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Pollution Control Technology for Pesticide Formulators and Packagers

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POLLUTION CONTROL TECHNOLOGY FOR PESTICIDE FORMULATORS AND PACKAGERS

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ABSTRACT

The pesticide formulation and packaging industry transforms bulk pesticidal chemicals (active ingredients) into packaged, ready-to-use forms for sale to the consumer. Most pesticides are formulated in plants completely separate from the site of active ingredient manufacture.

The industry is structured into three categories: pesticide-producer formulators, independent formulators, and small packagers for whom pesticide formulation is usually a minor part of their operation.

About 32,000 formulated products are federally registered to approximately 3,400 companies for interstate sale. Over two-thirds of the products are registered to companies marketing five or fewer pesticide products. Most pesticide products, however, are apparently formulated in the 200 to 300 large formulation plants located throughout the country.

Techniques currently used to dispose of process wastewater include evaporation, landfill disposal, and contract disposal services. Pretreatment of process wastewater before discharge into municipal systems is not universally practiced, and the techniques currently being used are generally inadequate to meet increasingly strict standards.

The best practicable wastewater treatment technology appears to be complete evaporation. Alternatively, partial evaporation with disposal of the concentrate in an approved landfill can be used. Air pollution resulting from these practices, however, has not been evaluated. The best available treatment technology appears to be a pretreatment-filtration-adsorption process now in the development phase.

Additional research on wastewater composition, evaporative transport of pesticides, and the demonstration of the pretreatment-filtration-adsorption process is needed.

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The study was made possible by the cooperation of two interested groups. The NACA membership, working through its Committee on Agricultural Chemical Environmental Quality, Mr. Robert E. Naegele, Chairman, provided much of the data that are contained in this report. The U.S. Environmental Protection Agency was quite helpful at both the regional and national levels in providing additional data on federal pesticide registrations and the operations of the pesticide formulation industry. Mr. David L. Becker, Effluent Guidelines Division, EPA Project Officer for the study, has aided in the coordination of the efforts of these two organizations. Dr. Robert R. Swank, Jr., of the Southeast Environmental Research Laboratory, EPA Co-Project Officer for this study, aided in providing technical input on possible treatment and disposal practices and in reviewing the project results.

SECTION I

CONCLUSIONS

The following conclusions apply to the pesticide formulation and packaging industry, and to the applicable wastewater control technologies. These conclusions are ordered according to their decreasing importance.

1. The best practicable control technology currently available for most plants in the industry appears to be an evaporative system having no effluent. For those plants that cannot effect complete evaporation of their process wastewater, partial evaporation in conjunction with disposal in an approved landfill appears to be the best alternative. A major limitation to the use of evaporative systems, however, is the possible pollution of air by toxic chemicals through various water-to-air transfer mechanisms.

2. The best available treatment technology appears to be a three-step process: (a) pretreatment (neutralization, precipitation, and/or deemulsification); (b) filtration; and (c) adsorption (activated carbon and/or resin). The specific treatment requirements can be expected to vary with the individual plant sites.

3. Only one formulation plant has been identified that is currently using wastewater treatment technology closely approximating this definition of best available technology. This plant's treatment process is still in the pilot-plant phase of development.

4. The expense of installing and operating equipment that is equivalent to best available technology as defined above, would have a significant impact on the capital investments required for many formulation plants.

5. Some plants are currently operating with no discharge of process wastewaters. By conservative water usage and improved operating and housekeeping practices, most plants can either eliminate or significantly reduce the volume of process wastewater generated.

6. Pretreatment practices that are now being used to process wastewaters before discharge into municipal systems appear to be generally inadequate.

7. The majority of pesticidal chemicals are formulated in 200 to 300 formulation plants located throughout the United States. Many of these plants produce 20,000,000 to 40,000,000 lb of formulated material per year.

8. The majority of pesticide registrations, both State and Federal, are held by small companies. Over two-thirds of these registrations are held by companies having five or fewer pesticidal products. The majority of these products are apparently formulated under contract in the 200 to 300 largest formulation plants.

SECTION II

RECOMMENDATIONS

The fundamental limitation in attempting to evaluate treatment technology for pesticide formulation and packaging wastewater is the lack of adequate quantitative and qualitative data. An overall recommendation, therefore, is that research and development studies be undertaken that will provide the necessary data. Recommendations for specific areas of study to provide these data follow. These are listed in their chronological order of need.

1. Studies should be made to characterize formulation wastewaters in terms of volumes, toxicant concentrations and overall pollution parameters. Pesticide formulation is largely a seasonal industry; for this reason, the wastewater characterization studies should be conducted for representative sites over a complete production season.

2. The potential for polluting air by evaporation of low solubility contaminants, such as pesticides, from water bodies is one of the major uncertainties in the use of evaporative treatment systems. Determination of the air pollution resulting from evaporative wastewater treatment systems is urgently needed. This study should be conducted concurrently with the characterization of formulation wastewater, and should also cover an entire production season.

3. The pretreatment-filtration-adsorption system, identified as potentially the best treatment system available for use on formulation wastewater, has not been fully demonstrated in terms of both technological performance and economic viability. The performance of this system should be evaluated, as well as modifications that would make it more efficient.

4. Longer-term studies should be initiated to identify effective methods for detoxifying the pesticidal chemicals in formulation wastewaters. The application of biological as well as chemical detoxification processes to formulation wastewaters should be included.

SECTION III

INTRODUCTION

The need to control potentially polluting emissions from agricultural chemical plants has been recognized for a number of years. One of the first sources of information on control techniques applicable to pesticide manufacturing and formulating facilities was a manual developed by a special National Agricultural Chemicals Association (NACA)-Industry Committee (the Grady Committee), and published by the NACA in 1965. This publication, "Manual on Waste Disposal,"[1/] has been widely used by the industry, and has become known as the "Grady Waste Disposal Manual."

The NACA manual has been a useful guide to wastewater disposal because of its general descriptions of wastewater treatment techniques, as well as of disposal methods for specific classes of pesticides. However, most of this information is addressed to disposal of wastewaters from pesticide manufacturing facilities or manufacturing-formulation complexes, rather than wastewaters from a separate formulation plant. Neither the "Grady Manual" nor any other available publication provides sufficient information to enable pesticide formulators and packagers to comply with the new system of national effluent limitations and performance standards. Because of this lack of information this study has been made, utilizing a research grant from the U. S. Environmental Protection Agency (EPA), to document information on control technology applicable to pesticide formulating and packaging plants.

Background

In 1965, the NACA published the "Grady Waste Disposal Manual" to provide "guidelines which might be followed in the disposal of waste from pesticide manufacturing and formulating operations."[1/] Although this manual contains much pertinent information, it is of limited usefulness in that it does not address the pesticide formulator as a specific audience. In fact, this document is now considered to be quite out of date, and is no longer in print.

In 1970, the Environmental Quality Committee of the NACA initiated efforts to provide a more current source of waste treatment information applicable to formulation plants. During 1970 and 1971, their work yielded draft revisions of many sections of the original manual, as well as the development of new sections for inclusion in an updated edition. It was later concluded, however, that the scope of revisions required was larger than the NACA could provide through its committee systems. One major element that expanded the disposal manual's scope over that which existed when the original edition was developed has been new water pollution control legislation.

The Water Pollution Control Act of 1972[2]/ outlines two national goals: (1) "by July 1, 1983, wherever possible, water that is clean enough for swimming and other recreational use, and clean enough to protect fish, shellfish and wildlife"; and (2) "by 1985 no more discharge whatsoever of pollutants into the Nation's waters."[3]/ To meet these goals, a series of actions is being taken by the EPA.

Limitations are being established on the maximum amounts of pollutants that can be discharged into a water body. To meet these effluent limitations, "best practicable" and "best available" water pollution control technologies are being defined on the basis of cost, age of the industrial facility, processes used, and the environmental impact of applying these controls. Industries must meet effluent limits equivalent to "best practicable" technology by 1 July 1977, and must meet effluent limitations reflecting "best available" technology by 1 July 1983. Where technically and economically achievable, the national goal is to eliminate pollutant discharge by 1 July 1985.

In addition, industrial discharges into publicly-owned sewage treatment plant will also be subject to effluent limitations. Pretreatment requirements, where specified, will take effect no later than May 1974 for new industrial sources, and no later than July 1976 for existing industrial facilities.

Study Objectives and Approach

The overall objectives of this study were to identify the "best" wastewater treatment technologies applicable to pesticide formulation plants, and to provide the pesticide formulation industry with a source of practical information on how to comply with effluent limitations.

Specific objectives were:

- characterization of the industry,
- characterization of the wastewater produced,
- assessment of applicable treatment technology,
- identification and assessment of best practicable, best available, and pretreatment technologies, and
- identification of research and development needs.

A dual approach was used to obtain the information needed to meet these objectives. The formulation industry, through the NACA membership, was surveyed to characterize its operation and identify plants already using good waste treatment practices. Key formulation plants were then selected for detailed case studies (see Appendix A). Concurrently, local, State, and Federal agencies were contacted to obtain available data on effluent characteristics and plant operations.

As an additional part of this study, data were compiled that had been generated to update the "Grady Disposal Manual," and integrated into the format of the original document. The updated manual has been included as Appendix B.

The scope of this study did not include provisions for analyses of plant waste streams, either to determine stream parameters, or to verify the reported effectiveness of treatment systems. Data are therefore limited to those made available by individual companies, found in the open literature, or obtained from local, State, or Federal agencies.

In addition, this study was not conducted as an official part of the EPA program to establish suggested effluent-limitation guidelines and standards of performance for specific industry categories, e.g., for pesticide formulators. Many companies have chosen not to make certain confidential information available.

The results of this study are presented in the following five sections: Industry Characterization; Wastewater Characterization; Current Wastewater Treatment Practices; Best Treatment Technologies; and Research and Development Needs. These sections parallel the five specific objectives outlined above.

SECTION IV

INDUSTRY CHARACTERIZATION

Pesticide formulation and packaging is the segment of the agricultural chemical industry that transforms bulk, highly concentrated active ingredients (technical pesticide) into convenient-to-use, effective forms ready for sale to the ultimate user. As the name of the industry indicates, two major operations are required to effect this transformation. The pesticidal materials must first be blended (formulated) with the necessary additives and inert carriers, and then packaged in appropriate containers.

Generally, the term "formulation industry" is used to include both of these operations because they are sequential steps normally conducted in the same plant. This meaning of the term is used throughout the report.

It was necessary to characterize the formulation industry before a meaningful assessment of pollution control technology could be made. Major considerations in the characterization were (1) what types of products are made, (2) how these products are manufactured, and (3) how the industry is structured. These considerations are discussed in the following three subsections.

Pesticide Formulations

Pesticidal chemicals (active ingredients) are normally manufactured in high concentration (80 to 99+%). Most active ingredients, however, cannot be used in their manufactured (technical) concentrations without being further processed into other forms. The usable forms (formulations) of pesticides must be biologically effective, as well as safe for the applicator to handle and use. These characteristics are obtained by dilution of the technical active ingredient with inert materials and conversion to appropriate physical forms designed for a particular method of application and end use.

The ultimate tests for a pesticide formulation are its effectiveness on the intended target, and the longevity of that effectiveness in storage. Major development work is often required to find a combination of ingredients that will meet these requirements. This effort is reflected in part by the dollar investment required to develop new pesticide products.[4,5]

For many pest control situations, complex formulations of active ingredients, solvents, stabilizers, synergists, emulsifiers, etc., are required.[6] Table 1, for example, lists the ingredients of one formulation that at one time was extensively used. The variety in formulation composition that is produced to meet specific applications and customer requirements is illustrated by Table 2. This table lists 25 potential diluents for use in dust

TABLE 1

COMPOSITION OF A SAMPLE EMULSIFIABLE CONCENTRATE FORMULATION[11/]

	Weight %
Active Ingredients:	
Toxaphene (90%)	42.1
DDT (100%)	18.9
Methyl Parathion (80%)	11.8
Solvents:	
Tenneco 500	10.6
HAN 132	10.6
Stabilizer:	
Epichlorohydrin	1.0
Emulsifiers:	
ATLOX 3404	2.5
ATLOX 3403F	2.5
	100.0

TABLE 2

DILUENTS USED IN INSECTICIDE FORMULATIONS[7]

Trade Name	Type	pH[a]
Attaclay	Attapulgite	7.5-9.0
Barden Clay	Kaolinite	4.0-5.0
No. 475 Bentonite	Montmorillonoid	8.5-9.5
Cab-O-Sil	Synthetic	4.5-6.0
Celite	Diatomite	6.0-7.0
Clatal	Talc	8.5-9.0
Continental Clay	Kaolinite	4.5-5.5
Dicalite 109-3	Diatomite	7.0-8.5
Diluex	Attapulgite	7.5-9.0
Frianite M3X	Diatomite	5.5-6.5
Glendon Pyrophyllite	Pyrophyllite	6.0-7.0
6 J Gray Talc	Talc	8.5-9.0
Hi-Sil 233	Synthetic	6.5-7.5
Hi-Sil 266X	Synthetic	5.5-7.0
Micro-Cel	Synthetic	8.0-10.0
Narvon 1F2	Kaolinite	5.0-5.5
Pikes Peak Clay	Montmorillonoid	4.5-5.5
Purecal O	Calcium Carbonate	8.0-8.5
Pyrax ABB	Pyrophyllite	6.5-7.0
No. 29 Pyrophyllite	Pyrophyllite	5.5-6.0
"Sierra Cloud" Talc	Talc	8.5-9.5
"Sierra White" IR	Talc	8.5-9.5
Silene EF	Synthetic	9.5-10.0
Zeothi 60	Synthetic	6.5-7.5
Zeosyl	Synthetic	6.5-7.5

a/ pH was determined on 5% by weight suspension in distilled water or from producer's literature.

formulations of one insecticide.[7] The lists of potential solvents and miscellaneous adjuvant chemicals are of comparable length.

Many factors are involved in the optimization of a formulation. Because of the complexities of these factors, trial and error techniques are still important elements in the development of successful formulations.[8] The composition of a formulation, except for the active ingredients and inert carrier or solvent, therefore, is usually considered confidential.

The number and types of pesticidal products sold, as well as the major type of formulations, are briefly discussed in the following section. More detailed information is available in a number of references for those requiring more specific data.[9,10]

Number of Products: The number of pesticide formulations produced and sold in the United States is difficult to determine accurately. Estimates have been made that as many as 900 pesticidal chemicals are formulated into over 60,000 products.[12] A more recent survey identified 550 pesticidal chemicals that are currently or have recently been commercially available in the United States.[13]

Accurate data are available on the number of pesticidal products having Federal registration for interstate sale. On 31 March 1973, there were 31,898 products having current Federal registration.[14]

Comparable data on pesticidal formulation registered for intrastate use, which are not included in the Federal registration listing, are not available. Table 3, however, summarizes available data on several key states. The number of Federally registered products are compared to the number of intrastate registrations for companies headquartered within the respective states. These data indicate that there are several thousand pesticide formulations marketed in addition to the nearly 32,000 sold under Federal registration.

Emulsifiable Concentrates: Emulsifiable concentrate (EC) formulations are solutions of active ingredients and emulsifiers in a solvent. These formulations are diluted with water or oil before application. Concentrations are typically 15 to 50% for a single active ingredient, to as high as 80% for formulations containing an active ingredient mixture. The concentration of emulsifiers is generally 5% or less.

Organic solvents are used for most emulsifiable concentrate formulations. Solvents commonly used include deodorized kerosene, xylenes, methyl isobutyl ketone, and amyl acetate.[15] The specific solvent selected for use depends on many factors, including solvency, specific gravity, flash point, safety to plants and animals, volatility, compatibility, odor, corrosiveness, and cost.[16]

TABLE 3

PESTICIDAL PRODUCT REGISTRATIONS FOR COMPANIES HEADQUARTERED IN REPRESENTATIVE STATES

	Number of Registrations		
State	Federal[a/]	State[b/]	State Registrations Not on Federal Listing
Arizona	123	535	-
California	2,790	6,234	-
Louisiana	238	341	-
Missouri	2,130	-	132
New Jersey	2,482	-	86

a/ Listing as of March 31, 1973.
b/ Based on 1972 data.

Water is used as the solvent for some of the water-soluble pesticides. The use of water is limited, however, and normally only certain herbicides are formulated with a water base.

Powders: Wettable or water-dispersible powders are mixtures of active ingredients, inert carriers, surfactants, and adjuvants that can be suspended in water for application. These powders generally contain a high concentration of active ingredient (15 to 95%), with 1 to 5% concentration of surfactant to improve wetting and suspendibility characteristics.

Soluble powders are similar to wettable powders except that they will completely dissolve in the appropriate diluent used in spraying. Normally, this diluent is water.

Dusts: The active ingredient concentration in dust formulations is usually low (0.1 to 20%), and therefore, the toxicity of these formulations is relatively low.

Dusts have long been used because they are relatively inexpensive and simple to apply. In the past few years, however, it has become a less important formulation because of its inherent dependence on climatological factors that cause variability in performance, as well as problems with drift.[17/]

The physical properties of dust formulations are determined by the properties of the carrier used and the particle size to which the formulation is ground. Some of the more commonly used carriers are organic flours, sulfur silicon oxides, lime, gypsum, talc, pyrophyllite, bentonites, kaolins, attapulgite, and volcanic ash (see Table 2, page 11). Selection of the carrier is critical, and is based on compatability with the active ingredient, particle size, abrasiveness, density, absorbability, wettability and cost.

These finely ground dry formulations typically contain active ingredient and inert carrier without the adjuvant chemicals found in powders. Dust formulations are directly applied without further dilution.

Granules: Granules are prepared by the impregnation of active ingredient on inert granular carriers such as clay, vermiculite, bentonite, sand, ground corncobs, carbon or diatomaceous earth. The granules are uniform in size, ranging from 15 to 60 mesh (15 to 30, 24 to 48, or 30 to 60 mesh) in diameter. The content of fine particles is tightly controlled in order to avoid dusting during application.

Granular formulations have advantages in that they avoid the problem of drift, and the rate of toxicant release can often be controlled by changing the ingredients of the formulation. The size of the inert granule, which is carefully controlled, also influences the redistribution of the active ingredient. This formulation is widely used for soil applications and is applied without further dilution.

Aerosols: Aerosol formulations normally contain low concentrations (less than 2%) of active ingredients in a suitable solvent solution with the necessary adjuvants. Solvents commonly used are organics, such as deodorized kerosene, and water. A wide range of special purpose additives may be included, depending on the intended use of the aerosol; for example, chlorbisan in a pet spray to suppress odor; copper oleate in some roach and ant sprays to prevent mildew; and isoparaffinic-based oil in livestock face fly sprays for the safety of the animals' mucous membranes.[18/] Synergistic chemicals are also commonly used, such as piperonyl butoxide, sulfoxide and propyl isomer. Pyrethrins are the active ingredients most commonly used.

Although millions of cans of pesticide aerosols are used each year in the United States, less than 1% of the total quantity of pesticidal active ingredients used is formulated in this manner.

Miscellaneous Formulations: In addition to these major pesticide formulations, a wide range of smaller volume products are manufactured. These other forms include baits (strips, grain, cubes, etc.), pastes, vapor and smoke generators, impregnated fertilizer, tablets, and treated seed.

Formulation Processes

Most pesticides are formulated in mixing equipment that is used only to produce pesticide formulations. The most important unit operations involved are dry mixing and grinding of solids, dissolving solids, and blending. Formulation systems are virtually all batch mixing operations. Formulation units may be completely enclosed within a building, or may be out in the open, depending primarily on the geographical location of the plant.

Individual formulation units are normally not highly sophisticated systems that require design and construction by an outside engineering firm. Rather, they are comparatively uncomplicated batch-blending systems that are designed to meet the requirements of a given company, location, rate of production, and available equipment. Production units representative of the liquid and solid formulation equipment in use are described below.

Liquid Formulation Units: A typical liquid unit is depicted in Figure 1. Technical pesticide is usually stored in its original shipping container in the warehouse section of the plant until it is needed. When technical material is received in bulk, however, it is transferred to holding tanks for storage. The technical material is transferred (frequently by gravity) to a scale, where the proper quantity is weighed out for a batch. The technical material is then pumped into a batch mixing tank. This tank is frequently an open-top vessel with a standard agitator. The mix tank may or may not be equipped with a heating/cooling system. When solid technical material is to be used, a melt tank is required before this material is added to the mix tank. Solvents are normally stored in bulk tanks located well away from the operating area of the plant. The necessary quantity of an appropriate solvent is either metered into the mix tank, or determined by measuring the tank level. Necessary adjuvants (emulsifiers, synergists, etc.) are added directly from their original container to the mix tank through the open top or a manhole. The components of the formulation are blended in the mix tank using its agitator and heating/cooling system as required. From the mix tank, the formulated material is frequently pumped to a hold tank before being put into containers for shipment. Before being packaged many liquid formulations must be filtered by conventional cartridge or plate-and-frame filters.

Air pollution control equipment used on liquid formulation units typically involves an exhaust system at all potential sources of emission. Storage and holding tanks, mix tanks, and container-filling lines are normally provided with an exhaust connection or hood to remove any vapors. The exhaust from the system normally discharges to a scrubber system or to the atmosphere.

Dusts and Wettable Powders: Dusts and powders are manufactured by mixing the technical material with the appropriate inert carrier, and grinding this

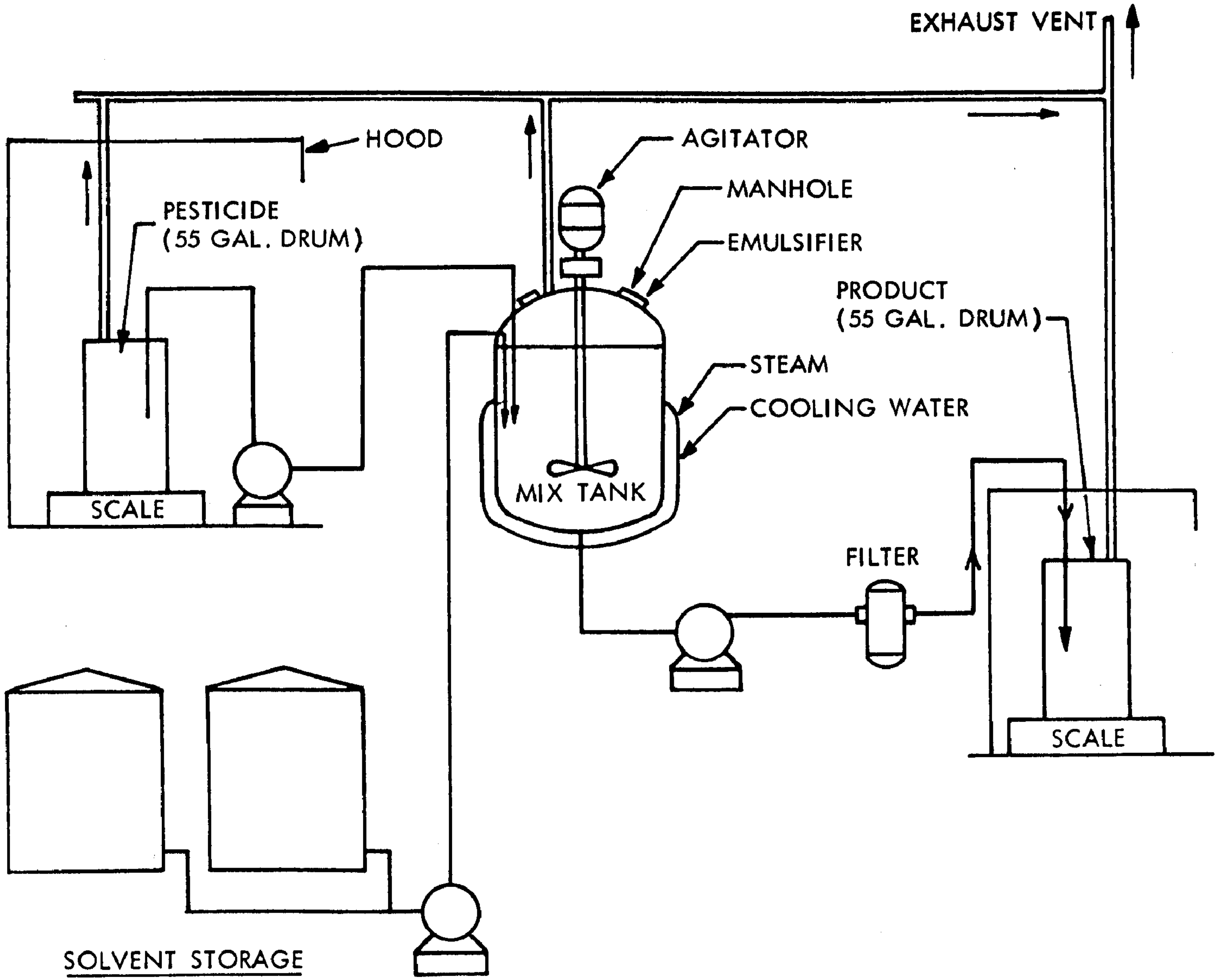


Figure 1 - Liquid Formulation Unit[19]

mixture to obtain the correct particle size. Mixing can be effected by a number of rotary or ribbon blender type mixers. Grinding is done in hammer, impact, roller or fluid energy (air) mills. As is the case with liquid formulation units, the exact configuration of a specific dust or powder unit depends on the production characteristics of the individual plant site.

Sulfur powder can be prepared in a rather simple unit (see Figure 2). Crude sulfur is transported from storage in open pits or in a warehouse, and loaded into a feeding hopper which feeds a roller mill. The material is then finely ground. The combustible nature of sulfur in air requires that the mill system be blanketed with an inert gas. The milled sulfur then goes to a cyclone collector from which the finished product is discharged into holding bins before being packaged.

Some production methods involve the use of a volatile solvent to impregnate the active ingredient on an inert carrier. After impregnation, the active ingredient-carrier mixture is ground, separated in a cyclone, and packaged.

One formulation process that has been used for DDT is a good example of more extensive processing required to produce some products: a two-stage process is used (see Figure 3). The first part of the process is the initial grinding of the active ingredient (Figure 3a) with silica. Flakes of technical material are emptied from bags onto a hopper, conveyed into a crusher, and mixed with finely ground silica before being pulverized. The coarse silica-active ingredient mixture is then mixed in a ribbon blender. This DDT formulation requires aging at this point before further grinding. The mixture is then fed into a ribbon blender where additional silica as well as wetting agents are added. This mix is conveyed to a high-speed grinding mill. A pneumatic system conveys the material to a cyclone separator which discharges into another blender. The blended material is finely ground by high-pressure air mill and conveyed to a reverse-jet baghouse that discharges into another blender. Final air grinding is repeated before the finished product is packaged.

Air pollution control in dust formulation units is accomplished primarily by baghouse systems. In some plants, however, water scrubbers are used. Water requirements for these systems are very low because the scrubbing water can be largely recirculated.[22]

Granules: Granules are formulated in systems similar to the mixing sections of dust plants. The active ingredient is absorbed onto a sized, granular carrier such as clay or a botanical material. This is accomplished in mixers of various capacity that generally resemble cement mixers. Ribbon blenders are not used because they tend to break down the granules.

