# Waste Problems of a Chemical Company

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**An area representing the drainage system of the Saginaw River in Michigan is described as an example of sources of pollution such as oil wells, oil refineries, beet sugar plants, chemical companies, and municipal sewage. Wastes from a chemical company are divided into five broad groups: nonhazardous, brine, taste- and odor-producing, phenolic and sediment-bearing.**

**Five methods of control are given: (*a*) Brine is ponded and released in periods of high river flows. (*b*) Scrubbing waters for removing taste and odor materials produced by cracking processes are settled in ponds and re-used, evaporation being made up by fresh river water. (*c*) Absorbing agents for halogens, halogen acids, sulfur dioxide, etc., are returned to the respective process when saturated, the value of returned products in many cases paying for the cost. (*d*) Weak water solutions of phenol and phenolic compounds are circulated over trickling filters having the proper bacteria inoculation and through detention ponds, and are then released to the river after 98 per cent or more of the phenol load has been destroyed. (*e*) Sediment-bearing wastes are made to flow through ponds where sediment largely settles out and dissolved oxygen is restored.**

THE Dow Chemical Company, originated in 1897 and located at Midland, Mich., on the Tittabawassee River, a tributary of the Saginaw River, has had many industrial waste disposal problems. Bay City, taking its water supply from Saginaw Bay, Saginaw, taking its water supply from Saginaw River, and Midland, taking its supply from the Tittabawassee or Chippewa, may be affected by any materials introduced into the streams. Oil, brine, and sugar beet wastes enter the water above Midland, and to these are added the wastes developing in the manufacture of over three hundred chemicals at the Dow plant (the total entering the Saginaw River). The company's responsibility is the condition of the Tittabawassee River below Midland. A great deal of information about the amount of pollution and what happens to it has been collected through years of study on 16 miles of the river below Midland before it enters the Saginaw River, at a cost of about five thousand dollars a year.

The Dow Chemical Company manufactures inorganic and organic, aliphatic and aromatic chemicals, comprising industrials, pharmaceuticals, insecticides, solvents, intermediate dyes, cellulose products, magnesium metal, etc. The operations are carried on in some three hundred buildings which spread over 400 acres of land.

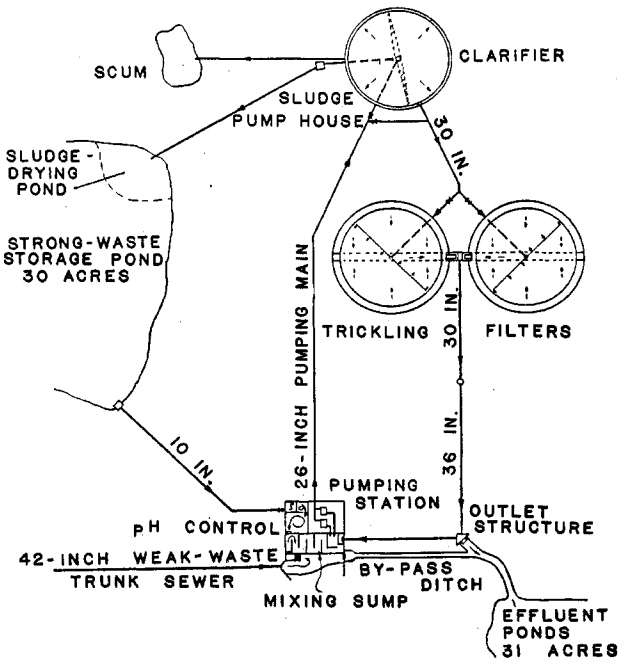



FIGURE 1. FLOW DIAGRAM OF PHENOLIC WASTE TREATMENT PLANT

The wastes from these processes are broadly classified as nonhazardous, brine, taste- and odor-producing, phenolic, and sediment-bearing.

