak ammonia liquors.

VOLUME AND CONCENTRATION OF WASTES

Figure 68 shows the source of waste from a gas-coke manufacturing plant. The usual volume of ammonia-still waste varies from about 20 to 35 gal. per ton of coal. The average is about 25 gal. The use of steam in the distillation of the ammonia increases the volume of the still waste over that of the weak ammonia liquor entering the still. The average increase is about 1.2 times the ammonia-liquor volume.

In most plants water used in the final cooler is recirculated. There is an occasional plant in which this water is discharged as a waste. The volume of this waste averages about 300 gal. per ton of coal.

In addition to the ammonia-still waste, all plants discharge a considerable volume of cooling water. The volume of this water has been roughly estimated at between 3,000 and 3,500 gal. per ton of coal. This is practically clean water, carrying little if any polluting material.

Table 63 shows the phenol content of ammonia liquor and ammonia-still waste from two plants. Phenol recovery, if practiced, is applied to the liquor before it passes to the still.

The reports from other plants have indicated a somewhat higher average phenol content than the average of the three plants shown in the table. The average phenol in ammonia liquors is expected to be about 2,200 p.p.m. and in still waste, about 1,800 p.p.m.

TABLE 63.—PHENOL CONTENT OF PHENOLIC WASTES

Source of Waste	Phenol, P.p.m.
Gas plant 1, ammonia liquor	1,313
Gas plant 1, still waste	796
Gas plant 2, ammonia liquor	1,560
Gas plant 2, still waste	1,085
Gas plant 3, ammonia liquor	2,310
Gas plant 3, still waste	1,932
Wood-distillation plant 1	115
Wood-distillation plant 2	61
Pentane-extraction plant	3,838

Using 20 gal. as the average volume of ammonia liquor per ton of coal and 25 gal. as the average still waste, the weight of

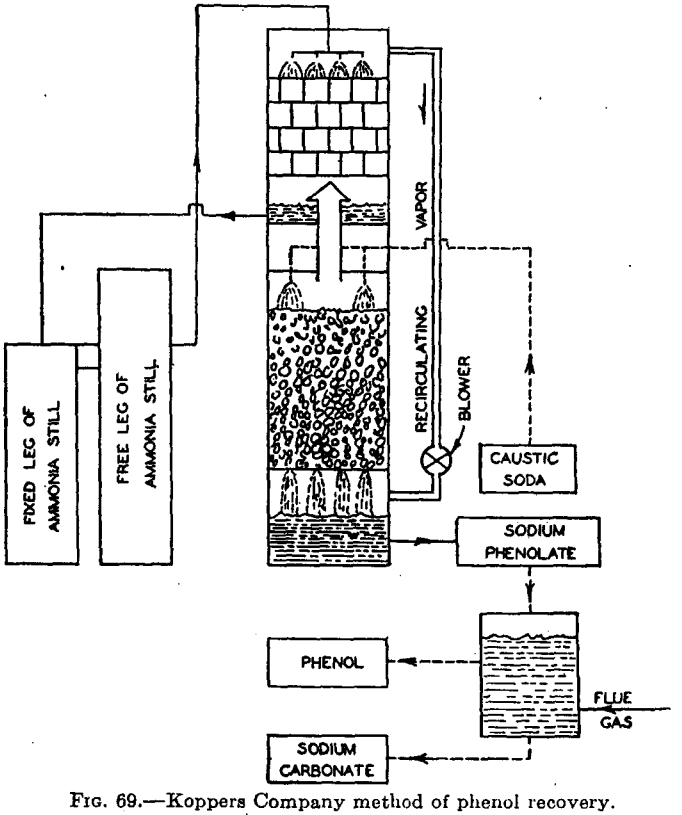

FIG. 69.—Koppers Company method of phenol recovery.

phenol discharged in the waste is 0.35 lb. per ton of coal. Little, if any, phenol is lost in passing through the still.

Table 63 also shows the phenol content of three other phenolic wastes, two from wood-distillation plants and one from a pentane-extraction plant. Wood-distillation-plant wastes are not high in phenol.

PHENOL POLLUTION

The major polluting effects produced by these wastes are caused by phenol and like substances (cresol and substitution products). These wastes have a demand for oxygen, but this demand is usually insignificant in comparison to the effect of the phenol. The wastes also contain other substances, such as the cyanides, the relative effect of which has not been definitely determined.

High concentrations of phenol are toxic to fish and aquatic life. The toxicity threshold of pure phenol has been shown by Hubbs[1] to be between 10 and 15 p.p.m. and for pure cresol between 15 and 20 p.p.m. However, the same investigation showed that gas-plant wastes gave entirely different phenol threshold. Dilutions of ammonia-still waste with phenol contents from 3 to 5 p.p.m. destroyed fish life in a relatively short time. Dilutions of ammonia liquor before distillation gave a toxicity threshold (based on the phenol content) of from 0.5 to 1.5 p.p.m. of phenol. The difference in the toxicity in these cases is apparently due not to phenol alone but to other toxic compounds contained in the ammonia liquor and still wastes.

Very small concentrations of phenol cause tastes in water supplies. Chlorination of the water intensifies the taste. About 0.1 p.p.m. phenol in water can be identified by some persons. Concentrations as low as 1 part in 50,000,000 of the chlorinated phenol produce a characteristic medicinal taste.

RECOVERY METHODS

There are three methods in general use for the recovery of phenol from gas- and coke-plant wastes. These methods are (*a*) steam distillation, (*b*) extraction with solvents, and (*c*) absorption by activated carbon. The object in most of these processes is to obtain the phenol in a marketable form. The methods are briefly described in the following:

Distillation.—The outstanding distillation process for phenol recovery is that developed by the Koppers Company, Hamilton,

Ohio.[3,4] The recovery plant is installed at the Hamilton Coke and Iron Company and treats upward of 35,000 gal. per day of ammonia-still liquor (see Fig. 69).

This plant consists of a steel tower, 95 ft. high and 7 ft. in diameter, divided into four sections. The still waste is sprayed in at the top of the tower, which is filled with vitrified tile, over which the waste flows. A mixture of air and steam is blown in the direction opposite to the flow of the liquor. The phenol is taken up by the mixture and passed through a section of the tower containing caustic soda. The sodium phenolate formed is then treated with flue gases which neutralize the alkali and liberate the phenol. The phenol content of the weak ammonia liquor is 2.5 to 3.0 g. per liter and of the effluent about 100 p.p.m., representing an extraction efficiency of 95 per cent.

Another notable process of distillation is the Heffner-Tiddy phenol-recovery process.[2,5] This method differs from the Koppers in that it depends upon the formation of the ammonia salts of the phenols. These salts are more volatile than phenol. The hot liquor is first treated with ammonia until the content is equivalent to that of the phenol. This solution is then steam-distilled. A temperature of 98°C. is maintained for the distillation. The distillate is treated with caustic soda to liberate the ammonia and then with flue gases to recover the phenols. The efficiency is about 85 to 90 per cent.

Extraction with Solvents.—Benzene is the most common solvent used for the extraction of phenols from phenolic wastes.[6 to 18] The method of extraction apparently originated from the studies made in the Emscher region of Germany. In its original form it was referred to as the Pott-Hilgenstock process. It is the most generally used method for phenol extraction at the present time.

The extraction takes place in steel towers, usually filled with vitrified tile. The ammonia-still liquor flows downward against a spray of benzene. The benzene-phenol solution is separated from the water and the two components obtained by distillation of the benzene. This distillation method for the recovery of the benzene was found to be expensive and has been replaced by treatment with caustic soda. The phenol is recovered from the caustic soda by acidifying with sulphuric acid or carbon dioxide.

The crude phenols thus obtained contain 12 per cent water, 51 per cent phenol, 26 per cent cresol, and 11 per cent residue.

In the operation of the Troy, N. Y., plant, sodium bicarbonate was substituted for sulphuric acid and carbon dioxide, and an increase in efficiency in phenol recovery resulted. The process was further modified by using sodium sulphide and hydrogen sulphide in separating the phenols.

The amount of benzene required for the extraction varies from 25 to 50 per cent of the volume of still liquor treated. For the average gas plant or by-product coke-plant waste (containing 2 g. per liter of phenol), 15 lb. of caustic soda, 5 lb. of benzene (loss), and 17 lb. of sulphuric acid or 9 lb. of carbon dioxide per 1000 gal. are required. About 16 to 17 lb. of crude phenol is obtained. The net cost for materials and operation at the Troy plant was 78 cents per ton of coal.

Trichlorethylene is sometimes used in place of benzene as a solvent. Crawford[19] recommends the use of a light tar oil, claiming a removal of 93 per cent of the phenol with this solvent.

Tricresyl phosphate is also suggested.[21] This substance is nonvolatile and very insoluble in water and allows a much better separation from the liquor. The phenol is from eight to twenty times more soluble in this compound than in benzene. The phenols are recovered by vacuum or steam distillation. Very little of the solvent is lost in the process.

Absorption by Activated Carbon.—Although activated carbon is used in a large number of water-treatment plants for the removal of phenolic-taste-producing compounds, it has not been applied to any great extent in the treatment of phenolic wastes. The principal difficulty encountered in the few instances reported was in the removal of the phenol from the carbon after it had been absorbed. Two processes have been suggested: (*a*) distillation with superheated steam and (*b*) extraction with benzene.

D. W. Parkes[22] reports the results of laboratory studies made in England in which the phenols were removed from the carbon by distillation. His first attempts at steam distillation in the presence of carbon dioxide resulted in the poisoning of the carbon and caused a rapid decrease in the absorption power. During the first 20 runs made with one sample of carbon, about 90 to 100 per cent of the phenol was absorbed. After the twen-

tieth, the percentage absorbed dropped off rapidly until at the thirtieth only 45 per cent was removed.

The poisoning of the carbon was found to be due to decomposition products of the phenols. A considerable portion of the decomposition was due to the carbon dioxide, although some took place during distillation.

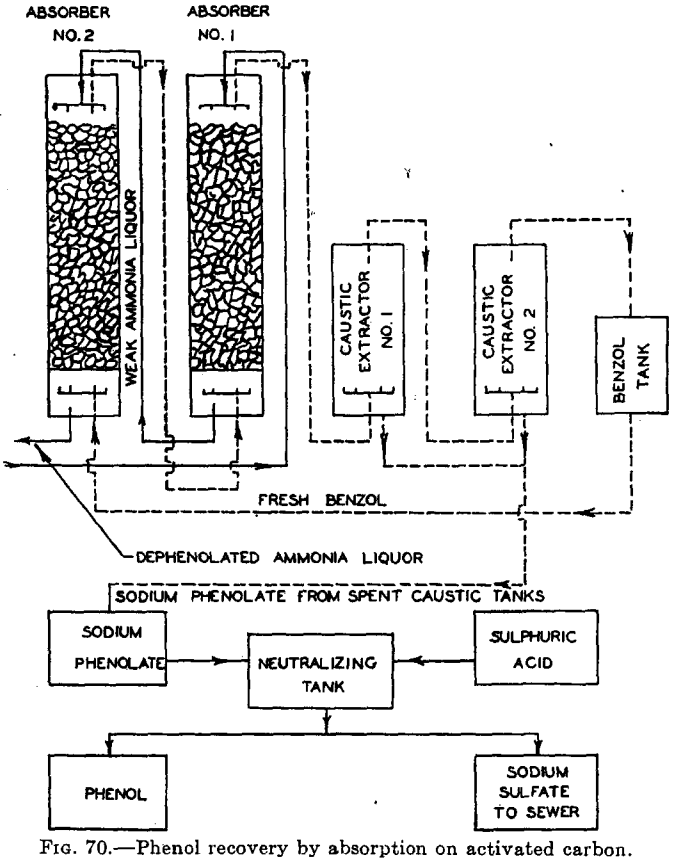

FIG. 70.—Phenol recovery by absorption on activated carbon.

