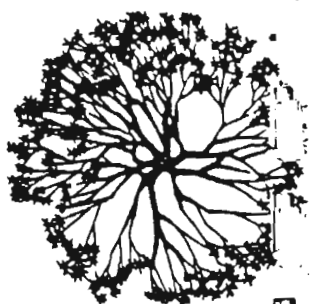


Treatment of Water and Wastes



Masters Guy, "Introduction to Environmental Engineering Science", Prentice-Hall, 1991.

Our planet is shrouded in water, and yet 8 million children under the age of five will die this year from lack of safe water.

United Nations Environmental Program

6.1 DRINKING WATER QUALITY

One of the first things that a world traveler learns to ask is whether or not the water is safe to drink. The unfortunate answer in most places in the world is no. It has been estimated that 80 percent of all sickness in the world is attributable to inadequate water or sanitation. Furthermore, an estimated three-fourths of the population in Asia, Africa, and Latin America lack a safe supply of water for drinking, washing, and sanitation (Morrison, 1983).

Developing and maintaining an adequate supply of safe drinking water requires the coordinated efforts of scientists, engineers, water plant operators, and regulatory officials.

The Safe Drinking Water Act

Legislation to protect drinking water quality in the United States began with the Public Health Service Act of 1912. In this Act, the nation's first water quality standards were created. While these standards slowly evolved over the years, it was not until the passage of the *Safe Drinking Water Act* (SDWA) of 1974 that federal responsibility was extended beyond interstate carriers to include all community water systems serving 15 or more outlets, or 25 or more customers. This

original Safe Drinking Water Act had two basic thrusts: (1) It required the EPA to establish national standards for drinking water quality and (2) it required the operators of some 60 000 public water systems in the country to monitor the quality of water being delivered to customers and to treat that water, if necessary, to assure compliance with the standards.

Twelve years later, in 1986, strengthening amendments were added to the SDWA. These required the EPA to quicken the pace of standard setting and required the equivalent of filtration for all surface water supplies and required disinfection for all water systems. The regulations also recognized the potential for lead contamination in water distribution systems, including the plumbing systems in homes and nonresidential facilities. To help prevent lead poisoning, the 1986 amendments require the use of "lead-free" pipe, solder, and flux for all such systems (in the past, solder normally contained about 50 percent lead; now it may contain no more than 0.2 percent lead).

Drinking water standards fall into two categories: *primary standards*, which specify *maximum contaminant levels* (MCLs) based on health related criteria, and *secondary standards*, which are unenforceable guidelines based on both aesthetic characteristics such as taste, odor, and color of drinking water, as well as nonaesthetic characteristics such as corrosivity and hardness. In setting MCLs, the EPA is required to balance the public health benefits of the standard against what is technologically and economically feasible. In this way, MCLs are quite different from National Ambient Air Quality Standards, which must be set at levels that protect public health regardless of cost or feasibility.

In setting standards, the EPA creates unenforceable maximum contaminant level goals (MCLGs; formerly known as recommended maximum contaminant levels, or RMCLs) set at levels that present no known or anticipated health effects, including a margin of safety, regardless of technological feasibility or cost. The Safe Drinking Water Act requires the EPA to periodically review the actual MCLs to determine whether they can be brought closer to the desired MCLGs.

Primary Standards

Contaminants for which MCLs and MCLGs are established are classified as being either inorganic chemicals, organic chemicals, radionuclides, or microbiological contaminants. Under the impetus of the SDWA, the list of substances in each category is continuously growing. A list of the standards for inorganic chemicals is given in Table 6.1. Additional inorganic chemicals for which MCLs are being proposed include asbestos and copper.

Organic chemical contaminants for which MCLs are being promulgated are conveniently classified using the following three groupings:

1. *Synthetic organic chemicals* (SOCs), are compounds used in the manufacture of a wide variety of agricultural and industrial products. This includes primarily pesticides and herbicides.