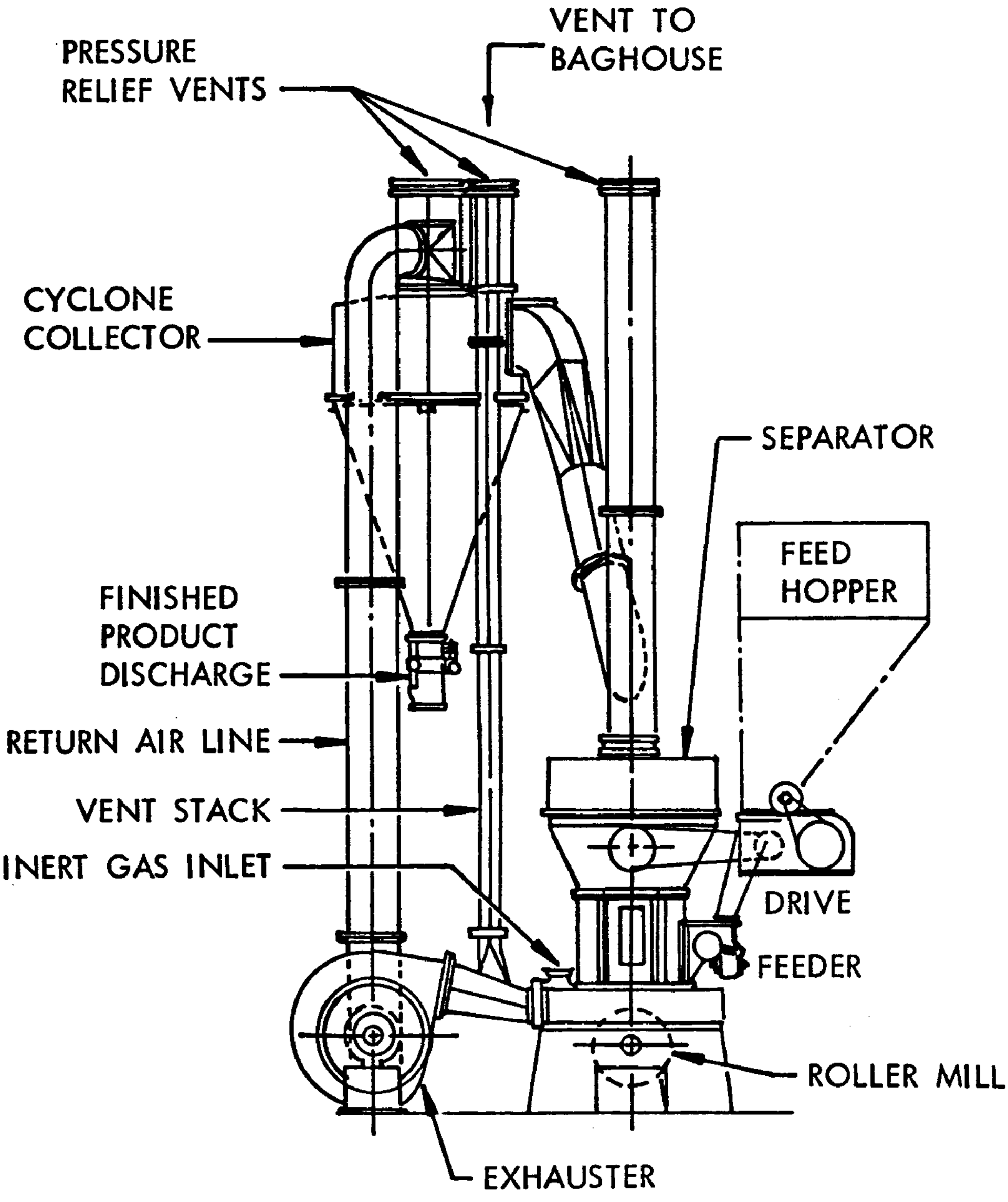
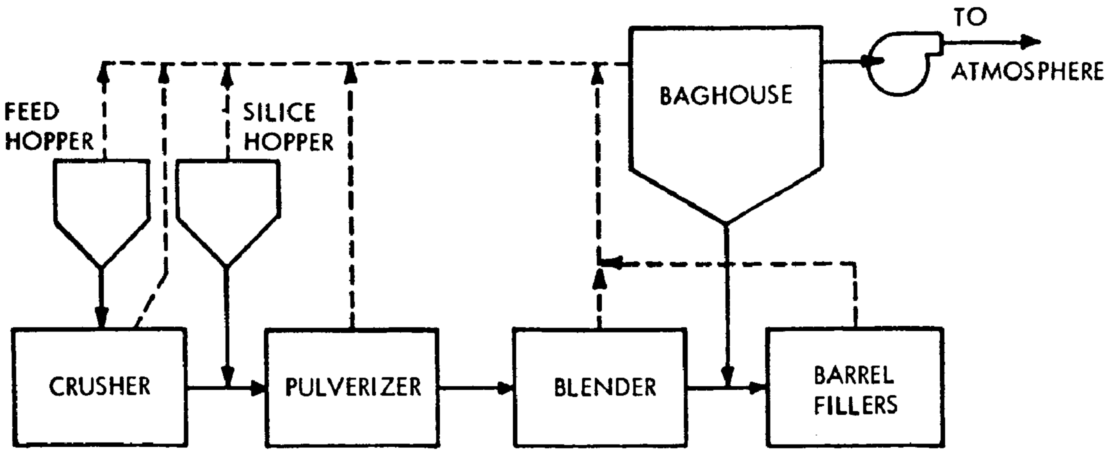
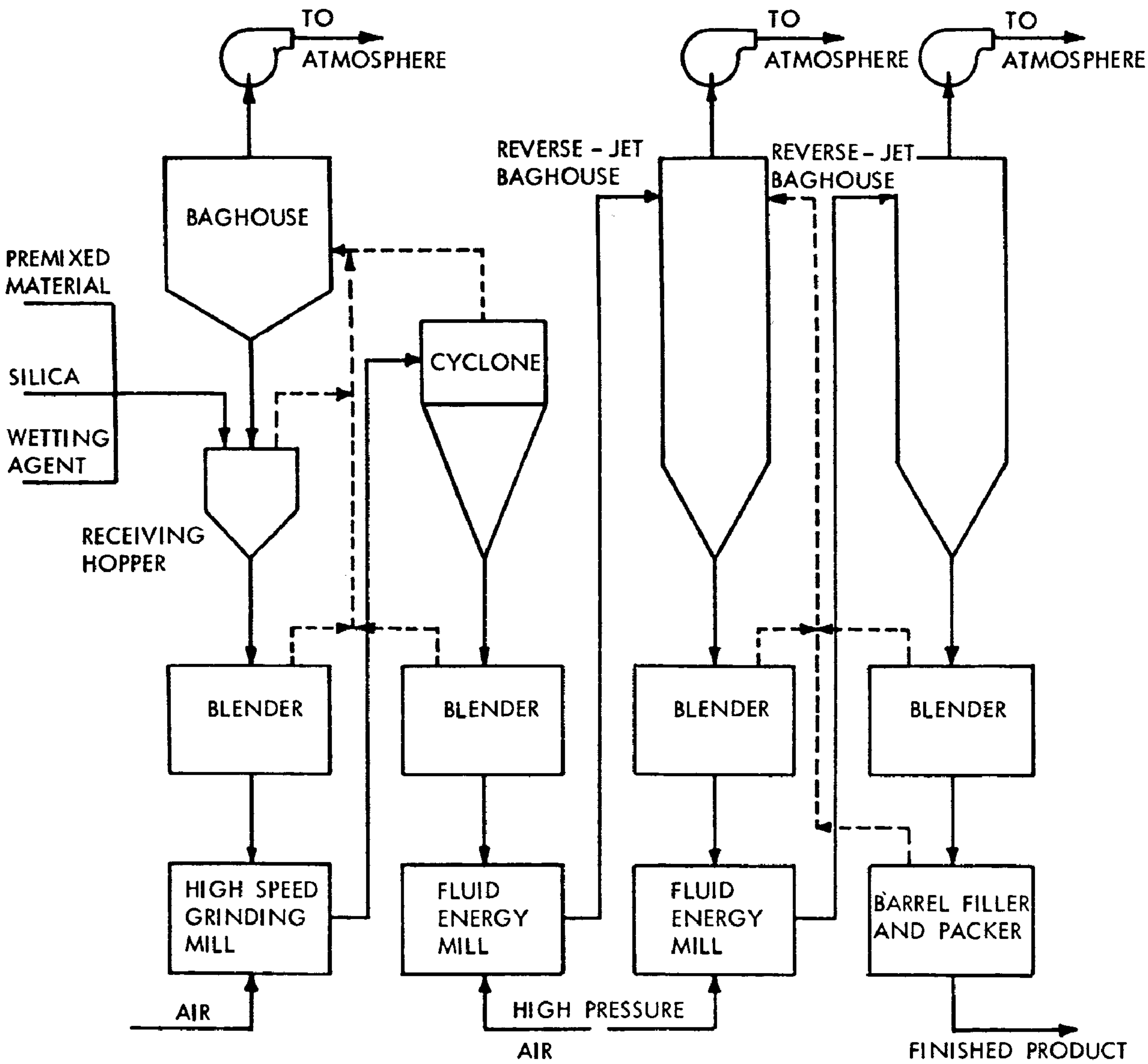


Figure 2 - Typical Sulfur Grinding Unit[20/]



a) Premix Grinding



b) Final Grinding and Blending

Figure 3 - Process for Formulating Dust[21/]

If the technical material is a liquid, it can be sprayed directly onto the granules. Solid technical material is usually melted or dissolved in a solvent in order to provide adequate dispersion on the granules. The last step in the formulation process, prior to intermediate storage before packaging, is screening to remove fines.

Packaging and Storage: The last operation conducted at the formulation plant is packaging the finished pesticide into a marketable container. This is usually done in conventional filling and packaging units. Frequent the same liquid filling line is used to fill products from several formulation units; the filling and packaging line is simply moved from one formulation unit to another. Packages of almost every size and type are used, including 1-, 2-, and 5-gal. cans, 30- and 55-gal. drums, glass bottles, bags, cartons, and plastic jugs.

On-site storage, as a general rule, is minimized. The storage facility is very often a building completely separate from the actual formulation and filling operation. In almost all cases, the storage area is at least located in a part of the building separate from the formulation units in order to avoid contamination and other problems. Technical material, except for bulk shipments, is usually stored in a special section of the product storage area.

A few formulators are able to ship formulated products in bulk containers to users in their immediate area. This technique, however, is limited to a few agricultural formulations.

Industry Structure

The formulation industry is such a dynamic one that detailed characterization of its organization and operation is difficult. The question, "Who formulates a given active ingredient, and in what quantity?", will have a different answer almost every year. Currently, there are about 3,400 companies who have Federal registrations for pesticide formulations. Those companies range in size from those who have one registered product, to those who have hundreds (see Figure 4). Almost three-quarters of the Federal registrants, however, have five or fewer registered products. Figure 5 shows the same type of distribution for State registrations, based on the data available (6 states). The State registration data also indicate a high concentration of registrants in the one-to-five registration range.

Characteristics that apply to all formulators of pesticides, however, can be discussed. These include ownership patterns, geographical distribution, and individual plant characteristics.

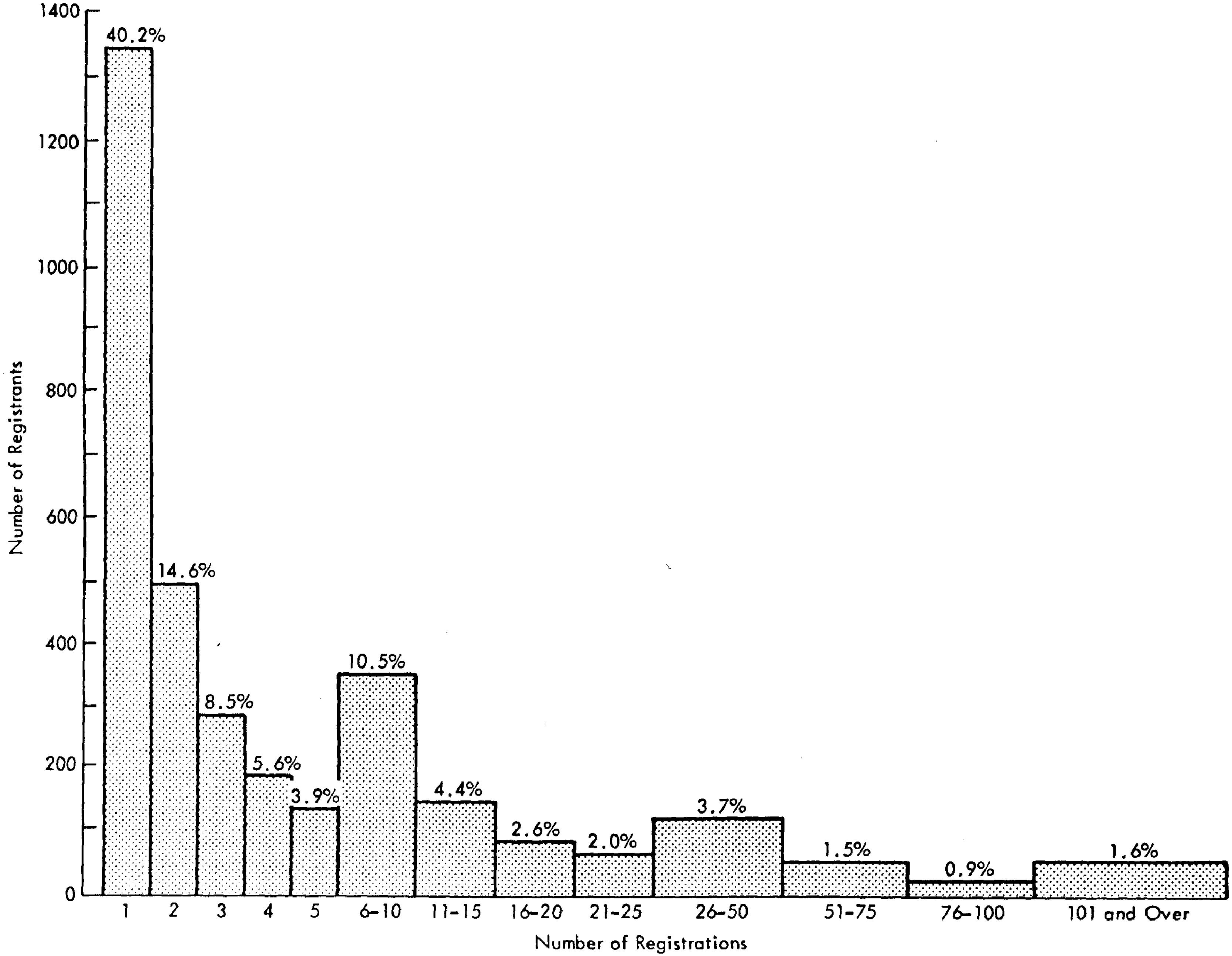


Figure 4 - Distribution of Registrants by Number of Federal Registrations

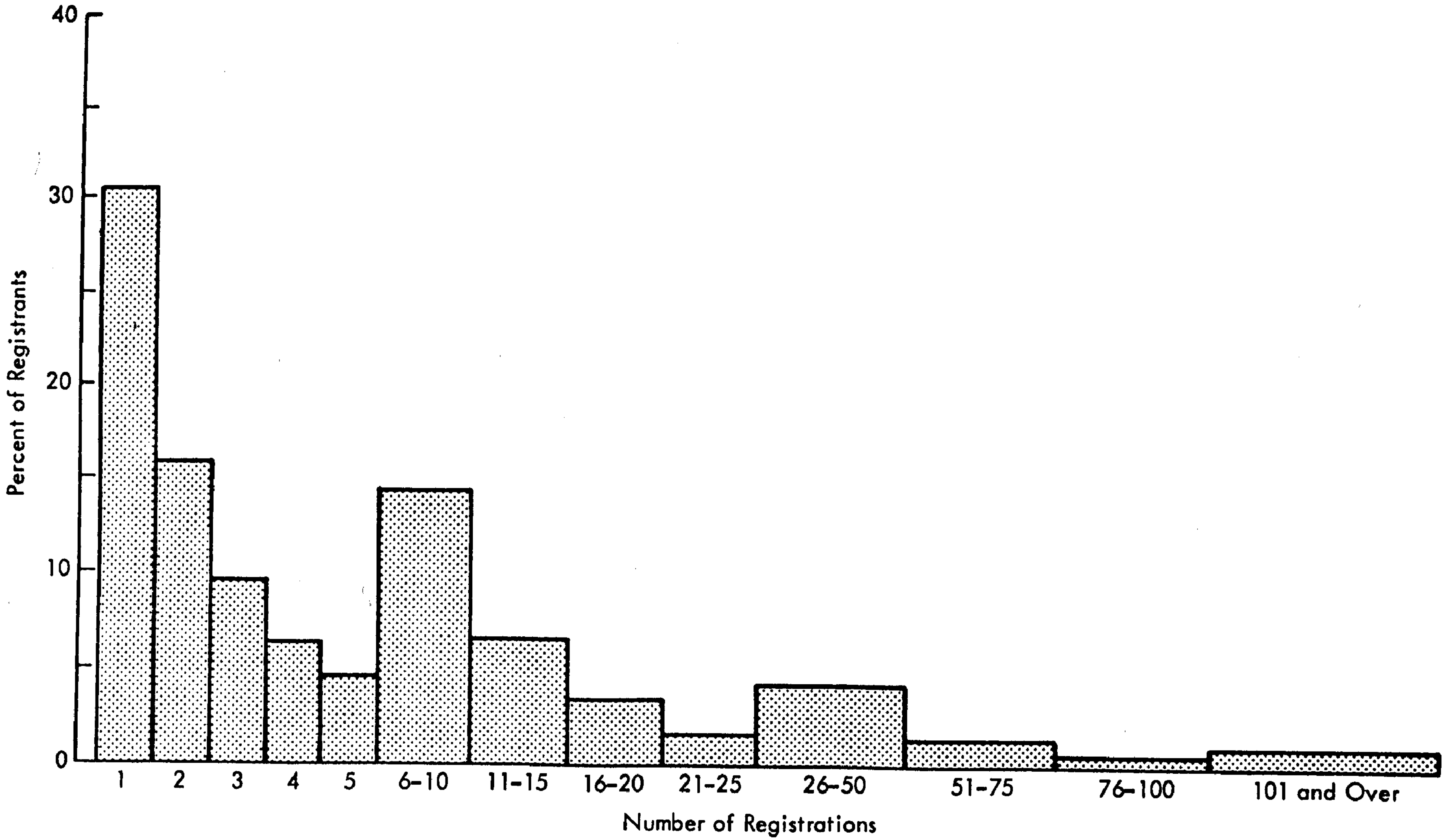


Figure 5 - Distribution of Registrants by Number of State Registrations

Ownership Patterns: Formulation plants can be categorized into three groups: the active ingredient producer-formulator, the independent formulator, and the small packager.

The producer-formulator is also referred to as an integrated producer. Such a company not only manufactures the pesticidal chemicals, but also formulates them in its own facilities. Frequently, formulating is done on the same plant site as the production of the active ingredient. Such formulation plants (i.e., satellite units of a production facility) have not been included in this study because they have access to waste treatment facilities and expert advice. Producer-formulator plants may also be located away from the production site of the active ingredient, e.g., close to or within the regions where the company's products are used. These plants may formulate the company's own products exclusively, or may formulate other products on a custom basis, and were included in this study, although they also usually have the expertise and help of the parent company to call on if needed.

The independent formulator produces products for sale under his own brand name and may also formulate products on a contractual arrangement. A number of the large pesticide manufacturers do not formulate any of their own products, and are, therefore, prime customers for the independent formulator. Under contractual agreement, the pesticide manufacturer furnishes the technology, active ingredient, and operational assistance to the formulator. The products are then sold under the basic manufacturer's labels. It is not uncommon for an independent formulator to have this type of contract with more than one basic manufacturer.

Most independent formulators also have pesticide formulations that they produce for sale under their own Federal or State labels. Examples of these operations are the farm cooperatives that formulate and sell pesticides. Products marketed under the formulator's own label can account for a small part of his production, or it can account for all of it.

In addition to contract formulation for basic active ingredient manufacturers, the independent formulator frequently has contracts with independent companies to formulate under their private labels. Most of the products sold with a department store's label, for example, are formulated under this type of contract.

The last major category of formulator is the small independent packager for whom pesticide formulations are only a small part of his business. These companies typically have one to five Federal or local registrations in their own name. Many of these small packagers actually formulate their labeled products in their own facility. A more practical arrangement for many, however, is to contract with one of the local independent formulators to do the actual formulating.

Geographical Distribution: The locations of large pesticide formulation plants identified during this study are shown in Figure 6. These plants were identified from information provided through the NACA as well as from two earlier studies of the formulation industry,[23,24] and do not include those formulation plants that are integral parts of pesticide manufacturing facilities.

A more complete picture of the formulation industry, however, can be gained by noting the numbers and locations of companies holding registrations for pesticides. Figures 7 and 8 show (a) the states in which corporations are headquartered who have Federal pesticide registrations, and (b) the number of Federal registrations, respectively. The significance of these data is limited because all companies and Federal registrations are shown in the state in which their headquarters are located. In many cases, and especially for the large companies, these locations are not sites of formulation plants. Smaller companies, however, constitute the bulk of the registrants (see Figures 4 and 5, pages 21 and 22), and their formulation facilities are often located on the same premises or in close proximity to their corporate offices.

Individual Formulation Plant Characteristics: Individual formulation plants are designed to meet the specific needs of the company and location. There is quite a range in the type of products formulated, the rates of production, and the age of the facilities in which they are manufactured.

The types of pesticides produced can be classified in two ways: by the chemical class of pesticide processed, or by the form of the product. Both measures are important when considering wastewater characteristics and volumes.

A recent study categorized 550 pesticidal chemicals into seven major categories, which were further divided into 42 subcategories.[13] (See Appendix C.) For the purpose of characterizing formulation plants, however, pesticidal chemicals can be classed as: inorganics, organophosphates, nitrogen-based, chlorinated hydrocarbons, and all others. Figure 9a illustrates the distribution of product mixtures found for 96 large formulation plants.

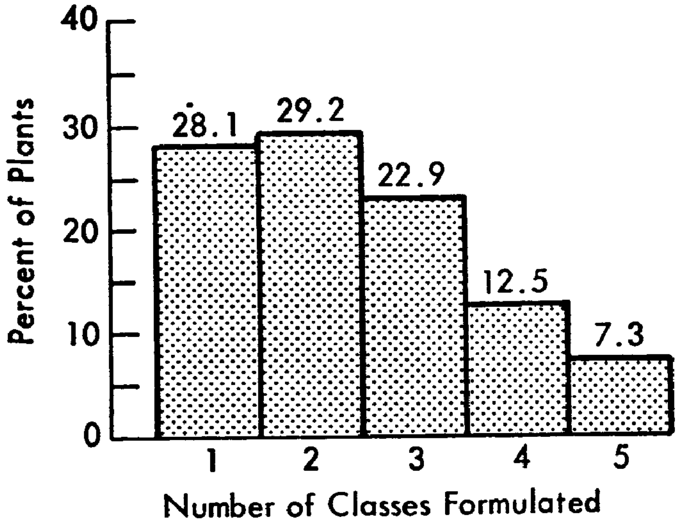
Pesticide formulations can also be classified as liquids, granules, dusts and powders, and all other forms. Figure 9b shows the distribution of 92 major formulation plants according to this classification.

The scale on which pesticides are produced covers quite a range. Undoubtedly, many of the small firms having only one product registration produce only a few hundred pounds of formulated pesticides each year. At least one plant has been identified that operates in the range of 100,000,000 lb of formulated product per year. The bulk of pesticide formulations, however, is apparently produced by independent formulators operating in the 20,000,000 to 40,000,000 lb per year range.

Figure 6 - Large Formulation Plant Locations

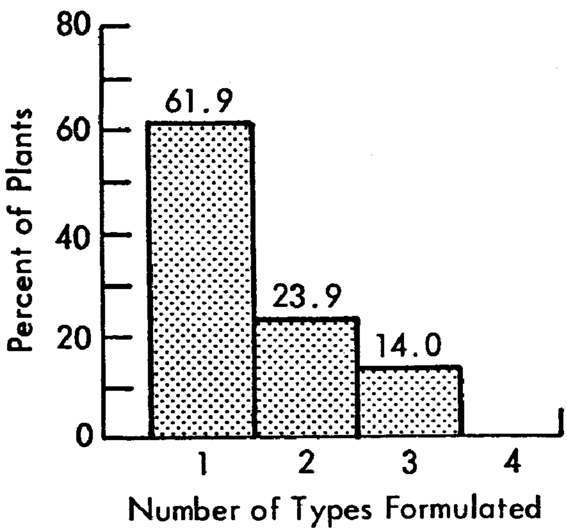
Figure 7 - Geographical Distribution of Companies Holding Federal Registrations

Figure 8 - Distribution of Federal Registrations by Company Location



Classes: Organophosphate, inorganic, chlorinated hydrocarbon, nitrogen based, and all others

a) Distribution by Chemical Class of Pesticde Formulated



Types: Liquids, powders and dusts, granules, and all others (strips, baits, etc)

b) Distribution by Type of Formulation

Figure 9 - Product Distribution for Large Formulation Plants

The ages of formulation plants identified during this study ranged from 1 to 53 years. Distribution according to age for 102 large formulation plants is shown in Figure 10.

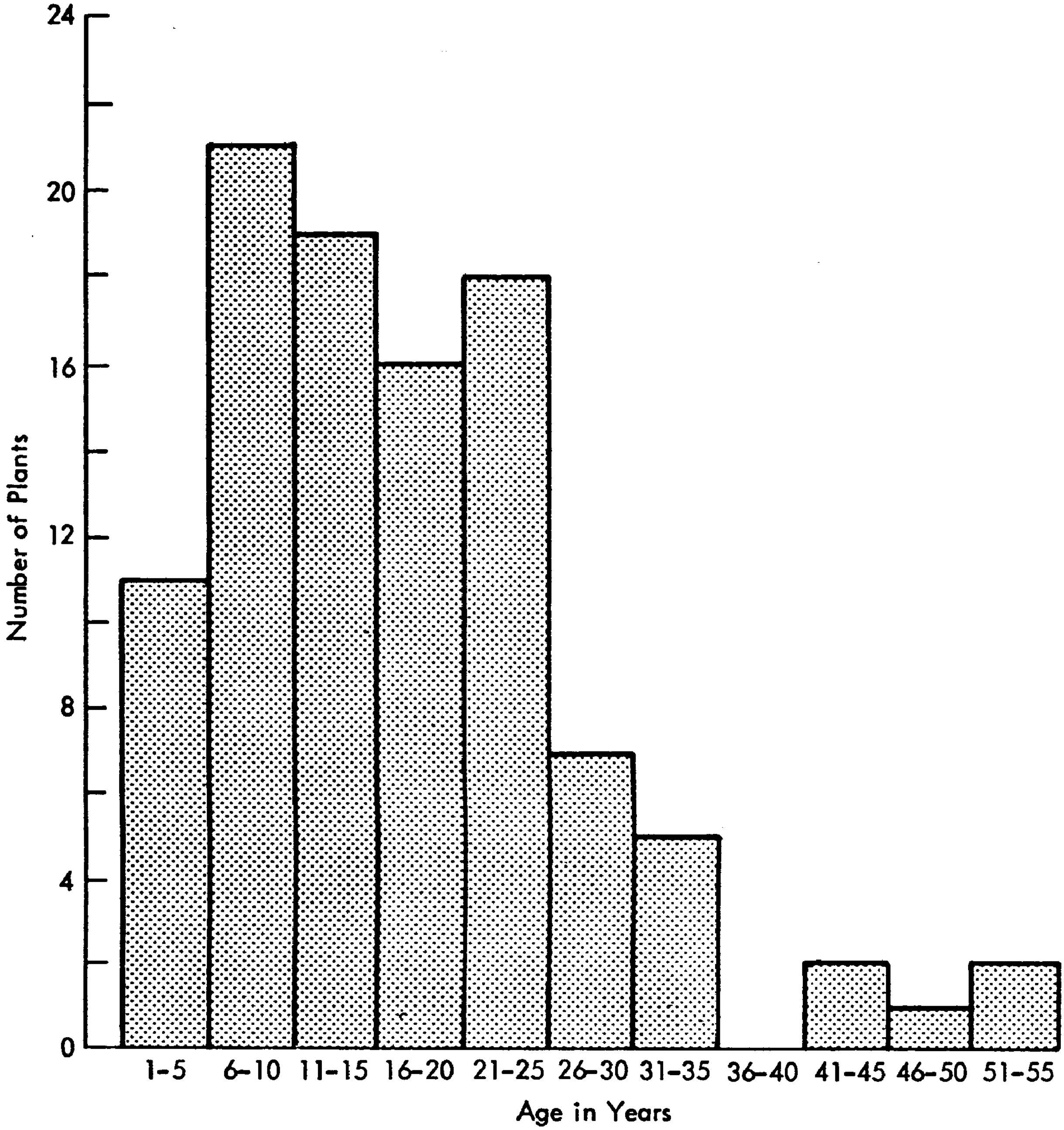


Figure 10 - Distribution of Plants by Age

SECTION V

WASTEWATER CHARACTERIZATION

The quantity and quality of wastewater generated by a formulation plant are determined by factors such as the type of formulations produced, the active ingredients used, the age and size of the facility, the plant's production schedule, and the company's operating philosophies and procedures. The ranges over which these factors can vary have already been discussed in Section IV. In this section, their effects on wastewater generation, as well as characteristics of the wastewater produced, are reviewed. The uses of water in a formulation plant, operating methods that control the volume of wastewater produced, and characteristics of process wastewater are discussed in the following subsections.

Water Uses and Wastewater Sources

Water is used for a number of purposes in a pesticide formulation plant. Some of these uses result in the generation of wastewater streams that contain various concentrations of pollutants. Other uses either generate no wastewater or yield an effluent that presents no significant pollution problem.

Cooling Water: Cooling water is required by several processes found in pesticide formulation plants. One of the most common uses is to cool air compressors used in conjunction with air mills that produce wettable powders. Cooling water is also required by many of the roller mills used for dust production.

Effluent from the cooling water loop is generally free from significant contamination, and, if kept separated from contaminated streams, can be discharged from the plant site via a conventional drainage system or into the sanitary waste.

Boiler Water: Steam is frequently used for space heating as well as in the actual formulation process. Blowdown water from the boiler system, as well as steam condensate that is not recycled, is generally free of toxicant contamination. These streams, if kept isolated, can also be disposed of with the other noncontaminated streams.

Steam is sometimes used to clean out formulation equipment. Condensate from such operations is not returned to the heating cycle, but is treated with equipment washdown water.

Formula Water: Some liquid formulations contain water as their base. Primarily herbicides are formulated in this manner. The formula water used in these formulations accounts for a major part of the water consumed by many formulation plants.

Sanitary Wastes: Sanitary wastes are generated at virtually all formulation plants. This category includes not only conventional sewage, but also the wastewater generated from shower facilities and washwater from work clothes processed on the plant site. Normally, this waste stream is treated as conventional sanitary waste, and discharged into municipal sewage treatment or septic tank systems.

At least one pesticide manufacturing-formulating plant, however, has removed lavatory effluent from the sanitary waste stream in order to ensure "zero discharge" of active ingredient.[25/]

Building Washdown: For housekeeping purposes, most formulators clean out the buildings housing formulation units on a routine basis, frequently once each year. Prior to washdown, as much dust, dirt, etc., as possible is swept and vacuumed up. The wastewater from the building washdown is normally contained within the building, and is disposed of in whatever manner is used for other contaminated wastewater.

Air Pollution Control Devices: Water scrubbing devices are often used to control emissions to the air. Most of these devices generate a wastewater stream that is potentially contaminated with pesticidal materials. One type of widely used air scrubber is the roto-clone separator. In this device, air is cleaned by the combined action of centrifugal force and mixing. Although the quantity of water in the system is high--about 20 gal. per 1,000 CFM--water consumption is kept low by a recycle-sludge removal system.[22/] Effluent from air pollution control equipment should be disposed of with other contaminated wastewater.

Drum Washing: A few formulation plants process used pesticide drums so that they can be sold to a drum reconditioner or reused by the formulator for appropriate products, or simply to decontaminate the drums before they are disposed of. Drum washing procedures range from a single rinse with a small volume of caustic solution or water, to complete decontamination and reconditioning processes. Wastewaters from drum washing operations are contained within the processing area and treated with other processing wastewater.

Control Laboratories: Most of the larger formulation plants have some type of control lab on the plant site. The control analyses performed range from determination of specific gravity only, to complete spectrophotometric analyses. Wastewater from the control laboratories, therefore, can range from an insignificantly small, slightly contaminated stream to a rather concentrated source of contamination. In many cases, this stream can be discharged into the sanitary waste stream. Larger, more highly contaminated streams must be treated along with other contaminated wastewater.