By the substitution of superheated steam for carbon dioxide a much better removal and recovery was obtained. In the former carbon dioxide method, the recovery of phenol varied from 29 to 65 per cent of that absorbed and increased with the age of the carbon. At the same time the amount absorbed per unit weight of carbon decreased.

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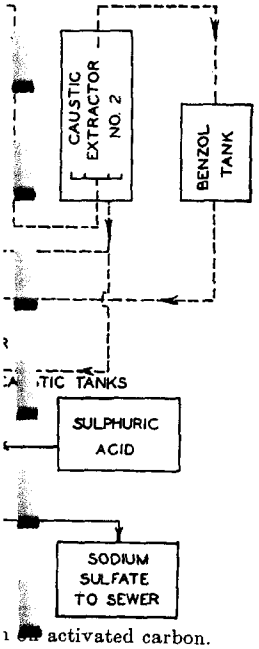

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In the superheated-steam method, the recovery was fairly constant at 75 to 80 per cent. In this process the carbon after the absorption of the phenol was first heated to about 370°F. in an electric furnace. Steam at 250 to 350°F. was passed through the carbon. The distillate contained about 5 per cent phenol and, in volume, amounted to about 10 per cent of the volume of still waste applied. Some of the carbons used deteriorated under this treatment.

Benzene has been used for the extraction of the phenol from the carbon in full-scale installations[23,24] (see Fig. 70). These plants consist of iron cylinders filled with about 2.2 tons each of carbon of a 1.5- to 2.0-mm. size. The waste, free from tar, is first passed through a benzene condenser that raises the temperature to about 65°C. It then enters the cylinders at the bottom at the rate of about 6,000 gal. per hour. About 99.5 per cent of the phenol is removed by the carbon. After about 4 hr., the waste is passed to the second cylinder and the first treated with warm benzene. The benzene enters at the top and leaves at the bottom. The extract contains 1.5 per cent phenol. The volume of benzene required is 12.5 per cent of the volume of waste treated.

After extraction, the cylinders are steamed out and are again ready for operation. The entire process requires about 4 hr. (3½ hr. for extraction and ½ hr. for steaming). The water is removed from the benzene by settling and is returned to the untreated waste. The benzene is then distilled at a low temperature, leaving the crude phenol.

The carbon losses by the process are from 35 to 40 lb. per ton of crude phenol recovered. Very little benzene is lost.

TREATMENT METHODS

The treatment processes to be discussed here are applied to phenolic wastes when the phenol concentrations are low. Wastes containing high concentration are most economically treated by means of one of the recovery methods given above. Effluents from the recovery processes may still contain too high a concentration of phenol to allow their discharge into a stream. These effluents require further treatment by the processes to be discussed below.

Phenols in low concentration are destroyed by biological-oxidation processes such as occur on the trickling filter or in the activated-sludge plant.

Phenols in natural waters are oxidized by the biological life normally present. According to Bach,[25] water containing 10 p.p.m. phenol showed no trace after 4 days. Amounts up to 25 p.p.m. were rapidly destroyed, but greater quantities retarded the oxidation process because of the toxic effect of the phenol on the organisms.

The Dow Chemical Company,[26] Midland, Mich., starting about 1927, made a complete and comprehensive study of methods of phenolic-waste treatment. As a result of this study a full-scale biological-filtration plant was constructed for the treatment of the phenolic wastes from this factory. The report of this study and the operation of the filter offers the most dependable information now available as the limits of phenol concentration and filter efficiencies.

TABLE 64.—PHENOL REMOVAL BY BIOLOGICAL FILTRATION

Influent, p.p.m.	Effluent, p.p.m.	Removal, p.p.m.	Removal, percentage	Lb. per 1,000 cu. ft. medium
5	0.0	5.0	100	0.31
20	0.0	20.0	100	1.25
25	2.5	22.5	90	1.42
30	0.5	29.5	98.5	1.85
40	3.0	37.0	92.5	2.33
70	8.0	62.0	88.5	3.88
80	8.0	72.0	90.0	4.53
100	30.0	70.0	70.0	4.40
115	40.0	75.0	65.0	4.72
120	60.0	60.0	50.0	3.77
140	80.0	60.0	42.8	3.77
190	132.0	58.0	30.0	3.65
270	224.0	54.0	20.0	3.14

The phenolic wastes from the Dow factory are diluted with river water to provide a constant supply of organisms for the biological filter. The applied concentration of phenol is between 20 and 30 p.p.m. The filters are 10 ft. deep and the rates of application from 9 to 18 m.g.a.d. The results of this full-scale

operation show that from 1.4 to 5.8 lb. of phenol was removed per 1,000 cu. ft. of filter medium, and a reduction in phenol of from 85 to 100 per cent was obtained.

The treatment plant consists of a settling tank, containing a sludge-collecting mechanism, and two trickling filters. The effluent from the filters is discharged into ponds that empty into the Tittabawassee River.

The author[27] made a study of phenolic-waste treatment using a shallow (3-ft.) filter and a pure phenol waste. Concentrations of from 5 to 270 p.p.m. phenol were applied. Complete removal was obtained with one application of waste containing 20 p.p.m. phenol or less. As the phenol content of the solution was increased, the amount removed increased up to 70 p.p.m. This occurred with phenol concentration of 85 to 115 p.p.m., after which the amount removed decreased. The maximum phenol removal was 4.72 lb. per 1,000 cu. ft. of filter medium. Table 64 shows the results of the studies.

The same studies showed that two-stage filtration using shallow filters removed all the phenol from a synthetic waste having an initial phenol content up to 180 p.p.m. When the same tests were applied to gas-plant wastes, somewhat different results were obtained. These wastes contain compounds that exert a toxic effect on the organisms of the biological filter. These toxic materials appear to accumulate on the filter medium if concentrations of waste above 50 to 55 p.p.m. are applied. They do not affect the treatment if the phenol concentration is kept below 30 to 40 p.p.m. For complete removal of phenol from a dilution of gas-plant wastes, the concentration of the phenol in the waste applied to the filter must be kept below 30 p.p.m. Continuous seeding with river water or sewage is necessary for continuous successful filter operation.

In view of these findings, it is apparent that the use of the biological filter alone for phenol removal from gas-plant wastes is impractical. The phenol content of the ammonia-still liquor may be greater than 2,000 p.p.m. In order to reduce this concentration by dilution to a point at which the waste may be applied to the filter (25 to 30 p.p.m.), the volume must be increased at least sixty-five times. Thus, if the volume of still was 10,000 gal. per day, the quantity of waste treated would be 650,000 gal., requiring a filter about 0.65 acre in area.

The treatment process for gas-plant wastes, therefore, must consist of one of the recovery processes discussed above, followed, if necessary, by the biological filter. Phenol-recovery processes in most cases cannot be expected to remove 100 per cent of the phenol. Situations that demand the entire elimination of the phenol usually necessitate the use of the filtration process as an adjunct to recovery.

Phenolic wastes from plants other than gas or by-products coke plants, as, for example, certain chemical companies and wood-distillation plants, may use biological filtration without preliminary recovery processes. In these cases, two-stage filters will allow the application of waste having a concentration of phenol up to about 180 p.p.m. The general arrangement and design of units for this purpose will be discussed in the following.

Wastes containing phenols may be successfully treated in municipal sewage plants having secondary-treatment processes (biological filtration or activated sludge), provided that the concentration of the phenol does not exceed 25 p.p.m. Gas plants using phenol-recovery processes may find a means of disposal for the residue from the process in the municipal system, eliminating the need for further treatment at the plant. The disposal of phenolic wastes in combination with domestic sewage will be discussed further in Chap. XVII.

TWO-STAGE FILTRATION

Figure 71 is a plan and elevation drawing showing the structures and their relative location necessary for the two-stage filtration of phenolic wastes. If single-stage filtration is desired the final filter is eliminated.

The successful operation of this process depends on a constant replenishment of the organisms on the filter, which is accomplished by the dilution of the waste with river water. This water is used to reduce the concentration to a point within the desired limits. In cases where the concentration is already within those limits, it is still necessary to use the river water for seeding the filter. The minimum quantity of seeding material depends on a number of factors and can be best determined by trial under existing conditions. Normally, where dilution is not required for reducing the phenol content, the minimum proportion of river water to waste is about 1 to 1. The arrangement of

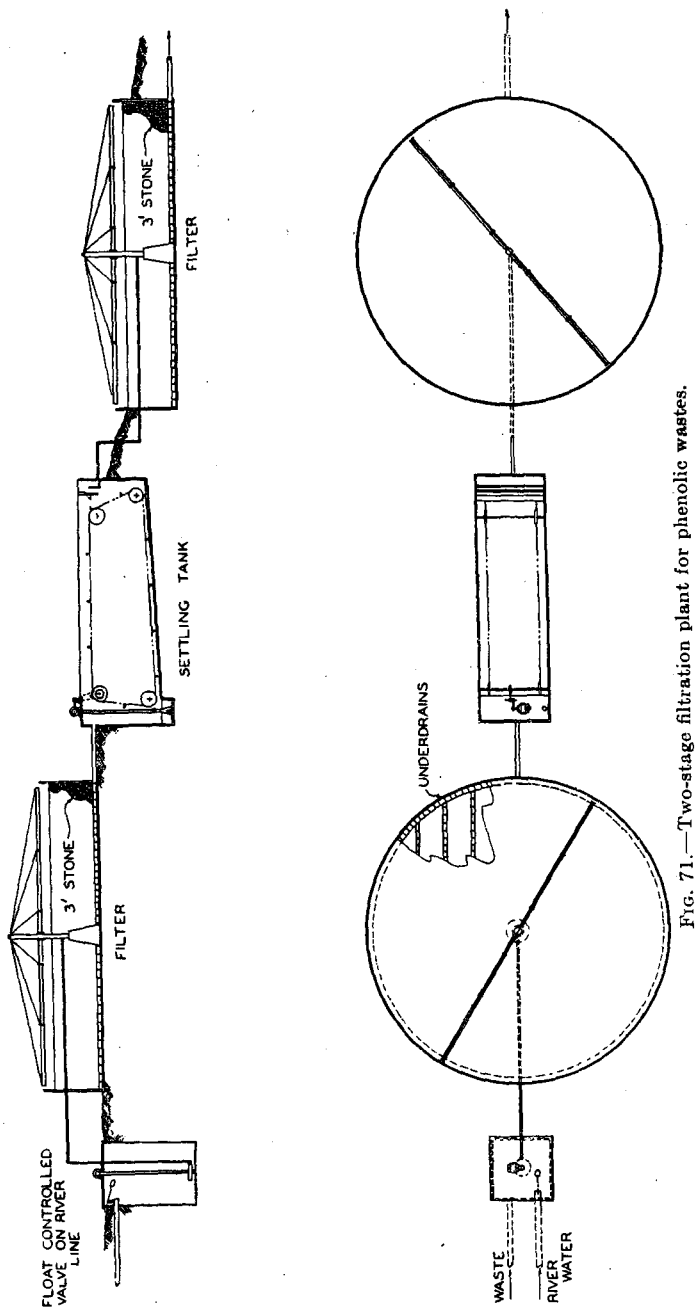

FIG. 71.—Two-stage filtration plant for phenolic wastes.

