

## CHAPTER 3

## NATURE AND ORIGIN OF WASTEWATERS

## 3-1. Introduction

While domestic wastewaters can be consistently classified as to their strength and constituents, industrial wastewaters and domestic/industrial discharges may be highly variable. The latter types of wastewaters are usually a complex rather than a simple mixture of constituents. Characterization of the waste stream by flow measurement and chemical analysis is used to identify the undesirable characteristics, to determine the source of these characteristics, and to implement a solution to control them to an acceptable level.

## 3-2. Wastewater characteristics

Wastewaters may contain any material which may be dissolved or suspended in or on water. Wastewater constituents are classified into organic, inorganic, particulate and pathogenic. Tests serve as a first step in determining the treatment requirements for a particular wastewater to preclude potential negative environmental impact.

*a. Primary organic parameters.* Organic materials in wastewater have traditionally been the major concern in the field of water pollution control. The decrease in dissolved oxygen due to the process of biodegradation is detrimental to the health of the receiving waterways and aquatic life. There are four major tests used to measure organic material in wastewater: the customary pollutant parameter, Biochemical Oxygen Demand (BOD); the noncustomary pollutant parameters Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), and Total Oxygen Demand (TOD).

(1) Biochemical oxygen demand (BOD). The BOD test is an indirect measurement of biodegradable organic material. The test does not measure specific organic materials but indicates the amount of oxygen required to stabilize the biodegradable organic fraction. This test was devised to simulate the impact of a particular wastewater on the dissolved oxygen level in the receiving waters. Adequate dissolved oxygen must be provided in order to maintain aquatic life. The BOD test measures the oxygen depleted after a period of five days in a closed system which contains a mixture of wastewater and an acclimated seed of microorganisms. The test may

also measure a quantity of reduced inorganic materials such as ammonia or sulfites.

(2) Chemical oxygen demand (COD). COD is another indirect measurement of organic material. COD measures the oxygen equivalent of the organic material oxidized by bichromate or permanganate during acid digestion. This parameter was developed in order to substitute for the more time-consuming BOD test.

(3) Total organic carbon (TOC). The TOC test is an indirect measurement of organic material. The test measures the quantity of carbon dioxide liberated during the combustion of the wastewater sample. Thus, TOC is the amount of carbon present in organic molecules contained in the wastewater sample.

(4) Total oxygen demand (TOD). TOD is an indirect method of measuring organic material concentration. However, it is the most direct measurement of oxygen demand. TOD is the difference in the oxygen content of a sample before and after combustion. TOD measures the amount of oxygen required to burn the contaminants in the wastewater sample.

*b. Organic parameter relationships.* A preliminary step in developing treatment alternatives for a specific wastewater should be an analysis of the organic parameter relationships. This analysis will provide the designer with a general idea of the treatment technologies most likely to be effective on the wastewater.

*c. Additional organic parameters.* As attention has been focused on the TOD, TOC, COD, and BOD parameters, it is necessary to recognize other important organic evaluations, such as oil and grease content, phenols, organics containing toxic functional groups, etc. Oil and phenol analyses are particularly significant when evaluating unit processes for the treatment of wastes containing petroleum distillates. Quantities of toxic organic compounds, such as pesticides, present in wastewaters entering the environment are extremely significant and require a great deal of effort to control. The need to analyze or treat these organic compounds is site specific. If a substance is used or manufactured in an industrial activity, then the possibility exists that it is present in the wastewater.

(1) Oil and grease. Oil and grease in wastewater is usually a characteristic of petroleum-

based chemical manufacturing, machining, vehicle maintenance, kitchen and restaurant wastes and, to a lesser degree, domestic wastewater. Oil and grease is an indirect measurement defined and quantified by an analytical procedure. Oil and grease is an expression of all substances extracted by the organic solvent (Freon) employed in the test procedure. Oil and grease may include hydrocarbons, fatty acids, soaps, fats, waxes, oils and any other Freon extractable substance that will not volatilize during the test procedure. Oil and grease, in large quantities, is a dangerous environmental pollutant. Oil and grease is difficult to remove by conventional treatment processes such as anaerobic or aerobic biological processes and is an interference in most physical-chemical treatment processes. Oil and grease treatment usually consists of removal by skimming or flotation and disposal by reuse, incineration, or landfilling.

(2) Phenol. Phenol is encountered most frequently in the petroleum refining and chemical processing industries, but is present where industrial activities utilize petroleum distillates. Phenol is very soluble in water, oils, carbon disulfide and numerous organic solvents. The wet chemical analysis of phenol measures directly a variety of phenolic compounds. Phenol is a toxic and mutagenic substance in high concentrations and may be absorbed through the skin. Phenols are, for the most part, biodegradable.

(3) Cyanide. Cyanide is found in metal plating, petroleum refining, plastics, and chemicals manufacturing wastewaters. The cyanide ion is highly toxic to aquatic life and humans at very low concentrations. Most cyanide appears as a chemical complex with a metallic compound. As a result, toxicity of cyanide depends upon the nature of the complex. Some cyanide compounds are harmless. Cyanide compounds are usually biodegradable and are otherwise treatable by alternate methods.

(4) Surfactants. Surfactants are found in household and industrial cleaning detergents and many industrial wastewaters. The presence of surfactants is indicated when there are large quantities of foam in the collection or treatment system.

(5) Other organic compounds of significance. Many wastewaters contain U.S. EPA identified toxic organic compounds not identifiable except by direct measurement using specialized analytical techniques such as infrared spectrophotometry, gas chromatography, gel chromatography and mass spectrometry. Other analytical methods may be required depending upon the substance.

*d. Wastewater solids.* Wastewater solids are present in nearly all wastewater discharges. Solids occur in wastewater as a result of stormwater runoff, sanitary discharge, chemical precipitation reactions in the waste and direct discharge of solid materials.

(1) Definitions. Waste solids are classified according to gross physical properties and chemical composition. The three basic types of solids include:

- settleable solids,
- suspended solids (TSS), and
- dissolved solids (TDS).

Settleable solids are particles which settle out of a wastewater sample during a 1 hour settling test using an Imhoff cone. Grit and most chemical sludges are settleable solids. They are denser than water and, therefore, cannot remain in suspension. Suspended solids are particles retained by filtering a wastewater sample. The suspended solids test may include settleable solids if the sample is thoroughly mixed. Dissolved solids are basically salts of organic and inorganic molecules and ions that exist in solution.

(2) Testing. Wastewater solids may be classified by direct gravimetric test methods. Suspended and dissolved solids are termed "volatile" if they are vaporized after ignition for 1 hour at  $1,022 \pm 122$  degrees F in a furnace. In wastewater treatment, solids are said to be non-filterable or insoluble if they are retained on the surface of a 0.45 micron filter. The filtrate is said to represent the soluble fraction of the liquid.

*e. Significant inorganic parameters.* There are many inorganic parameters which are important when assaying potential toxicity, general characterization, or process evaluation. Although special situations require the evaluation of any number of inorganic analyses, it is the intent here to discuss only the more prevalent ones.

(1) Acidity. The acidity of a wastewater is important because a neutral or near neutral water is required before biological treatment can be effective. In addition, regulatory authorities have criteria which establish strict pH limits to final discharges. Acidity is attributable to the non-ionized portions of weakly ionizing acids, hydrolyzing salts, and certain free mineral ions. Microbial systems may reduce acidity in some instances through biological degradation of organic acids, or they may increase acidity through vitrification or other biochemical processes. Acidity is expressed as mg/L  $\text{CaCO}_3$ .

(2) Alkalinity. Alkalinity may be considered the opposite of acidity and it is also expressed as mg/L  $\text{CaCO}_3$ . Alkalinity is imparted by carbonate,

bicarbonate and hydroxide components of natural water supplies. Industrial wastes often contain these species in addition to mineral and organic acids. Alkalinity determinations are useful in determining wastewater neutralization requirements.

(3) PH. pH represents the hydrogen ion ( $H^+$ ) or proton concentration in waters or wastewaters. pH is an extremely important wastewater parameter as it affects the solubilities of metals, salts and organic chemicals, the oxidation-reduction tendency and direction of wastewater components, and the rate of chemical activity in wastewater solutions. Gross wastewater characteristics affected by pH include toxicity, corrosivity, taste, odor, and color. The pH of pure water is given the value of 7. Acid solutions have a pH below 7 and alkaline or basic solutions have a pH above 7.

(4) Nitrogen. In wastewater treatment, the nitrogen forms of primary concern are:

- Total Kjeldahl nitrogen (TKN),
- Ammonia nitrogen ( $NH_3-N$ ),
- Nitrate nitrogen ( $NO_3-N$ ), and
- Nitrite nitrogen ( $NO_2-N$ ).