Formulation Equipment Cleanup: The major source of contaminated wastewater from pesticide formulation plants is equipment cleanup. Formulation lines, including filling equipment, must be cleaned out periodically to prevent cross contamination of one product with another. Infrequently, equipment must also be cleaned out so that needed maintenance may be performed.

Liquid formulation lines are cleaned out most frequently, and generally require the most water. All parts of the system that potentially contain pesticidal ingredients must be cleaned (see Figure 1, page 16). More than one rinsing of process vessels and lines is required to get the system clean. As a general rule, the smaller the capacity of the line, the more critical cleanup becomes in order to avoid cross contamination. Thus, larger volumes of washwater are required, relative to production quantity, for smaller units.

Granule as well as dust and powder lines also require cleanup. Liquid washouts are generally required, however, only in that portion of the units where liquids are normally present, i.e., the active ingredient pumping system, scales, and lines. The remainder of these production units can normally be cleaned out by "dry washing" with an inert material, such as clay.

Spills: Spills of technical material or material in process are normally absorbed on sand or clay, and are disposed of with other potentially toxic solid wastes. If the spill area is washed down, the resultant wastewater should be disposed of with the other contaminated wastewaters.

Runoff: Natural runoff, if not properly handled, can become a major factor in the operation of wastewater systems simply because of hydraulic loading. Isolation of runoff from any contaminated process areas or wastewaters, however, eliminates its potential for becoming significantly contaminated with pesticides. Uncontaminated runoff can be allowed to drain naturally from the plant site.

In some plants, formulation units, filling lines, and storage areas are located in the open. The runoff from these potentially contaminated areas, as a rule, cannot be assumed to be free of pollutants and should not be allowed to discharge directly from the plant site.

Catastrophic Events: In addition to routine generation of wastewater, there exists the possibility of polluted water resulting from a catastrophic event, including fires, floods, and major spills. Diking of the formulation plant is the most common method for minimizing pollution from such a source. Segregation of materials in storage as well as preventive cooperation with local fire, police, and health departments also help to isolate the polluted area and prevent unnecessary dispersion.

Operating Methods Affecting Wastewater Volume: There are a number of techniques, if made a part of the routine operation of a formulation plant, that can help minimize the volume of process wastewater, i.e., water potentially contaminated with significant quantities of pollutants. In most cases the degree to which these are applied are more a factor in determining the wastewater volume than scale of production. The following discussion lists minimization techniques that are applicable to most plants.

Segregation: Many effluent streams have little potential for containing pollutants, including cooling water, boiler water, and most sanitary wastes. These "clean" streams should be kept isolated from contaminated areas and streams so that they can be discharged directly from the plant site.

Scheduling: Production runs should be scheduled wherever possible so that the number of equipment cleanups is minimized. Production of liquid formulations containing active ingredients A, B, and C, for example, would be sequenced so that those containing only A would be produced first; then those containing A and B; and finally those containing A, B, and C. Such a sequence would require no cleanups between runs to avoid contamination. Use of this technique, however, is limited because of the frequency with which formulation plant production schedules are revised.

Water Conservation: When water washing is required, a minimum volume of water must be used. Although this seems a trite statement, it is one of the best ways to reduce the volume of wastewater. Water conservation techniques include the use of specified volumes of water, rinsing out rather than filling and flushing, and use of timers on water lines.

Solvent Washouts: Organic solvents can often be used rather than water to clean up a formulation unit. The solvent used for cleanup can be saved, and stored in drums until the next time the previously formulated ingredient is produced. The retained solvent can then be used as part of the production batch. This technique not only eliminates the generation of washwater, but it also can save small quantities of product that otherwise would be lost. Application of this method is limited, however, by a lack of storage space as well as the production of "one time only" formulations.

Sumps: Sumps can be installed in new plants to collect and contain contaminated wastewater or spills. When used in conjunction with curbing around formulation units, sumps minimize area cleanup and washwater requirements.

Dry Cleaning: The major portion of granule, dust, and powder formulation units can be sufficiently cleaned out by processing an appropriate inert carrier through the system. The inert carrier can be retained for use in the next similar batch, or can be discharged with other potentially toxic solid wastes. In either case, the dry wash technique can reduce the water required to clean out solid formulation units.

Product Separation: Companies having more than one formulation plant or those producing a limited number of active ingredients can reduce their wastewater volumes by two techniques.

The first involves the consolidation of product formulation. A number of firms have found that they can competitively produce all of a given product at one or two locations, thereby simplifying their overall operations, and reducing the number of cleanouts required. This approach, however, is not only limited to the few companies who have multiple site operations, but also has the economic disadvantage of increased transportation costs.

Some plants have been able to dedicate certain formulation lines to the production of specific active ingredients or formulations, and have thereby reduced clean-out requirements. Application of this technique, however, is also rather limited.

Wastewater Characteristics

Comprehensive data on the volume and quality of wastewater from pesticide formulation plants are virtually nonexistent. This is due in part to the fact that many of the formulation facilities operated by active-ingredient manufacturers are actually part of the pesticide manufacturing complex, and effluents from the formulation section of these plants have not been isolated and characterized. Another factor is that effluent analysis has not been heretofore required for many other formulation plants. A large part of this industry did not come under the provisions of the permit program implemented under the River and Harbor Act of 1899 (33 USC 407), and most formulation plants have simply never analyzed their wastewater.

Some generalizations on formulation plant wastewater can be made based on the data obtained from visits to key formulation plants, as well as limited data from regulatory agencies. The absence of complete sets of data (wastewater quality and quantity, as well as production quantities and characteristics), however, precludes the extrapolation of these generalizations into quantitative values, such as pounds of pollutant per unit of product.

Process Wastewater Quantity: The quantity of process wastewater, i.e., water containing pesticidal materials as a result of the plant's operation, is influenced by many factors, as outlined in the preceding sections. From the available data, relative volumes of wastewater produced cannot be directly correlated with any one of these factors. Higher quantities, however, are more frequently associated with plants that do not segregate runoff from process wastewater.

There is apparently a wide range in the volume of wastewater generated. The key formulation plants studied (see Appendix A) generated from less than 1 to more than 25 gal. of wastewater per ton of formulated product. Volumes of wastewater near the top of this range were generated by plants that isolate the runoff as well as those who did not.

Process Wastewater Quality: A limited amount of quantitative data on formulation plant effluents was obtained during the course of this study.

Data were obtained, for example, on a synthesized sample that had been prepared in order to evaluate its waste treatment requirements. Analysis of the samples showed:

pH	5.7
Total Organic Carbon	420 mg/liter
Suspended Solids	70 mg/liter
Conductance	290 μmho/cm
Toxicant Concentration	Not determined

One analysis made of the effluent from a formulation plant showed:

COD	483 mg/liter
Suspended Solids	661 mg/liter
Total Dissolved Solids	631 mg/liter
Arsenic	37 mg/liter
Flow Rate	~ 26 gpm
Toxicant Concentration	Not determined

Analyses of effluent from another formulation plant, performed by a regional EPA office, showed:

pH	Not determined
Total Organic Carbon	Not determined
Suspended Solids	Not determined
Total Dissolved Solids	Not determined
Flow Rate	Not determined
2,4-D	28.5 to 1,190 mg/liter
2,4,5-T	3.91 to 162 mg/liter
Malathion	2.06 mg/liter
Methoxychlor	0.13 mg/liter

Two indexes against which formulation effluent can be measured are shown in Tables 4 and 5. The first of these is a classification system for ranking industrial wastewater. On this scale of low, average, and high, process wastewater for this industry probably would be classified as follows:

BOD_5	Average to high
COD	Average to high
Suspended Solids	Low
Total Dissolved Solids	Low
pH	Low to average

TABLE 4

CLASSIFICATION OF INDUSTRIAL WASTEWATER CHARACTERISTICS[26]

	Classification		
Parameter	Low	Average	High
BOD_5, mg/liter	<200	200-300	>300
COD, mg/liter	<300	300-400	>450
Suspended Solids, mg/liter	<200	200-300	>300
Total Dissolved Solids, mg/liter	<500	500-600	>600
Ammonia, mg/liter	< 15	15-25	> 25
Total Phosphorus, mg/liter	< 8	8-12	> 12
Temperature, °C	< 15	15-25	> 25
pH	< 6	6-8	> 8

TABLE 5

GUIDELINES FOR PESTICIDE CONTENT OF WATER

Pesticides	New Drinking Water Guideline[27/] (mg/liter)	Proposed Criteria for Water Quality[28/] (μg/liter)	Proposed Toxic Pollutant Effluent Standards[29/] (μg/liter)
Aldrin	0.001	0.01	0.5[b/]
Chlordane	0.003	0.04	-
DDT	0.05	0.002	0.2
Dieldrin	0.001	0.005	-[b/]
Endrin	0.0005	0.002	0.2
Heptachlor	0.0001	0.01	-
Heptachlor Epoxide	0.0001	-	-
Lindane	0.005	0.02	-
Methoxychlor	1.0	0.005	-
Toxaphene	0.005	0.01	1.0
2,4-D	0.02	-	-
2,4,5-TP (Silvex)	0.03	-	-
2,4,5-T	0.002	-	-
Organophosphate and Carbamate Insecticides	0.1[a/]	-	-

a/ Expressed in terms of parathion-equivalent cholinesterase inhibition.

b/ Effluent standard for aldrin and dieldrin combined.

Ammonia concentration, phosphorus concentration and temperature can be expected to range from high to low, depending on the individual plant.

As a baseline for comparison, proposed guidelines for pesticides in various waters are shown in Table 5. Pesticide concentration in formulation wastewater reportedly ranges from < 10 to over 1,000 ppm. Most frequently, however, toxicant concentrations range from 10 to 200 ppm.

The data above are not indicative of unusual operating conditions, e.g., spills. Wastewater generated during periods of unusual operation can be expected to rank "high" on all pollutant parameters.

SECTION VI

CURRENT WASTEWATER TREATMENT PRACTICES

The treatment techniques currently being used for formulation plant wastewater can be grouped into several general categories: evaporation, sewer system, landfill, contract disposal, activated carbon adsorption, incineration, and miscellaneous pretreatment processes. The following discussions of these techniques are arranged according to their decreasing frequency of use by large formulation plants (see Figure 6, page 25).

Evaporation

Evaporation is the wastewater treatment technique most frequently employed. Evaporative systems range from those that just concentrate wastes by partial wastewater evaporation, to processes that evaporate all wastewater produced.

Evaporative systems can be used in most parts of the country (see Figure 11), depending primarily on the characteristics of the individual plant's operation. Systems range in size from 2,000 to over 1,000,000 gal. of wastewater evaporation per year.

Designs of the systems vary with the plant (see Case Studies Nos. 1, 2, and 8 in Appendix A). General considerations in all designs, however, revolve around the need to maintain an adequate evaporation rate.

A pretreatment step is sometimes required to break emulsions. This is usually done by batch-wise addition of a deemulsifying agent followed by gravity separation of the organic layer. This layer is usually disposed of by incineration, or in the case of spray oil formulation, by use as road oil.

After pretreatment, the wastewater is pumped into an evaporation pond where it is allowed to evaporate. These range from shallow, concrete pads to large (1 acre or more) man-made earthen ponds. When earthen ponds are used, they are preferably sealed with bentonite, plastic, or other lining materials to prevent percolation into the soil.

The natural rate of evaporation is normally not adequate to accommodate all process wastewater in a pond of reasonable size. In addition, as can be seen from Figures 12 and 13, few parts of the country have net annual evaporation of rain water. For these reasons, almost all wastewater evaporation systems employ additional techniques to obtain adequate evaporation.

Roofs: Many of the small evaporation ponds (up to 50 ft x 50 ft) use roofs to keep out rain water. Permanent roofs, even those made of "transparent" plastic materials, however, reduce the rate of natural evaporation.

Figure 11 - Formulation Plants Using Evaporative Treatment Systems

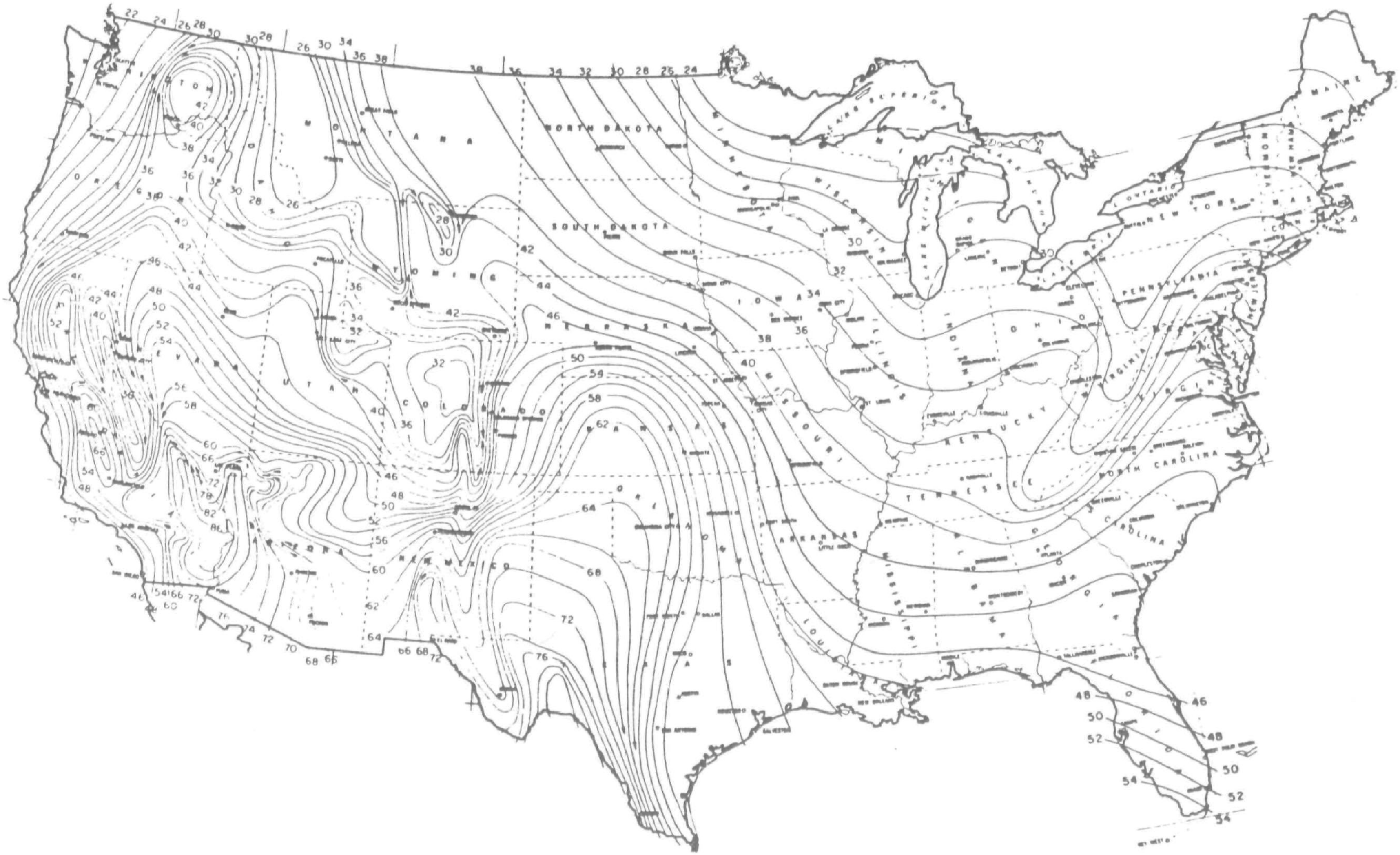


Figure 12 - Mean Annual Inches of Lake Evaporation30/

Figure 13 - Mean Annual Inches of Precipitation[31]

Awning-type coverings, that can be moved when not needed, overcome this deficiency, but obviously add to installation and operation costs.

Aeration Systems: To aid natural evaporation, aeration systems are frequently used. These are normally simple, low cost pumping systems used to spray the wastewater into the air. A number of variations are possible, including the use of burlap strips, waterfalls, etc., to increase the effective evaporative area. Aeration has the added advantage of oxygenating the water and thereby accelerating the decomposition of many pesticide chemicals.

Supplemental Heat: Supplemental heating also is used to aid the evaporation rate. Most frequently, this is done by the addition of conventional electrical or gas powered immersion heat exchangers to the evaporation pond. Supplemental heat is normally required for only a few months each production season.

Limitations: One of the major limitations of this system is the uncertainty of air pollution problems that may be created. This problem is discussed in more detail in Section VIII (page 55) of this report.

Sewer Systems

Many smaller and a few large formulation plants discharge into local municipal or industrial sewer systems. Pretreatment techniques used by the formulation plant in conjunction with these systems are minimal (see Miscellaneous Pretreatment Processes, page 47). The pH of the effluent is normally adjusted to neutrality or to that of the local groundwater. Effluents from a few plants are filtered before discharge. Limitations are established by local authorities on the concentration as well as the daily quantity of toxicants that can be discharged. Some municipal sewer systems, however, have not established criteria on the toxicant (pesticide) content of wastewater that can be discharged to their treatment systems.

The limitations of many existing treatment plants, with regard to their ability to remove pesticides from water, are well documented.[32-35] For these reasons, it is critically important that capabilities of the individual treatment system be determined before discharge of formulation wastewaters into the system is considered.

Landfills

Small formulation plants as well as larger plants producing small volumes of wastewater (< 10,000 gal/year) are frequently able to dispose of their wastewater in landfills. The landfill facilities in use include cut-and-fill operations located on the plant site, as well as a wide range of municipally and industrially operated sites.

The actual disposal procedures used at the landfill also are quite varied. Most frequently, the small volumes of wastewater are sealed in used 55-gal. drums. The wastewater drums are then treated like any other item of solid waste. Another practice in use, however, is to convey the wastewater to the landfill site in a bulk container, and spray it on the fill area.

Sites in which formulation wastewaters are disposed of normally have not estal lished criteria on the quality of the wastewater allowed and do not maintain records of the quantity or location of wastewater in the fill.

Almost all of the landfill sites apparently operate under some type of permit, either local or state. Very few, if any, of these sites, however, qualify as "specially designed landfill" operations that have been defined for use in pesticide waste disposal.[36] (See "Special Landfill" in Appendix B, page 111.)

Contract Disposal

The next most frequently practiced method for disposing of process wastewater is the use of a contract disposal service. The availability of this service in the immediate area, as well as the cost involved, are major factors in its selection. Care must be taken, however, to ensure that the wastewater is properly processed by the contractor. (See "Contract Services' in Appendix B, page 118.)

Activated Carbon Adsorption

The effectiveness of activated carbon in removing low concentrations of many pesticides in water has been well documented.[33,35,37] A limited number of formulation plants are attempting to apply activated carbon adsorption technology to treatment of their effluent streams. (See Case Studies Nos. 7, 9, and 10 in Appendix A.)

Most of the plants using carbon, however, apparently are doing so only on an experimental basis. None of the plants identified during this study are considered by the operating firms to be in full-scale operation; rather, they are in various stages of development.

Incineration

Incineration in appropriate facilities is the method of choice for disposal of all pesticides except for organometallics and inorganic compounds.[36] Adequate facilities, however, are generally not available to the independent and contract pesticide formulators. In fact, the only formulation plants identified as using incineration to dispose of their process wastewaters were those in chemical manufacturing complexes. Incinerators are used, however, by some contract waste disposal services.

Miscellaneous Pretreatment Processes

A small number of plants are using an assortment of miscellaneous unit operations to treat their wastewater. None of these, however, can be considered a complete treatment process; rather, they are pretreatment processes used to treat wastewater before it is discharged.

Conventional pretreatment processes as well as the protective functions that they serve are shown in Table 6.[26/] Only four of these are practiced to any significant degree by the pesticide formulation industry.

Neutralization: Many plants treat their wastewater with caustic before it is discharged. This is done primarily to produce a neutral effluent, or because it is thought that this will help detoxify the pesticidal chemicals. The frequently used generalization that alkaline conditions reduce the toxicity of pesticidal chemicals by hydrolysis, however, is not universally true.[38/] The formulator should determine the desirability of high alkalinity based on the active ingredients being formulated before adopting this practice.

Chemical Precipitation: Many inorganics can be removed from wastewater by precipitation. One plant that formulates primarily mercurial pesticides, for example, uses sodium hydroxide to precipitate the mercury, which is then filtered and recovered for reprocessing.[13/] Use of chemical precipitation processes, however, is not commonly practiced.

Solids Separation: Some plants filter their wastewater before discharge. When used in conjunction with precipitation or flocculation, this process apparently can effect some reduction of pesticide content of the wastewater. Filtration alone, however, is not considered to be a complete treatment process.

Equalization: Equalization, i.e., elimination of wide variations in wastewater quantity and quality before discharge, is practiced by some plants. As this is essentially a retention and dilution system, it does not effect a significant reduction in the total quantity of toxic pollutants that is eventually discharged. It can, however, prevent short discharges of highly toxic wastes which might cause a fish-kill or environmental damage.

TABLE 6

PRETREATMENT PROCESSES AND THEIR PROTECTIVE FUNCTIONS[26]

Pretreatment Process	Protective Function: Collection System	Pumping Equipment	Treatment Plant and Operating Personnel
Screening	X	X	
Grit Removal	X	X	
Neutralization	X	X	X
Oil Separation	X	X	X
Equalization	X	X	X
Cooling			X
Solids Separation			X
Chemical Precipitation			X
Foam Control	X	X	X
Spill Protection	X	X	X

SECTION VII

BEST TREATMENT TECHNOLOGIES

The establishment of "best practicable" and "best available" technologies for the treatment of various industrial wastewaters is required by the Federal Water Pollution Control Act of 1972.[2]

By 1 July 1977, industries are expected to meet effluent limits that reflect the use of best practicable control technology. This technology is to be based on end-of-the-line treatment techniques rather than on modification or cleaning up of the production process itself. Parameters to be considered in the definition of what is best practicable are the age of the facilities involved, the engineering effort required to apply various types of control technology, and the cost of effecting reductions in pollutant discharge.

By 1 July 1983, industries are to meet effluent limits that reflect the use of best available control technology. As a national goal, by 1985, industries must completely eliminate the discharge of pollutants wherever this is technologically and economically achievable.[2,3]

Best available technology includes in-process control technology as well as processes for treating wastewater. These guidelines will be applied to all plants within an industry category.

As a part of this study, we have attempted to define best treatment technologies for pesticide formulation plants. As has been done throughout this study, formulation plants that are an integral part of a chemical manufacturing facility have not been included.

Cost estimates also have been made in order to establish the order of magnitude of the economic impact that would result from application of these systems to the formulation industry. Conservative (optimistic), yet realistic cost data as well as readily available, off-the-shelf items of equipment have been used in developing these estimates so that costs for the minimum adequate system could be evaluated. These same procedures, built to the more exacting specifications used by many of the larger producer formulators, could cost 10 times our conservative estimates.

Best Practicable Technology

The best practicable wastewater treatment technology, based on the treatment practices in use within the industry, appears to be evaporative systems with no discharge of water for most plants in the industry. For plants not able to effect complete evaporation of their process wastewater, partial evaporation used in conjunction with disposal in an approved landfill and in accordance with EPA guidelines appears to be the best alternative. (See Appendix B, "Burial," page 110.)

The operational and design characteristics of evaporative systems have been discussed in Section VI of this report (see "Evaporation," page 41). Obviously, each system would have to be tailored to the needs of the individual plant site.

A preliminary design of an evaporative system is shown in Figure 14. A surge tank would be required to accumulate wastewater for batch-wise de-emulsification, if required. Wastewater would then be pumped into an evaporation pond that was fitted with such ancillary equipment as required to obtain the needed rate of evaporation.

Preliminary process designs show that a system capable of treating the effluent from a large formulation plant (one producing 40,000,000 lb/year of formulated product and generating 500,000 gal. of process wastewater) can probably be constructed for less than $10,000 (exclusive of land value) and operated at a cost less than 1¢/gal. (See Appendix D, Cost Estimate No. 1, and Appendix A, Case Studies Nos. 1, 2, and 8.)

An integral part of this system is the minimization of process wastewater. Operating methods that reduce the volume of wastewater must be used to the fullest extent possible. (See Operating Methods Affecting Wastewater Volume, page 34.)

The major uncertainty in the use of evaporative systems is the air pollution that may be created. The extent or seriousness of the air pollution caused by the evaporation of pesticides from the wastewater has not been established. Recent study has shown, however, that the transfer of contaminants (e.g., pesticides) from water to air by evaporation may be occurring much faster than has been generally realized.[39/] When aqueous solutions of DDT were evaporated, for example, it was shown that 97% of the DDT initially present (dissolved) had evaporated when only 5.2% of the water had been evaporated. In addition, the losses of pesticides by other water-to-air transfer mechanisms are quite possible.

Best Available Technology

The best wastewater treatment technology available appears to be a process including pretreatment (neutralization, precipitation, and/or deemulsification), filtration, and adsorption on activated carbon and/or resin.

Processes that included these basic concepts have been applied to a number of industrial effluents.[40-42/] Adsorption techniques also have been found to be highly effective in removing toxic chemicals, e.g., pesticides, from various wastewaters.[43,44/]

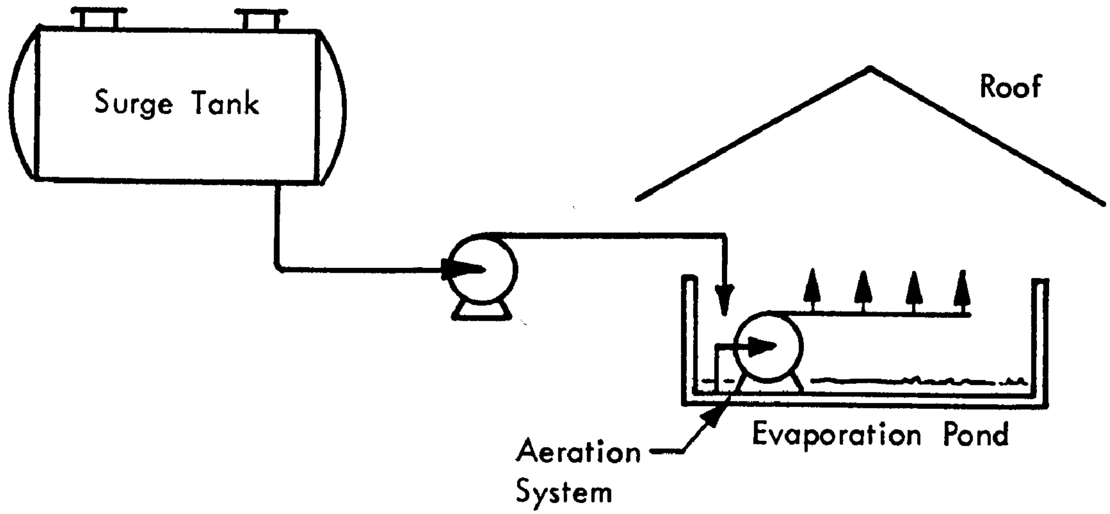


Figure 14 - Evaporative Wastewater Treatment

One of the large pesticide formulation plants in the United States is currently experimenting with a pilot plant using essentially this process. (See Appendix A, Case Study No. 7.)

The plant has been able to routinely produce an effluent containing less than 0.1 ppm total toxicants (pesticides).

Figure 15 shows the potential flow diagram for such a system based on the results of one pilot plant's operation and standard carbon adsorption design parameters.[45] A preliminary cost estimate has been made in order to estimate the capital and operating cost of such a system. (See Appendix D, Cost Estimate No. 2.) The preliminary data indicate that process wastewater from a plant producing 40,000,000 lb of formulated product/year can probably be treated for a cost of about 2¢/gal. Capital costs for the minimal system are estimated to be in the order of $20,000 (exclusive of land value).

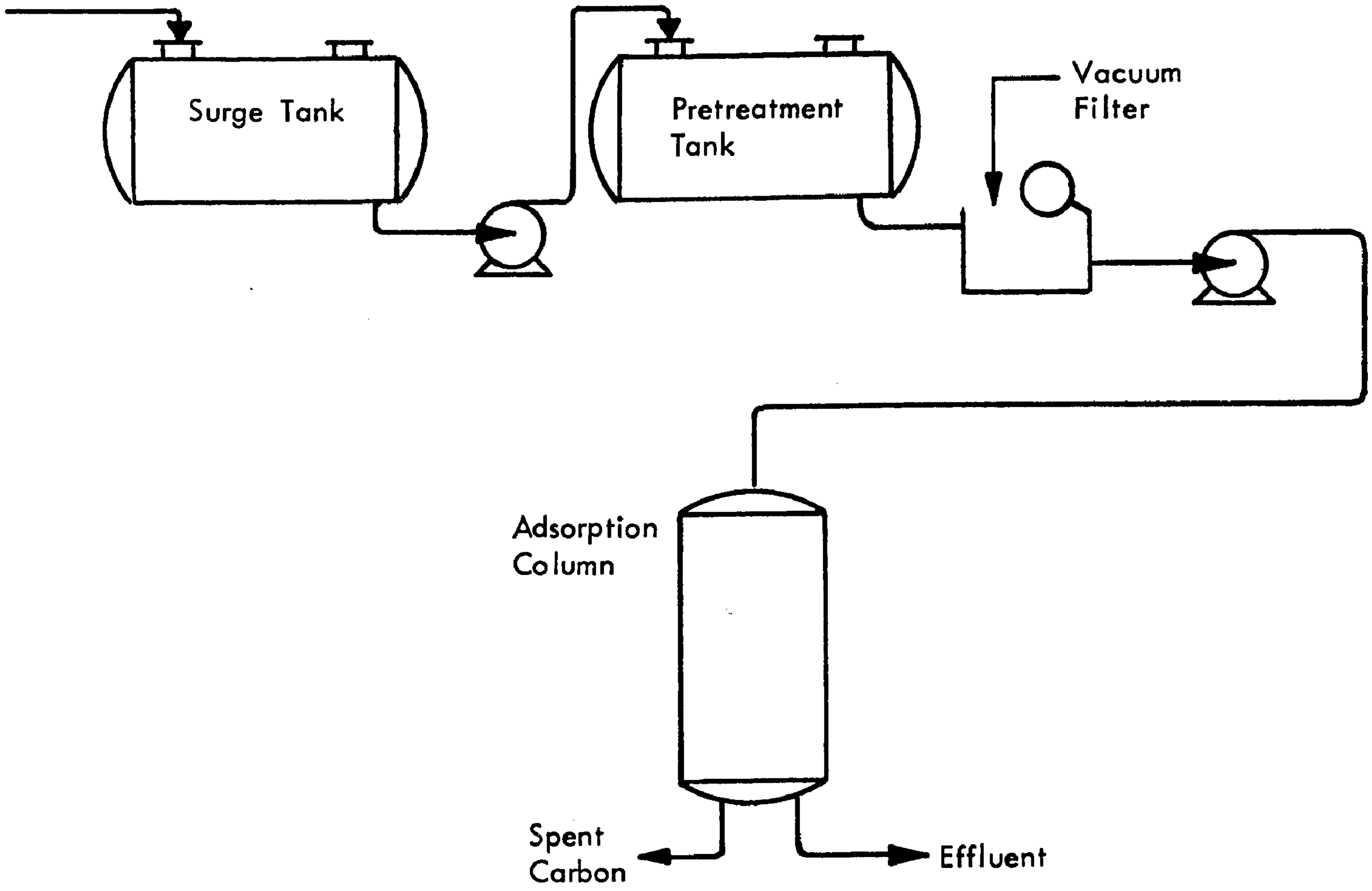


Figure 15 - Pretreatment-Filtration-Adsorption Systems

SECTION VIII

RESEARCH AND DEVELOPMENT NEEDS

A significant amount of research and development work is needed to characterize formulation wastewater from pesticide formulation facilities, and to evaluate methods for its treatment. For example, not one complete set of data (quantitative and qualitative information on both production and wastewater) was found during the course of this study.