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the units should be sufficiently flexible, however, so that the quantity of river water applied may be varied to suit the conditions.

River water and waste are discharged into a pump sump having considerable capacity. A regulating box on the river water is arranged in such a manner that the water in the pump sump is always at the same level. This ensures the continuous operation of the filter and a constant replenishing of the seeding. It is accomplished by a float-controlled valve on the river-water line. The dilution necessary to keep the phenol content below 180 p.p.m. is determined by the volume and strength of the waste. This dilution is provided for by regulating the rate of discharge of the pump. A valve on the pump discharge is used to provide some flexibility in the regulation of the dilution to fit changing river and waste conditions.

The primary filter is of the conventional type, with an open and well-ventilated underdrainage system. The waste is applied with a hydraulic-operated rotary distributor. The rate of distribution and the area of filter required are based on the phenol loading. The design loading is 5 lb. of phenol per 1,000 cu. ft. of filter medium. A medium depth of 3 ft. is provided. Medium consists of hard granite stone or blast-furnace slag, clean and free from soft stone. The size is specified as follows:

In.	Per Cent Passing Screen
4	100
3½	90
3	65
2½	15
2	3

In cases where two-stage filtration is required, a settling tank is installed between the primary and secondary filter. This tank is designed for a 1-hr. detention period. It is of the conventional type, either straight-line or circular (see Chap. III). It is used to remove the suspended material that normally "sloughs" off the filter medium. The sludge that collects in the tank is pumped or drawn by gravity to a lagoon. The quantity is small.

The final or secondary filter is located at an elevation about 6 in. below the surface of the water in the settling tank. This filter is also of conventional design and is of the same size and depth as the primary filter. In order to save head, the rotary

distributor is operated by a motor-driven mechanism. If head is available (12 to 18 in.) a hydraulic-drive distributor may be used.

The size of medium in this filter is somewhat smaller than in the primary. The following specifications are given for this medium:

In.	Per Cent Passing Screen
3	100
2½	90
2	60
1½	20
1	3

DISPOSAL BY QUENCHING COKE

The use of the phenol-containing wastes for quenching coke gives rise to many serious objections. Perhaps the most important of these is the production of a coke of poor quality. Coke quenched with ammonia-still waste produces odors when used for domestic and some industrial purposes. These odors are due to the volatilization of the phenols and other compounds retained in the coke. Coke produced in this manner has a limited sale and must be sold at a lower price than can be obtained for the water-quenched product. Another serious disadvantage is the corrosive character of the calcium chloride contained in the still waste and its effect on metal equipment with which it comes in contact.

This method of disposal, however, has certain advantages and is used in cases where the odors produced by the burning coke are not objectionable. These include certain industrial uses in which combustion is more complete than is possible in domestic heating appliances. The principal advantage of the method is the complete evaporation and elimination of the still waste.

There still remains the objectionable corrosion of equipment resulting from the use of the still liquor. To eliminate this undesirable feature, some plants have installed a distillation process. The still liquor is distilled with steam, which removes the phenol with the distillate. This distillate is used to quench the coke, thus eliminating the phenol. The residue that contains the corrosive materials is discharged to waste. Such a procedure provides a relatively cheap and simple method of phenol removal.

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Industrial Waste Treatment Practice

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CHAPTER XV

WASTES FROM OIL FIELDS AND REFINERIES

For the purpose of this discussion of waste-disposal problems, the oil industry has been divided into two operations: (*a*) operation of the oil-producing fields and (*b*) operation of refineries for the crude oil. Much of the authentic data collected on these problems is contained in the report of the Committee on the Disposal of Refinery Wastes of the American Petroleum Institute.[1] Other sources of information for the material contained in this chapter are the Michigan Stream Control Commission survey of 1939[2] and the U.S. Public Health Service Industrial Waste Guide.

OIL-PRODUCING FIELDS

In the operation of oil wells, the oil and salt brine is pumped into tanks, where the two components are separated by flotation. The oil is pumped to tank cars for shipping or by pipe line direct to refineries. The brine is wasted. The separation of the oil and brine in these tanks is not complete, and a certain amount of oil is wasted along with the brine. To the oil contributed from this source is added a considerable amount from careless spills, leaks, washing of equipment, and other sources. The oil from the separation is either in an emulsified condition or in the form of free oil.

Oil Films.—Both oil and brine are objectionable if discharged to a stream. Oil films on water surfaces are discernible, even if extremely thin. These films may spread to the thickness of one molecule. Films of oil disappear from the surface of water in from 5 to 24 hr., depending on the thickness of the film. The disappearance is due to several factors and does not mean that the oil has been destroyed. Agitation may cause formation of an emulsion that disperses through the water, or suspended matter may absorb the oil and cause it to settle to the bottom of the stream, from which it may later be released and appear as floating oil.

The following data have been presented to show the relation between the thickness of an oil film, its general appearance, and the approximate quantity of oil involved:

Thickness of film, in.	Appearance	Quantity, gal. spread per sq. mi.
0.0000015	Barely visible	25
0.0000030	Silvery sheen	50
0.0000060	First trace of color	100
0.0000120	Bright bands of color	200
0.0000400	Colors begin to dull	666
0.0000800	Colors are much darker	1,332

Pollution by Oil.—Oil in stream water is objectionable for the following reasons:

1. It interferes with surface reaeration, especially in quiet water. This may result in a depletion of oxygen.
2. Oils and emulsions are toxic to certain types of fish and aquatic life.
3. If in water used for municipal and industrial purposes, oil causes tastes and is troublesome in the operation of water-treatment plants. Oil coatings on sand grains results in the compacting of the sand in water filters.
4. Oil on the surface of water in large amounts is a fire hazard.
5. Oil causes unsightly conditions on stream banks and beds, destroys vegetation, and produces black floating-sludge areas.

Brine from Oil Wells.—Brine usually occurs in formations either just above or below the oil formation. In a carefully operated field much of the brine may be eliminated by bottom-plugging or casing off the brine formation. In some cases the brine appears along with the oil and must be pumped with it. Most wells of this type produce an increasing proportion of brine as the well is pumped down.

Brine also enters streams from abandoned oil wells which have not been plugged or in which the casings have corroded. Contamination of underground fresh-water strata with brine from similar sources is often encountered.

Sodium chloride is the chief constituent of most brines, although brines from certain sections of the country may contain

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	Quantity, gal. spread per sq. mi.
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	50
	100
r	200
	666
r	1,332

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varying amounts of calcium and magnesium chloride or sulphate. Most brines also contain a small amount of bromide. The concentration of mineral solids in brines varies from 2.0 to 25 per cent by weight.

Pollution from Brine.—The chief objection to the entrance of brines into either ground or surface waters is the increase in mineral solids in those waters. Chlorides in excess of 250 to 300 p.p.m. in water cause a taste that is readily discernible. The increase in the hardness of the water causes difficulties in municipal and private water-softening units and adds considerably to the cost of water treatment.

Cases are on record of the poisoning of cattle and especially hogs by the brine present in water to which they have access. Usually, however, cattle and other livestock will refuse to drink water that contains sufficient salt to cause death.

Fish and other aquatic life can stand only a limited concentration of the various minerals contained in brine. Concentrations up to 5,000 to 10,000 p.p.m. do not permanently affect most types of fish unless these concentrations are maintained for a period longer than 24 hr. Where the mineral content is continuously high, concentrations of 500 to 1,000 p.p.m. will eventually result in the death of the fish. The probable order of toxicity of the various chemicals found in brine is as follows: potassium chloride, potassium sulphate, magnesium chloride, calcium chloride, and sodium chloride.

Brines cause wild fowl to seek fresher water. Vegetation is soon destroyed in localities and streams into which there is a continuous discharge of brine.

Disposal of Oil and Brine Wastes.—Care exercised in the separation of oil from brine in the flotation tanks results in a considerable decrease of oil discharge with the brine. An auxiliary tank or pond is often provided for the further separation of the oil and for a protection against loss due to spills and breaks.

The amount of brine pumped by a well can be reduced to a minimum by properly plugging and sealing wells. Abandoned wells must be sealed with a material that will be permanent. Mud and cement are extensively used. The use of 1 sack of cement to 54 barrels of "mud fluid" with a specific gravity of 1.2 is an effective seal.

In some sections of the country, brine is disposed of by evaporation and seepage in large ponds. This practice is definitely limited to areas where contamination of fresh-water strata is not possible and where the soil is light and sandy. Such an arrangement can scarcely be considered permanent, since eventually the ponds become full. In most cases, the brine is discharged from the ponds during high water, when it will cause the least trouble.

In other sections, brine from a rather limited amount up to the entire production from a field is disposed of by returning it to dry or abandoned wells. In certain parts of Pennsylvania and New York, brine is pumped back into the formation to "repressure" producing wells. Repressuring is subject to government regulation, but the return of brine to subsurface formation is usually allowed rather than to have conditions of pollution caused by its discharge to streams.

Under certain conditions it is possible to evaporate the brine, or at least a portion of it, by using waste gas as a fuel. The recovered salts may be sold on the market, although there is seldom sufficient return to warrant the extensive use of such a process.

Brine disposal is largely controlled by local conditions. In all cases, careful operations to reduce the quantity are certainly essential. Wherever possible, return to subsurface formations definitely disposes of the brine. Ponding and regulated or controlled discharge during high water is a practice that also may be satisfactory as a means of disposal in some localities.