(a) Total Kjeldahl nitrogen represents the organic nitrogen plus ammonia nitrogen indicated in the Kjeldahl test procedure. Following measurement and removal of the ammonia nitrogen, the organic nitrogen in the wastewater sample is converted to ammonia nitrogen by catalyzed acid digestion of the wastewater. The resulting  $NH_3-N$  is then analyzed and reported as the organic nitrogen fraction. Not all organic nitrogen compounds, however, will yield ammonia nitrogen under catalyzed acid digestion. Acrylonitrile and cyanuric acid are examples of compounds that are only partially hydrolyzed by the Kjeldahl test procedure.

(b) Ammonia nitrogen ( $NH_3-N$ ) as well as organic nitrogen is present in most natural waters in relatively low concentrations. Concentrations as low as 0.5 mg/L have been reported to be toxic to some fish and concentrations as high as 1,600 mg/L have proved to be inhibitive to biological waste treatment plant microorganisms. The toxicity of ammonia is a function of pH, being highly toxic at an alkaline pH and less toxic at an acidic pH. Ammonia nitrogen is also an essential nutrient in biological waste treatment systems and a slight residual (0.5 to 1.0 mg/L) is recommended for optimum biological activity.

(c) Nitrate nitrogen ( $NO_3-N$ ) may appear in wastewaters as dissociated nitric acid,  $HNO_3$ , or may result from the biological nitrification of ammonia to nitrate. Nitrate nitrogen should be

restricted from drinking water supplies because it inhibits oxygen transfer in blood. Maximum  $NO_3-N$  concentrations of 10 mg/L are allowed in drinking water under National Interim Primary Drinking Water Regulations.

(d) Nitrite nitrogen ( $NO_2-N$ ) is most commonly found in treated wastewaters or natural streams at very low concentrations (0.5 mg/L). Nitrite is a metabolic intermediate in the nitrification process. It is rapidly converted to  $NO_3-N$  by nitrifying organisms. Nitrite is an inhibitor to the growth of most microorganisms and for this reason is widely used as a food preservative.

(5) Phosphorus. Phosphorus occurs naturally in rivers and streams as compounds of phosphate. Elemental phosphorus does not persist naturally in aquatic systems as it is quickly oxidized by molecular oxygen to phosphate. Phosphates are commonly found in industrial and domestic wastestreams from sources including corrosion inhibitors, detergents, process chemical reagents, and sanitary wastes. Phosphorus is an essential nutrient in biochemical mechanisms. A residual of 0.5 to 1.0 mg/L total phosphorus is usually required in biological waste treatment systems to ensure efficient waste treatment. Excessive phosphorus in natural waterways, however, can be very harmful resulting in algal blooms and eutrophication.

(6) Sulfur. Sulfur occurs naturally in rivers and streams as compounds of sulfur. Elemental sulfur does not persist naturally in aquatic systems as it is oxidized by molecular oxygen to sulfate. Due to the cathartic effect of sulfate upon humans, the drinking water limit for sulfate has been placed at 250 mg/L in waters intended for human consumption.

(a) In some industrial waste streams sulfate and sulfur compounds are present in high concentrations and may be a major component of TDS and conductivity. Sulfates can cause odor and corrosion of sewer pipes under the proper conditions. The malodorous gas, hydrogen sulfide, is produced by the anaerobic biological reduction of sulfate to hydrogen sulfide. As pH is increased, the chemical equilibrium favors the ionization of sulfur and prevents the formation of hydrogen sulfate ( $H_2S$ ). As pH is decreased, the formation of  $H_2S$  is favored.

(b) Crown corrosion of sewers occurs when the  $H_2S$  gas is released and rises to the crown of the sewer. At the crown, condensed water and  $H_2S$  form sulfuric acid which dissolves concrete.

(7) Chlorine. Chlorine is widely used as a disinfectant for drinking water supplies and for treated sanitary discharges. Chlorine is toxic to

all forms of life in the proper concentrations but does not persist in aquatic systems. These two qualities have helped promote the use of chlorine as a disinfectant. However, chlorine does react with other chemical compounds such as ammonia and certain hydrocarbons to form the toxic chloramines and potentially toxic or mutagenic chlorinated hydrocarbons. For this reason, chlorination is not recommended for certain industrial and combined domestic/industrial waste streams.

(8) Chlorides occur in all natural water systems and many industrial waste streams. Seawaters are very high in chlorides. Chlorides are relatively harmless to humans in low concentrations. At a concentration of 250 mg/L, drinking water is found to have an objectionable taste. In some cases, water containing concentrations of chloride up to 1,000 mg/L are consumed without ill effects. Chloride concentrations of 8,000 to 15,000 mg/L have been reported to affect adversely biological waste treatment systems.

(9) Heavy metals. Some of the heavy metals of interest are copper (Cu), chromium (Cr), cadmium (Cd), zinc (Zn), lead (Pb), nickel (Ni), and mercury (Hg). These materials may be measured directly. These elements may be inhibitive or toxic to aquatic and terrestrial organisms and the microorganisms employed in biological waste treatment systems.

(a) Copper. The primary sources of copper in industrial wastewaters are metal process pickling baths and plating baths. Copper may also be present in wastewaters from a variety of chemical manufacturing processes employing copper salts or a copper catalyst. Copper is an essential nutrient for most organisms including humans. Copper can impart a bitter taste to water in concentrations above 1 mg/L. Copper salts are used to control algae growth in reservoirs and farm ponds.

(b) Chromium. Chromium is found in metal plating and anodizing wastes, tannery wastes, and in certain textile processing wastewaters. Chromium commonly appears in the hexavalent (+6) and the trivalent (+3) valence states and also exists in less soluble complexes. Hexavalent chromium is highly toxic to microorganisms.

(c) Cadmium. Cadmium is present in wastewaters from metallurgical alloying, ceramics, electroplating, photography, pigment works, textile printing, chemical industries and lead mine drainage. Cadmium is relatively abundant in the earth's crust and the metal and its salts are highly toxic.

(d) Zinc. Zinc is present in wastewater streams from steel works, rayon manufacture,

battery manufacture, sodium hydrosulfite manufacture and other chemical production. Zinc is a nutritional trace element but is toxic at higher concentrations.

(e) Lead. Lead is present in wastewaters from storage battery manufacture, drainage from lead ore mines, paint manufacture, munitions manufacture, and petroleum refining. Lead is toxic in high concentrations.

(f) Nickel. Nickel is present in wastewaters from metal processing, steel foundry, motor vehicle and aircraft, printing and chemical industries. Nickel may cause dermatitis upon exposure to the skin, and gastrointestinal distress upon ingestion.

(g) Mercury. Mercury is used in the electrical and electronics industries, photographic chemicals, and the pesticides and preservatives industries. Power generation is a large source of mercury release into the environment through the combustion of fossil fuel. Mercury in its methylated form is a highly toxic compound. In its elemental form, it is readily absorbed by inhalation, skin contact and ingestion.

*f. Additional wastewater characteristics.*

(1) Temperature. Temperature is a very important wastewater characteristic. The chemical equilibrium of complex wastewaters is very temperature dependent. Different reactions may be found at higher temperatures as compared to lower temperatures. Waste treatment system efficiency is affected by extremes in temperature. At low temperatures (39 degrees F), biochemical and chemical reaction rates are extremely slow, and waste treatment operations are often severely limited. At temperatures greater than 100 degrees F, many waste treatment plants experience operating difficulty. Biological processes are impaired, air and oxygen solubility becomes limited, and other physical properties such as sludge density and settling rate affect overall waste treatment.

(2) Tastes and odors. Tastes and odors in water are generally associated with dissolved inorganic salts of iron, zinc, manganese, copper, sodium, and potassium. Phenolics are a special nuisance in drinking water supplies especially after chlorination because of their very low taste and odor threshold concentration (less than 0.2 parts per billion). Petrochemical discharges and liquid wastes from the paper and synthetic rubber industries often cause taste and odor problems. Sulfides from these sources cause odors in concentrations of less than a few hundredths of a part per million. Tastes and odors may also be associated with decaying organic matter, living algae and other microorganisms containing essential oils and other odorous compounds, specific or-

ganic chemicals such as phenols and mercaptans, chlorine and its substituted compounds, and many other chemical materials.

(3) Color. Color in water and wastewaters may result from the presence of metallic ions such as chromium, platinum, iron, or manganese from humus and peat materials such as tannin and algae. Color caused by suspended matter is said to be "apparent color". Color caused by colloidal or soluble materials is said to be "true color". True color is the parameter by which color is evaluated. An arbitrary standard is employed to evaluate color. The color produced by 1 mg/L of cobalt-platinum reagent is taken as one color unit. Dilutions of cobalt-platinum reagent are made in the 0 to 70 unit range and placed in special comparison tubes. Water samples are then compared and matched between the cobalt-platinum standard dilutions.