There are at least four problem areas which will have to be evaluated before "closed loop" wastewater systems or the complete elimination of pollutant discharge can be effected. These areas of research are discussed in the following subsections in the sequence in which they should be undertaken.

Wastewater Characterization

The first area requiring additional work is the characterization of wastewater produced from formulation plants. This would include both quanitative and qualitative determinations. The sources and the properties of contaminated wastewater must be determined. Wastewater must be characterized not only in terms of conventional quality parameters (temperature, pH, BOD, COD, total organic carbon, suspended solids, etc.), but also in terms of the concentration of toxicant chemicals present.

The formulation industry is a seasonal operation, with a wide range of types and sizes of facilities. Representative formulation plants, therefore, must be monitored for a complete production season in order to develop accurate wastewater data.

Evaporative Wastewater Treatment Systems

Evaporative systems are widely used to process formulation wastewater, and have been identified in this report as the best practicable control technology currently available.

One of the uncertainties involved in the application of evaporative processes to wastewaters containing pesticide, however, is the potential air pollution problem. The evaporative loss of pesticides when spread over large crop areas has been an acknowledged problem for a number of years and has been the subject of a number of studies.[45] A recent research study, however, as discussed in the preceding section on Best Practicable Technology (page 49), has shown that the transfer of contaminants, e.g., pesticides, from water to air environments may occur much faster than has been generally realized.

A research study is needed to quantify the air pollution resulting from the use of evaporative systems to process pesticide formulation wastewater. This study would also require monitoring of representative sites for a complete production cycle.

Pretreatment-Filtration-Adsorption System

The system of pretreatment (neutralization, precipitation, and/or deemulsification), filtration and adsorption (activated carbon and/or resin) of formulation wastewater has not been completely demonstrated. Operating and design criteria as well as the system's economic viability must be determined before this system can be defined as the best available technology for treatment of formulation wastewater.

In order to make an evaluation, the operation of a representative pilot plant system would have to be monitored for at least one complete production season.

Detoxification Processes

The ultimate process for treatment of toxicant-containing wastewater is a detoxification system. The waste treatment systems currently being used to process wastewater from active ingredient manufacturing sites are well documented.[46/] Many of these are chemical and biological detoxification processes that have potential application to formulation plant wastewater.

A study of the applicability of the treatment technologies should be conducted concurrently with the three research studies outlined above.

SECTION IX

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APPENDIX A

FORMULATION PLANT CASE STUDIES

Site visits were made to several pesticide formulation plants throughout the United States. The following 10 case studies are presented as an appendix to this report in order to document the quantity and quality of data made available to the project team, as well as to illustrate, as specifically as possible, the operational characteristics of pesticide formulation plants. The range of detail in which these case studies are reported is indicative of the extent to which corporate philosophies differ over what data are confidential.

CASE STUDIES

Case No.	Location	Production Rate	Wastewater Treatment Technique	Page No.
1	Gulf Coast	35 to 50 million lb/yr	Total evaporation	65
2	Pacific West	Large	Total evaporation	68
3	Midwest	40 million lb/year	Contract disposal	71
4	East North-Central	Small	Landfill	75
5	Midwest	Medium	Land spreading	78
6	Midwest	5 million gal/yr	Contract disposal	79
7	West North Central	40 million lb/yr	Pretreatment/ Filtration/ Adsorption	80
8	Middle Atlantic	Small	Total evaporation	83
9	West South	Large	Adsorption	86
10	South	3 million gal/yr	Adsorption	88

CASE STUDY NO. 1

General Information

This formulation plant is one of about a dozen that are owned and operated by a major manufacturer of pesticidal chemicals. The plant, the original part of which is about 20 years old, is located on a 15-acre site near the Gulf Coast.

Production ranges from 35,000,000 to 50,000,000 lb of formulated product per year. A large portion of this production (~ 20,000,000 lb) is sulfur powder. Liquid and granular formulations containing ~ 3,500,000 lb of active ingredients are produced. The thiocarbamates make up ~ 75% of the liquids. No parathion is formulated, and none of the formulations produced are water-based.

At one time, drums were cleaned at this plant site before being sold for reconditioning and reuse. This operation, however, has been discontinued.

Quality control samples are analyzed on-site.

Process Information

The formulation equipment at this plant is typical of that used in the industry. A Raymond mill is used to grind sulfur; this operation requires a small volume of cooling water (~ 1 gpm). The grinding unit is located within a building.

Liquids are formulated in four batch units ranging in sizes from 3,000 to 20,000 gal. Typically, batch sizes are in the 3,000 to 15,000 gal. range. The four liquid units are located outside on concrete pads. Filling and packaging equipment is moved from unit to unit as needed. This liquid system is only 3 or 4 years old.

Organic solvents are used to wash out process equipment between production runs. The solvent is redrummed, and stored until it can be used in the next appropriate production run.

Wastewater Characteristics

The use of organic solvents for equipment washout virtually eliminates one of the most common sources of wastewater. The small volume of process wastewater (estimated to be 2,000 gal. per year) that is produced by washdowns, etc., flows into a retention pond whose level is maintained by evaporation.

Sanitary wastes go into the plant's own septic system.

Cooling water from the milling operation and from air compressors is used to water grass and trees on the plant site. Excess cooling water from these two sources is discharged from the plant site into a drainage ditch.

Runoff, as well as the process wastewater, is channeled into the evaporative pond. Although analysis has not been made of the wastewater runoff that drains into the pond, extensive data have been developed on the quality of the water within the pond (Figure A-1).

Typical 1973 analysis of the water in the evaporative pond shows:

Dissolved oxygen	5 to 10 ppm
CO_2	5 ppm
pH	4 to 7
Phenol	0
Methyl orange	34.2
Total hardness	750 to 850
Toxicants	$<$ 1 ppm

Wastewater Treatment System

All process wastewater, as well as the runoff from the production area, flows into a man-made evaporative pond. The pond is about 1 acre in size and has a working capacity of about 1,000,000 gal. The pond is equipped with an aeration system that pumps approximately 1,000 gpm of water some 25 ft into the air (four streams). This aerator consists of a salvaged 15-hp, three-stage water pump supported on a float which was fabricated by plant personnel from used 55-gal. drums. The aerator is held in place in the center of the evaporative pond by cables.

The only costs directly associated with the operation of this system are the electrical and maintenance costs for the pump and the laboratory support required to monitor the pond. No operating expenses are separately charged against the system's operation although about 3 man-hours per week of analytical time are required. Land value in this area is about $4,300 per acre.

Miscellaneous Information

This plant site has a state permit to operate an incinerator for the disposal of solid wastes.

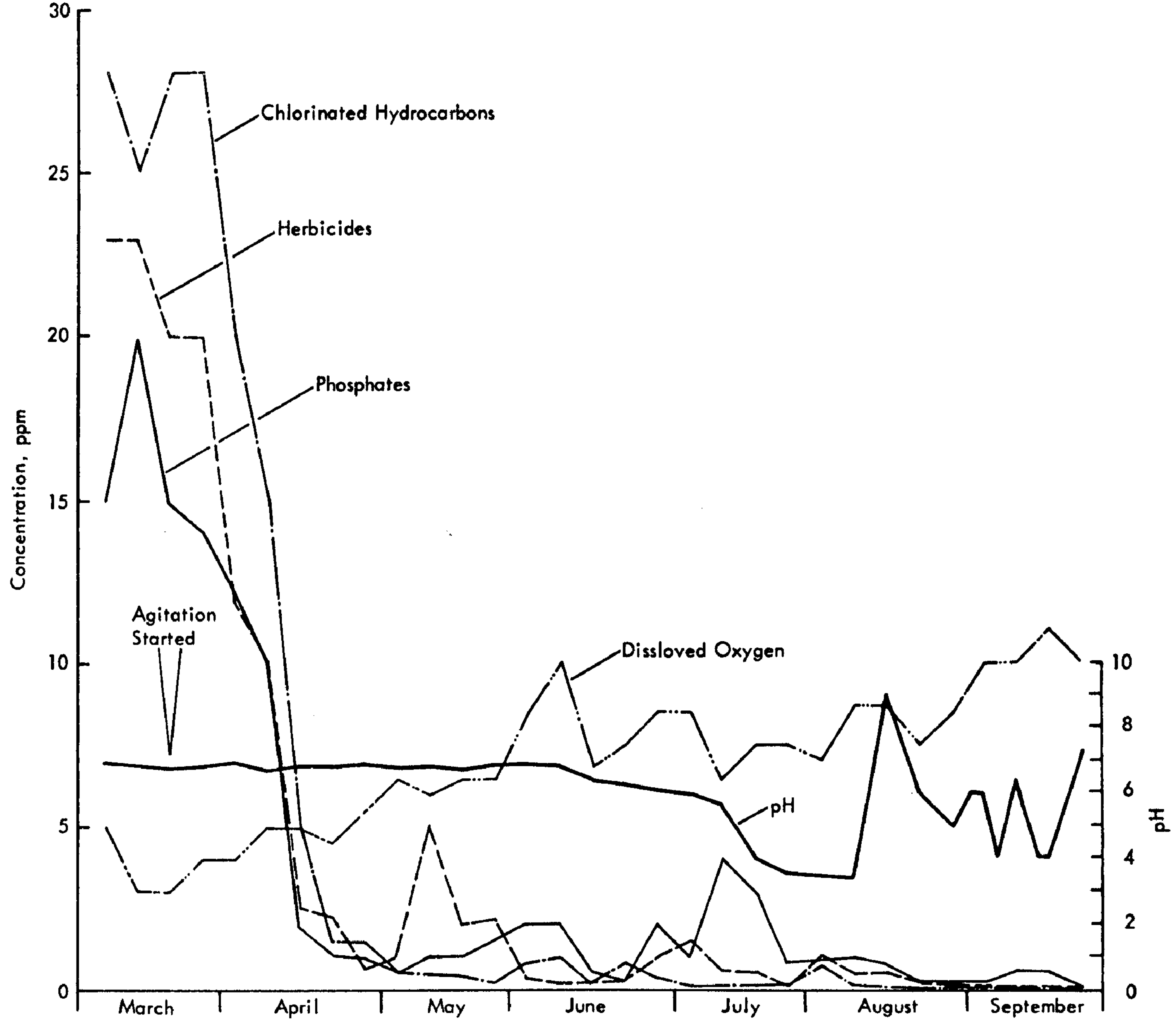


Figure A-1 - Holding Pond Analysis, 1971

CASE STUDY NO. 2

General Information

This plant is one of the oldest and largest visited during this study. It has been in operation in the Pacific West since the 1920's, and annually produces a large volume of solid formulations, as well as a significant volume of liquids. About one-half of the solid formulations are sulfur powder. The active ingredients which are formulated include major organophosphates, chlorinated hydrocarbons, carbamates, as well as spray oil. Organophosphate pesticides account for about 60 to 75% of the liquid formulations, some of which are water-based.

The plant is located on about 12.5 acres within an industrial district, and runs year round, normally on a one shift per day, 5 days per week basis. During the peak season of February through May, however, two or three shifts per day may be used. About 12 to 15 formulation unit turnarounds are required per month during this peak period.

There are five liquid formulation units, ranging in size from 100 gal. to 3,000 gal. capacity. If necessary, all units could be run concurrently, although they normally are not.

In addition to pesticide formulation, this plant also washes drums for reuse (for one inorganic pesticide and spray oil only). Washwater from this operation goes into the process wastewater system.

The liquid formulation lines as well as the Raymond mill used for powders are conventional batch units.

This plant maintains its own control lab on-site, and retains batch samples for a 2-year period.

Wastewater Characteristics

Total water usage for the plant site was about 25,000 gal. per month in 1969. Although no data have been developed since that time, current water usage is estimated to be lower because of operational changes that have been instigated. Water is obtained from wells located on the plant site.

This plant is not connected to the local sewer system, and uses a septic system to dispose of its sanitary wastes.

Primary sources of process wastewater are washdown of formulation equipment and the washing of drums. Neither qualitative nor quantitative data, however, are available on these wastewaters. Estimates have been made that the drum washing operation and the actual pesticide formulation activities each generate about 2,000 gpd of wastewater.

Wastewater Treatment System

Three separate systems are used for handling water: evaporation of rainwater, evaporation of drum washings and runoff from the production area, and evaporation of process wastewater.

Rainwater from most of the plant site (office buildings, parking area, etc.) drains to a sump from which it is pumped to a low section of land about 1.5 acres in area and allowed to evaporate.

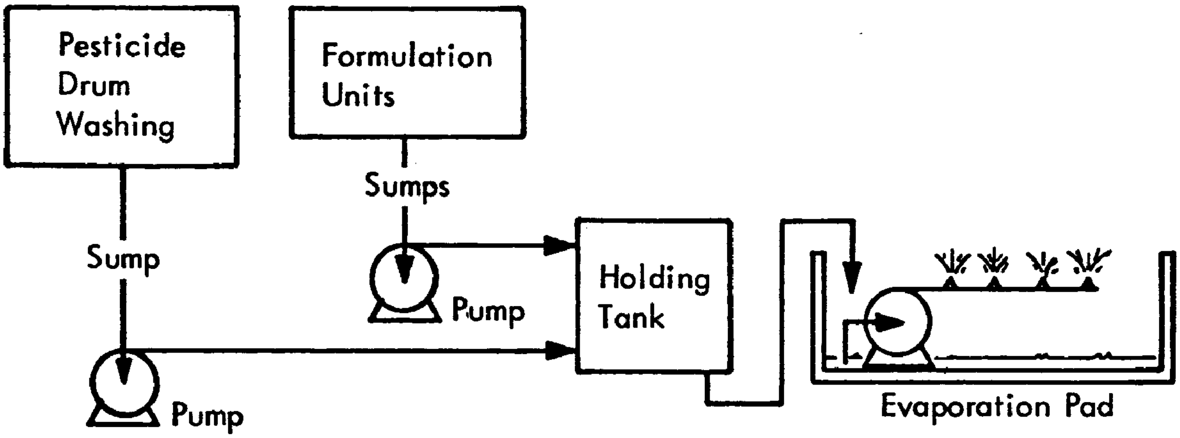
Wastewater from the production lines, as well as the effluent from pesticide drum washing, drains into sumps and is pumped into a 600,000-gal., open-top holding tank (see Figure A-2a). Caustic is used to adjust the pH to approximately 7. From the holding tank, water flows into a 50-ft wide x 50-ft long x 1-ft deep concrete evaporation pad. This pad is also equipped with a 5-hp, 100-gpm pump which pumps the wastewater through an aeration system consisting of a manifold of spray nozzles. A 10-ft burlap fence has been installed on two sides of the pad to prevent vapor drift.

Water from spray oil drum washing is collected via a sump, and is pumped into a 30,000-gal. tank (see Figure A-2b). A deemulsifier is added to the washwater, and the oil phase is removed from the tank for use as road oil. The water is then pumped from the tank into a 40-ft wide x 450-ft long x 2-ft deep fenced, bentonite-lined evaporation pond and is allowed to evaporate. Rainwater that falls on the production area of the plant site flows to a sump, and is pumped into this pond and allowed to evaporate.

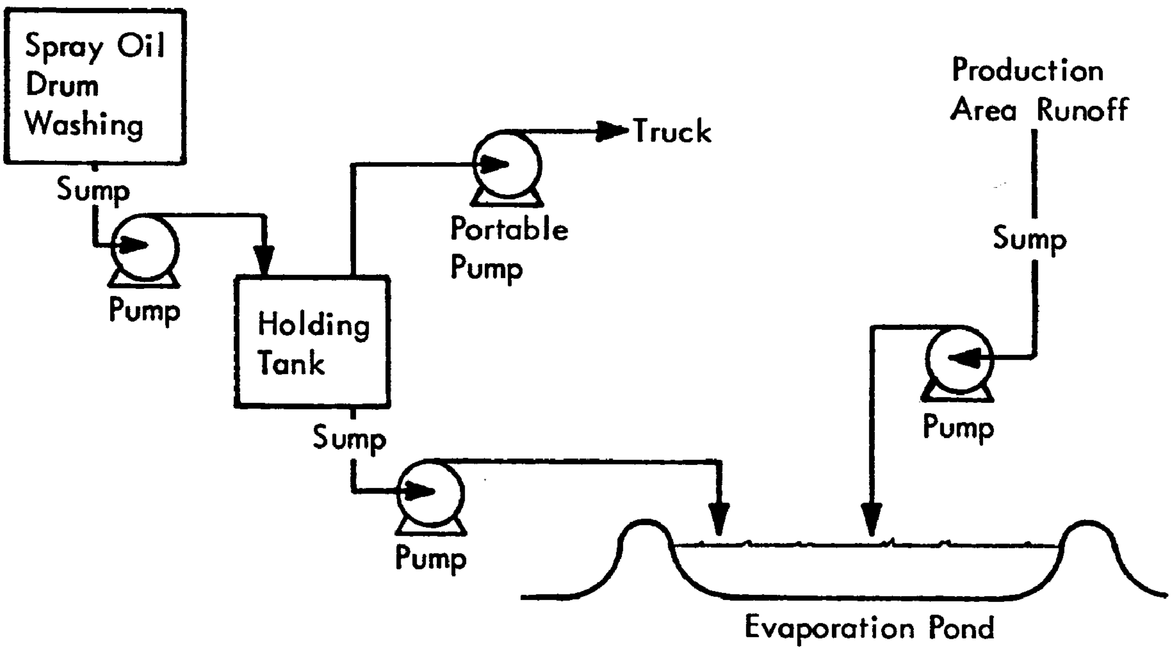
No operating costs are split out for the wastewater treatment system. About $1,400 worth of caustic and deemulsifier, however, are used each year. Less than 10% of one worker's time is required to monitor the system's operation.

Miscellaneous Information

Solid wastes such as sludge and empty containers are disposed of by a contract disposal service in an approved cut-and-fill dump. Cost for this service is about $1.00 per cubic yard, or about $300 to $500 per month. An incinerator (two combustion chambers) is used to burn combustible wastes. Land in this area costs about $6,000 per acre.



a) Process Wastewater Evaporation System



b) Evaporation Pond System

Figure A-2 - Water Handling Systems

CASE STUDY NO. 3

General Information

This formulation plant is located on about 10 acres of land in a large city in the mid-United States, and is owned by one of the large manufacturers of pesticidal chemicals. The plant came on stream in the early 1950's. Although production has expanded steadily since that time, no major changes in the liquid filling line have been made in several years. The current rate of growth in production volume is about 10% per year.

This plant produces a wide variety of insecticides and herbicides. Annual production is in excess of 40,000,000 lb of formulated products, which includes about 2,000,000 gal. of liquid formulations. Most of the liquids (~ 95%) are chlorinated hydrocarbons, while the remainder (~ 5%) are organophosphates. All but a small faction of the liquid products carry the company's own label.

The plant runs year round with an operating staff of about 60. As with most formulation facilities, monthly production rates vary with the season of the year (maximum production has been 5,000,000 lb per month). Custom formulation work, as well as all vacations, is scheduled during the June through August slack period.

Process Information

The dust and liquid lines are both typical batch operations. Liquid batches are usually 3,500 to 6,000 gal.

Water is used as the inert carrier for some of the liquid formulations as well as for washdown between process runs (typical water usage for the entire plant site is 56,000 gal. per month). Up to three turnarounds per week are required on the liquid formulation system (when changing from a petroleum to water base, herbicide to insecticide, etc.). These cleanups are made by water washdown. The same production units are used for both herbicides and insecticides. A caustic wash solution is used to clean up after parathion runs; one liquid formulation unit is used exclusively for parathion. Both the formulation units and the filling line are located inside a large building.

Wastewater Characteristics

Effluent from this plant site can be divided into three categories: sanitary waste, process wastewater, and runoff.

Sanitary wastes are currently processed through a sand filter, into a holding pond, and eventually discharged into a small creek. Plans call for connection with the local sewer system within the year.

Runoff is channeled into a gravity separator and then into a small holding pond. This water is also discharged into the creek. The separator-holding pond system provides a means for controlling large spills before they reach a nearby creek.

Process wastewaters result primarily from the washdown of the liquid lines between product runs and decontamination after parathion is formulated. Due to limited storage space, organic solvent is not used for equipment cleanup and retained for later use.

A complete analysis of the process wastewater has never been made. The only parameter that is checked is pH, which remains essentially neutral. It is estimated that this waste stream is about 30% organic (solvent, etc.) and 70% water. About 12,000 gal. per month of process wastewater are generated.

Recent efforts to minimize water usage have resulted in reducing the quantity of wastewater. Volumes of wastewater from individual systems have been specified, based on vessel sizes, length of lines, etc.

Spills of technical material normally do not reach the wastewater system. Rather, spilled material is absorbed by a solid carrier, such as clay, and is disposed of with the conventional solid wastes.

<u>Wastewater Treatment System</u>

The wastewater from the formulation process is kept isolated from sanitary wastes and runoff by a special collection system (see Figure A-3). Washwater from the liquid formulation lines as well as the line used exclusively for parathion formulation goes via floor drains to a collection sump located in the formulation building. A similar system is used in the filling area. From the two sumps, wastewater is pumped into one of two open-top holding tanks whose combined capacity is 5,500 gal. Periodically, the tank is emptied into tank trucks which transport the wastewater to the municipal sewage treatment plant. Before the water is transferred to the tank truck, however, the pH is checked and adjusted to that of local groundwater (8.0-8.1). Potash is used to adjust the pH. Lime is not used at the plant and there are no agitators in the storage tanks.

The major costs associated with this system are: a charge of $20 per 1,500-gal. load of wastewater (total cost for transportation and dumping), and $20 per load for the potash treatment. Current local cost to replace the

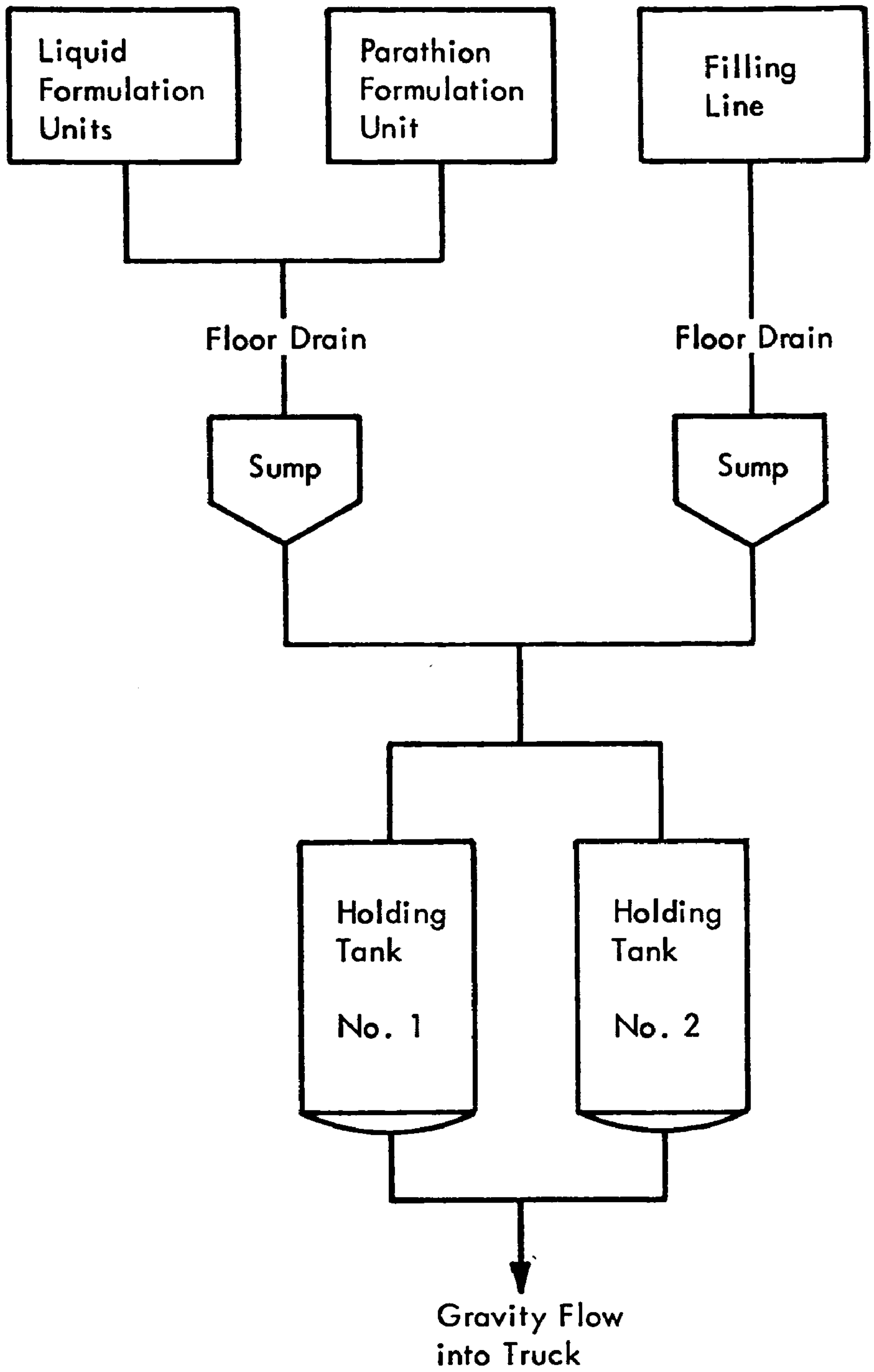


Figure A-3 - Process Wastewater

wastewater system would be about $7,000. No allocation of operating costs are made against the waste disposal system.

Miscellaneous Information

This plant has had no interaction with local Federal agencies other than the investigation of its sanitary waste system.

Solid waste is removed by a local disposal service. There is potential for recovery of solvent and active ingredients from the wastewater system.

CASE STUDY NO. 4

General Information

This plant, which first formulated pesticides in 1966, is located in the East North-Central United States. The facility is owned by a large pesticide manufacturer, although most of its production (~ 95%) is done on contract.

Production during the past 3 years has been essentially constant. Annual production of liquid formulations (none of which are water-based) and granules has been relatively small. Primarily, organophosphates, chlorinated hydrocarbon pesticides, and spray oils are formulated.

This is a rather small facility, having only two liquid formulation units whose capacities are 300 and 1,000 gal. No major modifications have been made to these units since they were installed. Both the liquid lines as well as the granule unit are conventional, batch units.

This plant is only operated about 9 months per year (one shift, 5 days per week schedule). During the busy season (November through April), the plant operates two shifts a day, 5 to 5-1/2 days per week. A total of 100 turnarounds are required during each operating season.

Most of the analytical control work is not done at this plant site. Rather, samples are sent to one of the company's larger facilities for analysis.

Wastewater Characteristics

Total water usage at this facility during the peak production season is about 27,000 gal. per month. The water is obtained from the local municipal water system.

An earlier company study estimated 200 to 250 gal. per day of process wastewater are generated. The process wastewater comes from three major sources: equipment washout, plant washdown, and steam condensate. The granule and liquid lines are washed out between production runs by using a minimum volume of water, which is collected in the same sump as condensate from the steam heating system. No analysis, however, has been made of this waste stream.

Drums that have contained technical organophosphate material are filled about one-fourth full with caustic solution. This water, however, is left in the drums when they are taken to the landfill for disposal.

Sanitary waste, which includes washwater from employee work clothing, goes into the local sewer system.

Rainwater is carried by natural drainage into a local stream.

Spills of technical material are not washed down with water. They are absorbed on clay, drummed, and disposed of with the other solid waste.

Wastewater Treatment System

The wastewater system used by this plant is depicted in Figure A-4. Both of the liquid formulation units are located in a pit that drains to a small collection sump. Washwater from the granule unit, which is located on ground level, is also routed to the sump system. From the collection sump, the wastewater is pumped into a small holding tank located at ground level. From the holding tank, the wastewater is periodically emptied into empty drums.

All of the waste from this site (both solid waste as well as the drummed wastewater) is transported to a local cut-and-fill dump where it is disposed of for a fee of $2 per ton (liquid or solid). No criteria have been specified for the liquid waste going into the dump.

The only direct cost for this system is the $2 per ton dumping fee and the expense of purchasing and operating the truck to haul the waste.