The following example is cited to illustrate the method of subsurface brine disposal. It is employed by the Ryan Consolidated Petroleum Corporation in the Bemis pool, Kansas.[7] Two leases in the Bemis pool produce together about 1,877 barrels of salt water per day. A disposal well 778 ft. deep was drilled to the Cheyenne sandstone. The sand was topped at 605 ft. and bottomed at 738 ft. A pocket of about 40 ft. was drilled below the sand. The first 60 ft. of pipe was 10¾ in. and was cemented to the surface. The lower 609 ft. was 7-in. out side diameter, also cemented. A closed system was used. Brine flows from the tank batteries to an 8- by 8-ft. steel tank. It is pumped to the well at 235 lb. pressure and at a rate of 186 barrels per hour over the entire 24 hr. daily. The disposal

volume amounts to 10,500 barrels of brine per month. The following cost estimate is given:

Drilling well and equipping lines	$2,721.00
Lead lines from two leases	820.00
Pumping station	2,521.00
Total cost	$6,062.00

OIL-REFINERY PROCESSES

The process of refining oil varies to some extent, depending on whether the oil is from a base of paraffin or asphalt or a mixture of both. Figure 75 is a flow diagram of an oil refinery. The process, in brief, is as follows:

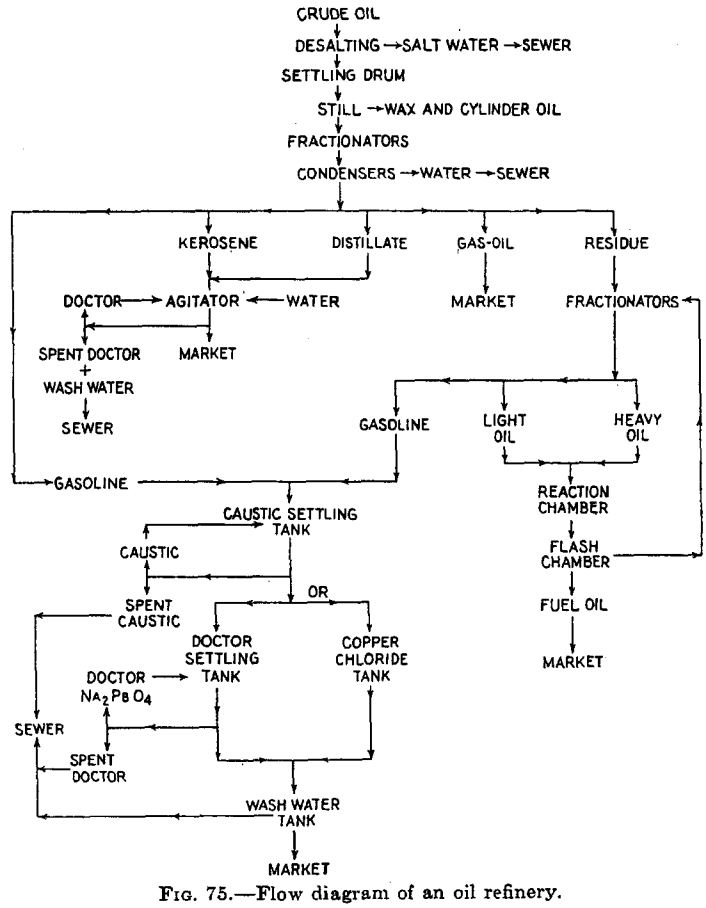

FIG. 75.—Flow diagram of an oil refinery.

Skimming of Crude Oil.—The crude oil is received from the fields by pipe line, tank truck, tank cars, or boat and is stored at the refinery. The crude material is first passed through heat exchangers, washed with water to remove the salt brine, and separated in a settling tank. The wash water containing the salt is discarded to the sewer.

The oil passes to a pipe still and then to the fractionating tower. Five fractions are usually taken from the tower: straight-run gasoline from the first tray; kerosene from the second; distillate from the third; gas-oil from the fourth; and residue from the fifth.

The first three fractions: gasoline, kerosene and distillate, are processed to remove hydrogen sulphide, mercaptans, and gums. The gas-oil is sold on the market, often without further processing. The residue may be sold for fuel oil or distilled for the recovery of asphalt if the original crude is of asphalt base; or it may be "cracked" for the manufacture of gasoline.

Cracking of Residue.—The residue in the cracking process is passed through a fractionating chamber at high temperatures. Three fractions are taken, consisting of gasoline, light oil, and heavy oil. The oils are passed through reaction and flash chambers and back to the fractionator, where a further recovery of gasoline is obtained. The flash-chamber residue is sold as fuel oil. About 51 per cent of the residue entering the process is recovered as gasoline, 40 per cent as fuel oil, and 9 per cent as gas.

Processing Gasoline.—The gasoline from the straight run is treated with a 15°Bé. caustic soda solution and passed through a settling tank, where the caustic and sludge are removed. The caustic solution is made up to the original concentration and reused until it becomes spent. Sludge and spent caustic are discharged to the sewer. In some cases sulphuric acid treatment is applied prior to the caustic soda and results in the formation of an acid sludge.

After the caustic treatment, sodium plumbate (Na_2PbO_4) is added. This is known as "doctor" treatment and results in the removal of sulphides and mercaptans. The mixture is again settled and the doctor reused after regenerating with caustic soda, heat, and air. Spent doctor solutions and the sludge from the settling tank are discharged to the sewer. In some

refineries, treatment with the doctor is omitted and copper chloride filtration substituted. This treatment eliminates the waste from the process.

Cracked gasoline is subjected to caustic soda treatment but usually is filtered through copper chloride in place of doctor treatment. Excess caustic is reused as before. The residue and spent alkali are discarded. The final process of the treatment is a wash with water to remove excess doctor and other impurities that remain in the oil. The wash water is discharged to the sewer.

Processing Kerosene and Distillate.—In most cases kerosene and distillate are treated by the batch process. The doctor is added to the material in agitators. The mixture is allowed to settle in a tank and the doctor and sludge removed. The doctor is reused. The product is washed with water and the water discarded to the sewer.

Composition of Crude Oil.—The above processes are those in general use. They are varied to suit the particular characteristics of the raw product and the products produced, since there is a rather wide variation in the composition of crude oil from the various fields. Table 67 shows the percentage of various products obtained from crude oils from different fields.

TABLE 67.—PRODUCTS OBTAINED FROM CRUDE OIL

Field	West Virginia	Pennsylvania	Mid-continent	Muskogee	Mexia-Powell
Gasoline and naphtha	38.67	30.59	21.34	34.92	20.33
Kerosene	18.37	16.94	9.77	14.29	28.52
Gas-oil	17.32	24.12	34.13	16.47	20.12
Neutral oils	5.96	4.75	5.88	4.47	5.26
Wax	1.21	1.46	1.88	0.68	0.26
Cylinder*	13.32	14.08	23.50		
Flux*	.....	.....	.....	22.46	21.09

* Run by the flux process.

Petroleum consists chiefly of compounds of carbon and hydrogen known as "hydrocarbons." There are also present small amounts of compounds containing oxygen, nitrogen, and sulphur. Metallic compounds, most of which originate from brine emulsions, may be found in limited amounts. A wide

variety of compounds of these elements exists as hydrocarbons and their homologues. From these compounds numerous by-products are possible.

REFINERY WASTES

Quantity.—There is very little information as to the quantity of waste from oil-refining operations. The U.S. Public Health Service, from measurements made at several refineries, has arrived at the value of about 1,000 gal. per barrel (42 gal.) of crude oil per day, including cooling waters. Of this quantity, about 80 to 90 per cent is cooling water that contains no substances from the process. The polluted-waste volume is therefore about 100 to 200 gal. per barrel of oil.

Measurements made in one refinery in Michigan having both skimming and cracking processes showed about 68 gal. of waste per barrel of crude oil or 68,000 per 1,000 barrels. Table 68 shows the average volume of waste from the various processes on the basis of each 1,000 barrels of crude oil processed. These values are roughly calculated from data contained in an unpublished report of the Michigan Stream Control Commission.[5] The following data are also taken from that report and are the basis for the values shown in the table.

1. About 1,500 gal. of 15°Bé. caustic is required per 500,000 gal. of gasoline from the skimming process. On this basis the discharge of spent caustic from a 1,000-barrel refinery amounts to 1,500 gal. every 45 days or 35 gal. per 1,000 barrels. This waste is discharged in batches.

2. Spent doctor waste amounts to about 1,000 gal. every 30 days or 35 gal. per 1,000 barrels.

3. Spent caustic from cracked-gasoline treatment amounts to 1,000 gal. per 1,350 barrels of residue or, on the basis of crude oil, about 150 gal. per 1,000 barrels.

4. The doctor used in the kerosene agitator maintains its efficiency over a long period of time. In some refineries it has not been necessary to dispose of this solution for a period of 2 years.

5. Waste water from the desalting unit amounts to about 4,000 gal. per 1,000 barrels of oil.

6. After gasoline from the skimming process is taken from the fractionating tower it is passed through a condenser to remove

entrained steam. The condensate amounts to about 1,300 gal. per 1,000 barrels of oil.

7. Wash water from the skimming of gasoline amounts to about 50 gal. per minute.

8. Wash water from the kerosene agitator amounts to about 1,000 gal. per 2,000 gal. of kerosene.

Spent solutions are dumped in batches. Most of the other waste is wash water and is more or less constant and continuous.

TABLE 68.—VOLUME AND PHENOL CONTENT OF INDIVIDUAL REFINERY WASTES

Waste source	Volume, gal. per 1,000 bbl.	Phenol content		
		P.p.m.	Lb. per 1,000 bbl.	Percentage of total
Desalting	4,000	4	0.13	0.5
Spent caustic (skimming)	35	1,500	0.44	1.7
Spent doctor (skimming)	35	2,500	0.73	2.8
Spent caustic (cracking)	150			
Condensate of raw-gasoline condenser	1,300	2	0.02	0.1
Wash water from gasoline	59,000	50	24.60	93.0
Wash water from agitators	4,000	15	0.50	1.9
Total	68,520	.....	26.42	100.0

Content of Refinery Wastes. *Oil and Finished Products.*—The wastes in general contain varying amounts of oil and the different finished products. This oil may be present as free or emulsified oil. The combined wastes from most refineries will contain less than 100 p.p.m. total oil.

Leaks, breaks, and spills account for the loss of a major portion of the oil or finished distillates. At times such accidents result in large amounts of oil reaching the sewer system. The cleaning of equipment and the drawing of oil sludges from settling tanks add to the losses. The effect of oil on stream water has already been discussed.

Phenols and Other Compounds.—There are a large variety of substances in the wastes from the different sources in the oil refinery. These substances are in true suspension, colloidal suspension, and in solution. They are mostly organic com-

pounds, being derivatives of the hydrocarbons and containing oxygen, sulphur, and nitrogen.

The chief of these are the phenols and phenol-like compounds. When wastes containing these substances are discharged into waters that are used for municipal supplies, they produce tastes and odors that are difficult to combat in the water-treatment plant. The very disagreeable taste imparted to chlorinated water that contains phenols may be detected in concentrations of phenol as low as 0.02 to 0.05 p.p.m.

Table 68 shows the phenol content as reported for some of the individual wastes.[5] Apparently the major contributor of phenol is the wash water from the gasoline treatment. Although this waste has a comparatively low phenol content because of the low volume, the total weight of the phenolic compounds contained in the waste is about 93 per cent of that from the entire refinery. The spent caustic and doctor solutions contain a high concentration of phenolic substances, but these wastes are low in volume and are discharged at infrequent intervals.

The substitution of the copper chloride filter for the doctor treatment in skimming processes eliminates the spent doctor and the washings. Thus, much of the phenolic pollution from the process may be eliminated by this change in the refining process.

Complex compounds of the sulphur group: mercaptans, sulphides, disulphides, and polysulphides, also produce intense tastes and odors. The odor produced by ethyl mercaptan may be detected in concentrations as low as 1 part in 50 billion.

RECOVERY PROCESSES

The practice of recovery of by-products from refinery wastes is growing, especially in the larger refineries. These by-products are either sold on the market or reused in the process. A few of the recovery processes and the by-products produced are briefly mentioned here:

1. Recovery of oil. Oil is recovered in separators or skimming tanks and is returned to the process. The design for separators for this purpose is discussed by the American Petroleum Institute[1] and will be given in detail later in this chapter.

2. Petroleum coke is produced by the destructive distillation of residues from the fractionating processes. This coke is used as a fuel or for the manufacture of electrodes.

3. Aromatic hydrocarbons and their derivatives have been recovered for the production of coal-tar products. The process is not profitable except during periods when the market for such products is abnormal.

4. Naphthenic acids are recovered from the alkaline liquors and have been used in the production of soluble oils and lubricants.