## Nonhazardous Wastes

Nonhazardous wastes comprise barometric condenser waters from evaporation of solutions such as sodium chloride, calcium and magnesium chlorides, sodium hydroxide, etc. This condenser water is warm, has nearly a saturated oxygen content, and is only intermittently polluted with the products evaporated. Sodium, calcium, and magnesium pollution from this source has little effect except in periods of very low flow in the river, as experienced in February, July, and early August. Sodium hydroxide may cause injury to fish for a distance of 20 rods below the point where effluent enters the river.

## Brine

Brine is the raw material for bromine, chlorine, sodium chloride, calcium chloride, and magnesium products. A total daily production of 51,600 barrels is required for bromine; 28,000 barrels of the total are processed for the other products, leaving 23,600 barrels to be disposed of per day.



FIGURE 2. CLARIFIER AND TWO TRICKLING FILTERS

This is too much to be released daily in the flow of the Tittabawassee River, which varies from 200 cubic feet per second in dry weather to over 6800 during spring runoff, and provides one of the major pollution problems for the company. In addition to causing increased softening expense to cities for their water supply, power plants, metal shops using cutting equipment, greenhouses, breweries, and vinegar manufacturers have complained that a high chloride content in their water was detrimental. Plants using barometric condenser water, such as the beet sugar factories, find that a large increase of calcium and magnesium ions causes calcium carbonate to separate in their pumps and lines to the extent that it is necessary to shut down for complete overhaul.

Two methods have been tried for disposing of the 24,000 barrels of brine. One is to return the brine to a formation in the ground that will receive it. Oil companies in certain fields of Michigan have been very successful with this method; they find that holes drilled for oil that have had small production or no oil at all returned brine at rates sufficient to take care of their needs. The Dow Chemical Company has not been so fortunate. It is obvious that spent brine should not be returned to the same stratum as that from which fresh brine comes; therefore a well was drilled to a stratum about 730 to 880 feet deep having 156 feet of Parma sand and being 300 to 400 feet above the brine producing Marshall sand. A filter was provided which clarified the brine to less than 10 p. p. m. of turbidity, and this brine was pumped down to the Parma sand by three pumps, one duplex and two triplex, operating at 500 to 550 pounds per square inch pressure. Up to 43,000 barrels were returned per 24 hours at a cost of 13 dollars per thousand barrels. This returning of brine was stopped after several days because it was finding its way back to the surface at every point where other wells pierced the Parma sand. Troubles were with pump breakage, packing, and filters.

The second plan was to impound brine during low-water months for release during high-water runoff periods. A pond comprising 146 acres was constructed. The dikes of this pond are protected by an interlocking steel sheet piling core driven 3 feet into clay underlining the pond. Seepage is collected in ditches encircling the pond and pumped back to storage. A second and larger pond is provided which makes the total storage available equal to more than a two-year excess production of brine. No steel piling has yet been driven in the second pond, but should its use be necessary, this would be done. Discharges of brine are carefully controlled through concrete and steel gate structures during periods of high-water flow in the river. Saginaw Water Works' intake to storage for raw water is protected by steel gates so that no effect is experienced during the passage of a brine release. Bay City is protected by reservoirs having about a week's capacity.