(4) Radioactivity. Regulatory agencies have established standards for the maximum allowable concentrations of radioactive materials in surface waters. It is possible to differentiate between the following three types of radioactivity:

- alpha rays.
- beta rays.
- gamma rays.

(a) Alpha rays consist of a stream of particles of matter (doubly charged ions of helium with a mass of four) projected at high speed from radioactive matter. Once emitted in air at room temperature, alpha particles do not travel much more than 4 inches. These particles are stopped by an ordinary sheet of paper.

(b) Beta rays consists of a stream of electrons moving at speeds ranging from 30 to 90 percent of the speed of light, their power of penetration varying with their speed. These particles normally travel several hundred feet in air and may be stopped with aluminum sheeting a tenth of an inch thick.

(c) Gamma rays are true electromagnetic radiation which travel with the speed of light, and are similar to x-rays but have shorter wave lengths and greater penetrating power. Proper shielding from gamma rays requires an inch or more of lead or several feet of concrete. The unit of gamma radiation is the photon.

(d) Radioactive materials commonly used in tracer studies in research in biology, chemistry, and medicine are the isotopes of carbon ( $C^{14}$ ) and iodine (125). In sewers and waste treatment plants certain isotopes, such as radioiodine and radiophosphorus, accumulate in biological slimes and sludges.

(5) Toxicity. Toxicity is most often related to aquatic organisms such as fish, arthropods, shellfish, and microorganisms. The toxicity bioassay test has been developed to evaluate the relative toxicities of individual wastewaters. The purpose of the test is to determine the lethal concentration of pollutant that will kill 50 percent of the test organisms ( $LC_{50}$ ) in a given period of time. The  $LC_{50}$  is an indirect method of measuring toxicity.

(6) Pathogens. Wastewaters that contain pathogenic bacteria can originate from domestic wastes, hospitals, livestock production, slaughterhouses, tanneries, pharmaceutical manufacturers, and food processing industries. The major pathogens of concern include certain bacteria, viruses, and parasites.

(a) The coliform group of bacteria has been used to indicate the bacterial pollution of water and wastewater. Generally used test parameters employed as water quality indicators are total coliform and fecal coliform. The total coliform test includes organisms other than those found in the gastrointestinal tracts of mammals.

(b) The fecal coliforms are differentiated from the total coliforms by incubation at an elevated temperature in a different, growth-specific medium.

(c) Fecal Streptococci are non-coliform bacteria which are widely used as indicators of pollution. Streptococci are particularly useful in that they are commonly found in heavily polluted streams and almost always absent from non-polluted waters. Other pathogenic bacteria of concern and related diseases are listed in table 3-1.

Table 3-1. Common enteric pathogenic bacteria and related disease

Bacteria	Disease
<u>Salmonella typhosa</u>	Typhoid fever
<u>Salmonella paratyphi</u>	Paratyphoid fever
<u>Salmonella typhimurium</u>	Salmonellosis
<u>Shigella sonnie, S. flexneri</u>	Shigellosis
<u>Vibrio cholera</u>	Cholera
<u>Pseudomonas aeruginosa</u>	Enteric infection
<u>Klebsiella sp.</u>	Enteric infection
<u>Diplococcus pneumonia</u>	Infectious pneumonia
<u>Clostridium botulinum</u>	Botulism
<u>Brucella sp.</u>	Brucellosis

(d) Viruses are submicroscopic obligate parasites which can only replicate in a host cell. However, viruses can survive for weeks, even months outside a host cell awaiting the opportunity to reinfect another host. Viruses cause a large number of diseases including the common cold, measles, poliomyelitis, mumps, hepatitis,

Table 3-2. Common parasites and related disease

Organism	Disease	Reservoir(s)	Range(s)
Protozoa			
<u>Balantidium coli</u>	Balantidiasis	Man, swine	Worldwide
<u>Entamoeba histolytica</u>	Amebiasis	Man	Worldwide
<u>Giardia lamblia</u>	Giardiasis	Man, animals	Worldwide
<u>Toxoplasma gondii</u>	Toxoplasmosis	Cat, mammals, birds	Worldwide
Nematodes (Roundworms)			
<u>Ascaris lumbricoides</u>	Ascariasis	Man, swine	Worldwide-Southeastern USA
<u>Ancylostoma duodenale</u>	Hookworm	Man	Tropical-Southern USA
<u>Necator americanus</u>	Hookworm	Man	Tropical-Southern USA
<u>Ancylostoma braziliense</u> (cat hookworm)	Cutaneous Larva Migrans	Cat	Southeastern USA
<u>Ancylostoma caninum</u> (dog hookworm)	Cutaneous Larva Migrans	Dog	Southeastern USA
<u>Enterobius vermicularis</u> (pinworm)	Enterobiasis	Man	Worldwide
<u>Strongyloides stercoralis</u> (threadworm)	Strongyloidiasis	Man, dog	Tropical-Southern USA
<u>Toxocara cati</u> (cat roundworm)	Visceral Larva Migrans	Carnivores	Probably Worldwide
<u>Toxocara canis</u> (dog roundworm)	Visceral Larva Migrans	Carnivores	Sporadic in USA
<u>Trichuris trichiura</u> (whipworm)	Trichuriasis	Man	Worldwide
Cestodes (Tapeworms)			
<u>Taenia saginata</u> (beef tapeworm)	Taeniasis	Man	Worldwide-USA
<u>Taenia solium</u> (pork tapeworm)	Taeniasis	Man	Rare in USA
<u>Hymenolepis nana</u> (dwarf tapeworm)	Taeniasis	Man, rat	Worldwide
<u>Echinococcus granulosus</u> (dog tapeworm)	Hydatid Disease	Dog	Far North-Alaska
<u>Echinococcus multilocularis</u>	Alveolar Hydatid Disease	Dog	Rare in USA

and distemper, to name only a few. The viruses of most concern found in wastewaters are of the Hepatitis, Coxsackie, Echo, Adeno and Arbo groups.

(e) Parasites and protozoa are widely found in sanitary wastewaters of the United States. Few of these organisms directly cause death but some do weaken the host and promote the possibility of contracting infectious disease. Table 3-2 lists the protozoans and multicellular parasites (nematodes and cestodes) of major concern.

### 3-3. Sources of industrial and sanitary wastewater

*a. Industrial waste waters.* Industrial wastewaters may be defined as all wastewaters other than those resulting from sanitary discharge or storm runoff. Industrial discharges include source from water treatment operations, vehicle wash racks, metal plating, motorpool and equipment maintenance shops, hospitals, laundries, x-ray and photographic and chemical laboratory operations. Discharges classified as industrial wastes often contain significant quantities of oils, soluble organic compounds, solid matter, dissolved metals, and other substances. Industrial wastes often require treatment operations not normally employed for domestic wastes are quite different from domestic wastes. This section of the manual discusses sources of sanitary and industrial wastewaters.

*b. Sanitary discharges.* Sanitary discharges originate from the use of restrooms, food preparation, clothes washing, and other domestic sources. When these activities are conducted on a large scale, they become an industrial source. Sanitary or domestic wastewater is commonly referred to as sewage. Table 3-3 summarizes average sanitary discharge loadings and sources from a typical domestic household of four members. Table 3-4 summarizes typical sewage volume and BOD for various services.

Table 3-3. Average pollutant loading and waste water volume from domestic household (four members) (100)

Wastewater Event	Number Per Day	Water Volume Per Use in Gallons	Total Water in Use in Gallons	BOD, in Pounds Per Day	Suspended Solids, in Pounds Per Day
Toilet	16	5	80	0.208	0.272
Bath/Shower	2	25	50	0.078	0.050
Laundry	1	40	40	0.085	0.065
Dishwashing	2	7	14	0.052	0.026
Garbage disposal	3	2	6	0.272	0.384
Total			190	0.695	0.797

*c. Industrial discharges.* Industrial wastewaters vary considerably in strength and composition

among military installations. This is due to differences in installation size and the type of site operations. Sources of industrial discharge common to many military posts are discussed below.

(1) Water treatment. Water treatment plants commonly employ chemical precipitation, sand filtration, carbon adsorption and chlorination as purifying operations. Sludges produced from the precipitation operation have high concentrations of minerals such as calcium, iron, and aluminum. These sludges vary in solids content from 2 percent to 25 percent and are most often handled in one of three manners:

- discharge to a municipal sewage treatment plant.
- discharge to an industrial waste treatment plant.
- dewater and landfill.

(2) Boiler water treatment blowdown. Boiler blowdown is required to control suspended and dissolved solids concentration. Boiler water is treated with chemicals, notably sodium and phosphate, to prevent scaling and corrosion. Boiler blowdown is typically high in pH, temperature, suspended and dissolved solids, and water treatment chemicals.