5. Sulphonic acid is extracted from the tar produced by sulphuric acid treatment. Ethyl alcohol is used to extract the acid. It is employed in the manufacture of low-grade soaps and cleaning agents. The process is usually not profitable.

OIL SEPARATORS

Two types of oil separators are in use in refineries. *Auxiliary* separators are installed on process wastes in which large quantities of oil are lost. They usually consist of steel skimming tanks designed to remove only the major portion of the oil. The *main* separators are used to protect the refinery against loss of oil and the stream against oil pollution. These units must be effective and should be capable of reducing the oil content of the waste water to below 30 p.p.m.

A number of different types of main oil separators are in use in oil refineries in this country. The American Petroleum Institute, prior to 1933, made a study of these types and from this study developed a design for a separator that seems best to meet the requirements for oil-pollution control. The institute design has been subsequently improved by the installation of more recently developed equipment. The separator that now seems to fit the needs of the industry is that described by J. B. Hill of the Sun Oil Company.[6] The general arrangement of this separator is shown in Fig. 76.

A.P.I. Recommendations.—The chief recommendations of the American Petroleum Institute[1] for the handling of refinery waste water and the removal of oil are briefly described below:

1. The location of a new refinery should be selected with due regard to the installation of an adequate drainage system.

2. Drainage systems should be provided with oil separators of proper design and adequate capacity.

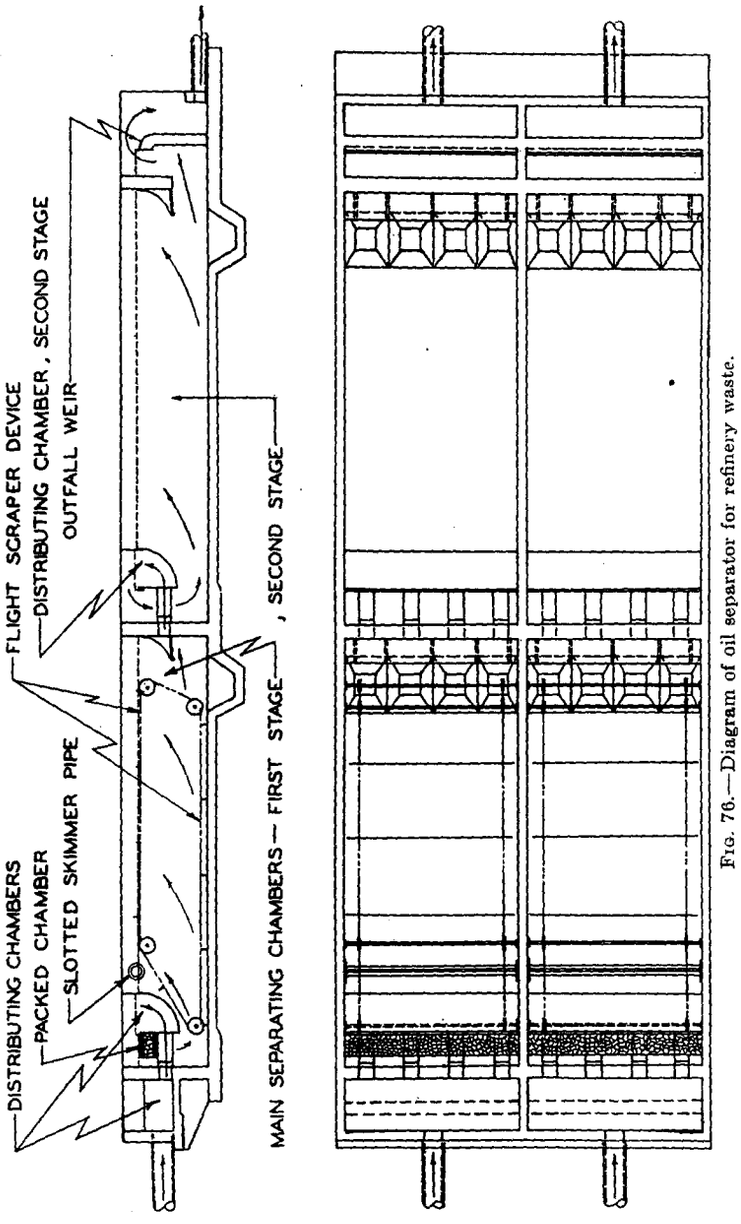

FIG. 76.—Diagram of oil separator for refinery waste.

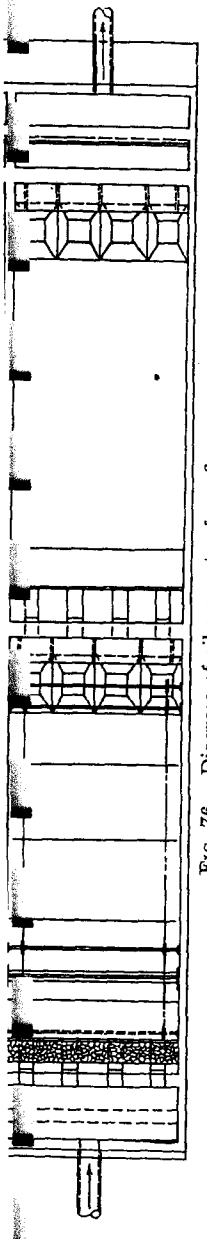

FIG. 76.—Diagram of oil separator for refinery waste.

3. Main separators should be constructed in at least two parallel sections to provide for shutdowns during cleaning and repairing.

4. Adequate equipment should be provided for the removal of the accumulated oil and sediment.

5. The oil pumps should be of high capacity to provide for the handling of large quantities of oil in case of emergency.

6. Auxiliary separators should be installed at points where considerable quantities of oil are lost to remove the major portion of the oil before it reaches the drainage system.

Separator Design.—The main separator is usually constructed of concrete. The capacity of the unit is such as to provide at least a 1-hr. detention period for the maximum flow of waste. The width and depth are such as to provide a velocity of flow through the tank not to exceed 2 ft. per minute. The A.P.I. recommendations for the dimensions of oil separators for various rates of flow are shown in Table 69. These dimensions give section velocities from 1 to 2 ft. per minute.

TABLE 69.—DIMENSIONS OF OIL SEPARATORS FOR REFINERY WASTES

Rate of flow, g.p.m.	Depth, ft.	Width, ft.	Length, ft.
250	5	13	35
500	6	16	57
750	6	18	67
1,000	6	20	75
1,250	7	21	85
1,500	7	23	90
1,750	7	25	95
2,000	8	26	100
2,250	8	27	104
2,500	8	28	107
2,750	8	28	110
3,000	8	29	112

The separator shown in Fig. 76 is constructed in two parallel sections, each divided into two stages. The waste enters a channel at the head end of the tanks and is distributed through submerged pipes into a second channel within the tank. It then flows over a weir and downward through a bed of crushed rock into the main body of the first settling compartment. The

purpose of the rock bed is to break up the oil film and cause the oil to collect in droplets. The oil rises to the surface and is pushed over the surface toward a slotted-pipe skimming trough which is located at the inlet end of the tank. The skimming mechanism is of the conventional type of sludge-scraper mechanism which, on its return flight along the bottom of the tank, moves any sludge that has settled to a series of hoppers. The water from the first compartment passes through submerged pipes into a channel in the second compartment. Here it is distributed over a weir into the settling portion of this compartment. Any residual oil is collected on the surface. The water passes under a baffle and over a weir into the outfall sewer. Only a small amount of oil is obtained in the second compartment, and it is usually removed by hand.

BREAKING EMULSIONS

In the operation of the separator it is important that chemical wastes be properly treated before going to the drain and that any permanent emulsions be broken up. Emulsions pass through gravity separators without breaking. Emulsions produced by the various refinery processes have different properties and require a somewhat different treatment. The emulsified mixtures must be collected and the emulsion broken before they are mixed with the other refinery wastes for oil separation.

There are two types of emulsions: (*a*) the oil-in-water emulsion, in which the oil is emulsified, and (*b*) the water-in-oil emulsion, in which the water is emulsified.

The oil-in-water emulsion appears as a milky mixture that is broken up when discharged into a stream, the oil appearing in the free state on the surface of the water. This type is usually found in refinery waste.

The water-in-oil emulsion is sometimes encountered, and its density may be such as to cause it to settle in the separator. This type may also be lighter than water and will accumulate along with the oil on the separator surface and add materially to the water content of the recovered oil.

The chief source of emulsions is in the treating of both light and lubricating oils and depends to some extent on the kind of oil treated. They most frequently occur in the wash water from

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the acid treatment of lubricating oil. Other sources are in the condensed water from cracking still and the distillation of crude naphtha and water drawn from the storage of still bottoms.

Emulsions are formed by the agitation of oil and water in the presence of some emulsifying agent. Some of the agents found in the oil or water of the refinery are sodium soaps of organic acids, asphalt, clays, calcium and magnesium soaps, lead sulphide from doctor-treatment operations, resins, and finely divided coke.

The difficulty attending the presence of emulsion wastes may be reduced by preventing the formation of the emulsion. The use of gravity flow wherever possible in place of the turbulence caused by pumps, the use of large-sized pipe to decrease the velocity of the mixtures, and the careful design of mixing equipment to minimize the agitation of oil and water all serve to decrease emulsion formation.

The American Petroleum Institute[1] lists the emulsion-breaking processes under three heads: physical methods, electrical methods, and chemical methods. Under physical processes are heat, distillation, and the centrifuge. Heat produces steam in the water-in-oil emulsions and breaks the film that holds the water in suspension. Distillation has an added advantage over heat in that the emulsifying agents are left in the residue. The centrifuge is rarely used to break emulsions unless the oil and water have widely different specific gravities.

Electricity is used to break emulsions by passing the mixture between electrodes connected to a high-voltage alternating current. The particles are charged and the film broken, causing the separation.

Chemical methods vary according to the properties of the emulsion. Often oil-in-water emulsions are easily broken by coagulation with some type of coagulating agent such as alum, ferric chloride, or lime. The coagulant in doses from $\frac{1}{8}$ to $\frac{1}{2}$ lb. per 1,000 gal. is rapidly mixed with the waste. The mixture is flocculated by a period of slow stirring for about 20 min., during which time the chemical floc forms. The colloidal oil adheres to the floc and is removed by a period of settling. The process can be accomplished in a single tank equipped with a mechanism for slow stirring. The sludge and clarified water may then be discharged to the drain leading to

the oil separator, or the sludge may be removed to a lagoon or sand bed.

The process adapted to the breaking of a particular emulsion must be worked out in the refinery. Sometimes considerable study is required to develop a satisfactory method.

TREATMENT OF ACID SLUDGES

Acid sludge is produced by the treatment of oils with sulphuric acid. The character of the sludge varies from a liquid of low specific gravity to an almost solid mass, depending on the type of treatment and the properties of the oil. Table 70 shows some typical analyses of acid sludges as given by the American Petroleum Institute.[1]

TABLE 70.—TYPICAL ANALYSES OF ACID SLUDGES FROM REFINERY PROCESSES

Specific gravity	Sulphuric acid, per cent	B.t.u. per lb.
1.05	10.12	11,260
1.15	2.20	12,440
1.19	24.70	11,850
1.22	30.97	11,155
1.37	67.07	9,000
1.41	28.50	16,425
1.41	52.20	7,700
1.43	48.50	6,940
1.66	76.60	
1.77	78.00	

Acid sludges should be handled in a closed system without access to the sewer. They are allowed to settle for about 3 hr. in order to separate any free oil before they are subjected to treatment processes. There are two types of treatment processes used for this sludge. One type involves the recovery of sulphuric acid; in the second type the sludge is burned in furnaces to carbon dioxide, water vapor, sulphur dioxide, and sulphur trioxide.