Surveys to determine the chloride concentration and its location in Saginaw Bay were made by The Dow Chemical Company and by the Michigan Stream Control Commission during 1933, 1934, 1935, and 1936. A conductivity cell was developed in our Physics Laboratory, consisting of a Wheatstone bridge with a double switch, connected to an electrode and resistance thermometer. A buzzer served in place of a galvanometer to indicate when the bridge was in balance. Readings on conductivity and temperature were made and related to chloride concentrations. By the use of this device chloride concentration could be determined for the surface, and any other depth that might be desired from a boat or by drilling holes through the ice in the winter. Over ten thousand such determinations were made. The procedure was to release a quantity of brine at Midland, follow its travel down the river to the bay, then, by use of a power boat traveling over compass courses covering the entire bay, determine how the area of high chloride moved with normal currents and what was the effect of winds. Samples taken through the ice March 2, 3, and 4, 1936, show the following results: from the surface, 10 to 20 and 20 to 40 p. p. m.; from mid-depth, an area of 100 to 200 p. p. m., and from the bottom, a much greater area of 100 to 300 p. p. m. Toward the northeast there is a narrow boat channel, 20 to 30 feet deep, leading to Lake Huron. During periods of ice coverage any releases of brine at Midland pass through the bay by moving along the bottom of the ship channel, spreading relatively little on either side. Releases of brine in the absence of ice move along the east shore of the bay except when easterly winds interfere. If a 2- or 3-day blow from the east occurs while a brine release is entering the bay, the high-chloride water is diverted west over the intake of the Bay City Water Plant. It is for such contingencies that the storage pond is provided. No evidence is available to show more than a week's duration of serious chloride conditions around the intake. Brine releases are not made during beet sugar manufacturing season, and other industries are notified before each release. Concentrations of 25,000 p. p. m. of sodium chloride cause discomfort to suckers, perch, and carp, but do not kill unless maintained for more than 20 to 30 hours. Concentration during releases is kept below 5000 p. p. m. at Midland to assure a concentration in the bay at the mouth of Saginaw River of not over 1000 to 1500 p. p. m.

### Taste- and Odor-Producing Wastes

Taste and odor chemicals classified as such at the present time include products from cracking oils and those bought and used, such as nitrobenzene and mercaptan but not phenol or phenol-related compounds. This is not the complete list of such offenders but does cover those affecting the river for miles below the plant. A 65-acre pond is now being utilized as a cooling and clarifying step for water used for quenching and scrubbing gases from the cracking plants. This hot, highly polluted water is pumped to the pond and, after a devious travel route through the pond, is pumped back for re-use. Evaporation is made up with clean river water, and no trouble has developed with oil and tar during one year's operation. Oil and tar are accumulating in this pond and will eventually necessitate a new pond or disposal of the oil and tar by burning.

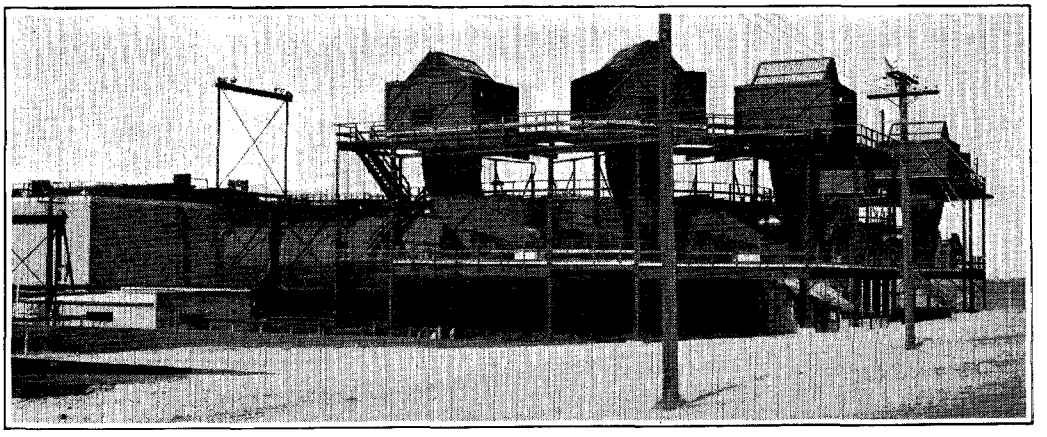


FIGURE 3. SPRAY CATCHER FOR HYDROBROMIC AND SULFURIC ACIDS

### Phenolic Wastes

Up to the present time phenol and allied products, such as chlorobenzene, aniline, salicylates, etc., have created the gravest need for complete elimination from plant wastes. Since 1927 phenol-polluted plant effluent has been impounded. At first, ponding and release during high river flow were used for solutions having over 10 p. p. m. of phenol. The high river flow always came before the temperature of the water was above 52° F. so that phenol contamination could be detected chemically for several days after a release. It was impossible to retain in ponds all the water that had only 1 to 2 p. p. m. of phenol. For seven or eight months of the year it really did not matter, but during December, January, February, March, tastes in water were attributed to this source.