(3) Cooling water. Cooling water originates from air conditioning systems and cooling towers. Most air conditioning cooling water is once-through water which is not recovered or reused. Occasionally, air conditioning cooling water is treated with biocides to prevent slime growth in the plumbing and the condenser heat exchangers. Cooling towers are used to cool process waters and vessels, and allow reuse of utility water. Cooling towers are treated with organic and inorganic biocides to control slime growth in the tower. Severe contamination of cooling tower discharges may occur when the heat exchangers leak process chemicals into the cooling water. In general, however, non-contact cooling water is very low in chemical strength.

(4) Aircraft and vehicle wash racks.

(a) Nearly all military installations have vehicle wash racks to clean vehicles returning from field exercise and for normal maintenance. The wash waters contain grit, soil, oil and detergents.

(b) Centralized Vehicle Wash Facility (CVWF) are being constructed at Army facilities which are complete recycle systems with no discharge to wastewater facilities.

(5) Motor pools.

(a) Motor pools have a variety of waste sources. These include: engine cleaning, spilled hydraulic engine and transmission oils, battery

Table 3-4. Sewage volume and BOD for various services (126)

Type	Volume (gal/capita/day)	BOD (lb/capita/day)
Airports		
Each employee	15	<b>0.11</b>
Each passenger	5	0.04
Bars		
Each employee	15	<b>0.11</b>
Plus each customer	2	<b>0.02</b>
Camps and resorts		
Luxury resorts	<b>100</b>	<b>0.39</b>
Summer camps	<b>50</b>	<b>0.33</b>
Construction camps	<b>50</b>	<b>0.33</b>
Domestic sewage		
Luxury homes	<b>100</b>	0.44
Better subdivisions	90	0.44
Average subdivisions	80	0.39
Low-cost housing	70	0.39
Summer cottages, etc.	50	0.39
Apartment houses	75	0.29
(Note: if garbage grinders installed, multiply BOD factors by 1.5.)		
Factories (exclusive of industrial and cafeteria wastes)	15	<b>0.11</b>
Hospitals		
patients plus staff	<b>150-300</b>	<b>0.67</b>
Hotels, motels, trailer courts, boarding houses (not including restaurants or bars)	<b>50</b>	<b>0.33</b>
Milk plant wastes	<b>100-225 gal/1,000 lb of milk</b>	<b>1.24 to 3.65/1,000 lb of milk</b>
Offices		
Restaurants		
Each employee	15	0.13
Plus each meal served	3 (per meal)	0.07 (per meal)
If garbage grinder provided, add	1 (per meal)	<b>0.07 (per meal)</b>
Schools		
Day schools (each person, student or staff)		
Elementary	15	<b>0.09</b>
High School	20	<b>0.11</b>
Boarding Schools	75	<b>0.39</b>
Add per person if cafeteria has garbage grinder		<b>0.02</b>
Swimming pools (Employees plus customers)	<b>10</b>	<b>0.07</b>
Theaters		
Drive-in, per stall	5	<b>0.04</b>
Movie, per seat	5	<b>0.04</b>



maintenance, spray booths, radiator cleaning and floor wash. Engine cleaning is frequently performed with a decreasing agent in conjunction with steam and detergent cleaning or, in modernized facilities with high-pressure hot water, eliminating solvents and detergents. Although most spent oils are recycled, spills in engine maintenance areas are frequently sent to floor drains.

(b) Scheduled maintenance platforms (SMP) have been provided to modernize some facilities. These will be covered to minimize wastewater and will include oil removal. High-pressure hot water has replaced steam cleaning, eliminating use of solvents and detergents.

(6) Laboratories. Hospital laboratories usually incinerate pathological solid and semi-solid waste products. Liquid waste may be disinfected prior to discharge to the sanitary sewer. X-ray and photographic laboratories commonly pretreat fixing solutions to recover silver prior to discharge (DOD Div. 4160.21-M). X-ray finishing and washing solutions are discharged directly to the sewer.

(7) Laundries. Laundry washwaters are a significant source of BOD and flow. Wastewater is usually filtered through a lint screen and sometimes cooled for heat recovery prior to discharge into the sewer. Dry cleaning solvents are normally recycled but a small volume may enter the sanitary sewer system.

(8) Coal pile runoff. Coal pile runoff wastewater results from the passage of water through coal deposits where disulfides, usually pyrites, are exposed to the oxidizing action of air, water and bacteria. Coal piles exposed to air and moisture will result in sulfide oxidizing to ferrous sulfate (copperas) ( $\text{FeSO}_4$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ). The major characteristics of this runoff flow include a high suspended solids concentration and turbidity, mainly from coal, a low pH and high  $\text{H}_2\text{SO}_4$  and  $\text{FeSO}_4$  concentrations. Major treatment and disposal methods involve settling, froth flotation and drainage control.

(9) Paint stripping. There are several paint stripping methods in use today: mechanical, chemical or molten salts. Chemical or solvent stripping uses either a hot or a cold method. Cold strippers may be further classified by material used into:

- Organic solvents.
- Emulsion type.
- Acid type.
- Combination of types.

Organic solvent stripping processes of modern paints, involving spray-on/spray-off stripping procedures, have exhibited high levels of phenolic

compounds in the associated wastewater. Older paints are removed by strippers containing mostly methylene chloride and hexavalent chromium with additional surfactants, thickening and wetting agents. High levels of lead compounds can be expected when stripping lead based paints. Viable treatment alternatives for phenolic waste include hydrogen peroxide oxidation and/or carbon adsorption.

(10) Metal plating. Metal plating process wastewater is defined as all waters used for rinsing, alkaline cleaning, acid pickling, plating and other metal finishing operations; it also includes waters which result from spills, batch dumps and scrubber blowdown. The cleaning, pickling and processing solutions may contain a variety of chemical compounds, most of which at very low concentrations have a toxic potential to aquatic life. At higher concentrations, they may also be toxic to humans. The suspended solids concentration is elevated due to components such as precipitated metal hydroxides, tumbling and burnishing media, metallic chips and paint solids. Treatment methods commonly used include batch treatment for cyanide destruction, continuous flow-through treatment for cyanide and chromium contaminated rinse waters and an integrated treatment system for cyanide and chi-omit acid process solutions. Lime precipitation can be used for the removal of other metals. When clarification of the treated rinse water containing precipitated metal hydroxide is required, it normally is accomplished with settling tanks or clarifiers or filtration using pressure filters.

(11) Munitions manufacturing. Propellants and explosives are materials which, under the influence of thermal or mechanical shock, decompose rapidly and spontaneously with the evolution of a great deal of heat and much gas. Some of the most common industrial and military propellants and explosives include gunpowder, nitrocellulose, nitroglycerin, ammonium nitrate, trinitrotoluene (TNT), picric acid, ammonium picrate, RDX, HMX, and lead azide. When these compounds are manufactured, the associated wastewater is an acidic, odorous flow sometimes containing metals, organic acids and alcohols, oils and soaps. Major treatment methods include flotation, chemical precipitation, biological treatment, aeration, chemical oxidation neutralization and adsorption.

3-4. Comparison of domestic and industrial wastewaters

a. *Composition and concentration.* All wastewaters differ in composition and concentration.