Land value in this area ranges from about $800 per acre for agricultural to $2,500 to $3,000 per acre for industrial areas.

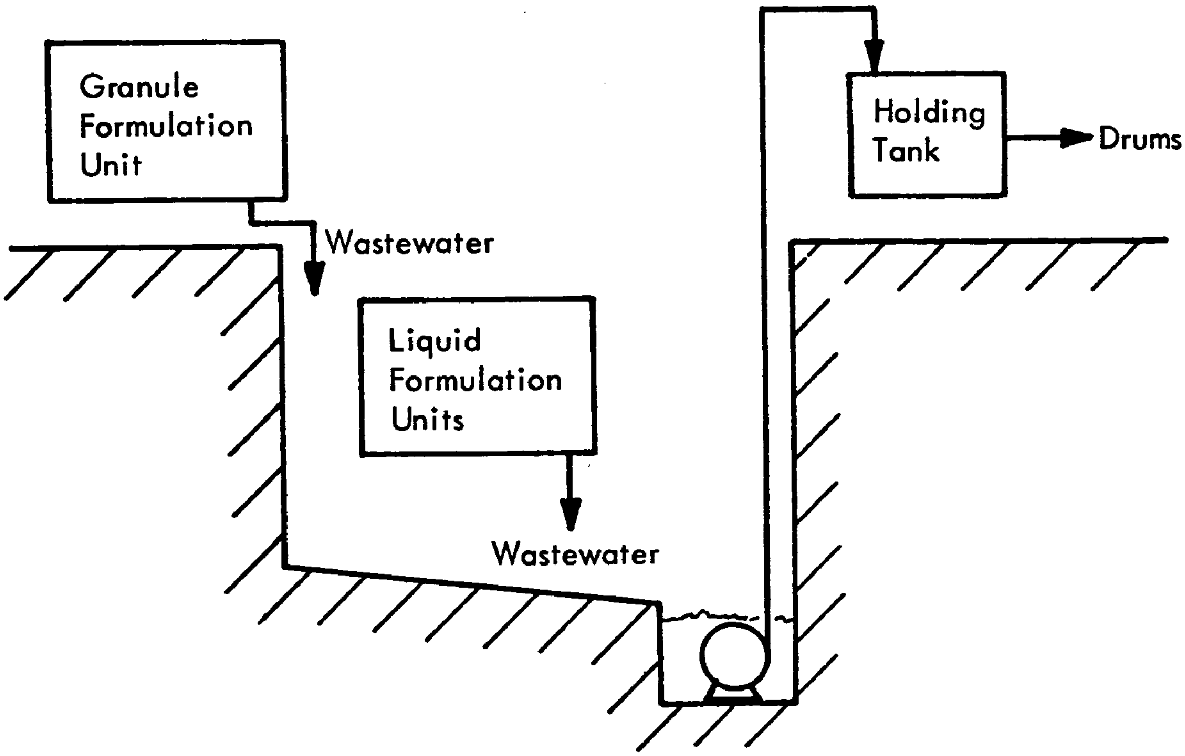


Figure A-4 - Waste Handling System

CASE STUDY NO. 5

General Information

This plant site formulates about 100 pesticidal products for sale under the company's own brand name. It is located on about 18 acres of land in an industrial section of a major metropolitan area. This independent formulator is a major supplier of home and garden products for Mid-America. Almost the complete range of active ingredients is formulated into liquids, dusts, wettable powders, and granules.

Wastewater Characterisitics

In 1972, typical water consumption for this plant site was 20,000 gpd. The water was used for sanitary waste, showers, boiler makeup, cooling, water-based products, equipment washdown, and air cleaning equipment. The contaminated wastewater from equipment cleaning and air pollution control was about 3,000 gpd.

Analysis of effluent from the plant site in March 1972 showed the following concentrations of toxicants:

2,4-D	28.5 to 1,190 mg/liter
2,4,5-T	3.91 to 162 mg/liter
Malathion	2.06 mg/liter
Methoxychlor	0.13 mg/liter

Revisions in the plant's operational procedure and production schedule have allowed for a significant reduction in the quantity of toxicant-containing wastewater produced. Equipment washdowns have been reduced to about 30 per year, yielding only about 60,000 gal. of washwater. This washwater is now disposed of by spraying on the company property.

CASE STUDY NO. 6

General Information

This formulation plant, which is owned by a large, diversified corporation, produces about 5,000,000 gal. of formulated material each year, all products carrying other company labels. Included in the production figure is a small volume of nonagricultural materials such as antifreeze that are simply repackaged for sale. All types of ingredients are formulated, including herbicides and insecticides. Both water and organic solvent formulations are packaged, although mostly water-based products are produced. The liquid formulation line in this plant is about 15 years old. The plant runs most of the year on a one-shift basis; three shifts are operated during the peak season. Water is obtained from the city. Usage during peak production is about 300,000 gal. per month.

Wastewater Treatment

Major sources of toxicant-containing wastewaters are equipment washdown and the waste from the quality control laboratory. This plant uses four holding tanks to accumulate wastewater before analyzing and discharging it into a local industrial district treatment system. Most runoff is also channeled into this system. The district system consists of primary treatment only.

The only requirements set by the industrial treatment system for discharge of formulation waste into its treatment plant are:

Toxicant concentration	$\leq$ 100 ppm
Total toxicants	< 10 lb/day
pH	6 to 8

This plant has had little difficulty in meeting these few requirements. The rare occasion where these specifications can not be met is usually the result of an unusual event, such as a spill. In this event, the wastewater is transferred to storage for subsequent treatment or removed by a contract disposal service to a state-approved landfill.

System Cost

This system utilizes the storage capacity of an abandoned secondary waste treatment plant that had been used to process waste from a herbicide manufacturing plant. Capital cost data on the system, therefore, are not meaningful. The operational costs charged against the operation of this system are one-half of one operator's time (~ \$3-4 per hr), and ~ \$10 per 1,000-gal. load that is removed by the contract disposal service. Infrequently, the pH of the wastewater must be adjusted to meet the 6 to 8 range, but the associated cost is not significant.

CASE STUDY NO. 7

General Information

This plant is operated by a large agricultural chemical manufacturer to formulate products for sale under the company's own label. The plant is located in the West North-Central United States, and has been in operation since 1955. This facility operates year round, and produces about 40,000,000 lb of formulated products each year. Active ingredients used include a number of thiocarbamate herbicides and organophosphate insecticides. No inorganics or metal-containing pesticides are formulated. Production is about evenly split between liquid and granule products.

Wastewater Characterization

The primary source of process wastewater is equipment washout. Dye is used for one of the major solid formulations, and is one of the main reasons for water-washing. All water from inside the dikes that surround technical material storage tanks also goes to the wastewater treatment system.

Effluent from the plant's wastewater treatment system has been analyzed by the local municipality into whose sewer system the water is discharged, and the quality of this water has been found to be acceptable. These analyses, however, were not available.

Where possible, solvent is used to clean out formulation equipment in order to minimize the volume of wastewater generated.

Wastewater Treatment System

The wastewater treatment in use at this plant site is depicted in Figure A-5. The system is still considered to be in the pilot plant phase, however, and for that reason complete design and operational data were not available. A general description of the system is given below.

Wastewater from the production units is collected in a sump and is pumped into a settling tank. Here, flocculating and deemulsifying agents are added. The wastewater is then continuously pumped to a vacuum filter unit. Sludge from the filter is disposed of with the other solid wastes. From the filter, the water is pumped to an aeration tank for secondary treatment. If necessary, water from the aeration tank can be recycled to the settling tank.

In the next step, the aerator effluent is passed through an activated carbon column and then into a 100-ft long x 6-ft wide "fish pond." The system effluent can be discharged to a garden plot, the city sewer, or to a recycling system.

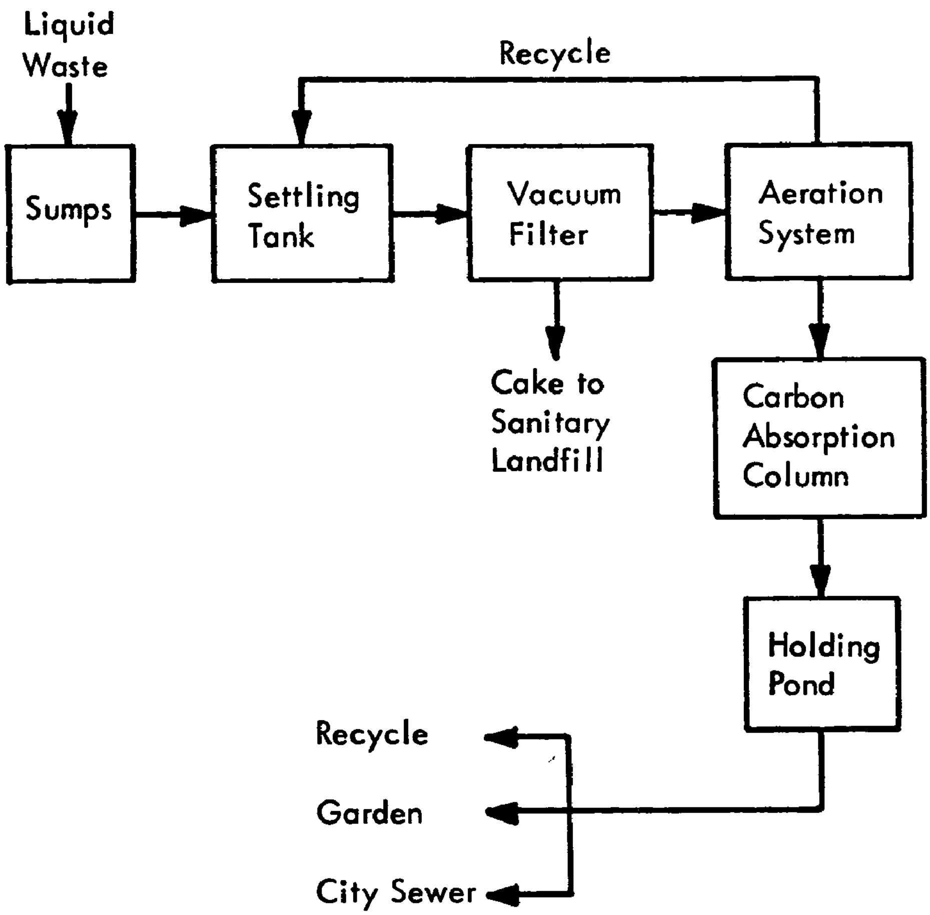


Figure A-5 - Pilot Absorption System

The design retention time for the system is about 30 days. The carbon column has been used up to 6 months between rechargings (about 540 lb of carbon). At the reported continuous flow rate of 2 to 5 gpm, a carbon capacity of 500 gal. per lb is indicated. This system has reportedly operated for short periods at a rate of 15 gpm.

Specific data on the quality of influent and effluent water for this system were not made available. However, data indicate that typical operation yields a reduction in total toxicants from an initial concentration of 140 ppm to an effluent containing < 0.1 ppm.

The actual capital cost of this plant is not significant because of its developmental status. Operational costs, however, are meaningful. This system requires the full-time attention of two people to operate the equipment and provide analytical services.

Miscellaneous Information

Solid waste is disposed of by shipping it to an approved landfill at a cost of about $1.25 per cubic foot (including freight). The disposal of drums and bags is not a problem as most technical materials are received in tank cars or tote tanks.

CASE STUDY NO. 8

General Information

This plant is located on a 2-1/2 acre site near a small Middle Atlantic town. The facility, which first came on stream in late 1962, is owned and operated by a large manufacturer of agricultural chemicals. The plant operates all year, with peak production during the January through July period. This is a one shift per day, 5 days per week operation except for 3 months in the spring when they operate 6 days per week. The plant work force is seven full-time employees.

Production at this facility typically includes small volumes of solvent-based liquid formulations (no water-based liquids), granules, and dust. All of these products carry the company's own label. These products include a broad range of organophosphates, chlorinated hydrocarbons and spray oil.

The plant facilities include two liquid formulation units, one granule unit, and a dust unit. All four of these units are typical batch operations of small capacity. Major modifications have not been made since 1966.

The plant's production schedule requires a number of turnarounds per year: 50 for the two liquid lines, six for the granule system, and 100 to 120 for the dust unit.

Approximately 500 55-gal. drums are reconditioned each year. To each drum, 1 to 1-1/2 lb of soda ash and about 1 gal. of water are added; the drums are placed on their sides, and are allowed to stand for several days before they are emptied. During this time, the drums are periodically rotated. Most of the washouts are made during the peak production season. Water, however, is generally not used to wash out the production units; solvent is used, and where practical, is saved until the next production run. About 50 gal. of water is required each time the granule system is cleaned out.

Quality control samples are not analyzed at this site, but are sent to another of the company's facilities for analysis.

Wastewater Characteristics

An on-site well is the source of water used at this plant. The consumption rate has not been determined.

All surface waters run off the plant site and eventually end up in a nearby stream. This area's water table is at about 6 ft, and a drain tile system has been installed.

Sanitary wastes from office and production areas go to two septic systems. Washwater from work clothes processed on-site also goes into one of the septic systems.

It is estimated that about 2,000 gal. of process wastewater are generated each year. The major sources of the wastewater are building washdown (approximately one time per year), granule unit turnarounds (approximately six per year) and drum cleaning (~ 500 drums per year).

The process wastewater from this plant has not been analyzed, and therefore no estimate of the toxicant content can be made. The volume estimate of 2,000 gal., however, was based on operating experience as well as knowledge of the wastewater treatment system's capacity.

Solid wastes are disposed of in a local landfill at no charge.

Wastewater Treatment System

Process wastewater from the formulation units as well as from the drum washings is disposed of by evaporation. The system used is depicted in Figure A-6. Wastewater from the liquid lines, from the granule unit, and from the yearly building washdown go into a collection sump in the bottom of the liquid line pit. From there, the wastewater is pumped into a 16-ft long x 4-ft wide x 3-ft deep concrete evaporation pit. The water is treated with soda ash to adjust the pH to 9, and is allowed to evaporate. This evaporation pit is covered with a plastic roof, and contains a series of burlap sheets that hang into the water to aid evaporation.

Washwater from drum decontamination is also emptied into this evaporation pit.

No direct expenses are allocated to the operation of this system. The concrete pit was installed by plant personnel, and would cost about $1,000 to duplicate today. About 5% of one person's time is required to monitor the system's operation.

Land value in this area is about $8,000 per acre.

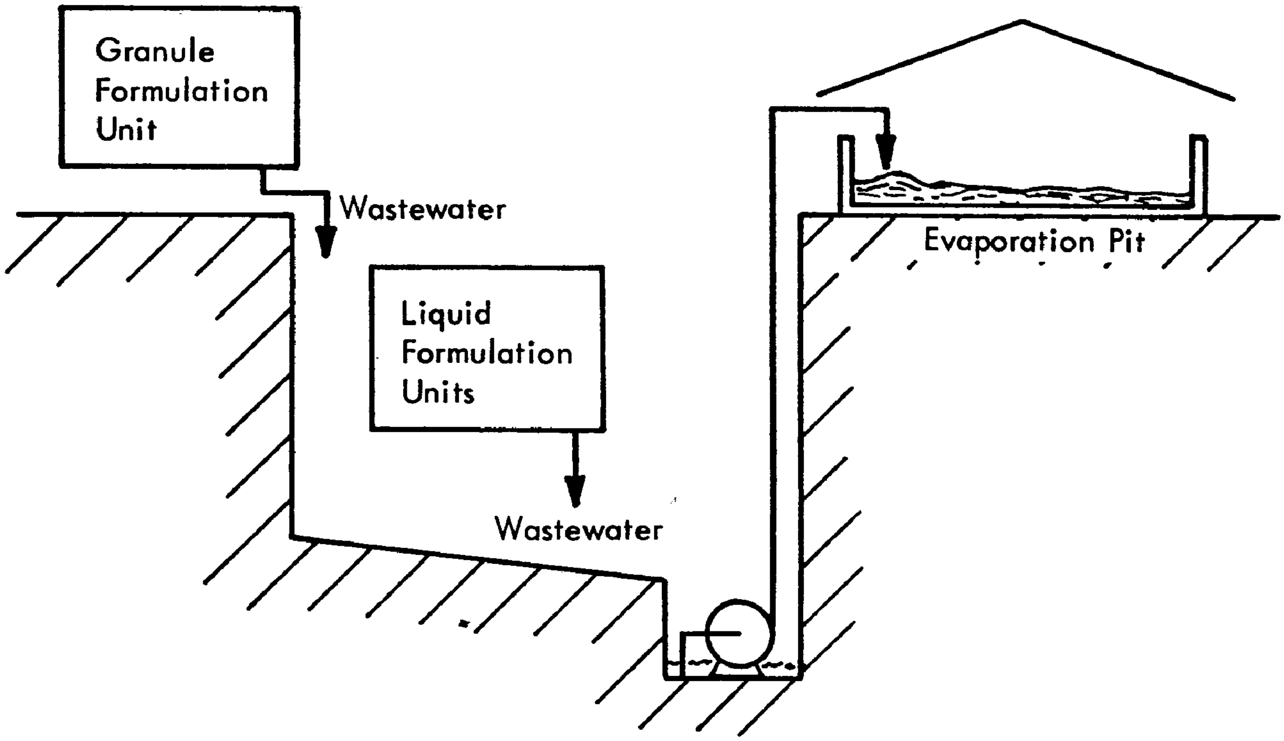


Figure A-6 - Wastewater System

CASE STUDY NO. 9

General Information

This is one of the larger pesticide-formulating facilities in the country, and is one of several plants operated by this company in the South. This firm is not involved in the manufacture of pesticidal chemicals. Annual production is estimated to be about 40 million pounds of dry and liquid formulations. Much of this volume is custom-formulated for other companies under their respective labels. The balance is formulated and marketed under the company's own label. The custom-formulating work is done for almost all major basic pesticide manufacturers in the country.

This facility, located in the West South United States, first started operation in the 1950's as a dust-formulating plant. An air mill unit for powder formulations was added in 1967, and liquid formulation units were added in 1968.

The plant operates on a year-round basis producing a complete range of products. About 40% of the products are insecticides, and 60% are herbicides. Arsenical-based formulations are also mixed. The solid formulation facilities include three air milling units. Long production runs are made wherever possible.

There are several liquid units where 1,000-gal. batches can be run simultaneously.

Wastewater Characteristics

The primary sources of process wastewater from this plant site are equipment washdown and the quality control laboratory effluent. Estimated wastewater volumes are 1,500 to 2,000 gpd (average), with a maximum of 4,000 gpd.

At one time, the plant attempted to use a carbon filtration system to treat process wastewater. This system included a pit 16 ft deep and 20 ft sq which was filled with layers of limestone (4 ft), charcoal (1 ft), and, on top, 4 more feet of charcoal. Wastewater from the entire plant was sprinkled over the top of this filter bed, and eventually discharged into a small stream. Use of this treatment system was discontinued, however, before operational data were developed.

The following analyses were made of the effluent from this plant by a state department of pollution control:

1. Five 24-hr composite samples (1970) showed:

COD	483 mg/liter
Total solids	661 mg/liter
Dissolved solids	631 mg/liter
Arsenic	37 mg/liter

2. One grab sample (1971) showed:

DDT	62 mg/liter
DEF	14 mg/liter
Aldrin	0.21 mg/liter

Plus indication of Chlordane and Toxaphene

3. One 24-hr composite sample for conducting bioassay, using bluegill, sunfish, and procedures according to Standard Methods, 13th edition. The 48-hr Median Tolerance Limit (MTL) was determined to be 0.023% concentration of the wastewater (1971).

This plant is currently attempting to obtain permission to discharge its effluent into the local municipal sewer system. Sanitary wastes are already going into this sewer system.

CASE STUDY NO. 10

General Information

This plant is one of several owned and operated in the South by a pesticide formulation company. This company does not manufacture pesticidal chemicals.

A wide variety of products are formulated, including granule, liquid, and powder forms of organophosphates, chlorinated hydrocarbons, and inorganics. Total liquid production is about 3,000,000 gal. per year, about 25% of which is water-based. Water-based formulations of MSMA/DSMA are produced.

A significant volume of solid formulations of proprietary pesticides are produced for several of the major agricultural chemical manufacturers.

Wastewater Treatment

Process wastewater is being treated by a pilot plant carbon absorption system. The wastewater is first collected in a 40-ft long x 22-ft wide x 4-ft deep, covered collection sump. From there the water is pumped into a holding tank. The holding tank discharges into a carbon absorption column made from three 55-gal. drums. No analytical data were available on either the raw wastewater or the effluent from the treatment process.

APPENDIX B

NATIONAL AGRICULTURAL CHEMICALS ASSOCIATION (NACA)
WASTE DISPOSAL MANUAL

FOREWORD

The original NACA manual, "Waste Disposal," was developed by a special NACA-Industry Committee (the Subcommittee on Waste Disposal of the Grady Committee) in 1965. The intent of this manual was to provide guidelines for the disposal of waste from pesticide manufacturing and formulation operations. The "Grady Disposal Manual," as it became known, has received wide use since its original publication.

In 1970, the Environmental Quality Committee of the NACA initiated efforts to update the original disposal manual. Revised sections as well as new data were developed by about 20 representatives of the agricultural chemicals industry. Unfortunately, the Committee was not able to complete the revision of the manual, and the new data on waste disposal have not become available to the pesticide industry.

As part of this study of waste treatment technology for pesticide formulators (Environmental Protection Agency Grant No. R-801577), data that had been generated to update the "Grady Disposal Manual" were compiled, and integrated into the format of the original document. The "updated" manual, which follows, has been used during this study to help develop baseline parameters, against which to evaluate treatment systems being used for formulation plant wastewater.

This appendix has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the view and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TABLE OF CONTENTS

INTRODUCTION

The suggestions in this manual have been developed by a special NACA-Industry Committee as guidelines which might be followed in the disposal of waste from pesticide manufacturing and formulating operations.

Of necessity, these suggestions are expressions of opinion and are based on practical experience and information correlated by researchers, operators, and executives who are qualified industry representatives. They are not intended to supersede any manufacturer's or supplier's specific instructions relative to individual products which may appear on the label or be supplied to the formulator in some other manner. They are also not intended to supersede any effective waste disposal practices now currently followed by individual plants.

To the extent that Federal, State, and local regulations pertaining to waste disposal exist, and require or prohibit certain practices, the suggestions in this manual are intended as supplementary information only. No guarantee or warranty is expressed or implied that adoption of the suggestions herein will ensure compliance with applicable laws and regulations pertaining to waste disposal.

In the preparation of this manual, a few classes of pesticides were selected, for purposes of illustration, for specific discussion as regards waste disposal practices. The fact that some pesticide or group of pesticides is not mentioned in the manual should not be interpreted as indicating that it presents no waste disposal problem. Most pesticides do present such a problem.

It is recommended that manufacturers and formulators of pesticides contact their suppliers for specific information and suggestions on any waste disposal problems which might be involved with the materials which they are supplying. Attention is also called to the fact that there are professional consultants on the matter of waste disposal.

PESTICIDES IN THE ENVIRONMENT

Pesticides have been used for several decades and have been a major factor in increasing the quantity and quality of man's food supply. It is only recently that their use or misuse has raised serious questions as to whether they are adversely affecting man's environment.

As of early 1965, the Pesticides Registration Division, U. S. Department of Agriculture, had registered approximately 60,000 products containing one or more of some 600 active pesticidal ingredients. Currently, about 32,000 products have Federal registrations from the Environmental Protection Agency. These pesticidal chemicals are separated into three major categories: inorganic; frequently so-called "natural" organic (or plant extracts); and synthetic organic pesticides.

Pesticides in Water

Pesticides can enter ground and surface watercourses by several means: direct application for the control of aquatic weeds, trash, fish, or aquatic insects; percolation; and runoff from agricultural applications. The discharge of industrial waste resulting from the manufacture of pesticides and the discharge of wastewater normally used for equipment cleanup have also contributed in some instances to pollution. There have been documented instances which indicate that effluents containing pesticides have damaged or killed various species of vegetation and fish. Pesticides, when found in water samples, are usually in very low concentrations. Although knowledge is lacking regarding the long-range effects of most pesticides on our water resources, it has been reported that these substances, with their accompanying diluents and solvents, are entering our natural waters and may have contributed to taste and odor problems. It is generally believed that many of the formulations exhibit low threshold concentrations and the tastes imparted are typical of the solvents used in the formulations. There is a paucity of laboratory information regarding the threshold taste and odor levels of organic pesticides.

The fate of the parent compounds of organic pesticides once they enter water, regardless of whether they are biologically degraded, absorbed, or chemically decomposed, is important. If the pesticide is of such type that it would persist and affect water quality for a long time, additional or special treatment may be required.

Pesticides in Air

Although air pollution control has been accelerating at a faster rate than other environmental health disciplines, the matter of air pollution control as it applies to the manufacture and formulation of pesticide chemicals imposes no major difficulties. The nature of the processes and the high cost of the pesticidal chemicals used dictate that the material losses be held to a minimum. To make the process economical and safe, dust collectors, such as cyclones and bag collectors, are widely used throughout the industry. Fumes are usually collected under a slight vacuum, condensed and/or scrubbed in a packed tower or an equivalent gas/liquid absorption type vessel which will clean the air. Solvents, when stripped from the final product, can frequently be reprocessed (recovered) for reuse.

The unloading and storage of some chemicals give rise to occasional emission of vapors or odors. The use of a closed system will minimize these losses. Vent losses of storage tanks can be controlled by connecting the vents to the process scrubbing system. Effluents from the scrubbers may require further treatment.

Regulatory Agencies

Air and water contamination, either by use or misuse of pesticides, can best be controlled at the local level. With the increasing demands on the part of everyone for a better environment, it is only logical to expect a closer interest displayed by State, interstate, and Federal bureaus whose responsibility lies in the field of pollution control. It is generally believed, particularly by both industry and State regulatory agencies, that pollution control is a complex technical problem which requires thorough study and long-range planning on the part of competent personnel. Industry recognizes the need for research and the need for highly technical field studies dealing with air and water quality and long-range planning.

The importance of the support and assistance of local regulatory agencies cannot be overemphasized. The disposal of processing waste and other materials containing pesticides will depend to a great extent upon local conditions. All local, State, and Federal regulations regarding health and pollution must be followed. The official agencies involved are normally the city or county health departments, and the State Department of Health or the State Water Pollution or Water Resources Commissions. The materials supplier is also a good source for this information.

POLLUTION CONTROL BY PREVENTIVE MEASURES

During the manufacture and formulation of agricultural chemicals, loss prevention, containment, recovery, and in some cases treatment of intermediate by-products and product losses, are of great concern.

The greatest potential for preventing air or water pollution in the manufacture of agricultural chemicals can be divided into two categories, each of which can be incorporated into the initial design of a plant. Such incorporation provides means for controlling potential pollutants before they reach the waste treatment system.

Process Design

It is apparent that pollution control can best be accomplished by a positive waste prevention and recovery program in the processing plant. In essence, this places a portion of the waste treatment system into the waste generating plant, a location where the operation of the recovery equipment is usually a money-making rather than a money-losing operation. It is much easier to contain and recover material from a single waste source which is at a minimum volume, rather than recover or treat large volumes of mixed wastes. Table B-1 lists some examples of prevention, control, and recovery measures that can be incorporated into the design of a new plant.

Waste-Treatment Buffer System

Experience has shown that a buffer unit, placed between the processing plant and the final waste treatment unit, is a very effective source of control, equilization, and stabilization. This buffer unit should be of sufficient size to contain releases of product or intermediates due to misoperation or accident, without increasing the feed quantity to the final waste treatment unit. If the maximum buffer capacity of the intermediate unit is reached, the waste-generating plant must be shut down, rather than exceed the design loadings of the final treatment plant. For example, a large receiving pond provides an equalization buffer against shock loads of waste material before final treatment. The buffer unit also serves as a trap so that high losses can be given additional or different treatment.

An example of a buffer system would be a sump equipped with a sump pump connected to a dumpster, with no sewer overflow connections. This system provides time and opportunity to make additional judgments in disposal of unexpected losses. Perhaps the buffer unit can be called a Fail-Safe Unit, since its greatest asset is to function properly during abnormal conditions. These units help ensure better and surer correct handling as compared to sewer samplers or alarms, which can break down, be turned off, or ignored.

TABLE B-1

METHODS FOR WASTE PREVENTION, CONTROL AND RECOVERY

Method	Comment
Record prints	Records of all sewers, sewer junction boxes, valve boxes, all underground lines, are beneficial in tracing and controlling waste losses.
Raw material purity	As a general rule, the purer the raw material, the less the potential for waste. Some wastes are made up of impurities; they combine with other raw materials or other impurities to give additional by-products, which may be greater pollutants than either.
Curbs and sumps	Curbs and collecting sumps around pumping areas and transfer tanks can collect pump drippings and accidental losses. The lost material may be returned directly back to the process.
Distillation	Distillation is not only an effective method of obtaining product purity, but collects higher boiling residues in a relatively small volume of burnable bottom tars.
Washing	During washing of products or intermediates in processing steps, the wash water might be acidified slightly or salt added, to minimize organic solubility (if permissible on the basis of the chemistry involved).
Shell and tube condensers on steam jets	The use of a shell-and-tube condenser for the exhaust of a steam jet (operating on a still, for example) is recommended over a direct water-quench condenser for several reasons. First, the condensate volume is about 1/100 that of the direct-quench condenser, plus the fact that this allows for a higher organic concentration, allowing for phase separation in some cases, or easier disposal.

TABLE B-1 (Concluded)

Method	Comment
Phase separation	When wastewater is separated from product in decanting tanks, a bull's-eye sight glass should be located well ahead of the final valve so as to prevent carryover of product with the water.
Filter cakes	Some filter cakes can be steamed on the filter press to remove absorbed product.
Bag filters	Where bag filters can be used on contaminated air, they are preferred to water scrubbers in that the material can be recovered if of value, or it can be destroyed by burning if small volumes are involved.
Recirculating scrubbers	A recirculating scrubber is preferred to a continuous pass scrubber in that concentration buildup is possible, making recovery feasible or disposal much more efficient.
Settling tanks	Settling tanks, of the proper size, are effective in removing entrained, insoluble contaminants.
Cleaning	Brooms or industrial vacuum sweepers should be used to pick up spills of dry materials, rather than hosing down.
Drain tile	Drain tile, connected to a collecting sump, can be an effective aid in providing an interception system for chemical contaminants that have soaked into the ground.
Operating instructions	Each operation should have carefully written job procedures for each operation that include specific instructions on the minimization of waste as well as on the correct ways of disposing of waste for each operation.