Two problems are presented: the impounding and disposal of solutions having over 5 p. p. m. of phenol, the volume of which varied from 2 to 5 hundred thousand gallons per day; and the disposal of solutions having less than 5 p. p. m., usually 1 to 2 p. p. m., and varying from 10 to 15 million gallons per day.

Atmospheric oxidations with catalyst and controlled pH made only slight improvement.

Extraction by use of solvents such as benzene and treatment with alkali were not practicable. Strong waste had too many different products in solution, and effluent still contained 1 to 5 p. p. m. of phenol derivatives.

Adsorption by active carbon was effective but expensive. Carbon did not reactivate well owing to mineral salts, particularly sodium sulfate.

Biochemical methods held most promise. Milwaukee Coke and Gas Company, working with the City Activated Sludge staff, observed that phenol was reduced by passage through the sewage plant. Records of phenol load entering and leaving sewage disposal plants, particularly the Emscher filter type in Germany, show marked reductions of the phenol. Our own observations conclusively established that weak phenol solutions lost their phenol when mixed with city sewage in warm weather.

On the basis of this information, a small pilot plant consisting of neutralizer, sedimentation tank, and two Emscher filters were put into operation for over a year. City sewage was first mixed with phenol-containing waste, the pH was adjusted to 7, and the mixture was conducted through the two Emscher filters in series. Then it passed to a settler where the clear liquid went to waste and the settled solids were divided; part returned in the feed to the filter and the balance to atmospheric drying beds. Phenol was reduced from 20 p. p. m. entering the filter to 0.5 p. p. m. in the effluent. There was a tendency for filter beds to clog, which disturbed the even distribution of air and increased the resistance to air passing through the bed. Air was supplied by a compressor at about 10 pounds per square inch pressure and constituted a major expense. The same results were obtained by operating a trickling filter in place of an Emscher filter. Air is supplied by natural draft through the bed, and with proper material for the bed no trouble is experienced with sludge. Soil bacteria, common in all surface waters, were found to be the active agents, so that the use of sewage was abandoned in favor of river water.

A plant to handle 2 to 5 hundred thousand gallons per day of strong phenol-polluted waste (up to 500 p. p. m. phenol) and 10 to 15 million gallons per day of weak phenol (1 to 5 p. p. m.) has been operating for twenty months with remarkable success. The phenol load to the filter is 13–30 p. p. m., and the effluent varies from 0.4 to 3.0 p. p. m.; this concentration is permitted, since the effluent passes through a 31-acre pond where action continues so that the effluent from the pond is averaging under 0.05 p. p. m.

A flow diagram of the phenolic waste treatment plant is shown in Figure 1. Strong and weak phenol wastes enter the mixing chamber, have pH adjusted to 6.8 by the addition of lime, and are pumped to a depth clarifier, 140 feet in diameter with 8-foot side walls; clear effluent flows by gravity to two trickling filters, and sludge is pumped to an area where the solids settle and the liquid runs to strong phenol storage. The trickling filters have a top diameter of 142 feet and a bottom diameter of 162 feet (Figure 2). The filter bed is blast furnace slag 10 feet deep, with the following screen size:

| % Passing | Screen Size, In. | % Passing | Screen Size, In. |
|---|---|---|---|
| 100 | 4 | 20 | 2.5 |
| 95 | 3.5 | 8 | 2.0 |
| 60 | 3 | Not more than 3 | 1.5 |

Filter bottom tile are laid in mortar over a concrete slab completely covering the wetted area.