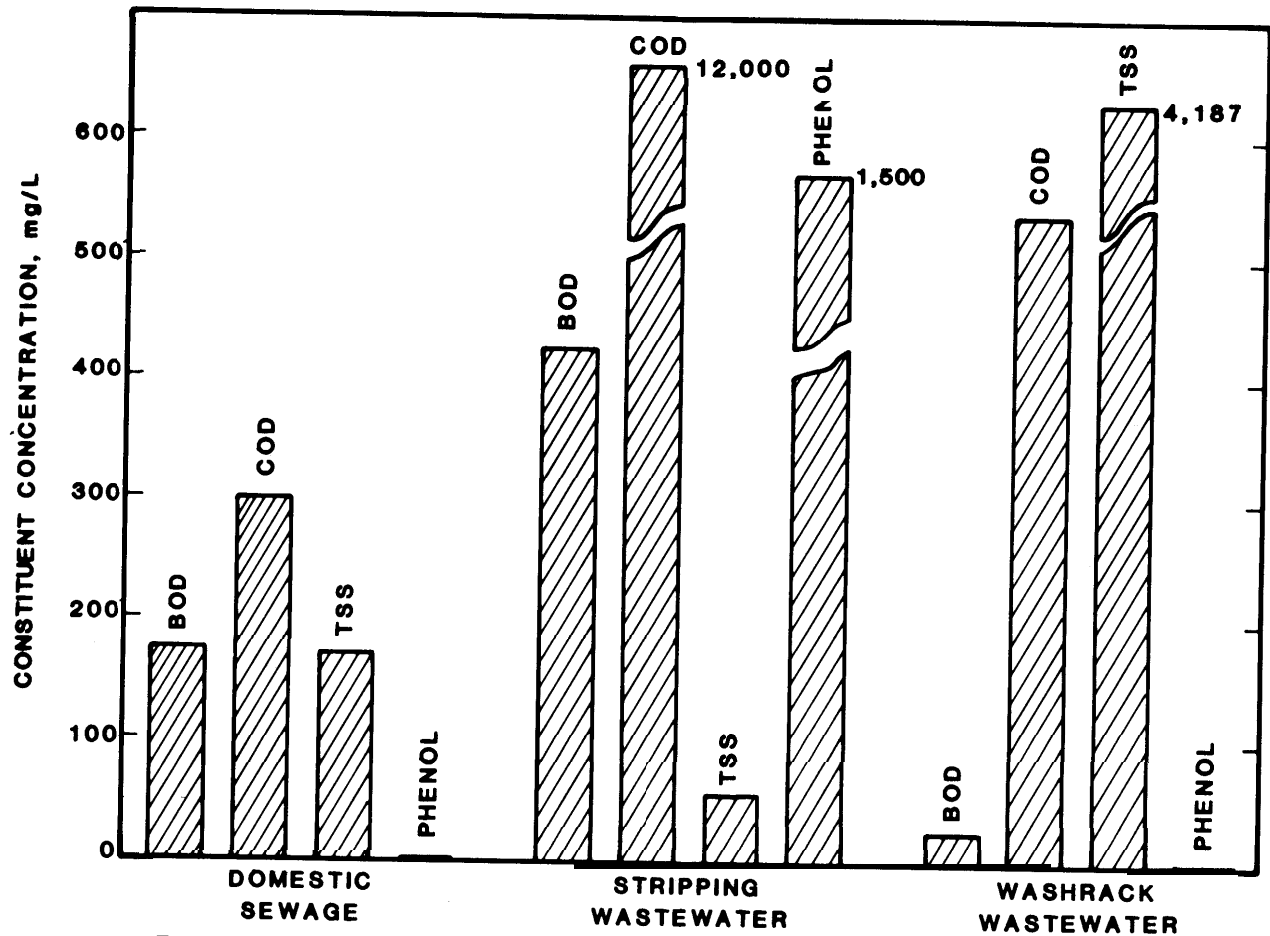


Figure 3-1. Comparison of domestic wastewater with selected military industrial wastewater.

For this reason comparison between domestic and industrial wastes is made on a case-by-case basis. However, some general conclusions may be drawn from the major differences between domestic and industrial wastes.

(1) First, a major portion of the BOD in domestic sewage is present in colloidal or suspended form while BOD in industrial wastewaters is usually soluble in character. The non-degradable COD in domestic sewage is low (usually less than 200 mg/L) while industrial wastewaters may have a non-degradable COD level in excess of 500 mg/L. Domestic sewage has a surplus of nutrients, nitrogen and phosphorus, relative to the BOD present. Many industrial wastewaters are deficient in nitrogen and phosphorus.

(2) Total dissolved solids (TDS) in domestic sewage primarily reflect the concentration of the carrier water, while many industrial activities substantially increase the TDS through the process areas. Certain industrial wastes contain pa-

rameters of special significance such as phenol or cyanide. Figure 3-1 schematically illustrates a comparison between domestic sewage and military industrial type wastewaters. Figure 3-1 and table 3-5 present a comparison between domestic sewage characteristics, aircraft stripping wastewater, and vehicle washrack discharges.

Table 3-5. Comparison of domestic waste water characteristics with selected military industrial wastewater (mg/L unless noted otherwise)

	Sanitary Wastewater	Aircraft Stripping Wastewater	Washrack Wastewater
pH (units)	6.8-7.5	6.2-7.5	7.0
BOD	75-276	375-478	10-29
COD	195-436	5,388-18,946	105-1,620
TSS	83-258	34-76	180-12,390
Phenol	Nil	71-2,220	Nil

b. Characteristics of domestic wastewaters. Domestic sewage is composed of organic matter

present as soluble, colloidal, and suspended solids. The pollutant contribution in sewage is usually expressed as a per capita contribution. A study of data reported by 73 cities in 27 states in the United States (96) during the period 1958-1964 showed a sewage flow of 135 gal/capita-day and a BOD and suspended solids content of 0.20 lb/capita/day and 0.234 lb/capita/day, respectively. The average composition of domestic sewage is shown in table 3-6. It should be recognized that the presence of industrial wastes in a domestic system may radically alter these concentrations. These levels may be expected to vary by about a ratio of 3 over a 24-hour period. Flow and BOD loadings generally peak between 1400 and 1900 hours. The lowest loadings generally occur between 0300 and 0500 hours.

Table 3-6. Average characteristics of domestic sewage (mg/L unless noted otherwise)

Parameter	High	Average	Low
BOD	350	200	100
COD	800	400	200
pH (units)	7.5	7.0	6.5
Total Solids	1,200	700	400
Suspended, total	350	200	100
Fixed	100	50	25
Volatile	250	150	75
Dissolved, total	850	500	300
Fixed	500	300	200
Volatile	350	200	100
Settleable Solids (mL/liter)	20	10	5
Total Nitrogen (as N)	60	40	20
Free Ammonia (as NH <sub>3</sub> )	30	15	10
Total Phosphorus (as P)	20	10	5
Chlorides (as Cl)	150	100	50
Sulfates (as SO <sub>4</sub> )	40	20	10
Alkalinity (as CaCO <sub>3</sub> )	350	225	150
Grease	150	100	50

c. *Characteristics of industrial wastewater.* Industrial wastes vary widely in composition and quantity. The purpose of this section is to describe the characteristics of major industrial discharges and particularly those discharges found on military installations. The major portion of wastewaters from most military installations are domestic in nature. However, military industrial wastewaters are produced from operations such as photographic processing, metal plating, laundry, maintenance, and munitions manufacturing.

(1) Aircraft and vehicle washing.

(a) Ground equipment is routinely washed to remove any accumulated oil film, grease, metal oxides, salts and dirt. This is normally accom-

plished by pressure spraying with water or cleaning compounds to remove surface films, followed by scrubbing with brushes and cleaners to loosen foreign matter, and finally rinsing thoroughly with water to remove emulsified oils and dirt. An alkaline, water-based cleaner normally is used. Wastewater flows and concentrations are highly variable. This is due primarily to the type vehicle being washed, type of washing operation, amount of water used, inclusion or exclusion of storm water, variation in type of cleaning agents, and sampling procedures used. Automobile and ground vehicle washing requires 30 to 50 gal of water per vehicle. Washwater characteristics determined from ground vehicles are presented in table 3-7. Principal wastewater constituents include free and emulsified oils, suspended dirt and oxides, phosphates, detergents, and surfactants.

(b) Aircraft are routinely washed to remove foreign material from the aircraft surface. The survey results indicate significantly higher waste loads than those experienced during ground vehicle washing. BOD values ranging from less than 100 to several thousand mg/L and oil and grease levels of less than one to several thousand have been observed.

(2) Wastes from paint stripping operations. Aircraft and other vehicles are stripped of paint periodically as routine maintenance in preparation for repairs or overhaul. Aircraft are usually repainted every three or four years to prevent corrosion of metallic surfaces. The paint-stripper is brushed on and allowed to set on the painted surfaces, causing the paint to swell and blister. This loosened paint is then removed with a high pressure water spray. Modern paints are stripped with a phenolic paint remover, while the older paints are removed by strippers containing mostly methylene chloride (dichloromethane) and hexavalent chromium with additional surfactants, thickeners, and wetting agents. Flows and characteristics are highly variable. For example, approximately 3,350 gallons of paint-stripper, 715 gallons of which is phenolic paint-stripper, are used for large aircraft; while smaller aircraft may require some 300 gallons of stripper. It is estimated that from 45 to 75 gallons of water are required to rinse each gallon of paint-stripper. The principal pollutants from a phenolic aircraft paint-stripping wastewater and the ranges of concentration are presented in table 3-8.