It is evident that these described categories use the most direct route to minimize pollution. Final treatment of some sort will be necessary. It should be recognized that the purpose of final treatment is to treat this irreducible minimum waste, and not wastes due to poor operation.

Active pursuance of these concepts will result in minimum waste that will require processing, thereby minimizing cost and pollution.

GENERAL CONSIDERATIONS

The methods of waste treatment and disposal that are generally used for industrial wastes have application to, or can with modification be employed for, pesticide plant wastes.

Within limits, there are treatment processes available that are versatile enough to remove almost any impurity that is considered harmful. However, the unit operations and processes that are called upon to achieve this objective may be complex, and several may have to be used in series. From a technical point of view, a means probably exists for removing a contaminant; the problem is reconciling the cost of removal with the necessity for achieving minimum contamination of the environment.

Need for Treatment

Some compounds are objectionable in small concentrations in water for several reasons. Principal among these reasons are:

- Potential toxicity to wildlife, fish, and man.
- Tainting of fish flesh.
- Taste and odor.

Wastewater Analysis

Waterborne wastes are characterized in part by reference to physical and chemical properties. The more common of these are:[1/]

- Biochemical Oxygen Demand (BOD) - That amount of dissolved oxygen which is utilized by microorganisms in stabilizing organic matter that can be consumed or metabolized. The test is performed by incubating an appropriate volume of the waste sample with oxygen-saturated dilution water under test conditions of 5 days at 20°C (68°F), unless specified otherwise. The test is a bioassay.

- Chemical Oxygen Demand (COD) - That amount of chemical oxidant which is consumed by reacting a waste sample under given laboratory conditions (usually 2 hr refluxing with dichromate in a 50% sulfuric acid medium, and determination of the oxidant remaining after this treatment).

- Suspended Solids - That quantity of particulate matter that is retained upon filtration of a given volume of the wastewater.

• pH - The intensity of acidity or alkalinity present. pH limitations are imposed, for example, to protect concrete sewers, ensure the effectiveness of waste treatment processes, and protect aquatic life in receiving watercourses. A permissible range of 5 to 9 is typical for plant effluents.

• Dissolved Oxygen (DO) - That quantity of oxygen present in solution.

• Others - Occasionally, additional properties are considered, and these may include temperature, color, dissolved gases, dissolved solids, and chlorine demand.

This section contains brief descriptions of treatment methods that can be used for pesticide wastes. The applicability of these techniques to specific pesticides or to individual classes of pesticidal chemicals is not discussed in this section, but is reviewed in the section immediately following.

Biological Treatment

Wastewaters containing decomposable organic matter exert a demand for dissolved oxygen when discharged into a watercourse. If the oxygen demand exceeds the rate of replenishment from the atmosphere and by photosynthesis, the dissolved oxygen in the watercourse becomes depleted. Anaerobic decomposition takes place with the evolution of gases, and nuisance conditions and foul odors result.

Biological treatment of wastewaters for removal of organic matter prior to discharge to a watercourse may be accomplished either aerobically (oxygen present) by use of trickling filters, the activated sludge process, oxidation ditches, aerated lagoons and oxidation ponds, or by anaerobic (oxygen absent) digestion. In each of these processes, the organic matter is used as an energy source (i.e., food) by microorganisms present in the wastewater and is converted to innocuous forms in an artificial environment and under controlled conditions.

Trickling Filter. The trickling filter or bio-filter is a packed bed of media over which wastewater is distributed from fixed or movable nozzles, or sprays. As the wastewater trickles through the media, the biological organisms present cling to the media surface and a slime growth develops. Using oxygen supplied by natural or induced means, organic matter present in the waste which is subsequently added is adsorbed and oxidized by the slime growth.

Filter media may be either random-packed blast furnace slag, crushed granite, limestone or traprock, or an engineered plastic material placed on a false bottom consisting of perforated filter blocks or grating and an under-drainage system. Rock filters contain 2-1/2 to 4 in. rock packing and vary in depth from 3 to 8 ft. Plastic packings, due to their light weight and greater surface area per unit of volume, are employed in depths up to 40 ft. Filters using plastic media are sometimes referred to as "oxidation towers."

Trickling filters are usually followed by a settling basin. The function of the settling basin is to remove the large masses of biological growths which intermittently "slough off" the filter media.

Where wastewaters contain a widely variable organic loading, trickling filters have been used ahead of an activated sludge system. This type of filter is often referred to as a "roughing filter." Using the trickling filter's inherent ability to absorb shock organic loadings with only a minimum loss of efficiency, the roughing filter reduces the loading to the polishing or second stage biological process.

For intermediate and high-rate filters, a portion of the wastewater which has passed through the filter is recycled for another passage through the filter for increased organic removal and to maintain a continuous loading.

A settling basin is generally employed ahead of the trickling filter where an economically justifiable proportion of the organics can be removed in this manner.

A typical trickling filter layout is shown in Figure B-1.

Activated Sludge. In the activated sludge process, the biological slimes are produced within the wastewater itself. The biological masses are either generated about suspended particles, or they are constructed of colonial growths of bacteria and other living organisms. The microorganisms, or activated sludge, multiply rapidly when maintained in contact with the organic matter present in the waste in an aerobic environment. As a result, the organic matter is rapidly oxidized, while the activated sludge tends to coagulate and form a precipitate that is readily settleable.

The two methods that are in general use for aerating the mixture of sewage and activated sludge (mixed liquor) are diffused air aeration and mechanical aeration. The former is accomplished by forcing compressed air into the wastewater through a diffusion device at the bottom of the aeration tank creating a bubbling action. As the bubbles rise to the surface, oxygen transfer occurs at the bubble/water interface. In mechanical or surface aeration, the wastewater is constantly stirred and exposed to the atmosphere. In some instances, a combination of air diffusion and mechanical aeration is used.

There are a number of modifications of the activated sludge process. Among these are: conventional activated sludge, extended aeration, contact stabilization, step aeration, tapered aeration, and high-rate activated sludge. Only the first three modifications, the most widely used, are discussed herein.

The conventional activated sludge process is the most commonly used, particularly for larger plants since it offers the best compromise between treatment efficiency and capital and operating cost. A schematic illustration of the process is shown in Figure B-2.

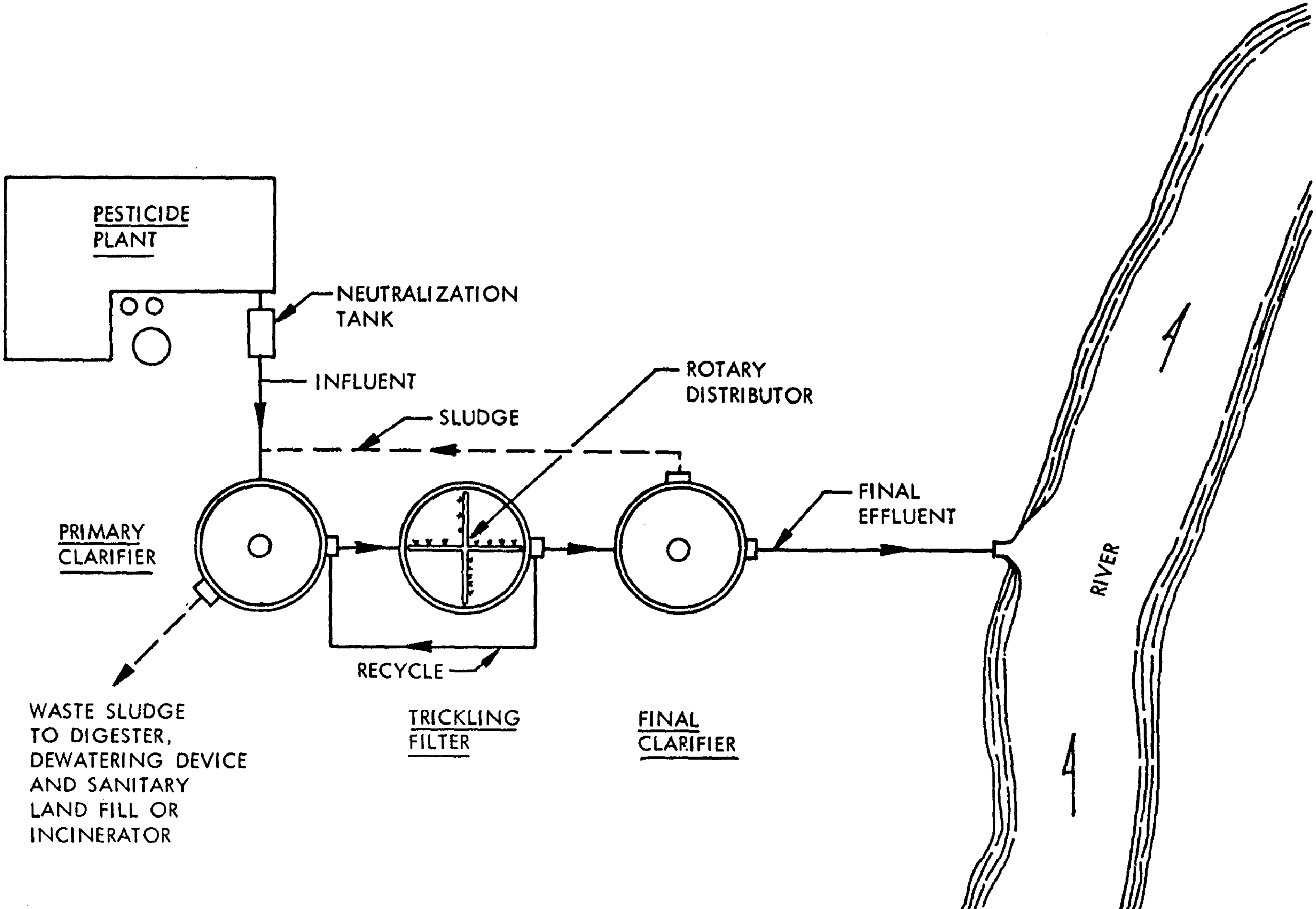


Figure B-1 - Wastewater Treatment by Trickling Filter

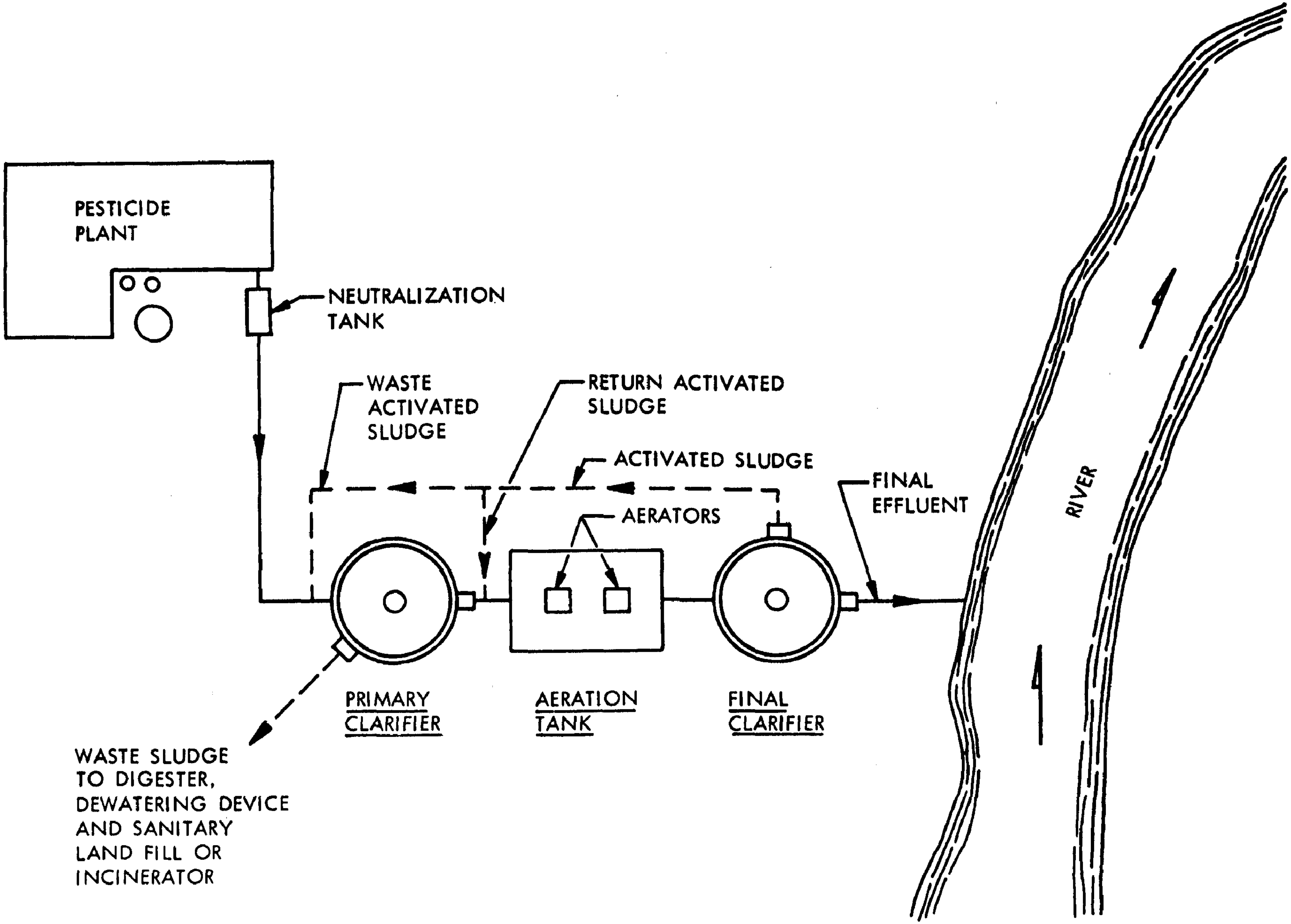


Figure B-2 - Wastewater Treatment by Conventional Activated Sludge

In the conventional process, clarification ahead of the aeration tank is generally practiced. Up to one-third of the organic matter present in the wastewater may be removed in this manner. Following aeration of the settled waste (usually for 6 to 8 hr), the aerated mixture is withdrawn to a final settling tank in which the activated sludge floc is separated by gravity, leaving a clear liquid for discharge to the watercourse. The greatest portion of the settled activated sludge is returned to the aeration tank (return activated sludge) to aid in the treatment of more wastewater. The remainder is wasted in order to prevent a buildup of solids in the aeration tank. Settled activated sludge is wasted by returning it to the inlet of the primary settling tank where it is resettled with the incoming raw sludge for ultimate disposal.

In the extended aeration process, organic removal is achieved by continuous aeration, generally for 24 hr. Since tankage requirements would be high for large volumes of waste, this process is generally restricted to use only at smaller installations.

Stabilization of wastes in the extended aeration process takes place in two stages. During the first stage of aeration, as in the conventional process, the biological organisms adsorb and oxidize the available organic matter. In the second stage, the biological cells formed undergo self-oxidation for further energy. Following aeration, the effluent is withdrawn to a final settling tank in which the sludge floc is separated by gravity. As in the conventional process, the greatest portion of the sludge is returned to the aeration tank and the remainder is wasted. Since only a portion of the biological sludge is nonbiodegradable, the quantity of waste sludge is minimized. Primary settling preceding extended aeration is not practiced.

In the contact stabilization process, organic removal is achieved by performing the two stages of stabilization previously discussed in separate aeration basins. In the first, the aeration period is maintained such that little or no oxidation of organic matter adsorbed onto the biological organism takes place. Effluent from this basin is then settled. A portion of the biological sludge is transferred to the second aeration basin where stabilization or reduction by oxidation occurs. Effluent from this tank containing the partially oxidized sludge is recycled to the first aeration basin. Sludge not returned to the stabilization basin is wasted. The degree of organic removal obtainable with the contact stabilization process is less than that of the conventional and extended aeration processes. Tankage volume requirements are smaller, however. Primary sedimentation is not used with this process.

Prefabricated, "package" treatment facilities utilizing either the extended aeration or contact stabilization process are available from several equipment manufacturers in sizes up to 1.5 million gal. per day.

Oxidation Ditch. The oxidation ditch is basically an extended aeration modification of the activated sludge process, characterized by a design retention time of at least 24 hr. A schematic layout of the process is shown in Figure B-3.

The aeration basin consists of an earthen or paved oval-shaped ditch in the form of a racetrack. Oxygen is suppled by a so-called brush aerator which also circulates the mixed liquor.

Final settling and returning and wasting of sludge is similar to the extended aeration process. Where sufficient, suitable land is available, the oxidation ditch offers an economical method of treatment.

Aerated Lagoon. An aerated lagoon is a basin of significant depth (6 to 12 ft) in which oxygenation is accomplished by mechanical or diffused aeration units and by induced surface aeration. The turbulence level maintained in the basin ensures distribution of oxygen but is usually insufficient to maintain solids in suspension. As a result, most inorganic suspended solids and biological solids which are not oxidized settle to the bottom of the basin where they undergo anaerobic decomposition. Need for removal is usually infrequent (10 years or more). The basin can be modified to include a separate sedimentation compartment to yield a more highly clarified effluent.

Detention time provided in the lagoon is a function of the degree of organic removal required and the rate at which it may be biodegraded. Since the organic removal rate is dependent on the liquid temperature, winter conditions are used in sizing the basin. Detention periods of 10 days are not uncommon. Because of this, use of aerated lagoons is generally restricted to applications where land availability is not a problem.

Aeration devices may consist of either platform mounted or floating mechanical surface aerators or submerged porous pipes of diffusers supplied with compressed air.

Basins for aerated lagoons can be of almost any size, shape and material. Walls can be vertical or sloped, concrete, stone rip-rap, paving or earth. Where there is a potential for contaminating groundwater by seepage, the lagoon must be lined with a plastic film, asphalt, concrete or certain clays. A schematic layout of a typical aerated lagoon installation is given in Figure B-4.

Oxidation Pond. An oxidation pond or waste stabilization lagoon is a large shallow pond usually 2 to 4 ft deep in which wastewater is stored under climatic conditions, namely warmth and sunshine, that favor the growth of algae. Bacterial decomposition of waste matter releases carbon dioxide,

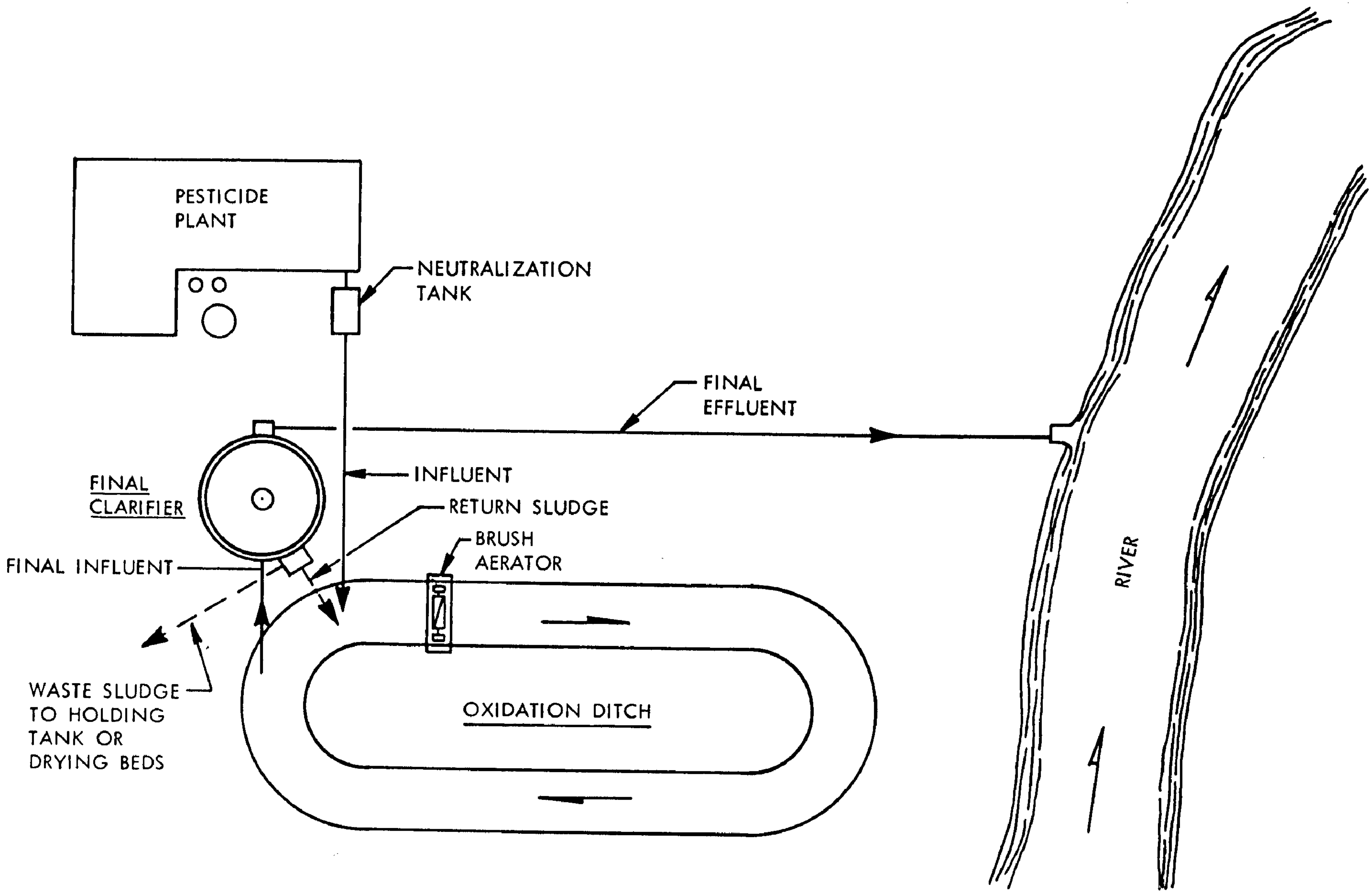


Figure B-3 - Wastewater Treatment by Oxidation Ditch

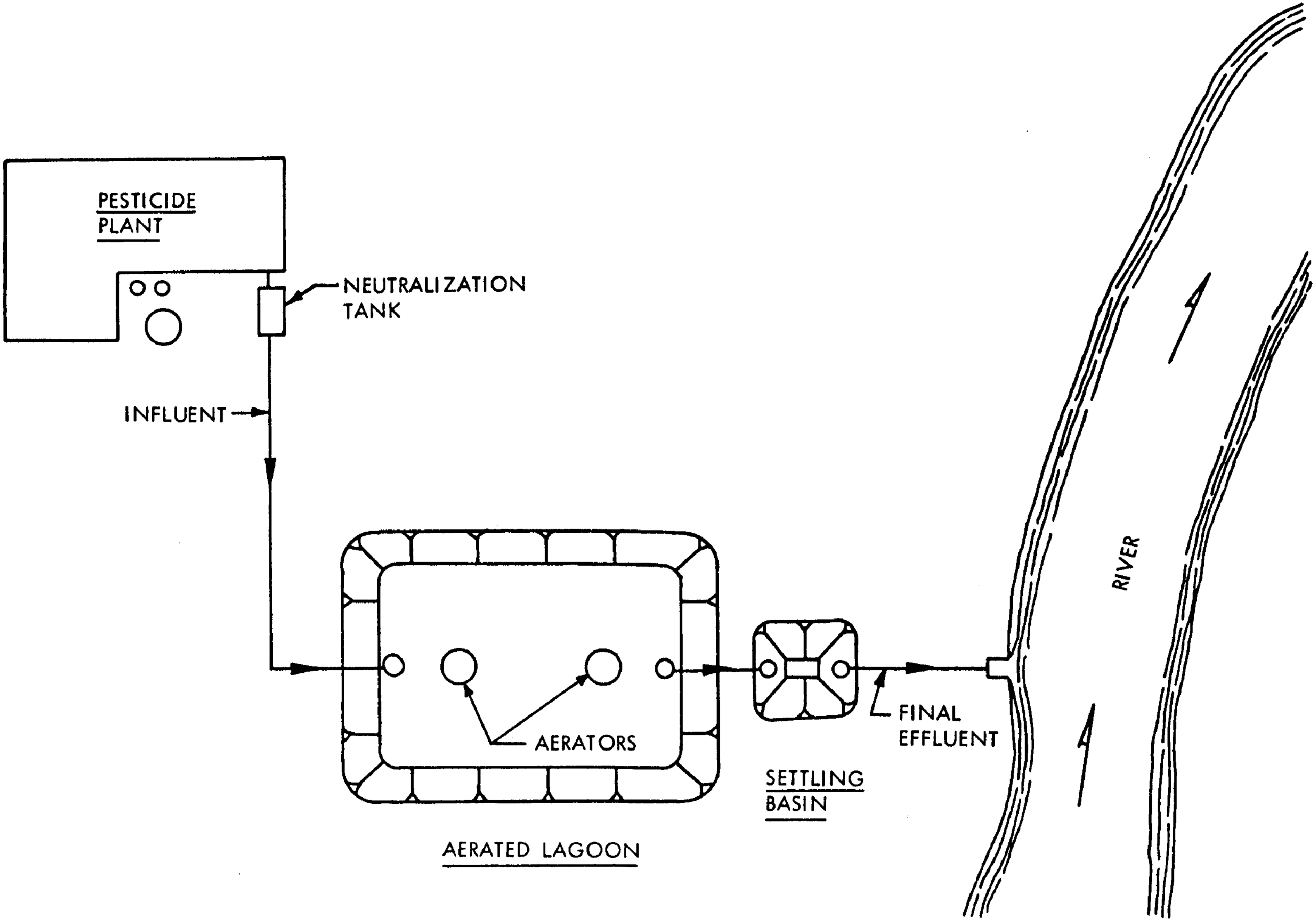


Figure B-4 - Wastewater Treatment by Aerated Lagoon and heavy growths of algae develop. By photosynthesis the algae use the carbon dioxide and inorganic minerals produced by the bacteria and convert them into new cell mass releasing oxygen in the process. Combined with the oxygen obtained by atmospheric reoxygenation induced by wind currents, the bacteria oxidize the organic matter. Organic matter which settles to the bottom of the pond (as in the aerated lagoon) is stabilized anaerobically. Ponds which combine aerobic and anaerobic stabilization are termed "facultative ponds."

Deep oxidation ponds (10 to 12 ft) stabilize waste primarily by anaerobisis. These ponds may be extremely odorous due to the gases created in the decomposition.

Since oxidation ponds rely on natural oxygenation and mixing, the organic loading which may be applied per unit of area is small. As a result, detention requirements and consequently land requirements are high. Ponds should have sufficient capacity to hold the maximum amount of rainfall as well as the maximum amount of wastewater. Evaporation and seepage must also be considered in determining the required pond capacity. Seepage may be controlled in a similar manner as for aerated lagoons.

Anaerobic Digestion. Anaerobic digestion is a commonly used method for disposal of concentrated organic solids removed from primary settling tanks and excess biological solids from trickling filters or the activated sludge process. Decomposition of the organic matter results from the activities of two major groups of bacteria. The first convert the organic matter to organic acids and the second convert the organic acids to methane and carbon dioxide gas. The kinetics of anaerobic decomposition are slow and as a result long detention periods are required to achieve a substantial reduction of organic matter. In order to shorten the detention period, the digester contents are often heated to increase biological activity.

Anaerobic digestion is usually performed in a circular tank with either a fixed or floating cover. Floating covers are used to store the gases produced which are combustible and may be used as a fuel for heating and mixing the digester contents. Mixing and recirculation of the contents are provided to evenly distribute the incoming raw sludge food for optimum contact with the microorganisms, to maintain consistency and to prevent buildup of scum and heavy bottom deposits. Drawoffs for removal of liquid supernatant, scum and stabilized sludge are provided.

In some cases, anaerobic digestion is performed in two tanks. The first is used for gasification and stabilization and the second for separation of the stabilized solids from the liquid.

Due to the long detention periods and large tankage volumes required, anaerobic digesters are generally sized to provide only an intermediate degree of stabilization of organic matter. The partially stabilized sludge may then be ultimately disposed of by drying on filter beds, dewatering by mechanical means for use as sanitary landfill or by incineration.

Ponding

A natural earthen depression or excavated pit can serve as a pond. The distinction between a "pond" and an "oxidation pond" is somewhat arbitrary, but refers to function or the processes that take place therein. No effort is made to exclude the entry of toxic materials into a pond, and the purification that results is due to chemical reactions, physical storage, and solar evaporation (provided there is a net loss of water; i.e., the total evaporation exceeds the total precipitation).

The capital costs for a pond are much less than those for accelerated biological treatment systems (trickling filters and aeration tanks), particularly if land prices are reasonable, and operating costs can be much less, too. Some disadvantages of ponds are:

- There is a potential for contaminating groundwater. This can be minimized by lining the bottom with plastic film, asphalt, certain clays, or concrete, but this adds to the first cost.

- There is a potential for producing undesirable odors. If biological conditions prevail, all the oxygen dissolved in the water may be utilized and hydrogen sulfide can result.

- There is a potential for chemicals in the pond to produce odors.

- Water-holding capacity. Ponds should have sufficient capacity to hold the maximum amount of rainfall as well as the maximum amount of waste chemical to be impounded. Evaporation, seepage, and annual rainfall, as well as the volume of waste to be handled, must be considered in determining the capacity of a pond.

Burial

Solids and trash may be disposed of by burial in an approved landfill, either in drums or packages, or in bulk, depending upon the material and the distance to a burial site. Sanitary landfill is the process of depositing refuse on the ground, usually in a depressed area, by compacting it thoroughly and covering it within 24 hr with approximately 24 in. of earth or equal material. This process "fills" the "land" and normally is "sanitary" from a public health point of view.