Sulphuric acid recovery is accomplished in two ways; by steam treatment and by incineration with the collection of the sulphur oxides in water. In the first method the sludge, after it has been settled and the free oil removed, is treated with steam and a

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light fluxing oil. This causes an oil or tar to separate which is used as a fuel. The sulphuric acid is recovered in a weak water solution and is concentrated for reuse in the refinery. The process of concentrating the acid is accompanied with the production of odors unless a high-vacuum concentrator is used. These odorous compounds are dispelled into the air through a high stack.

The second method of sulphuric acid recovery is a variation of the process of disposal by incineration. Specially designed furnaces are required, and the sludge must be incinerated at high temperatures in order to destroy compounds that have odors. Although the sludge itself usually has a B.t.u. value sufficient to cause incineration, auxiliary fuel must be used to bring the furnace to temperature and to maintain the high temperature required for the destruction of odorous compounds. Details for the construction and operation of the furnace for acid-sludge disposal are given by the American Petroleum Institute in "Disposal of Refinery Wastes," Sec. II, page 20.

SPENT CAUSTIC

The spent caustic contains sodium sulphide, sulphate and hydrosulphide, mercaptides, and phenolic compounds. The waste is neutralized with acid recovered from acid sludge or by passing the gases from the boiler stack through it. The flue gases contain carbon dioxide, which neutralizes the alkali and forms carbonates. The gas and any odor-producing compounds that are carried with it are dispelled to the atmosphere by way of the boiler-house stack.

Neutralization of the caustic causes a liberation of the phenolic compounds, which collect on the surface as an oily mass and are removed and burned in the furnace. The water from the process contains some residual phenolic compounds in solution and, when necessary, is treated for further phenol reduction with other low-concentration phenolic wastes, as discussed later.

SPENT DOCTOR

The spent-doctor sludge is composed largely of insoluble lead compounds. Because of the value of these compounds, the sludge is almost universally reactivated. The sludge is treated with soda and aerated to reform sodium plumbite, which is then

reused in the process. The liquid material from the process contains phenolic compounds and mercaptides and is treated for further reduction of these compounds along with other wastes.

TREATMENT OF PHENOLIC WASTES

Wastes from the refinery, when combined for oil separation in the main separator, may contain from 25 to 50 p.p.m. phenol. By mixing the alkaline and acid wash waters and by the neutralization of strongly alkaline or acid wastes, the total refinery waste water should be almost neutral in reaction.

The treatment of phenolic wastes for the reduction of phenolic compounds and the oxidation of oxygen-demanding material are accomplished by the use of the biological filter. This method of treatment and its limitations are discussed in Chap. XIII. Details for the construction of suitable units for this purpose are also given in this chapter and will not require repetition here.

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CHAPTER XVI

TREATMENT OF COMBINED INDUSTRIAL WASTE AND DOMESTIC SEWAGE

Many industries are located within the limits of municipalities and in most of these cases have access to the municipal sewer system. It is generally desirable, from the standpoint of both the city and the industry, that these facilities remain available for the disposal of the industrial waste. Industries are an asset to the city, and every effort is usually made to maintain satisfactory conditions for their continued operation. On the other hand, industry must have an outlet for certain waste products, and one of the most convenient is through the municipal system.

Industrial wastes in municipal sewerage systems unfortunately are often the cause of numerous and complicated problems. As long as these systems act only as a means of transporting the sewage and waste to the stream for direct disposal, the presence of the industrial waste affects only the size of the system required and the material of which it is composed. With the introduction of sewage-treatment facilities, consideration must be given to the possible effect of the wastes on the treatment process and on the size of the various structures.

Increasing industrial activity of recent years has been accompanied by new treatment problems both for the designer of proposed treatment plants and for the superintendents or officials in charge of their operation. In the case of new plants, the engineer is faced with the problem of providing proper and adequate facilities for the treatment of wastes from established industries within the corporate limits. These wastes may be of sufficient significance to govern completely the type of treatment adopted. In some cases it may be necessary to provide preliminary treatment of the waste or to remove it entirely from the municipal system. The cost of combined facilities is often a limiting factor, since, with sufficient capacity and the proper type of units or processes, most combinations of industrial waste

and sewage may be successfully treated. In other words, there is usually a process that may be adapted to treatment of these combinations, but the cost of the necessary structures may prohibit its use.

Existing sewage-treatment plants are often called on to handle the additional load resulting from wastes of either new industries or those which have not previously been connected to the system. Before such wastes are admitted, it is necessary to make a complete and careful study of the possible effect of the waste on the treatment process and on the plant structures. The presence of these wastes may completely disrupt the existing process.

Although the methods of treating domestic sewage are more or less standardized, the treatment of combined trade and domestic wastes has not been standardized to any great extent. Because of the differences in character, strength, and volume of wastes from various types of industry and their proportion to the total sewage flow, the problems are extremely variable. The difficulties experienced in handling them in combination with domestic sewage vary with each of these factors. The problems, therefore, become individual and must be solved as such. However, it is possible to establish certain general principles that will act as guides in attacking these individual problems.

GENERAL CHARACTERISTICS

Geyer[1] has given the following items as necessary for satisfactory sewage-plant operation where biological processes are involved. There are many other factors involved in plant operation, but the items listed are those most likely to be affected by the presence of industrial wastes.

1. The sewage must be as uniform as possible in rate of flow and composition
2. The load of suspended matter should not be too high
3. The sewage should not be excessively acid or alkaline
4. It should be free of toxic substances
5. The carbohydrate content should be low
6. The sewage should be low in grease and oil content

It is essential, therefore, that a strict control be maintained on industrial discharges in order that these operating require-

ments may be met. The following characteristics are undesirable in an industrial waste when combined with domestic sewage for treatment:

1. Intermittent discharges of strong wastes, such as vat dumpings in the tanning and metal industries
2. Large quantities of sand, silt, leaves, fibers, grains, and other material such as are discharged from beet-sugar factories, pulp and paper mills, and distilleries
3. Acid and alkaline wastes, as, for example, the discharges from pickling of metal and the plating of metal parts
4. Toxic reactions as caused by phenols, cyanides, metals, and certain other chemicals
5. High carbohydrate content such as occurs in starch-factory wastes, some cannery wastes, milk waste, and others.
6. Oil from garages and refineries and grease from packing houses, textile industries, and laundries.

Although these characteristics are undesirable, it does not necessarily follow that wastes having them cannot be treated in combination with domestic sewage. The dilution may be such that the effect of the waste is not noticeable. The discharge of intermittent wastes may be regulated. Acid and alkaline waste may be partially or wholly neutralized. These and other factors influence the various problems, showing the necessity for careful study of individual cases. Such a study should include the determination of answers to the following questions:

1. Will the waste deteriorate the sewer system?
2. Is the nature of the waste such that it will respond to existing treatment processes?
3. Is the strength of the waste such that it will not interfere with the treatment process?
4. Are the various units of the plant of sufficient size to handle the additional load due to both the strength and volume of the waste?
5. How will the additional load affect the final effluent?

Each of the wastes discussed in previous chapters has certain characteristics that may or may not influence sewage-treatment processes and structures. It is the purpose of the discussions that follow to point out these characteristics and their possible effects and insofar as possible to suggest the additional facilities

required for handling each of these wastes in combination with domestic sewage.

BEET-SUGAR-FACTORY WASTE

In Chap. IV it was shown that the average volume of the combined wastes from a beet-sugar factory is from 3.0 to 4.0 m.g.d. Large factories may discharge as much as 6.0 to 7.0 million gallons. Of this total about 72 per cent is flume water, 22 per cent process water, 3 per cent lime slurry, and 3 per cent Steffens waste.

The flume water, although large in volume, is comparable in strength to average municipal sewage. The flume-water waste from the average factory is equivalent to the sewage from a population of about 21,000. One of the major problems in the handling of this waste is grit removal, since it contains an average of 11 cu. yd. of grit per million gallons or about fifty times that of domestic sewage. The usual grit chambers of existing sewage-treatment plants are entirely inadequate for handling this quantity of material. The use of continuous-grit-removal equipment is essential, and provision must be made for the disposal of the large quantity of grit collected. Grit chambers designed for this combination of sewage and flume water should have a detention period of at least 40 sec. at a velocity of flow of 1 ft. per second.

Another major problem introduced at the treatment plant by the presence of flume water in the sewage is that of handling a very large volume of a very heavy sludge. About 9,000 gal. of sludge having from 10 to 15 per cent solids is obtained from each million gallons of flume water. This sludge is low in volatile matter, and, although it will add considerably to the required sludge-digestion capacities, it will not contribute gas in proportion to the solids it contains.

The following facilities must be provided if the average beet-sugar-factory flume water is to be admitted to the sewage-treatment plant: The flowing portion of the grit chamber must be increased in order to maintain a velocity of 1 ft. per second for the additional volume. In case of the average factory, this increase will amount to about 240 cu. ft. Continuous-grit-removal facilities must be provided. Settling-tank volumes must be increased by about 325,000 gal., the sludge tanks by 140,000

cu. ft. for the average factory, and sludge pumping and drying equipment must be increased accordingly. Unless the municipality is large and the volume of flume water less than about 10 per cent of that of the sewage, this waste can be best and most economically treated separately by methods discussed in Chap. IV.

The process water from the average beet-sugar factory amounts to about 700,000 to 800,000 gal. per day. Its strength is about five to six times that of domestic sewage and its population equivalent, about 40,000. Process water contains considerable fine pulp and may require fine screening prior to its entrance to the sewer system. Since a large portion of the organic material present is in solution or colloidal suspension, this waste will add considerably to the load on secondary-treatment units. Sludge-handling facilities will also be affected.

Process waste from the average factory will require additional sedimentation facilities amounting to about 70,000 gal. If filters are in use as secondary treatment, about 2 acres of additional area will be required to handle the added load.

During the beet-sugar campaign of 1940, the Michigan Sugar Company factory located at Lansing attempted to dispose of their process-water waste through the medium of the Lansing sewage-treatment plant. This plant employs the activated-sludge process as secondary to sedimentation and sludge digestion. The average sewage flow is about 9 m.g.d. Starting with a small portion of the process water, the quantity was increased until about 350,000 gal. or 75 per cent of the waste was received at the sewage plant. The effects of this waste on the plant were (*a*) an increase in sludge index of the activated-sludge aeration-tank mixed liquor from a normal of about 50 to 120; (*b*) an increase in effluent B.O.D. of from a normal of 10 to about 40 p.p.m., (*c*) a large increase in suspended solids in the effluent due to the bulking condition of the activated sludge; (*d*) an increase in air requirements up to the total capacity of the plant that amounted to 2.0 cu. ft. of air per gallon of sewage. The proportion of process water to sewage was only 3.7 per cent, yet it is apparent from this experience that this proportion was too high for satisfactory sewage-plant operation.

Lime slurry can seldom be disposed of through the municipal sewer system or sewage-treatment plant. Even the supernatant

liquor from lime ponds is undesirable, especially in plants employing the activated-sludge process. The high sugar content causes bulking of the sludge and results in much the same conditions as indicated above for process water.