TABLE 3-7

Summary of Wastewater Quality From Maintenance and Exterior Cleaning Activities

	Grease and Oil (mg/L)	Suspended Solids (mg/L)	Settleable Solids (mg/L)	Total Dissolved Solids (mg/L)	BOD mg/L	COD (mg/L)	Alkalinity	pH	Orthophosphate mg/L
Yakima Firing Center Maintenance Exterior	37-1,448	1.72-10,900	1-25						
Fort Stewart Exterior - Old	0.5-86.4	3.2-2,390	6.5-32		10.36	100-1,620			
Fort Polk Maintenance Exterior	174	4,780	22	1,720	340	156	82		
Fort Lewis TMP Maintenance Exterior	9-13	65-454				24-32			
Fort Lewis Maintenance - New Exterior	20- ,673 5-110	92-1,060 25-1,420	.1-4.5	71-346	1.8-20	20-356		60-8.1	
Fort Lewis Maintenance - New Exterior Old	553-18,855	957-2,260	.25-6.2	135-160		1,020-1,800		7.5-8.0	
Fort Knox Exterior Old	.6-32.9	3,559	4.3			117.5		0.8	0.07
Fort Hood Exterior Old	1,467-16.1 (PPM)	2,864 (PPM)	60	175-230 (PPM)		336-829 (PPM)	131.0 (PPM)	8.1-8.3	

TABLE 3-7 Cont'd.  
 Summary of Wastewater Quality From Maintenance and  
 Exterior Cleaning Activities

	Grease and Oil (mg/L)	Suspended Solids (mg/L)	Settleable Solids (mg/L)	Total Dissolved Solids (mg/L)	BOD (mg/L)	COD (mg/L)	Alkalinity pH	Orthophosphate mg/L
Fort Drum Maintenance Exterior	4-22 <b>5.9-268.5</b>	<b>1,500-10,000</b> <b>603-1,100</b>	<b>1.6-4.0</b>	<b>15.5-43.8</b>		<b>20-1,200</b> <b>110-289</b>	<b>65-137</b>	<b>7.1-7.4</b> <b>0.8-2.6</b>
Fort Carson Maintenance Exterior	1-3,096	2-7,844			3-1,078	1-3,366		
Fort Carson Maintenance Exterior	25-3,096	30-15,700		8-1,078			7.0-8.1	

Source: U.S. Army Corps of Engineers, Construction Engineering Research Laboratory

Table 3-8. Characteristics of phenolic aircraft paint-stripping waste water (mg/L unless noted otherwise)

Parameter	Concentration
Phenols	1,000-3,000
Methylene Chloride	1,000-3,000
COD	5,000-30,000
Chromium	50-200
Suspended Solids	100-1,000
Oils	100-2,000
pH (units)	8.5-8.5

(3) Wastes from machine shops. The machining of metal parts for aircraft, ground vehicles, and large guns is an operation where the major water flows are used for cooling purposes. However, there are large amounts of both lubricating and cooling oils which eventually must be wasted. This operation is often incorporated in a large equipment rebuilding and maintenance depot but may be present in tactical posts. The major pollutants are soluble, emulsified, and free oils; and metal ions, shavings, and flakes.

(4) Wastes from vehicle mechanical maintenance. Engine maintenance on military installations can result in a number of wastewater flows. Waste sources from engine maintenance areas include: steam cleaning condensate, spilled hydraulic, engine and transmission oils, battery maintenance, radiator cleaning, and fuel tank cleaning. A major source of contamination from maintenance shops is solvents, especially petroleum distillates.

(5) Laundry wastes. Most military installations have a large central laundry facility to clean uniforms and work clothes. Wastewaters from laundries vary in composition due to the type of laundry operation, the type of detergents used, the use of dyes, and the condition of the clothing being laundered. Table 3-9 lists typical laundry waste characteristics. TM 5-842-2 indicates wastewater flows and characteristics will vary depending on the type of laundering operations used, the type of detergents used and the condition of the incoming laundry.

Table 3-9. Typical laundry waste characteristics (mg/L unless noted otherwise)

Parameter	Maximum	Average	Minimum
pH (units)	11	8	5.1
Temperature (degrees F)	140	100	50
BOD	3,810	700	45
Grease and Oil	1,410	800	150
Total Solids	3,310	1,700	120
Suspended Solids	784	160	15
Detergents (as ABS)	126	55	3
Phosphates	430	150	1
Free Ammonia	—	3	—

(6) Photographic laboratory wastes. Most military bases have one or more photographic laboratories on site. Photographic wastes normally represent a very small fraction of a facility waste load. However, separate treatment of photographic wastes is sometimes required to remove toxic materials or to recover silver.

(a) There are a number of different types of photochemical processes and each results in a different type of wastewater. Color processes produce more pollutants than black and white processes. Photographic wastes are a combination of spent process chemicals and washwater. Some spent process chemicals, notably fixing agents, are often treated separately for silver recovery. The three most common types of silver recovery processes are: metal replacement, electrodeposition, and precipitation. Metal replacement involves passing the wastewater through a fine steel wool screen. The iron in the steel wool replaces the silver in solution resulting in a settled silver-rich sludge. Electrodeposition involves plating nearly pure silver on the cathode of an electrolytic cell. Precipitation of silver is usually achieved by the addition of chlorine and sulfide to form insoluble silver chloride or sulfide.

(b) The other constituents of a typical combined photographic wastewater are listed in table 3-10. This analysis represents the combined process chemical and wash wastewaters. The toxic chemicals of concern include silver, chromium, cyanide, and boron.

Table 3-10. Analysis of photographic processing waste water discharge

Constituent	Concentration (mg/L)
COD	2,234
Dissolved Solids	5,942
Suspended Solids	70
Oils and Grease	22
Surfactants (as LAS)	13
Phenols	0
Nitrates	48
Phosphates	380
Nitrates	1,100
Sulfates	260
Cyanides	6.70
Silver	1.96
Iron	0.20
zinc	0.08
Copper	0.05
Manganese	0.05
Chromium	0.05
Lead	0.05
Cadmium	0.01

(c) Silver ion is highly toxic to aquatic organisms. However, silver in photographic wastes is largely precipitated as silver chloride or

silver sulfide and in these forms represents minimal risk of toxicity.

(d) Chromium is present in the hexavalent form ( $\text{Cr}^{+6}$ ) in some bleach solutions. However, hexavalent chromium is reduced to the trivalent form ( $\text{Cr}^{+3}$ ) by strong reducing agents present in photographic wastewaters.

(e) Cyanide is present in bleaching solutions as potassium ferrocyanide. After chemical action by other reducing agents and by oxidation of silver, complex insoluble cyanide compounds are formed. These cyanide complexes are potentially dangerous as their degradation releases toxic cyanides.

(f) Boron is present in photographic wastes in small quantities and is usually precipitated as calcium borate.

(7) Metal plating wastes. Metals are plated onto both metallic and nonmetallic surfaces for decoration, corrosion inhibition, increased wear resistance, or improved hardness. Commonly plated metals are copper, cadmium, chromium, nickel, tin, and zinc. The surface to be plated serves as a cathode. An electrode made of the metal being deposited in most instances acts as the anode. With some metals, such as in chromium plating, an inert anode is used and the plating bath supplies the metal deposited. Nonmetallic surfaces to be plated must be made conductive by application of a conductive material such as graphite. Metal stripping, cleaning, pickling, and phosphatizing are preparation steps for the actual plating operation. Anodizing of aluminum in a chromate bath is considered a related operation since it produces a waste similar in characteristics to plating waste.

(a) A wide range of processing steps is used in the plating operation. Selection of such steps is based on the type of material receiving the plated layer, the type of metal being plated, individual plating technique preferences, and various final product requirements. A typical plating operation will include the following steps:

- Cleaning by solvent decreasing and/or alkaline cleaner.
- Rinsing.
- Acid cleaning or pickling.
- Rinsing.
- Surface preparation such as phosphatizing.

- Flash plating.
- Principal plating.
- Rinsing.
- Drying.

(b) The major waste sources are rinse water overflow; fume-scrubber water; batch-dumps of spent acid, alkali, or plating bath solutions; and spills of the concentrated solutions. Important parameters include pH, cyanides, emulsifying and wetting agents, and heavy metals. Cyanide is converted to highly toxic hydrogen cyanide gas at low pH; therefore, cyanide-plating solutions must not be mixed with acid-cleaning or acid-plating solutions.

(8) Wastes from munitions manufacture. Wastes generated from munitions manufacture originate from manufacturing areas as well as loading, assembling, and packing (LAP) areas. Wastewaters are generated from the manufacture and use of explosive chemicals such as trinitrotoluene (TNT), nitroglycerine, cyclonite (RDX), HMX, and tetryl. The amount and composition of munitions wastewaters varies with the explosive being produced.

(a) TNT ( $\text{CH}_3\text{C}_6\text{H}_2(\text{NO}_2)_3$ ). In TNT manufacture, toluene is reacted with nitric acid in a three-step process, using fuming sulfuric acid as a catalyst and drying agent. Excess acids are washed away from the crude TNT, forming in a waste stream known as "yellow water". Unwanted beta- and gamma-TNT isomers are selectively removed from the desired alpha-TNT in a solution of sodium sulfite (sellite). This purification step generates a dark red-colored waste known as "red water". The purified TNT is then recrystallized, dried and flaked. TNT contains up to 0.4 percent dinitrotoluene (DNT) which also is an explosive and considered hazardous. The washdown water from processing areas contains suspended TNT and is known as "pink water". Originally, production was a batch-type operation, however nearly all plants have been converted to continuous-type systems, as shown in figure 3-2. The continuous operations normally employ chemical recycle and result in a smaller quantity of more concentrated waste than the batch-type operations. Typical wastewater characteristics from both types of operations are presented in table 3-11.