Land Availability. The availability of land which would benefit from a sanitary landfill operation is an important consideration. The materials should either be stable or of such nature that they become stable in the environment produced by burying. Unless the quantity of refuse to be disposed of is sufficient to fully utilize at least a single piece of digging, moving, and compacting equipment, the economics may be unfavorable.

Pollution Potential. A sanitary fill must not be used if there is any possibility of polluting either surface or groundwater supplies. Relatively insoluble substances can still dissolve or leach into groundwater and this fact must be given critical attention. Thorough compaction and proper surface drainage, however, minimize the possibilities of water leaching through the refuse.

Choosing Mechanics of Operation. After the limitations of a landfill have been considered and its feasibility seems attractive, the mechanics of operation demand attention. There are two general types--the trench method and the area method.

- The trench method. The trench method is used normally where the grade of the area to be filled is not exceptionally lower than adjacent land. Usually a bulldozer or front end digger is used to make trenches between 4 and 12 ft deep and 15 to 40 ft wide. The dirt removed from the trench is used as cover after the deposited refuse is thoroughly compacted. The same tractor compresses the refuse by riding back and forth over it after it is deposited.

- The area method. The area method of landfill is employed where land that is used is at an elevation considerably lower, over a fairly extensive area, than the surrounding land. Normal equipment is the back hoe, clam shell, or dragline bucket. This type of equipment can stand on solid high ground adjacent to the fill area and reach into the low area. Compaction is accomplished by dropping the bucket on the deposit.

Landfill Precautions. Other specifications and precautions, although important collectively, are minor compared to the one item upon which a successful operation is dependent; and that is, a sanitary landfill operation must be considered an engineering project. Careful planning must be followed by constant high-quality supervision.

Special Landfills. The use of a "specially designated landfill" is the procedure recommended by the Environmental Protection Agency for disposal of small quantities of certain classes of pesticides:2/

> "Specially designated landfill" means a landfill at which complete long term protection is provided for the quality of surface and

subsurface waters from pesticides, pesticide containers, and pesticide-related wastes deposited therein, and against hazard to public health and the environment. Such sites should be located and engineered to avoid direct hydraulic continuity with surface and subsurface waters, and any leachate or subsurface flow into the disposal area should be contained within the site unless treatment is provided. Monitoring wells should be established and a sampling and analysis program conducted. The location of the disposal site should be permanently recorded in the appropriate local office of legal jurisdiction. Such facility complies with the Agency Guidelines for the Land Disposal of Solid Wastes as prescribed in 40 CFR Part 241.

Burial should not be used for the disposal of wastes unless:

- The landfill operation will not pollute either surface or subsurface water supply because of the location chosen.

- The nature of the material to be disposed of is such that disposal by this method is economical, environmentally acceptable, and does not lead to loss of materials which should be salvaged.

- The chemical and physical properties of the bulk of the waste to be disposed of are of such a nature that they can be safely compressed.

- A sufficient quantity of the waste to be disposed of exists so that a landfill operation of sufficient size to achieve economy can be made.

- An adequate amount of suitable land for the operation is available.

- The ultimate use of the land used for the fill will benefit from the fill operation.

Burial is, or can be, a relatively economical method for disposing of many types of industrial waste and trash in a sanitary nonnuisance manner wherein both public and employee relations are improved. In some cases, reclaiming of submarginal land results.

Incineration

Incinerators have been used for many years for the disposal of municipal refuse and garbage, and recently a number have been built specifically to handle chemical wastes efficiently and safely. In the simplest concept incineration amounts to burning a substance to yield the harmless gases, carbon dioxide and water vapor, together with more or lesser amounts of residual ash. The application of this operation to the disposal of pesticides, however, is subject to complicating factors.

For complete destruction of these materials, combustion must be conducted at about 1800°F with a residence time of one to several seconds at this temperature. The vapors generated can be toxic if the combustion is incomplete and, perhaps more often than not, they include acid constituents. With some pesticides the residual ash presents yet another disposal problem.

A schematic diagram of one facility capable of incinerating pesticide wastes is shown in Figure B-5. The major considerations involved in the design of such a facility are discussed in the following section.

Character and Quantity of Wastes. Materials exhibiting pesticidal properties number in the hundreds, and formulations containing one or more of these materials number in the thousands. Pesticidal chemicals may be classified in major groupings as inorganic, organic, and botanicals or "natural" organic materials. The inorganic group includes sulfur and phosphorus compounds, borates and chlorates, arsenicals, mercurials and other heavy metal derivatives. The botanicals include materials such as rotenone and pyrethrum. The organic group of materials also includes salts and metal derivatives as well as many compounds containing one or more of the following elements: sulfur, phosphorus, nitrogen, chlorine, bromine and fluorine. Frequently encountered materials in the latter category include:

2,4-D (isooctyl ester of 2,4 dichlorophenoxyacetic acid)

Picloram (potassium salt of 4-amino-3,5,6-trichloropicolinic acid)

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine)

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea]

Trifluralin (α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine)

Bromacil (5-bromo-3-sec-butyl-6-methyluracil)

DSMA (disodium methanearsonate)

DNBP (alkanolamine salt of 4,6-dinitro-o-sec-butyl-phenol)

Dicamba (2-methoxy-3,6-dichlorobenzoic acid)

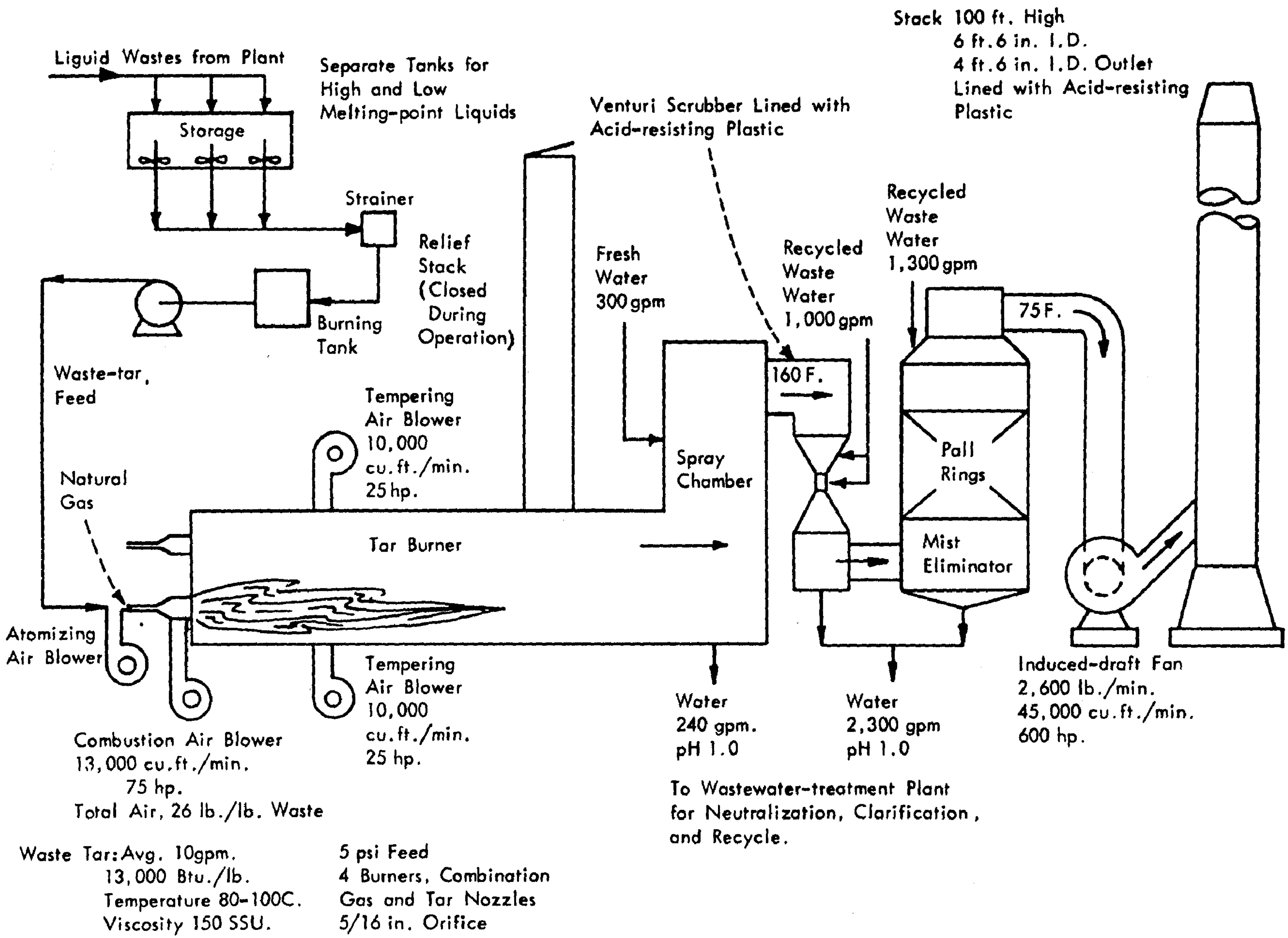


Figure B-5 - Waste-Tar Burner

Dalapon (sodium salt of 2,2-dichloropropionic acid)

Paraquat (1,1-dimethyl-4,4-bipyridylium salt)

Vernolate (s-propyl dipropylthiocarbamate)

2,4,5-T (trichlorophenoxyacetic acid)

Carbaryl (1-napthyl N-methyl carbamate)

DDT (dichlorodiphenyl trichloroethane)

Dieldrin (hexachloroepoxyoctahydro-endo, exo-dimethanonaphthalene)

Malathion (0,0-dimethyl dithiophosphate of diethyl mercaptosuccinate)

PMA (phenyl mercuric acetate)

Zineb (zinc ethylenebisdithiocarbamate)

Nemagon (1,2-dibromo-3-chloropropane)

Considering that pesticide waste disposal problems will be met by the applicator, distributor, formulator, and manufacturer, it is obvious that requirements and quantity aspects will cover a very broad spectrum. The problems can range from the disposal of empty containers and the disposition of material from minor spills and broken containers all the way to containment and destruction of highly toxic vapors and wastes from manufacturing operations, which can involve tonnage operations.

Collection and Identification of Waste Materials. Wastes should be collected in suitable containers, properly labeled for transfer to incineration, unless of course, the incinerator is an integral part of a manufacturing or formulating operation. Depending upon quantity, containers should preferably be metal pails, drums or tanks, or in some instances, fiber packs if the wastes are dry solids. Identification should include trade name, type of material, active concentration, weight. If the wastes are solids, the unit quantity will need to be compatible with the incineration facility. If the wastes are liquid and represent a continuing and sizable consideration, receiving tanks at the incineration site will be necessary for proper segregation and blending.

Selection of Incineration Facilities. With few exceptions, facilities required for the proper incineration of pesticides cannot be justified for small-scale operations. The applicator, distributor, and many formulators will find it expedient to contract for the services of a municipal or commercial incinerator equipped to meet all governmental regulations.

For the incineration of flammable liquid wastes in those cases where a gas scrubber is not required it may be quite satisfactory to mount an oil burner and refractory burner block (such as supplied by National Aeroil Burner Company) on a pedestal in the open with or without a pile of rubble as a "target." Conventional vertical refractory lined incinerator units capable of handling liquids having a high water content and operating at rates up to several thousands of pounds per hour are supplied among others by Thermal Research and Engineering Corporation, John Zink Company, Prenco Division, Pickards Mather and Company, and Surface Combustion Division, Midland-Ross Corporation.

Present practice in the combustion of solid wastes employs multiple-chamber incinerators wherein the combustion proceeds in two stages. The primary or solid phase combustion occurs in an ignition chamber which is followed by a secondary or gaseous phase occurring in a secondary combustion zone. Heat release is ordinarily in the range of 25,000 to 50,000 Btu per hour per cubic foot of combustion volume. The Bigelow/Phillips Incinerator represents a large-scale application of this configuration. The "Cleanaire Radicator" furnished as a package unit by the Midland-Ross Corporation has a capacity of several hundred pounds per hour and with adaptation for vapor scrubbing might be suitable for pesticide formulation or small-scale manufacture.

For large-scale operation a rotary kiln incinerator has certain advantages, among which is the ability to handle a large variety of feed including packs and drums of solid waste chemicals. The Dow Chemical Company operates an incinerator of this type and a Dow subsidiary has designed a similar installation for another company.

A further type of incinerator coming into prominence is the fluid bed unit which has special application when an inorganic residue such as sodium sulfate or sodium chloride will be produced. Dorr-Oliver and Copeland Systems, Battelle Memorial Institute, the Dow Chemical Company, and others, have been active in this field.

Fumes and air-dispersed mists can be incinerated in equipment similar to that used for liquids. The concentration of combustible contaminants will usually be well below the lower limit of flammability, but it may be possible to pass the entire stream through a burner after adding a small amount of natural gas as auxiliary fuel and adjusting the air to effect complete combustion. Fuel oil can, of course, be accommodated as supplementary fuel in fume incinerators as well as in any other type.

The two most critical factors in incineration are temperature control and retention time. The incinerator must be capable of maintaining a set temperature with minimal fluctuation. Retention time is fixed by operating parameters such as amount of excess air and by the volume of the combustion chambers which should be large enough to provide several seconds residence for the gaseous products of combustion. The temperatures required for the complete destruction of most pesticides will be about 1800°F. An extensive study in this regard has been reported by M. V. Kennedy, et al.,[3/] as a contribution from the Mississippi Agricultural Experimental Station under a grant from the U. S. Department of Agriculture.

Conventional fuel oil burners are used for burning waste liquids. All the air necessary for combustion can be supplied as primary air, or primary air may be used to control flame character while secondary air is introduced through openings in the burner block to provide additional requirements for complete combustion. To achieve proper burning, the waste liquid, or supplemental fuel when required, must be finely atomized. High-pressure air atomization, low-pressure air atomization, steam atomization and mechanical atomization have all been used satisfactorily.

Temperatures in the separate combustion zones are controlled by strategically located thermocouples which cause fuel (or waste) and air flows to respond to the temperature settings. Draft gauges, flowmeters, and stack gas analyzers are most useful in properly controlling incinerator operation. Ignition and flame detection systems operating in conjunction with purge arrangements and other safety features and interlocks are necessary accessories which should be provided in a manner to meet Factory Insurance Association requirements.

Liquid wastes are strained, segregated and blended as necessary and are preheated if required for proper atomization in an oil type burner. The feed pump should be a positive displacement type such as a vane, gear or screw pump and it should be equipped with a variable speed drive actuated by furnace temperature control. When handling solids, it is likely that provisions would be made for directly injecting pails and drum quantities of solid wastes into the incinerator. Typically, refuse other than full drum or pails would be dumped into a refuse pit from which an overhead hoist would transfer the material to a charging hopper.

The disposal of halogen-bearing pesticides and solvents presents complications of no small matter. These materials release the corresponding acid vapors when burned, thus precluding the use of simple pits or furnaces.

The incinerator stack gas must be scrubbed with water or an alkaline medium, and the scrubber effluent should be sent to a wastewater treatment plant employing secondary treatment. If the wastes contain sodium salts, a simple packed tower will probably be inadequate and a high-energy Venturi type scrubber may be required. Under any circumstances, appropriate governmental approval must be obtained for release of gases to the atmosphere or discharge of liquids to municipal sewers or to other waterways. Figure B-5 shows schematically a system (now in use) which was worked out jointly by Bigelow Liptak and the Dow Chemical Company for the disposal of chlorinated wastes.

Operating Considerations. In addition to mechanical safety features for the physical plant, other considerations require attention to assure the safety of the operator, the public and environment. These may range from container and ash disposal to material properties such as thermal stability, shock sensitivity, flash point, flammable limits, auto ignition and toxicity.

Operating records, such as temperature charts, wind direction and velocity data, character and quantity of material handled, etc., should be retained. Composite samples of ash and scrubber water should be collected and analyzed from time to time and the stack gas should be monitored for composition and particulate content.

High temperature operation will require frequent inspection and routine maintenance. Accurate operating and maintenance records are obviously important. Burners firing liquid waste and heavy fuel are subject to deposits in the burner nozzle and may require cleaning daily. Shutdown and safety systems should be tested at scheduled intervals in accordance with written procedures.

Contract Services

Private processors of industrial waste frequently operate in communities of moderate to large size for the convenience of plants not large enough to warrant in-plant disposal service. Municipal collection agencies also exist, and depending upon the nature of the waste, as well as upon relative economics, a choice can be made between municipal or a private service.

However, it must be emphasized that getting some organization to "cart the waste away" does not always solve the problem. From a legal standpoint, should an adverse event occur as a consequence of improper handling or disposal, the company as well as the contractor can be liable. If there are details or handling precautions that a prudent knowledgeable industrialist would consider, it is incumbent upon him to communicate these to the contractor; or the contractor's inadvertent mishandling may come back to haunt the company.

Information on the availability of these facilities in your area can be obtained from the U. S. Government Environmental Protection Agency. Addresses and telephone numbers of Regional EPA offices are listed below.

Region	Address
I	Environmental Protection Agency John F. Kennedy Federal Building, Room 2304 Boston, Massachusetts 02203 617-223-7210 (Maine, New Hampshire, Vermont, Massachusetts, Rhode Island, Connecticut)
II	Environmental Protection Agency 26 Federal Plaza New York, New York 10017 212-264-8958 (New York, New Jersey, Puerto Rico, Virgin Islands)
III	Environmental Protection Agency 6th and Walnut Philadelphia, Pennsylvania 19106 215-597-9875 (Pennsylvania, West Virginia, Maryland, Delaware, District of Columbia, Virginia)
IV	Environmental Protection Agency Suite 300 1421 Peachtree Street, N.E. Atlanta, Georgia 30309 404-526-3454 (North Carolina, South Carolina, Kentucky, Tennessee, Georgia, Alabama, Mississippi, Florida)
V	Environmental Protection Agency 1 North Wacker Drive Chicago, Illinois 60606 312-353-5756 (Michigan, Wisconsin, Minnesota, Illinois, Indiana, Ohio)

Region	Address
VI	Environmental Protection Agency 1600 Patterson Street Suite 1100 Dallas, Texas 75201 214-749-1461 (Texas, Oklahoma, Arkansas, Louisiana, New Mexico)
VII	Environmental Protection Agency 1735 Baltimore Avenue Kansas City, Missouri 64108 816-374-3036 (Kansas, Nebraska, Iowa, Missouri)
VIII	Environmental Protection Agency 1860 Lincoln Street Denver, Colorado 80203 303-837-3849 (Colorado, Montana, Wyoming, Utah, North Dakota, South Dakota)
IX	Environmental Protection Agency 100 California Street San Francisco, California 94111 415-556-0218 (California, Nevada, Arizona, Hawaii)
X	Environmental Protection Agency 1200 6th Avenue Seattle, Washington 98101 206-442-1296 (Washington, Oregon, Idaho, Alaska)

Chemical Methods

Chemical means of waste treatment prior to the ultimate disposal of particulate waste are varied. Some convenient categories of treatment applicable to pesticide wastes are:

Ion Removal by Chemical Precipitation. Dissolved substances that combine to form a compound having low solubility may be readily removed by filtration or settling of the precipitate.

Ion Exchange. Toxic, deleterious, or valuable dissolved substances may be concentrated for ultimate disposal or reuse by removal from solution onto an ion exchange resin.

Coagulation. Coagulation is a process in which chemicals are added to an aqueous system for the purpose of creating rapid-settling aggregates out of finely divided, dispersed matter with slow or negligible settling velocities. The specific coagulant and technology used vary with the waste, but common coagulates include lime, alum, ferric chloride, ferrous sulfate, and the newer synthetic organic coagulants known as cationic polyelectrolytes. As an example, trace amounts of DDT have been removed from water supplies by this method.

Oxidation. Chemicals that react with organic impurities and have found application in treatment of aqueous wastes include: hydrogen peroxide, potassium permanganate, ozone, oxygen, chlorine, and chlorine dioxide.

Alkaline or Acid Destruction. Certain chemicals may be decomposed by being subjected to acidic or alkaline conditions; e.g., some chlorinated hydrocarbons are decomposed under acidic conditions, others under alkaline conditions; trace amounts of phosphate insecticides have been destroyed by alkaline hydrolysis.

Adsorption. To be precise, adsorption is a physical-chemical phenomenon, but its potentially wide application in water and waste treatment warrants its inclusion. By definition, adsorption is the concentration and collection of contaminants at the surface of a solid. The most efficient adsorbent is activated carbon, but coal has been used. Adsorption can take place in fixed beds under pressure provided with regeneration facilities. An efficient adsorption process has been installed by a herbicide manufacturer producing 2,4-D acid, MCPA acid, 2,4-DB acid and their esters. Phenolics were removed from a waste stream by passing through two fixed bed adsorbers containing granular activated carbon. Carbon is regenerated in a furnace. The treated effluent from this system consistently contains less than 1.0 mg/liter phenolics and is compatible with a municipal sewage system.

Municipal Treatment

When a plant has access or connection to a sanitary or industrial sewer, it may be possible to contract for treatment and disposal with a municipality. In such a case, a company can devote all its efforts to production and allow a municipality to handle the treatment and disposal. In no event, however, should the plant consider itself relieved of responsibility by such an arrangement. It should be recognized that this would be another form of contract services which has been discussed previously. Specifications contained in local sewer ordinances or in specific contractual arrangements must be adhered to. Where the concentration of specific substances exceeds the allowable, pretreatment measures will have to be taken within the plant property. Reduction in strength of waste may be achieved by:

- Process changes.
- Equipment modifications.
- Segregation of strength waste.
- Equalization and proportionation of waste.
- By-product recovery.
- pH control through neutralization.
- Collection of floating or settleable matter by passage through: manually cleaned baffled traps, detention and settling; tanks with endless chain scrapers; manual or mechanical screens; filters; and other "packaged plants" or facilities available from engineered equipment manufacturers in the liquid conditioning field.

The cost of this type of waste treatment and disposal is dependent on the municipality and the characteristics of the waste. In many cases, it may be the most economical means of treatment because of economics of size, lower cost, labor and the benefits of low municipal bond rates of interest. It is most important that the specifications for the waste discharged into the municipal system not be exceeded because of the danger of bad public relations.

Deep Well Injection

This method is usefully applied in those areas where the subsurface geology is favorable. Basically, it requires the injection of clarified fluids into formations containing noncommercial and compatible saline waters. The wells and surface equipment are designed for the particular problem and the installation should be made, or at least supervised, by firms or individuals known to be technically experienced and competent in the field. The plant management, prior to approaching the regulatory agency, should have had a feasibility study performed. The report should include a description of the subsurface geology, an estimate of the expected hydrologic performance during injection, a definition of the chemical and physical properties of the waste in question, a detailed description of the well to be installed and a summary of the surface equipment to be used. The feasibility report should also contain cost estimates, including the costs of operation.

Depths of industrial disposal wells have varied from 1,000 ft to over 12,000 ft. It generally is not considered good practice to install a well less than 2,000 ft deep; the most frequent depth is from 3,000 to 6,000 ft. Volumes injected vary from 10 gpm to over 1,000 gpm. In some parts of the United States, capacities may approach or exceed 5,000 gpm. Volumes injected most frequently range from 30 gpm to 200 gpm.

Particular care must be exercised in designing and operating the system so that natural resources can be properly protected from damage or contamination. Once the system is placed in service it should be operated and controlled with the care and attention to detail required by other industrial installations and not relegated to some unsupervised or poorly regulated status that will result in operating failures.

DISPOSAL OF SPECIFIC CLASSES OF PESTICIDES

The applicability of a given waste treatment technique to a specific waste stream is determined by a number of factors, the most important of which is the pesticidal chemical involved. The following section contains a brief discussion of the applicability of specific treatment methods to individual families of pesticides. Representative classes have been selected for discussion. The omission of certain pesticide families from this discussion, therefore, should not be interpreted as indicating that these pesticides present no waste disposal problem, or that the treatment techniques discussed would not be applicable to their treatment.

Chlorinated Hydrocarbons

Waste materials from plants manufacturing or formulating chlorinated hydrocarbon pesticides may be in several forms:

- Solids (technical materials, wettable powders, dust concentrates, and granules).

- Liquids (technical materials, oil solutions, and emulsible concentrates).

- Gaseous (true vapors, or aerosols).

It is suggested that the disposal systems described in the preceding sections of this manual be reviewed and considered for applicability in a particular chlorinated hydrocarbon pesticide plant situation.

Waste materials must not be flushed down sanitary sewers. Most of the chlorinated hydrocarbon pesticides pass through normal sewage treatment plants unchanged and may enter public water supplies.

Incineration. Incineration is undoubtedly the most positive system for the disposal of chlorinated hydrocarbon pesticides in a solid, liquid, or gaseous state. A variety of systems, all of which are somewhat expensive to construct, maintain, and operate, have been developed for incineration of wastes. Most commonly, the resulting hydrogen chloride gas is reacted with an alkali to form a salt. Under certain circumstances, however, it may be desirable to recover the hydrogen chloride as an aqueous solution for other uses.[4,5]

Biological Treatment. A search of the literature has revealed that little published work on this technique is available at this time. Discussions with several of the major manufacturers of chlorinated hydrocarbon pesticide indicate that research is now in progress to develop commercial biological treatment techniques. They agree that the technique has promise for a specific product, but has little likelihood of success on mixtures such as the wastes from a formulating plant handling a variety of pesticides.[7/]

Organic Phosphates

The physiological action of toxic organic phosphates is due to their ability to combine rapidly and in very small concentrations with cholinesterase in the central nervous system. This anticholinesterase material permits the acetylcholine to continue its stimulating effects which immediately cause an interference in the muscular system and possible complete paralysis is the result. Acute poisoning from these toxic organic phosphate compounds can result from absorption of the material through the skin, from inhalation of its vapor or dust, or from swallowing the material. Prompt first-aid and medical treatment is essential in all cases of organophosphorus poisoning.

The handling and disposal of waste organic phosphates is a specialized field. These and other related waste materials may be safely disposed of by proper selection and utilization of a combination of the normal waste disposal methods of hydrolysis and filtration, incineration, burying, deep sea dumping, and deep well disposal.

The best overall prescription for waste disposal is the philosophy and simple economics of waste control--the smaller the quantities to be disposed of, the easier and less expensive the solution to the problem.

Hydrolysis and Filtration. Many organic phosphate compounds can be hydrolyzed and, in general, the rate of hydrolysis is dependent upon the pH and temperature of the aqueous solution. Liquid wastes containing toxic organic phosphorus compounds are normally collected, adjusted to the desired pH by the addition of an alkaline agent, then passed through a hot water heater. The neutralized waste effluent should then be collected in a large surge tank, analyzed for toxicants, and the detoxified waste pumped into the wastewater of the sanitary sewage disposal system. This type of detoxified waste material should remain as a separate entity and not be passed through the sanitary waste system if any adverse reaction will occur with the dissolved chemicals and the clarifier-digester of the typical sewage disposal system. Formulators should check with their suppliers as to whether any problems may be involved.

An effective control practice is to maintain a recording pH meter and a flowmeter on the waste effluent line just before the effluent leaves the control of the industrial facility. Minute particles of suspended solids in the waste effluent can be removed by passing the neutralized waste through a filter.

Incineration. This procedure can be safely used to destroy organic phosphate waste materials. Sufficient heat (1800°F) must be generated during the incineration to destroy the pesticide, as well as the container, diluents, and solvents. Proper safety precautions must be taken as to distance from habitation, trees, and other living things.

Burying. In some instances, burying organic phosphate waste material can be considered a satisfactory procedure for disposing of contaminated waste but there are so many external factors to be considered that this procedure should only be used as a last resort. Location of the pit, types of soil, land drainage, predominant wind direction, water sources, and possible future use of the land are among the many factors that must be considered. In any event, detailed records of the actual location of the "burial ground" must be maintained (see "Burial," p. 110).

Deep Well Disposal. Deep well disposal can be applied to organic phosphate wastes.

Spills and Broken Containers. When a leaking, sifting, or damaged container is discovered, isolate the area and use the following precautions:

- Safety equipment for personnel. Equip the man who will process package with a Pulmosan C-241 respirator with type GMP cartridge or equivalent, heavy gauntlet neoprene or rubber gloves, and washable clothing, also rubber boots if necessary. The man should not carry cigarettes, chewing gum, etc., in the pockets of his clothes. Tell him that he will be safe if he avoids all skin contact and washes well after the operation. All precautionary statements on the label should be carefully read and observed.

- Small bag removal. Standing to windward, the operator should remove undamaged bags from carton, wipe bags with barely damp cloth (to be burned later) moistened with a strong soda ash solution and transfer to new carton. Broken bags and original carton are to be held for reworking or disposal in a sealed metal drum, properly labeled and with a poison label.

- Fiber drums. Remove to suitable hood with exhaust ventilation or to remote open area. Standing to windward, slowly transfer powder, creating a minimum of dust, to new drum and re-label. Burn old drum (avoid fumes) or bury if burning is not permitted.

- Metal containers. Alter position of container to place leak flow on top. (Avoid skin contact!) Remove to suitable hood with exhaust ventilation or to remote open area. (a) If feasible, transfer contents to new drum via bung fittings. (b) If existing bungs cannot be used, equip a new drum with a large funnel. Position leaking drum over funnel so that it leaks into it.

Spills can be decontaminated by the following procedure: Fill old drum with caustic soda solution; discharge on ground in burial area and cover with dirt. Rinse drum and decontaminate or discard in a safe manner. (See NACA "Manual for Decontamination and Disposal of Empty Pesticide Containers."[7/])

• Spilled dusts and powders. Cover dust or powder spills with double its volume of damp (not wet) hydrated lime, clay, or sawdust. Gather carefully with old broom. Sweep into a disposable container. Burn or bury broom and container.

• Liquid spills. Cover liquid spills with an inert absorptive substance such as hydrated lime, sawdust, clay, or fuller's earth. After the liquid has been absorbed into the drying material, carefully gather with old broom. Sweep into disposable container. Burn or bury container and broom.