The same is true of Steffens waste unless the volume of sewage is at least 250 times that of the waste. Even with this dilution the B.O.D. of the sewage will be increased by 40 to 50 p.p.m. The coagulating power of the Steffens waste will have a tendency to increase the removal in the primary units and will offset to some extent the effect of the additional B.O.D.

MILK WASTES

Milk-products-factory wastes are probably the most common industrial wastes found in municipal sewage. Almost every city or town of any appreciable size has one or more milk plants. In large cities the proportion of milk waste to sewage is usually not sufficient to have a noticeable effect on the treatment processes. However, occasionally a situation arises, especially in small towns and villages, where the waste does become a factor.

The waste from this industry arises mainly from the washing of milk cans, floors, and utensils in receiving stations, bottling plants, condenseries, creameries, and cheese factories. Buttermilk and whey from the latter two types of factories are usually considered to be by-products and are not often discharged into the sewer systems, since they have some value as a food for human or animal consumption.

Milk waste is highly organic in nature and has an average 5-day B.O.D. of about 1,000, which is from five to seven times that of normal domestic sewage. The average milk plant whose daily milk intake is near 100,000 lb. will produce 20,000 to 30,000 gal. of waste per day. On a B.O.D. basis this waste is equivalent to the sewage from 1,500 people.

Milk waste can be successfully treated in combination with domestic sewage if certain conditions are fulfilled. Since the organic matter is mostly in solution or colloidal suspension, B.O.D. reductions cannot be expected from primary sedimentation. The waste has very little effect on sedimentation or sludge-disposal equipment, except as the capacity of these units must be increased to accommodate the added volume.

Sedimentation-tank effluents containing the mixed wastes will respond to oxidation on trickling filters if the waste is applied in a fresh condition. In cases where the proportion of milk waste to sewage is large, sedimentation periods over 1 hr. are not recommended for mixed wastes for the reason that acidification takes place which may inhibit bacterial growths on the filter medium.

Although the standard trickling filters are adaptable to the treatment of domestic sewage containing milk wastes, there are many limitations to their application. A few general rules to be followed in this respect are:

1. If a final B.O.D. up to 80 p.p.m. is acceptable, a mixed waste having an initial B.O.D. up to 300 p.p.m. may be applied up to a rate not to exceed greatly 1 m.g.a.d.

2. If a B.O.D. below 40 p.p.m. is desired the proportion of milk waste to sewage should be such that the initial B.O.D. will not be greater than 200 to 250 p.p.m. at the same rate or a loading of not more than 120 cu. ft. per pound of B.O.D.

3. Where the filter area available is such that rates above 1 m.g.a.d. are necessary, the B.O.D. limits must be decreased accordingly.

4. If the volume of milk waste is greater than 25 per cent of the volume of the sewage or if the B.O.D. of the mixed waste is in excess of 300 p.p.m., pretreatment of the milk waste is desirable to reduce the combined B.O.D. to or below that value.

The recirculating filter may be applied to advantage in connection with the treatment of combined sewage and milk waste. Higher loadings and greater B.O.D. reductions are possible by the proper application of this process than are obtained with the standard filter. For recommended loadings see Chap. V.

Much the same rules apply to the treatment of combined sewage and milk waste by the activated-sludge process. The capacities of the various units must be such as to provide for the additional volume and B.O.D. load contributed by the waste. Air requirements, return-sludge facilities, and aeration periods are affected according to the load. Initial B.O.D. values may be higher than recommended for the biological-filtration process, if proper conditions are maintained. For the conventional plant, however, best results are obtained if the B.O.D. of the mixed waste is kept below 300 to 400 p.p.m.

Another consideration of importance in accepting milk waste for treatment in the municipal-sewage treatment plant is the possible increase in odors due to the decomposition of the milk solids. It is especially essential to prevent the accumulation of solids in channels, grit chambers, and pump wells. Butterfat has a tendency to adhere to the walls of these units as well as to those of sedimentation and filter units and must be continuously removed if the production of odors is to be prevented. In many cases, prechlorination for odor control becomes necessary.

CANNERY WASTES

Perhaps the second most common organic industrial waste found in municipal sewage is that from canneries. There are many different types of canning factories. Some are limited to the canning of a few special products; others are full-line factories operating on a wide variety of raw materials.

In the full-line cannery, the major portion of the wastes, so far as volume is concerned, is made up of the washings of the raw product and equipment. Usually the volume of waste from the full-line cannery is large and the strength comparable to or only slightly greater than domestic sewage. These wastes respond to biological processes and, if allowance is made for them in the treatment plant, they can be successfully treated in combination with the sewage.

Canneries operating on special products such as peas, tomatoes, squash, etc., usually present a more difficult problem, since the volume of waste is low and the strength high. The following B.O.D. values are typical of some of these special wastes: peas, 1,400 p.p.m.; corn, 625 p.p.m.; tomatoes, 840 p.p.m.; squash, 10,800 p.p.m.; and red beets, 7,000 p.p.m. Although these specialized wastes also respond to biological treatment, they contribute a much greater load in proportion to their volume than the full-line wastes.

One of the first requirements in the treatment of any cannery waste is fine screening. This should be accomplished at the factory before the wastes are discharged to the sewer. A 28- to 40-mesh screen of the revolving type is recommended.

Cannery wastes contain considerable solid matter in suspension and will influence sedimentation and sludge-digestion units.

Both must be increased in proportion to the amount of cannery waste admitted to the system. If the proportion is great, an acid condition may develop in the digestion tank, resulting in foaming of the sludge and a very poor supernatant liquor. The gas produced under these conditions will be high in carbon dioxide and low in heat value. The required conditions to be maintained are similar to those necessary for the successful treatment of garbage in sewage-digestion tanks.

The solids of cannery wastes are light and do not settle so rapidly or so completely as do sewage solids. For this reason, chemical treatment as a means of coagulating and settling the combined waste and sewage is recommended. Canning operations are seasonal, and chemical treatment, if employed, should be so arranged as to allow its use only during the period when the factory is running. Ferric chloride (or sulphate) and lime are recommended as coagulants. The quantities of each required will depend on the type and proportion of cannery waste in the sewage and can be determined only by trial. Sedimentation capacities should be provided for a 2-hr. detention period during factory operations. Additional sludge capacities required may be calculated on the basis used for sewage solids (from 2 to 3 cu. ft. per capita). On this basis the required capacity will be from 10 to 15 cu. ft. per pound of dry solids added to the digester per day.

Of the secondary-treatment processes, filtration is probably the more dependable where the ratio of cannery waste to sewage is high. The activated-sludge process is more likely to be upset by the seasonal change in the material applied and by the changes that occur during the pack as the various types of products are processed.

Filters should be designed so as to allow the application of maximum flows at a rate not greater than 1 m.g.a.d. unless recirculation is available. If the proportion of cannery waste is high, the filters may be built in two or more units, one or more of which will be used during the canning season. These filters may be developed by applying sewage for a week or so prior to the opening of the canning factory. The filters must be followed by secondary sedimentation. Chlorination for odor control may be necessary, since odors, especially from the filters, are usually more noticeable than with sewage alone. The loading

for standard filters is about 120 cu. ft. per pound of B.O.D. and for the recirculating filter about 50 cu. ft.

Although the cannery waste can be treated in combination with sewage, it is not generally recommended unless the ratio of this waste is comparatively low. Where the cannery waste represents more than 25 per cent of the combined volume or where more than 50 per cent of B.O.D. of the combined wastes is due to cannery waste, it should be treated separately or should be subjected to pretreatment before it is discharged to the system. Individual treatment under these cases will usually be more effective and economical.

MEAT-PACKING-PLANT WASTE

The liquid wastes from the smaller meat-packing plants and slaughter houses consist mostly of the washings from the killing floor, blood, and some paunch manure and grease. These wastes are not large in volume and consequently will not greatly affect the capacities of sewage-treatment units. In many of the smaller houses no effort is made to save the blood from the killing floor. This material is very high in oxygen demand and although it will respond to biological treatment, it may, in its concentrated form, upset certain of the processes.

The wastes from small plants located in the larger cities may be so diluted with the sewage as to pass through the treatment plant without any apparent effect. In the smaller cities, however, the waste may be a factor in the treatment and may necessitate some form of control.

The major portion of the blood should be collected at the house, and in no case should the paunch manure be washed into the sewer system. Both blood and manure can be easily disposed of elsewhere, and such disposal will eliminate possible difficulties with the system and treatment plant. Adequate grease traps, located in the packing-house sewer lines, will eliminate much of the difficulty of scum formation. This grease has some value as a by-product and if collected in sufficient quantity may be sold.

In the majority of cases the washings from the killing floor of small plants, when proper care is exercised in collecting the blood, grease, and manure, may be treated in the municipal

plant without difficulty, although some grease may pass by the traps and will increase the scum on sedimentation units.

The wastes from the very large packing plants present a somewhat different problem. In the majority of cases these wastes require some degree of pretreatment prior to their admission to the municipal system, unless the municipal plant is particularly designed to handle the combination. Pretreatment processes have been outlined in Chap. X. One of the most important factors is the removal of grease, which can be done to a great extent at the packing plant. However, there is usually sufficient grease entering the sewer system to necessitate the installation of grease-collecting equipment at the treatment plant.

Some paunch manure will be washed into the system and will affect sludge disposal and sedimentation in proportion to the amount present. Secondary-oxidation units will be affected to a greater extent than primary units, since much of the blood will pass through to the secondary process. Activated-sludge treatment has been successfully used as secondary treatment for combinations of sewage and meat-packing-plant wastes. The loading on these units is based on the B.O.D. value of the combined sewage and waste as previously given. If the proper loading is applied, either activated sludge or filtration can be expected to be successful as secondary treatment.

TANNERY WASTES

There are two processes used for the tanning of leather, the vegetable and the chrome processes. The beamhouse wastes from each process contain large amounts of lime, hair, fleshings, and grease. The tan liquor from the vegetable-tan process contains soluble organic compounds, is acid in character, and has a high oxygen demand. That from the chrome process contains chromium salts that precipitate with lime. This liquor does not have as high an oxygen demand as do the vegetable-tan liquors.

Generally speaking, tannery wastes should not be treated in municipal plants unless the plant is particularly designed for them. Much more effective and economical treatment is possible if they are handled separately. However, there are a few instances in which tannery waste and domestic sewage are treated in a municipal sewage-treatment plant.

One of the first considerations, if the waste is to be handled in combination with sewage, must be the manner by which the wastes are discharged by the tannery. Spent limes, bates, soaks, and tan liquors are dumped intermittently. Such an intermittent discharge of concentrated wastes is not favorable to treatment-plant operation. Arrangements must be made whereby these wastes can be stored in tanks and admitted to the sewers at a more or less constant rate over the major portion of the day.

The nature of tannery wastes is such as to affect the sedimentation and sludge-handling facilities in particular. Experience has shown that the solids settle and concentrate very slowly, necessitating much greater sedimentation capacities than are usually provided for sewage settling. A minimum of 3 hr. should be provided on the basis of the combined flow.

Large quantities of a fairly inert sludge are obtained from tannery-waste sedimentation. This sludge may be highly alkaline because of the limes and bates and does not digest rapidly, if at all. In fact, unless the proportion of sewage sludge is comparatively large (greater than 50 per cent), sludge digestion should not be attempted. Much more satisfactory sludge disposal may be accomplished if the raw sludge is dried on the vacuum filter and incinerated or disposed of by spreading on land.