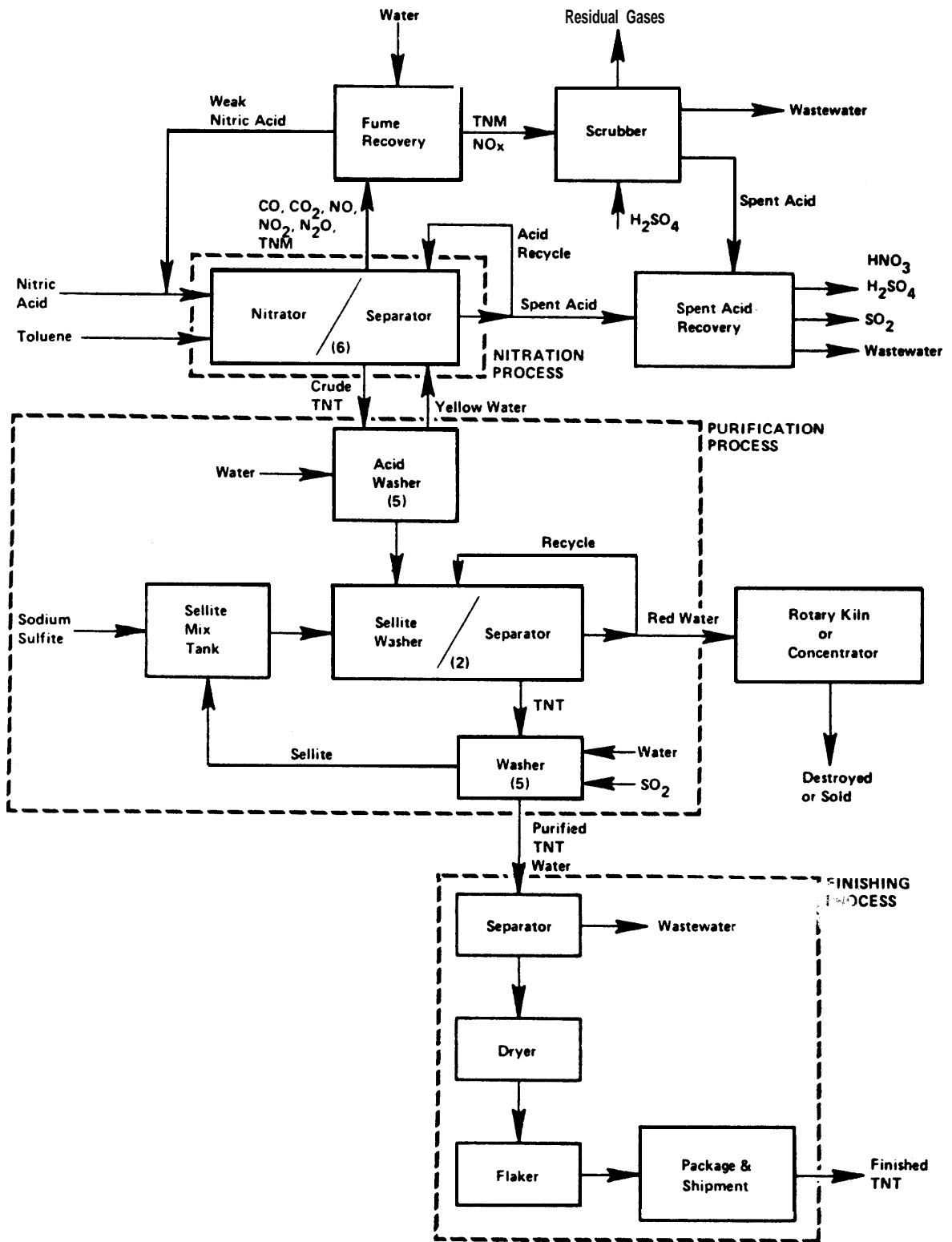


Figure 3-2. Typical TNT production process.



Table 3-11. Typical TNT waste water characteristics (mg/L unless noted otherwise)

Parameter	Continuous-Type Process		Batch-Type Process
	24-Hour Composite Sample	Grab Sample	
TNT	20.3	145	—
pH (units)	2.5	2.05	2.6
COD	64	274	673
Nitrate (as N)	213	53	107
Sulfate (as SO <sub>4</sub> )	1,821	842	638
Color (units)	161	228	6,700
Total Solids	2,792	1,160	2,048
Volatile Solids	1,377	960	850
Suspended Solids	619	224	98
Temperature (degree F)	95		—
Flow (gal/lb of TNT)	—		11.2

(b) Nitroglycerine (CHNO<sub>3</sub>(CH<sub>2</sub>NO<sub>3</sub>)<sub>2</sub>). Nitroglycerine is produced by mixing glycerine with concentrated nitric and sulfuric acids, similar to the TNT manufacturing process. The acids are then decanted, and the nitroglycerine is washed with water and soda ash to remove any residual acids. The two principal wastewaters are the waste acid and the soda ash washwaters; and both contain nitroglycerine. Typical wastewater characteristics are presented in table 3-12.

Table 3-12. Typical nitroglycerine waste water characteristics (mg/L unless noted otherwise)

Parameter	Maximum	Minimum
Nitroglycerine	315	0
pH (units)	9.9**	1.7
COD	340	10
Nitrate (as N)	1,920	0.5
Sulfate (as SO <sub>4</sub> )	470	15
Color (units)	80	5
Total Solids	25,000	110
Suspended Solids	40	1
Temperature (degrees F)	80	50
Flow (mgd)	0.17	0.04

\*\*High values indicate a dump of the soda ash washing solution.

(c) HMX and RDX, HMX ((CH<sub>2</sub>N<sub>2</sub>O<sub>2</sub>)<sub>4</sub>) and RDX (CH<sub>2</sub>N<sub>2</sub>O<sub>2</sub>)<sub>3</sub>) are very similar chemical compounds and are manufactured by essentially the same process, except for different operating temperatures and raw material feed ratios. Hexamine, acetic anhydride, nitric acid, and ammonium nitrate are fed into a reactor, forming crude HMX or RDX; which is then aged, filtered, decanted, and washed with water. Wastewaters result from spillage of raw materials or product, discharge of cooling water, washwater and filtered water; and flows from equipment and floor cleanup operations. HMX and RDX wastes typically have a BOD of 900 to 2,000 mg/L and a pH ranging

from 1.6 to 6.0. Analysis of wastewater must be made to determine specific treatment needs.

(d) Nitrocellulose (C<sub>6</sub>H<sub>7</sub>O<sub>5</sub>(NO<sub>2</sub>)<sub>3</sub>). To produce nitrocellulose, purified cellulose in the form of cotton-linters or wood-cellulose is treated with a mixture of sulfuric acid, nitric acid and water. The nitrated cellulose is then purified by a combination of centrifugation, boiling, macerating, solvent extraction or washing operations. The nitrocellulose ("green powder") is then combined with other explosive materials to be processed into various propellants. Waste materials generated include the cellulose- and nitrocellulose-contaminated acid waters from the vitrification and purification steps, alcohol and ether solvents, and other waste material from the refining and processing steps. Accidental fires caused by processing of nitrocellulose into propellants are often extinguished by automatic sprinklers, generated highly contaminated wastewater.

(e) Black powder. The industrial classification used by the Bureau of Mines defines black blasting powder as all black powder having sodium or potassium nitrate as a constituent. Black powder and similar mixtures were used in incendiary compositions and in pyrotechnic devices for amusement and for war, long before there was any thought of applying their energy usefully for the production of mechanical work. Where smoke is no objection, black powder is probably the best substance that is available for communicating fire and for producing a quick hot flame. It is for these purposes that it is now principally used in the military. (129)

(f) Nitroguanidine (NO<sub>2</sub>NHC(NH)NH<sub>2</sub>). Nitroguanidine exists in two forms. The alpha-form invariably results when guanidine nitrate is dissolved in concentrated sulfuric and the solution is poured into water. This is the form which is commonly used in the explosive industry. When alpha-nitroguanidine is decomposed by heat, a certain amount of beta-nitroguanidine is found among the products. Beta-nitroguanidine is produced in variable amounts, usually along with some of the alpha-compound. This is accomplished through nitration of the mixture of guanidine sulfate and ammonium sulfate which is formed from the hydrolysis of dicyanodiamide with sulfuric acid. Nitroguanidine on reduction is converted first into nitrosoguanidine and then into aminoguanidine (or guanylhydrazine). The latter substance is used in the explosives industry for the preparation of tetracene.