The rate of feed to the filters is about 16 million gallons per acre per day with an average phenol content of 13 to 30 p. p. m. The effluent (0.4 to 3.0 p. p. m. of phenols) enters a 31-acre detention pond from which it flows to the river with less than 0.05 p. p. m. Temperature of feed to the filters must be 70° F. for this rate; lower temperatures necessitate slower rates, and below 50° F., practically no action takes place.

### Sediments

Plant effluents carrying appreciable amounts of turbidity pass through ponds several feet deep spreading over 42 acres, where the greatest proportion of solids settle out and dissolved oxygen is restored to nearly saturation. A satisfactory disposal for solutions that may cause precipitates when mixed with one another or when mixed with river water is still being sought. Sulfur chloride and waste water precipitates a very fine sulfur when mixed with effluents from sulfur insecticide plants and carbon disulfide wastes. This is comparatively harmless but causes unsightly turbidity for long distances downstream from the plant. It may be possible to segregate most inorganic acids so that the main body of the wastes will not precipitate sulfur. Experimental work is now in progress toward a solution of this problem.

### Atmospheric Pollution

Chemical vapors such as chlorine, bromine, sulfur dioxide, hydrogen chloride, ammonia, sulfur dichloride, carbon disulfide, etc., are prevented from escaping to the atmosphere by scrubbing vent gases of all processes in towers with the proper absorbent (Figure 3). The value of products recovered often pays for the expense. Absorbents are the usual ones—alkalies, acid, and charcoal. Odors from storage ponds may be a nuisance in warm weather. As an example, acid waste contacts alkaline sulfides and liberates hydrogen sulfide. Faulty operation of scrubber towers may do damage to lawns, trees, and shrubbery, may cause corrosion of steel equipment, discoloration and destruction of painted surfaces, and, with certain conditions of humidity and temperature, may cause fogs.

# Biological Processes for Treating Waste

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**Biological processes are applicable to wastes from industries using biological raw materials primarily. Three essentially distinct biological processes have been applied to the treatment of such industrial wastes: bioprecipitation which results in oxidation and precipitation, anaerobic fermentation which converts organic matter to insoluble gases, and production of valuable by-products. Examples of the first two are discussed, and data are given to show limits of applicability and results obtained. The third type of process is largely in the experimental stage.**

THE purpose of this paper is to discuss certain biological processes which are broadly applicable to the stabilization of all organic wastes. The term "trade wastes" as ordinarily used applies to the water-carried wastes discharged by manufacturing plants. A few of these waste liquors carry mineral salts or acids which are responsible for more or less damage to the stream. By far the larger number discharge organic material of a biological origin which, on decomposing, causes putrefactive odors and a depletion of the oxygen of the stream below the requirements of normal fauna and flora. We are primarily concerned with this latter class of wastes in the discussion of biological processes in industrial waste treatment.

The primary object of treatment processes is to prevent oxygen deficiency in the streams. Oxygen deficiency is the basic cause of nuisance and destruction of fish and other aquatic life as well as normal vegetable life. The elements carbon and hydrogen and to a small extent nitrogen are the chemical factors responsible for consumption of dissolved oxygen; therefore the problem is to remove substances containing unoxidized compounds of these elements.

BACTERIA of various sorts are capable of accomplishing this in two ways—namely, to form relatively insoluble gases or solids from the carbon in the organic matter. These processes might be classified as fermentative (gas producing) and precipitating (bioprecipitating). A more common classification of the processes for biological stabilization is made on the basis of the classes of bacteria and other microorganisms which are responsible for the results produced. This classification divides the stabilizing processes into the aerobic and anaerobic groups—that is, those produced by organisms requiring air or oxygen and those carried on in the absence of oxygen.

Except in the case of very simple substances, such as acetic acid or glucose, aerobic and anaerobic action both yield solid and gaseous end products under practicable conditions. When carried to the extreme, the solids may be almost, if not completely, gasified by both processes.

The character of the solids and gases is distinctly different in the two cases. The aerobic process naturally yields carbon dioxide, and the hydrogen forms water. The solids produced