• Follow-up treatment for area. Revisit spill area and either, (a) sprinkle with hydrated lime or soda ash (1 handful per square foot), dampen slightly with hose or sprinkling can, rope off area, allow to remain overnight, flush away in morning. If yellow coloration appears, repeat until color does not appear, or (b) cover the contaminated surface with undiluted household bleach, scrub the area with long-handle scrub brushes for at least 25 min. (Avoid breathing vapors from this process.) Take up the scrubbing liquid with absorbent clay or similar material. Repeat the whole process, allow treated area to dry. Dispose of the contaminated absorbent in a safe manner.

• Follow-up by personnel. It is imperative to take a bath after these operations. Launder clothes before reuse. Read label carefully for first-aid instructions.

General Considerations. Any reaction muds or waste process materials which cannot be reused should be removed from manufacturing or storage vessels and transferred to drums which are removed for incineration or burial in an approved, supervised area.

In the manufacturing area for pesticide products, drains should be eliminated to avoid any washing of spills to the main plant sewers. Material should be picked up manually or by vacuum and either returned to process area for rework or transferred to the dump where it is incinerated or buried.

Dust collecting facilities should be provided on all major process equipment, and, in addition, high velocity suction points should be provided at all critical areas on the packaging lines.

Carbamate Pesticides

The major carbamate pesticides in use today include the insecticide carbaryl (SEVIN®) and the herbicides IPC and chloro-IPC (isopropyl-N-phenylcarbamate and chloroisopropyl-N-phenylcarbamate).

Characteristics of Carbaryl. Principal characteristics of carbaryl of interest in waste disposal are the following:

- Low toxicity to warm-blooded animals, fish, fowl, wildlife.

- Decomposes relatively quickly in soil.

- Under alkaline conditions it breaks down fairly rapidly.

- It is insoluble in water (less than 0.1%) and only moderately soluble in organic liquids (toluene--5%, acetone--20%, deodorized kerosene--5%).

- Carbaryl will burn fairly readily. (CAUTION: Carbaryl dusts are explosive!)

- Dilute suspensions of carbaryl are amenable to treatment by biological disposal systems. Standard tests have shown that carbaryl exerts a 5-day biochemical oxygen demand (BOD_5) of about 0.2 lb of oxygen per pound of carbaryl. This value increases to about 0.6 lb per pound after acclimation of the seed bacteria. No gross bacterial toxicity was noted up to a concentration of 100 mg/liter. Suspensions containing up to 100 mg/liter per liter of carbaryl which were fed to laboratory activated sludge units were oxidized quite efficiently after acclimation of the bacteria. No adverse effects on the biological populations were noted. Similar results were obtained in a simulated sewage oxidation pond although carbaryl rates were generally somewhat lower.

The carbamates listed are subject to alkali hydrolysis and can be decomposed by the addition of strong alkali. Adequate mixing with the alkali is necessary. A stirred vessel should be used. Reaction products from this step should then be routed to the sewage treatment facility.

For disposing of small volumes of carbaryl suspended in water, caustic treatment in a settling tank may be sufficient. For each 5 lb of carbaryl carried into the tank, addition of 2 lb of flake caustic will provide a

50% excess of the minimum required to react with the carbaryl. Reaction time will vary depending upon dilution and temperature but 24-hr treatment time should insure completeness of reaction.

Where continuous treatment of wastes with this technique is necessary, a pair of settling tanks would be required in order to permit holding of wastes for the needed treating time period. Size of the tank, of course, would be dictated by the volume of water expected to accumulate in each 24-hr period.

Where water used in flushing floors or equipment needs to be disposed of only occasionally, it may be simplest to drain this to an outside holding pit for caustic treatment as described above before it is permitted to drain from the plant area.

Solid wastes, which cannot be easily treated by reaction in water with caustic or biologically oxidized, should be buried through landfill techniques. Lime should be dumped or mixed with the carbaryl waste in ratio of one part lime to five parts of waste.

The landfill should be located above grade and so situated that leaching of buried wastes and their being carried away by surface runoff water is not possible.

Where fires in open fields are permissible, this allows convenient disposal of empty bags from carbaryl technical. Under some combustion conditions, carbaryl burning can produce methyl isocyanate which is a toxic material.

Exposure to smoke and gases from the burning bags should be avoided.

Normally designed incinerators will permit achieving of higher temperatures (1800°F) at which carbaryl is more completely oxidized to harmless products.

Air pollution aspects need to be kept in mind. In most areas, particularly those more heavily populated, open burning is forbidden by law.

Where burning or controlled combustion cannot be safely accomplished and where air pollution is a factor, then burial of empty bags as described above is the preferred disposal technique.

IPC and Chloro-IPC Treatment. The chemical treatment for IPC and CIPC (isopropyl-N-phenylcarbamate and chloro-isopropyl-N-phenylcarbamate) wastes as well as suggestions for incineration and burial are the same as for carbaryl.

Dithiocarbamate Pesticides

Formulators handling dithiocarbamates should give serious consideration to waste handling and disposal. In many areas, local governments have specified the procedures that must be used for disposal of liquid and solid wastes. In these areas the prescribed method is then the minimum level of care that must be taken.

We believe the following control on wastes should be considered the minimum in cases where there is no municipal control or where the specified control is less than that now outlined.

Handling of Solids. Empty fiber containers, drum liners, paper bags, dust bags, or other combustible refuse contaminated with dithiocarbamate should be collected in a metal container, provided with a lid, and then sent to a municipal incinerator or burned in a private incinerator under strict control to meet all local ordinances. (Sulfur dioxide is one of the products of dithiocarbamate combustion.)

Metal or other nonburnable containers that are to be discarded due to damage or because salvage would be too costly should be disposed of in a sanitary landfill operation, or if sold to scrap dealers, should be steam cleaned and washed before leaving the premises.

Metal containers that are to be reused can be safely used for nonfood products if they are reconditioned by a "Drum Reconditioner" who processes them by the standard treatment at drum reconditioning plants. (See NACA "Manual for Decontamination and Disposal of Empty Pesticide Containers"[7/] for full recommendations concerning drum decontamination and reconditioning.)

Solid dithiocarbamate recovered from dust collectors, vacuum cleaners, floor-sweepings, equipment cleanout, etc., should be packaged in steel drums and then disposed of in a sanitary landfill where a trench is made, the drums dropped in and the trench backfilled with earth. These operations are usually under municipal control and are in locations where ground percolation will not contaminate the local water supply.

Handling of Liquids. The sewer lines in buildings handling dithiocarbamates should run into a settling basin where solids can settle out and be removed for disposal as outlined above. Soluble dithiocarbamates can be precipitated by the addition of zinc salts in slight excess if it becomes necessary to remove dithiocarbamates to satisfy the requirements of a sewage treatment plant. The clear effluent can then be treated in a municipal sewage disposal plant if the local authorities will accept it. The dilution accomplished by blending this waste into the total waste stream going to the sewage disposal plant dilutes it to an acceptable level.

Botanicals

Botanicals such as rotenone, pyrethrum, sabadilla, and ryania, as well as synergists useful with botanicals, must be considered as having potential for causing injury to fish, if allowed to enter streams, lakes, or groundwaters. The many formulations of botanicals include dusts, oil solutions, emulsifiable concentrates, and liquids in pressurized containers (aerosols).

Again, it must be recognized that the first step to safe disposal of these materials is to reduce to an absolute minimum the amount of such wastes to be disposed of by utilizing the best manufacturing, formulating, and housekeeping methods.

Wastes of a botanical nature can then be handled as follows:

Burial. Burial of solid botanical formulations can be accomplished in those locations where the burial site is free from groundwater movement. This is particularly important in view of the fish toxicity of rotenone and other botanicals. Local authorities should be consulted in making a choice of burial site.

Liquid botanical wastes can be buried if first absorbed on a suitable diluent. Diatomaceous earth, fuller's earth, and other highly absorptive diluents are examples of materials upon which liquid wastes can be absorbed before burial.

Incineration or Burning. Both liquid and solid wastes containing botanicals can be safely destroyed by incineration in a suitable unit. Open burning of botanicals is not recommended, largely because of the poor combustion occurring near the soil surface. Thus, seemingly destroyed material can remain behind to cause subsequent pollution due to movement by wind or rain. Also, many of the solid wastes consist of the botanical on a noncombustible carrier and open burning cannot be depended upon to heat the mass to the decomposition point.

Liquid formulations of botanicals are even more amenable to incineration in a well-designed burner due to the usual presence of solvents in the formulation and these help support combustion.

Municipal Sewage Treatment. A small, regulated flow of botanical wastes can be accommodated by municipal sewage treatment plants using secondary treatment consisting of either trickling filters or activated sludge. Permission must first be obtained from local authorities to permit this approach and a means of controlling the amount to be discharged must be incorporated in the discharge system.

Phenoxy Acids, Salts, and Esters

The manufacture of phenoxy herbicides and their formulations presents potential water pollution problems.

Formulation of phenoxy herbicides starting with the active acids or esters and addition of amines and water, or oils and emulsifiers, respectively, generate very little waste as such, if due consideration is given to design, operation and control of inadvertent spills by use of dikes and collecting pits. Good initial drainage and rinsing with diluent used in the formulation so that the rinse can be used in future runs, along with efficient final washing and rinsing would result in minimal volume of low concentration of wastes to dispose of by methods to be described.

2,4-D and 2,4,5-T. These phenoxy herbicides are not widely used in the free acid or sodium salt form because of low solubility and limited herbicidal activity. User perference and need are usually better met through enhanced herbicidal activity, which results when the parent compound is altered to the ester, an oil-soluble form, or to the amine salt, a water-soluble form. The most common forms of 2,4-D and 2,4,5-T are shown in Table B-2.

TABLE B-2

COMMON ESTER AND AMINE FORMS OF PHENOXY HERBICIDES[8/]

2,4-D (2,4-Dichlorophenoxyacetic Acid)		2,4,5-T (2,4,5-Trichlorophenoxyacetic Acid)	
Esters	Amines	Esters	Amines
Isopropyl	Ethanol amines	Glycol ethers	Triethyl
Butyl	Mixed alkanol amines		
Iso-octyl	Dimethyl amine		
Glucol ethers	Triethyl amine		

Other Phenoxy Herbicides. Other phenoxy herbicides include MCPA (2-methyl-4-chlorophenoxyacetic acid), sesone, silvex, 2,4-DB [4-(2,4-dichlorophenoxy) butyric acid], and erbon.

The amine salt formulations are generally 4 lb acid equivalent per gallon of the amine salt dissolved in water. Small amounts of sequestering agent are added to the formulation to prevent precipitation of calcium and magnesium salts in the sprayer. Formulations intended for the home gardener usually contain lesser amounts of active ingredient per gallon and include an alcohol, such as isopropanol, as an antifreeze.

The ester formulations are made by dissolving the ester in a suitable solvent and adding emulsifier. The emulsifier is frequently a minor part of the total formulation, usually less than 5%, and usually consists of a blend of non-ionic and anionic emulsifiers. Perhaps the most troublesome portions of the formulation from a waste disposal standpoint are the aromatic solvents and fuel oil or kerosene used as diluents.

Incineration. At least 1800°F and 1 sec detention time when using a straight combustion process must be provided. Catalytic combustion can lower this temperature to levels of about 900°F.

Chemical Treatment. Chlorination can be accomplished by adding sodium hypochlorite solution or gaseous chlorine to the liquid waste in a suitable reactor until a residual chlorine level is achieved. Temperatures somewhat above 85°F, at pH 3, and retention times of at least 10 min are required to render many of these materials nonherbicidal.

Strong solutions of acid, amine, or other salts of 2,4-D and 2,4,5-T can be precipitated with calcium or magnesium salts to reduce the quantity of herbicide in a gross manner. This technique is not useful with esters.

Biological Treatment.[9/] Proper biological treatment is highly temperature-dependent and requires temperatures about 75°F for effective operation and removal of the active herbicide. Biological treatment would include trickling filters, activated sludg , and sewage lagoons.

Assuming a concerted effort on the part of all employees in a plant to keep herbicide wastes out of the water, then the small amounts that do occur in an unavoidable fashion can be treated adequately by biological means. Such compounds include:

2,4-D acid
2,4,5-T acid
MPC acid

isopropyl ester 2,4-D
propylene glycol butyl ether ester 2,4-D
propylene glycol butyl ether ester 2,4,5-T
butyl ester 2,4-D
alkanol amine salt 2,4-D
dimethyl amine salt 2,4-D

Pesticide plant operators faced with the necessity of supplying treatment methods for contaminated wastewater should not overlook the favorable economics possible through use of sewage stabilization ponds or lagoons. In warmer climates, this can be an effective method of disposal with throughputs of 20 to 40 lb biochemical oxygen demand (BOD) per acre per day. Many states already provide information on design and construction of such ponds, as does the U. S. Public Health Service.[10/]

Biological treatment of wastes where space is not available for a pond or where soil conditions preclude its use can be accomplished with package treatment units embodying activated sludge units or the new vertical trickling filter units containing biological oxidation media.[11/]

Deep Well Disposal.[12/] Deep well disposal consists of pumping liquid wastes into a deep well drilled to a natural subterranean stratum capable of accepting the volume of such liquids to be pumped. Identification of such strata must consider the possibility of leakage to potable water sources and surface streams. However, where such discrete strata exist, deep well disposal can be considered where permitted by local regulatory agencies.

Inorganic Pesticides

Arsenicals. Two methods for disposal of arsenicals are generally applicable.

- Burial. Since most of these compounds are quite insoluble, disposal of solid residues by burial in an approved location is a recommended practice.

- Municipal system or receiving water. The permissible level of 0.05 mg/liter of arsenic (as As) established for public water supplies is the governing factor.[13/] Waters from the disposal area must be monitored to make sure this limit is not exceeded.

Borates. Borates can be disposed of by burning under controlled conditions.

Chlorates. Chlorates are best disposed of by careful burning in small amounts so as to avoid any great hazard from the oxidizing power of these materials. Extreme care should be taken to prevent chlorate wastes from being mixed with any organic matter, as explosive conditions can result.

The Environmental Protection Agency has made the following recommendations for the disposal of small quantities of inorganics.[2/]

". . . inorganic pesticides should be disposed of according to the following rank order of procedures:

"(1) Chemically deactivate the pesticides by conversion to nonhazardous compounds, and recover the heavy metal resources. It is intended that such methods as are appropriate will be described and catalogued according to their applicability to the different groups of pesticides.

"(2) If chemical deactivation facilities are not available, such pesticides should be encapsulated and buried in a specially designated landfill. Records sufficient to permit location for retrieval should be maintained.

"(3) If none of the above options is available, place in suitable containers (if necessary) and provide temporary storage until such time as adequate disposal facilities or procedures are available."

Triazine Herbicides

The most important triazine herbicides are:

simazine (2-chloro-4,6-bis (ethylamino)-s-triazine),
propazine (2-chloro-4,6-bis(isopropylamino)-s-triazine),
atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine),
prometone (2,4-bis(isopropylamino)-6-methoxy-s-triazone),
prometryn (2,4-bis isopropylamino-6-methylthio-s-triazine),
ametryn (2-ethylamino-4-isopropylamino-6-methylthio-s-triazine), and
terbutryn (2-tert butylamino-4-ethylamino-6-methyl-thio-s-triazine).

Table B-3 shows some of the important properties of these compounds.

TABLE B-3

PROPERTIES OF TRIAZINE HERBICIDES

Herbicide	Molecular Weight	Melting Point[a]	Solubility in Water[b]	Stability[c] H_2O	Stability[c] 0.1N HCl	Stability[c] 0.1N NaOH	Toxicity Rate[d]
Simazine	201.6	223-225	5	>1800	5.1	2.2	5000
Propazine	229.7	212-214	8.6	>1800	5.6	3.6	>5000
Atrazine	215.7	173-175	33	>1800	5.4	2.9	4050
Prometone	225.3	91-92	750	>1800	24.1	141	2980
Prometryn	241.4	118-120	48	>1800	22.2	1200	3750
Ametryn	227.3	84-86	185	>1800	22.9	1440	1405
Terbutryn	241.4	104-105	58	>1800	22.0	>1800	2980

a/ Noncorrected °C.
b/ ppm at 20-23°C.
c/ Half-life time, in days, at 25°C.
d/ Oral LD_{50} in mg/kg.

Since these compounds and their decomposition products or metabolites are of relatively low mammalian toxicity, the main concern in disposal of wastes is to ensure that the herbicidal properties are destroyed or diluted to ineffective levels before release to the environment. The decomposition products of these compounds do not have herbicidal activity.

Incineration. Incineration in a properly designed municipal or industrial incinerator is the most effective way of ensuring destruction of the herbicide. Gases from the incinerator should be scrubbed to avoid releasing acids to the atmosphere. The effluent from the scrubber in form of gases to the atmosphere and liquid to the sewer should be monitored to ensure that they are free of herbicide. Ash from the incinerator should be buried in a sanitary landfill.

Incineration lends itself to the safe disposal of all types of formulations and packaging materials, except metal cans and drums, as well as the herbicidal compound and its by-products. The contents of metal containers can be incinerated and the containers can be disposed of separately. (See NACA "Manual for Decontamination and Disposal of Empty Pesticide Containers."[7])

Open air burning should be avoided.

Chemical Treatment. The properties tabulated in Table B-3 indicate the susceptibility of the triazines to acid and alkaline hydrolysis. This method is an effective way of treating aqueous effluent from the reaction and formulation processes. The rate of hydrolysis is dependent upon the pH and temperature of the aqueous solution. After adjusting to pH of 1, the solution should be passed through a hot water heater and discharged into a holding pond. The concentration of herbicide in the holding pond should be monitored to determine when it is safe to discharge the solution to the sewer.

This procedure does not lend itself to disposal of large quantities of waste chemicals, formulations, or packaging.

Deep Well Disposal. Solutions and slurries of triazine herbicides can be pumped into properly located deep wells. To be effective, a deep well must provide access to a rock-bound stratum with enough capacity to hold the volume of liquid to be pumped. There must be no possibility of leakage to water sources and surface streams.

This method of disposal is less desirable because the decomposition of the herbicide is not accomplished before release to the environment and it is difficult to determine the potential of a given well to leak. This method also does not provide for disposal of empty containers.

Burial. Disposal by burial of untreated wastes should be considered only as a last resort. If no other alternative is available, the burial must be done only in an area approved by local authorities that is free of groundwater movement. Liquids should be absorbed on diluents such as attapulgite, montmorillonite or diatomaceous clays before burial.

Contract Services. If disposal is accomplished through a company or municipality that provides this service, the contractor should be advised of the proper means of disposal and checked to ensure that proper means are being used.

Substituted Ureas

The urea herbicides (monuron, diuron, etc.) possess a comparatively low order of mammalian toxicity but will exert herbicidal activity at very low concentrations. Care must be taken, therefore, to prevent atmospheric or aqueous effluent contamination. Solubility in water ranges from 5 to 4,000 ppm and activity is exhibited at the 1-ppm level.

Members of the urea class of compounds are used as both selective and nonselective herbicides. Among the nonselective uses are prevention of weed growth on plant sites. The selective uses include weed control in crops such as cotton and soybeans. Formulations are available as wettable powders, water dispersible liquids, pellets and granules.

Handling of Solids. Process vapors or ventilation air, carrying even low concentrations of these herbicides, should be passed through scrubbers or filters prior to discharge into the atmosphere. Contaminated equipment or clothing should be cleaned in such a manner that herbicidal content of effluents will not be discharged into the plant aqueous effluent at active levels.

Use of a vacuum cleaner to pick up spills and dust is preferred to flushing contaminated areas with water, since aqueous effluents require additional treatment (see paragraph "Disposal of Liquid Wastes" below).

Solids recovered from dust collectors, settling tanks, filters, etc., should be reworked insofar as this is possible. Where rework is not feasible, special disposal methods such as incineration or on-site burial should be used.

Disposal of Liquid Wastes. Aqueous effluents containing urea herbicides should be handled by extracting the soluble herbicide content by washing the aqueous effluent with a suitable solvent prior to discharge.

Nonaqueous waste streams containing urea herbicides can be disposed of by incineration or burial. Since many urea herbicides contain a halogen, the combustive products from incineration will contain acid halides. A gas scrubber may be required to remove the acid halides before discharge to the atmosphere.

Chloroacetamide Herbicides

The major chloroacetamide herbicides in use today are:

Ramrod®, 2-chloro-N-isopropylacetanilide
Lasso®, 2-chloro-2', 6'-diethyl-N-methoxymethyl acetanilide
Machete®, 2-chloro-2', 6'-diethyl-N-butoxymethyl acetanilide, and
Randox®, 2-chloro-N, N-diallyl acetamide.

These products, used as solid and liquid forms, are relatively insoluble in water. All decompose quite quickly in soil.

Persons handling and using chloroacetamide herbicides should carefully consider the disposal of wastes and containers. Of course all local regulations should be rigorously followed.

Disposal of Liquids. Liquid wastes may be disposed of by burning at temperatures exceeding 1800°F in a suitable incinerator. The products of combustion are CO, CO_2, NO, NO_2, and HCl. These gases should be passed through a water scrubber. The effluent from the latter, after lime treatment, can be sewered or imponded.

In cases of spills of liquid chloroacetamide products, it may be preferable to absorb the spilled material in clay, lime, sawdust, or other absorptive material. These wastes should then be disposed of by the methods suggested for treatment of solids.

Disposal of Solids. Empty containers made of paper, fiber or polymeric materials, along with other contaminated, combustible wastes may be burned in a suitable, controlled incinerator where local laws permit. Open burning is not recommended. In areas where incineration is not permitted, containers should be buried in carefully controlled landfill operations.

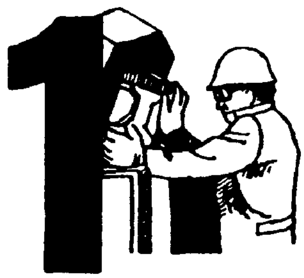
Metal containers may be reconditioned for nonfood product use. Reconditioning should be carried out in carefully controlled operations. The methods outlined in NACA "Manual for Decontamination and Disposal of Empty Pesticide Containers" are recommended.[7/]

Solid chloroacetamide wastes (technicals, wettable powders, dusts and granules) should be buried in controlled landfill operations which are described in the "Burial" of this manual, p. 110.

PESTICIDE CONTAINER DISPOSAL

The National Agricultural Chemicals Association has developed a quick, easy procedure for draining and rinsing all single-trip containers. This procedure, when conscientiously followed, significantly reduces the hazard associated with empty pesticide containers.

Four simple steps are required:



Empty container into spray tank. Then drain in vertical position for 30 seconds.

Add a measured amount of rinse water (or other dilutent) so container is 1/4 to 1/5 full. For example, one quart in a one-gallon container.

Rinse container thoroughly, pour into tank, and drain 30 sec. Repeat three times. Add enough fluid to bring tank up to level

Crush pesticide container immediately. Sell as scrap for recycling or bury. Do not reuse.

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APPENDIX C

CLASSIFICATION OF PESTICIDAL CHEMICALS

The following classification of pesticidal chemicals was developed in a recent study (Lawless, Edward W., et al., "Methods for Disposal of Spilled and Unused Pesticides," (Draft), EPA Contract No. 68-01-0098, Project 15090 HGR, July 1973). Pesticides were categorized according to their potential for detoxification.

Pesticide Classification	Number of Pesticides
Inorganic and metallo-organic pesticides	
Mercury compounds	28
Arsenic compounds	17
Copper compounds	11
Other heavy metal compounds	6
Cyanides, phosphides, and related compounds	6
Other inorganic compounds	11
	79
Phosphorus-containing pesticides	
Phosphates and phosphonates	19
Phosphorothioates and phosphonothioates	34
Phosphorodithioates and phosphonodithioates	27
Phosphorus-nitrogen compounds	8
Other phosphorus compounds	5
	93
Nitrogen-containing pesticides	
N-alkyl carbamates, aryl esters	22
Other n-alkyl carbamates and related compounds	7
N-aryl carbamates	6
Thiocarbamates	10
Bithiocarbamates	13
Anilides	13
Imides and hydrazides	9
Amides	6
Ureas and uracils	20
Triazines	14
Amines, heterocyclic (without sulfur)	18
Amines, heterocyclic (sulfur-containing)	12
Nitro compounds	26
Quaternary ammonium compounds	6
Other nitrogen-containing compounds	19
	201

Pesticide Classification	Number of Pesticides
Organochlorine, bromine or iodine pesticides	
DDT	1
DDT-relatives	8
Chlorophenoxy compounds	12
Aldrin-toxaphene group	16
Aliphatic chlorinated hydrocarbons	15
Aliphatic brominated hydrocarbons	5
Dihaloaromatic compounds	10
Highly halogenated aromatic compounds	19
Other chlorinated compounds	4
	90
Sulfur-containing pesticides	
Sulfides, sulfoxides and sulfones	6
Sulfites and xanthates	4
Sulfonic acids and derivatives	5
Thiocyanates	4
Other sulfur-containing pesticides	4
	23
Botanical and microbiological pesticides	19
Organic pesticides, not elsewhere classified	
Carbon compounds	41
Anticoagulants	4
	45
Total	550

APPENDIX D

ESTIMATED COSTS FOR BEST TREATMENT TECHNOLOGIES

Order-of-magnitude estimates were made for capital and operating costs for best practicable and best available technologies. These estimates were made for large formulation plants (40,000,000 lb/year production) that generate relatively large volumes of wastewater (25 gal/ton of product, or 500,000 gal. of wastewater/year).

Conservative (optimistic), yet realistic cost data as well as readily available, off-the-shelf items of equipment have been used so costs for the minimum adequate system could be determined. Design parameters were largely determined from actual plant or pilot plant data. (See Appendix A, Case Study No. 7, p. 80.)

These same wastewater treatment systems, if built to the higher specifications required by many of the large producer formulators, could cost five to 10 times our estimates. For comparison purposes, therefore, high side estimates are shown in the last column of each estimate (10 times the conservative estimate). This high side represents the estimate of maximum cost for a waste treatment facility constructed to more exacting specifications, i.e., those using specially designed equipment, and outside engineering and construction. The costs of treatment are shown at the bottom of the cost estimate.

COST ESTIMATE NO. 1

BEST PRACTICABLE TECHNOLOGY - EVAPORATION

Basis for Calculations

Formulation rate - 40,000,000 lb/year (formulated product)
Process wastewater rate - 25 gal/ton of formulated product
Waste treatment process - 250 day/year, 8 hr/day, 2,000 gal/day operation

Capital Costs	Low	High
Pump	$ 400	$60,000
Surge tank (4,000-gal. gas tank)	1,100	
Concrete evaporation pad (15 ft W x 30 ft L x 3 ft H)	2,000	
Aeration pump system	1,000	
Roof	1,500	
Total	$6,000	$60,000

Yearly Operation Costs	Low	High
Deemulsifier	$ 350	$ 350
Electricity	75	75
Labor (250 hr at $4/hr)	1,000	1,000
Fixed charges (25% of capital cost)	1,500	15,000
Total	$2,925	$16,425
Cost per gallon of wastewater	0.6¢	3.3¢
Cost per pound of product	0.007¢	0.04¢

COST ESTIMATE NO. 2

BEST AVAILABLE TECHNOLOGY - PRETREATMENT-FILTRATION-ADSORPTION

Basis for Calculations

Formulation rate - 40,000,000 lb/year (formulated product)
Process wastewater rate - 25 gal/ton of formulated product
Waste treatment process - 250 day/year, 8 hr/day, 2,000 gal/day operation

Activated Carbon Criteria

120-min contact time
500 lb of carbon/166,650 gal. of wastewater processed 2-gpm flow rate (based on Case Study No. 7 data)

Capital Costs	Low	High
Surge tank	$1,100	
Pump	400	
Pretreatment tank	1,100	
Filter and vacuum pump	6,000	
Carbon column pump	200	
Carbon column (10 ft x 2 ft diameter fabricated from pipe)	500	$167,500
Initial carbon charge	650	
Installation	1,200	
Piping	1,500	
Electrical	1,100	
Contingencies	1,500	
Engineering	1,500	
Total	$16,750	$167,500

Yearly Operating Costs	Low	High
Carbon	$1,050	$1,050
Sludge removal	300	300
Deemulsifier and/or caustic	700	700
Diatomaceous earth	200	200
Labor (1,000 hr at $4/hr)	4,000	4,000
Utilities	200	200
Fixed charges (25% of capital cost)	4,200	42,000
Total	$10,650	$48,450
Cost per gallon of wastewater	2.1¢	9.7¢
Cost per pound of product	0.03¢	0.12¢

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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4. TITLE AND SUBTITLE Pollution Control Technology for Pesticide Formulators and Packagers		5. REPORT DATE November 1974; Approval
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7. AUTHOR(S) Thomas L. Ferguson		8. PERFORMING ORGANIZATION REPORT NO.
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15. SUPPLEMENTARY NOTES
Prepared in cooperation with the National Agricultural Chemical Association's Committee on Agricultural Chemical Environmental Quality

16. ABSTRACT

The pesticide formulation and packaging industry transforms bulk pesticidal chemicals into packaged, ready-to-use form for sale to the consumer. Most pesticides are formulated in plants completely separate from the site of active ingredient manufacture.

About 32,000 formulated products are federally registered to approximately 3,400 companies for interstate sale. Most are apparently formulated in the 200 to 300 large formulation plants through the country.

Techniques used to dispose of process wastewater include evaporation, landfill disposal, and contract disposal services, including municipal systems. Current pretreatment and treatment techniques for process wastewater discharge are generally considered inadequate to meet increasingly stringent standards. The best practicable wastewater treatment technology appears to be complete evaporation. The best available treatment technology appears to be a pretreatment-filtration-adsorption process under development.

Additional research is needed to: characterize the wastewater; assess the air pollution potential due to pesticides; and demonstrate the pretreatment-filtration-adsorption process.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Agricultural Chemicals, -Pesticides, Water Pollution Sources, Air Pollution, -Wastewater Disposal, Evaporation, Landfills, -Wastewater Treatment, Adsorption, Chemical Degradation, -Solids Wastes, Incineration, Landfills	Pesticide formulation industry, Pesticide formulator wastes, Pesticide packager wastes	06/06

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