(g) Lead azide (PbN<sub>6</sub>). Lead azide is manufactured by treating sodium azide with lead acetate or nitrate. Sodium azide is formed from sodium amide and nitrous oxide. Lead azide is used where it is desired to produce, either from flame or from impact, an initiatory shock for the detonation of a high explosive such as found in compound detonators and in the detonators of artillery fuzes. The commercial preparation of the azides is carried out either by the interaction of hydrazine with a nitrite or by the interaction of sodium amide with nitrous oxide.

(h) Lead styphnate (PbC<sub>6</sub>H<sub>4</sub>O<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>). Lead styphanate is commonly prepared by adding a solution of magnesium styphnate to a well-stirred solution of lead acetate at 158 degrees F. Dilute nitric acid is added with stirring to convert the basic to the normal salt, and the stirring is continued while the temperature drops to about 86 degrees F. The product consists of reddish-brown, short, rhombic crystals. Lead styphnate is a poor initiator, but it is easily ignited by fire or by a static discharge. It is used as an ingredient of the priming layer which causes lead azide to explode from a flash. (132)

(i) Projectiles and casings. The manufacture of the lead slugs, bullet jackets, and shell casings generates wastewaters different in composition than those from explosives manufacture. Waste constituents include heavy metals, oils and grease, soaps and surfactants, solvents, and acids. Lead slugs are manufactured by extruding lead wire, then cutting and forming the lead for insertion in the bullet jacket. Alkaline cleaners, soluble oils, and cooling waters constitute the wastewater flow. Typical characteristics include high pH of about 11 and a moderate COD of 286 mg/L. Small arms bullet jackets and casings are normally brass (copper and zinc alloy), although either may be made of steel for certain applications. The larger artillery shells are generally steel. The manufacturing processes used for both brass and steel are essentially the same, consisting of stamping out plugs from metal sheets, then drawing, trimming, tapering, and shaping the plugs into either a shell, bullet jacket, or casing. Conventional metal conditioning operations, such as alkaline cleaning, pickling, phosphatizing, and metal coating occur between steps. One quality control check involves the use of a mercurous nitrate solution, creating an opportunity for mercury pollution. Total wastes have widely fluctuating pH with heavy metals (mercury, copper, zinc, and iron), oils and surfactants. Table 3-13 indicates typical munitions metal parts wastewater characteristics.

Table 3-13. Typical munitions metal parts waste water characteristics (mg/L unless noted otherwise)

Parameter	Maximum	Average
Temperature (degree F)	120	65
pH (units)	9.2	3.3
Alkalinity (as CaCO <sub>3</sub> )	370	0
Total Solids	5,000	650
Suspended Solids	725	27
Zinc	18	7
Copper	32	0.6
Lead	less than 0.2	—
Iron	21	less than 3.0
Oil	168	0

(j) Loading, assembling and packing (LAP).

The main LAP operations are explosives receiving and melting operations, cartridge and shell-filling operations and shell-renovation. Figure 3-3 is a schematic of a typical shell-filling and renovating facility showing major waste flows. Wastewater is generated from the four following sources:

- air-scrubbing.
- shell-filling.
- shell-washout water.
- cleanup water.

Dust from the unloading operation and fumes from the molten explosives are scrubbed from the air with water. When the shells are being filled with explosives, any spillage or over-filling will contaminate the water bath unless the water is covered. The washout water from rejected or renovated shells is heavily contaminated with explosives. The metal-cleaning and metal-treating rinse waters are contaminated with alkali soaps and surfactants, as well as dissolved copper. A complete washdown of all areas and equipment which could be contaminated with explosives is usually performed at least weekly, resulting in large flows of highly contaminated water. Table 3-14 indicates typical total wastewater characteristics.

Table 3-14. Typical LAP facility industrial waste water characteristics (mg/L unless noted otherwise)

Parameter	Maximum	Average	Minimum
pH (units)	8.4	7.9	6.8
Total Solids	1,790	1,401	903
Suspended Solids	336	138	22
Total Volatile Solids	956	548	426
Total (Kjeldahl) Nitrogen	25	17	10
TNT	235	178	156
RDX	180	145	88

(k) Coal pile runoff. Large quantities of coal are used at many military facilities for power generation. The coal that is stored for this purpose is maintained in large outdoor storage piles. Rain infiltration generates a coal pile runoff

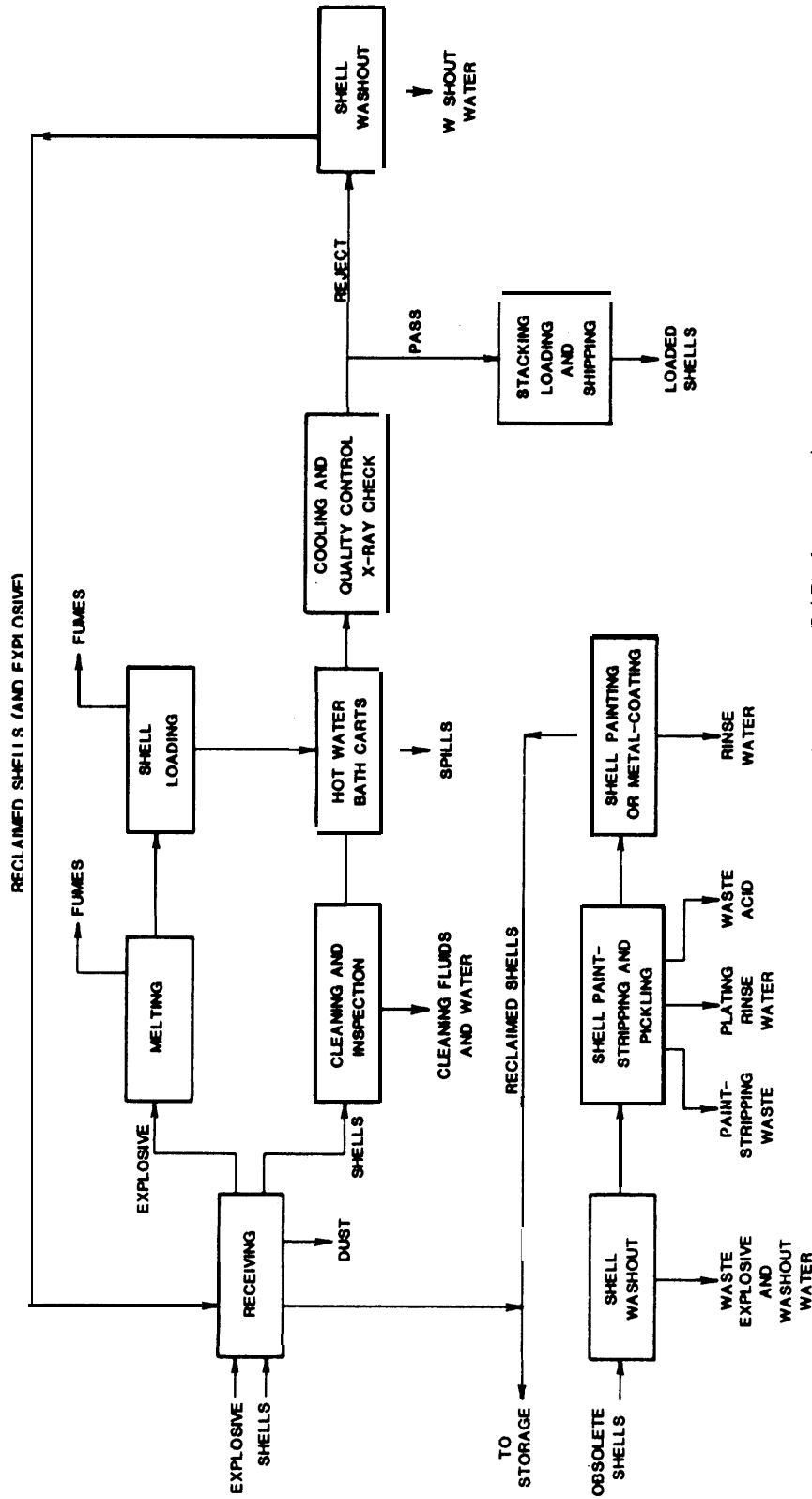


Figure 3-3. Typical shell-filling and renovating (LAP) plant operations.

**TM 5-814-8**

flow which must be treated due to its elevated TSS and turbidity, as well as an increased  $\text{FeSO}_4$  and  $\text{H}_2\text{SO}_4$  concentration resulting from the coal oxidizing environment. Construction of a retaining curb surrounding the area of potential contamination, as well as a collection sump for short

term storage, will allow for complete collection and routing of this flow to the wastewater treatment system. Construction of a coal pile cover, where applicable, would negate the need for flow collection as well as protect the coal from environmental influences and degradation.