Concentrated limes may contain as high as 8 per cent solids, especially those used in sole-leather tanning processes. These limes cause difficulties in sludge-removal equipment by packing into a compact, heavy mass. If possible, limes of this nature should be lagooned at the tannery and the dried material sold or given away to farmers for land treatment.

Primary-sedimentation effluents from tannery waste and sewage combinations contain considerable finely divided material in suspension and a considerable amount of soluble organic matter. The secondary treatment of this combination may be accomplished by means of either the activated-sludge or biological-filtration processes, the latter being preferred. The material contained in the waste is not so rapidly oxidized as that of some other wastes. Deeper filters and lower loadings are desirable. Eight-ft. depths at loadings of from 120 to 140 cu. ft. per pound of B.O.D. are considered necessary if an effluent of fair quality is to be obtained. Even with loadings of this nature

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TEXTILE WASTES

There are many different types of textile wastes, as has been indicated by the discussion in Chap. IX. These wastes contain spent chemicals such as alkalies, soda ash, dyes, sulphite, chromates, and hypochlorites. Some of them, particularly the deterging wastes, are very concentrated and have a high oxygen demand. Others, such as the dye wastes, have a low demand but require treatment to remove color.

In small cities, combined treatment of textile wastes and sewage is usually much more expensive and much less desirable than separate treatment. Large city systems, of course, can absorb a considerable quantity of these wastes without material effect on the treatment processes.

Textile wastes are largely chemical in nature and therefore do not respond so readily to biological processes as they do to chemical precipitation. For this reason plants required to treat the combined sewage and waste should involve chemical treatment as at least the primary process. Secondary biological processes may follow if necessary. However, the successful application of secondary processes requires careful control and manipulation of the primary treatment. Alkali must always be neutralized, chlorine must be destroyed, and in most cases the dyes must be decolorized before the waste is in condition for the application of biological processes.

Chemical treatment applied to the combination of these wastes and sewage should be on the same basis as described for textile wastes in Chap. IX, except that in most cases sludge digestion is practical. This will depend to some extent on the proportion of sewage solids present; however, a portion of the textile solids may respond to anaerobic digestion when mixed with the sewage sludge.

Textile mills practicing deterging operations, where large quantities of grease and strong chemicals are discarded, should be required to install recovery processes. This applies especially to wool-scouring wastes.

LAUNDRY WASTES

Laundry wastes have been known to cause considerable difficulty in the operation of certain sewage-treatment plants, although in the majority of cases they have no great significance. The problem is more likely to be present in plants serving institutions than in those serving municipalities.

These wastes are strongly alkaline and contain grease, dirt, soap, and soda ash. Much of the suspended matter is light and floats on the surface of sedimentation tanks, thereby increasing the scum-removal problem. The B.O.D. of laundry waste may be several times that of domestic sewage.

Where the difficulties resulting from the presence of laundry wastes are largely due to floating suspended matter, it becomes necessary to provide adequate skimming facilities. This involves some satisfactory arrangement for the disposal of the scum. In many plants the scum is pumped to the sludge-digestion units. The insoluble soaps and grease of laundry-waste origin, when present in large proportions, often disturb the digestion process. In this case, some other means of disposal becomes necessary, and often lagooning of the scum is the only other method available. When the situation becomes acute, pretreatment of the laundry waste by methods already discussed in Chap. XI is desirable.

PULP- AND PAPER-MILL WASTES

The major wastes from mills manufacturing pulp from wood result from the treatment of the stock by either the sulphite or sulphate process. Calcium bisulphite is used in the sulphite process for extracting the lignin and other impurities from the wood fibers. This extraction results in the production of a waste known as "sulphite liquor." Treatment of this liquor in a municipal sewage-treatment plant is never attempted, since the chemical constituents completely upset the treatment processes.

Sulphate mills use large quantities of soda ash, caustic soda, and sodium sulphate in extracting the impurities from the pulp. Most of these active ingredients are recovered from the waste liquor. This type of mill discharges a considerable quantity

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of water containing odor-producing compounds. This waste is usually not subjected to treatment in municipal plants.

Paper mills produce two general types of waste, namely, the "white water" from the paper machines and the "conversion" wastes from the washing of rags, straw, or old paper stock. White water is large in volume and contains a varying amount of fiber, clay, filler, alum, resin, and starch. Of these constituents, the chief one is fiber. Most of these substances are of some value to the industry, and the problem of waste disposal is largely one of reclamation rather than waste treatment.

Conversion wastes are also large in volume and contain some fiber and a considerable amount of clay, ink, casein, starch, and other material washed from the cooked stock. At present, there is no known use for the material that may be recovered from conversion wastes.

If conversion wastes are to be treated in municipal sewage-disposal plants, increased sedimentation and sludge-disposal facilities must be provided because of the large volume and high suspended-solids content of the waste. For example, a study made of a conversion mill for old paper stock in Michigan showed a combined volume of ink-washer and bleach-washer wastes of 828,000 gal. per day. This waste contained about 11,700 lb. of suspended material, about 50 per cent of which could be removed by plain settling. The remainder of the solids were finely divided or colloidal and required chemical treatment for effective removal. The disposal of this waste by way of the municipal plant would require facilities for chemical treatment and coagulation, an additional settling capacity of about 9,000 cu. ft., and digester and sludge-drying capacities for about 6 tons of solids daily. Since the sludge does not decompose when added to sewage sludge in the digester, it materially increased the required sludge-drying-bed area. If the difficulties attended with the clarification of this waste and the disposal of the sludge are considered, it does not seem advisable to attempt treatment in combination with municipal sewage.

The major waste from mills manufacturing strawboard is a composite of the water from the paper machine and the alkaline waste from the washers where the straw pulp is washed following digestion in the cookers. The volume of these combined wastes averages about 40,000 gal. per ton of production. The sus-

pended solids average about 2,500 p.p.m. or about 800 lb. per ton. The B.O.D. is approximately 900 p.p.m. and the population equivalent, 1,800 per ton. This waste is very high in putrescible material and decomposes rapidly. If combined with sewage for treatment, its effect would be applied throughout the entire plant. Unless the mill is located in a large city where the waste is but a small portion of the sewage flow, strawboard wastes may be best treated separately rather than in combination with the municipal sewage.

METAL-TREATING AND -PLATING WASTES

The principal wastes from the metal-treating industries are (*a*) acid liquors from pickling vats, (*b*) cyanide wastes from plating and heat-treating rooms, and (*c*) metals or metallic salts from plating, etc. The picking liquors consist largely of sulphuric acid and ferrous sulphate. These wastes in large amounts have a deleterious affect on sewer systems and completely upset biological types of sewage treatment unless they are neutralized prior to their discharge from the factory. Since sewage is normally alkaline, small proportions of acid waste may be neutralized by dilution with the sewage. This results in the precipitation of the iron salt and may aid in the clarification of the sewage. In fact, in several cases, acid pickling liquors are used as coagulants and if added in controlled amounts are a decided aid to settling. The usual practice, however, is to dump the liquor over a very short period. This procedure results in an undesirable condition, both in the sewer system and plant for this period. A controlled discharge over a long period of time may be feasible under certain conditions. However, as a general rule, acid pickling liquors should be at least partially neutralized before they are discharged to the municipal system.

Cyanide wastes result from the washing of the metal parts taken from the cyanide baths, the dumping of vats containing spoiled plating solutions, or the waste cyanide from the heat-treating process. These wastes are extremely toxic and unless diluted to a considerable degree are harmful to all types of biological processes.

Usually the dilution afforded by the sewage is sufficient to prevent the washings from plating rooms from causing trouble at the sewage-treatment plant. These washings may contain as

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Spoiled cyanide solutions cannot usually be disposed of in the sewer system, especially when the entire vat of solution is dumped at one time. There are exceptions to this statement, of course, since the dilution in the systems of the larger cities may be such as to reduce the concentration of cyanide below the toxic limit. In other cases, these solutions may be disposed of by spreading the discharge over a long period of time. Pretreatment to reduce the cyanide content must be resorted to when the possibilities of controlled disposal by dilution have been exhausted.

Copper and chromium in washings and other wastes from metal plating often cause trouble in municipal treatment plants. These metals as they are discharged from the factory are usually in the form of soluble cyanides, chlorides, etc. They are precipitated in the sewage, probably as sulphides or oxides, and settle in the sedimentation units from which they reach the sludge-digestion tanks. The effect of these compounds is cumulative, since the concentration tends to build up until the digestion process is seriously inhibited.

MALTHOUSE AND DISTILLERY WASTES

Malthouse wastes consist of the water from the steeping and germination of the grains. The quantity of this waste is comparatively large, and the B.O.D. is about two to three times that of domestic sewage. This waste responds readily to biological processes and may be treated in combination with municipal sewage if the required capacities are provided. As is the case with other wastes of this type, the feasibility of combined treatment depends chiefly on the comparative proportions of waste and sewage. If the industry is located in small cities, it is generally more economical and satisfactory to treat the waste separately or at least to pretreat the waste prior to any attempt at combined treatment.

The average volume of malthouse waste was shown in Chap. XIV to be about 500,000 gal. per day and the B.O.D. about 400 p.p.m. Thus, the population equivalent is approximately 10,000 on the basis of B.O.D. The suspended-solids content of the waste is not high. On the basis of suspended solids, the

population equivalent is about 1,600. These data indicate that, although sedimentation capacities will be required for the additional volume of waste, digestion capacities will not be affected in the same proportion. The additional load on digesters will require on the above basis about 3,200 cu. ft. of digester space. Secondary units, either activated sludge or biological filtration, will be required to carry an additional load of about 1,700 lb. of B.O.D.

Beer or distillery slops are extremely concentrated wastes. Table 66 shows them to contain from 2 to 5 per cent solids. This concentration of solids is comparable to raw primary-sewage sludge. If these slops are to be handled at all in the sewage plant, they should be added direct to the digester rather than mixed with the sewage. Digester capacity being available, it is entirely feasible to digest sewage sludge and beer slops in combination. Whether it is economical depends on the local conditions. Chapter XVI gives a more or less detailed discussion of the requirements for the anaerobic digestion of beer slops. The volume of waste per bushel of grain averages between 45 and 55 gal. per day.

PHENOLIC WASTES

Gas-plant and other phenolic wastes, after the tar has been removed, have been successfully treated in combination with domestic sewage. The effect of these wastes is mainly applied to secondary-oxidation processes, since the phenols are soluble compounds. There is some divergence of opinion as to the maximum allowable phenol content of the mixed sewage. It is generally conceded that a maximum of 50 p.p.m. phenol may be applied to either trickling-filter or activated-sludge units. Gas and other coal by-products plants should install efficient tar separators through which the wastes are passed before being discharged to the sewer.

OIL WASTES

Garage and other oil-containing wastes in quantity should not be allowed to discharge into the municipal system unless some form of oil separation is provided ahead of other treatment units. Usually it is much easier to separate the major portion of the oil at its source and to keep it from entering the system than to

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remove and dispose of it at the treatment plant. In some cases it is impossible to eliminate all the oil from an industrial waste. Floor washings in factories and garages and street washings usually contain oil. As a rule, the oil from such sources is not sufficient to cause serious difficulties in the treatment plant.

References

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