TABLE 6.1 MAXIMUM CONTAMINANT LEVELS (MCLs) FOR CERTAIN INORGANIC CHEMICALS

Contaminant	Principal health effects	Maximum contaminant levels (mg/L)
Arsenic	Dermal and nervous system toxicity effects	0.05
Barium	Circulatory system effects	1.0
Cadmium	Kidney effects	0.010
Chromium	Liver/kidney effects	0.05
Fluoride	Skeletal damage	1.8 (at 20 °C)
Lead	Central and peripheral nervous system damage; kidney effects; highly toxic to infants and pregnant women	0.05
Mercury	Central nervous system disorders; kidney effects	0.002
Nitrate and nitrite	Methemoglobinemia (blue-baby syndrome)	10.0 (as N)
Selenium	Gastrointestinal effects	0.01
Silver	Skin discoloration (argyria)	0.05

Source: Based on USEPA (1986a).

2. *Trihalomethanes* (THMs) are the by-products of water chlorination. They include chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), dibromochloromethane (CHBr_2Cl), and bromoform (CHBr_3).

3. *Volatile organic chemicals* (VOCs) are synthetic chemicals that readily vaporize at room temperature. These include degreasing agents, paint thinners, glues, dyes, and some pesticides. Representative chemicals include benzene, carbon tetrachloride, 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), and vinyl chloride.

A list of organic chemicals for which MCLs had been set as of 1986 is given in Table 6.2.

Radioactivity in public drinking water supplies is the third category of contaminants regulated by the Safe Drinking Water Act. Some radioactive compounds, or *radionuclides*, are naturally occurring substances such as radon and radium-226 (which are often found in groundwater), while others, such as strontium-90 and tritium, are surface water contaminants resulting from atmospheric nuclear weapons testing fallout. The MCL for the combination of radium-226 and radium-228 is 5 pCi/L, while the gross α -particle activity MCL (including radium-226 but excluding radon and uranium) is 15 pCi/L. The MCL for β -particle and photon radioactivity is an annual dose either to the whole body or to any particular organ, of 4 mrem/year (USEPA, 1976).

The most significant radionuclide associated with drinking water is dissolved radon gas. It is a colorless, odorless, and tasteless gas that occurs naturally in

TABLE 6.2 MAXIMUM CONTAMINANT LEVELS (MCLs) FOR CERTAIN ORGANIC CHEMICALS

Contaminant	Principal health effects	MCL (mg/L)
Endrin	Nervous system/kidney effects	0.0002
Lindane	Nervous system/kidney effects	0.004
Melchiorchlor 2,4-D	Nervous system/kidney effects	0.1
2,4,5-TP Silver	Liver/kidney effects	0.01
Toxaphene	Cancer risk	0.005
Trihalomethanes (THMs)	Cancer risk	0.10

Source: Based on USEPA (1976, 1986a).

some groundwater. It is an unusual contaminant because the danger arises not from drinking radon contaminated water, but from breathing the gas after it has been released into the air. When radon-laden water is heated or agitated, such as occurs in showers or washing machines, the dissolved radon gas is released. As will be discussed in Chapter 7, inhaled radon gas is thought to be a major cause of lung cancer.

The fourth category of primary MCLs is *microbiological contaminants*. While it would be desirable to evaluate the safety of a given water supply by individually testing for specific pathogenic microorganisms, such tests are too difficult to perform on a routine basis or to be used as a standard. Instead, a much simpler technique is used, based on testing water for evidence of any fecal contamination. In this test, coliform bacteria (typically *Escherichia coli*) are used as indicator organisms whose presence suggests that the water is contaminated. Since the number of coliform bacteria excreted in feces is on the order of 50 million per gram, and the concentration of coliforms in untreated domestic wastewater is usually several million per 100 mL, it would be highly unlikely that water contaminated with human wastes would have no coliforms. That conclusion is the basis for the drinking water standard for microbiological contaminants which specifies, in essence, that on the average, water should contain no more than one coliform per 100 mL.

The assumption that the absence of coliforms implies an absence of pathogens is based primarily on the following two observations. First, in our society it is the excreta from relatively few individuals that adds pathogens to a wastewater stream, while the entire population contributes coliforms. Thus, the number of coliforms should far exceed the number of pathogens. Second, for many of the waterborne diseases that have plagued humankind, the survival rate of pathogens outside the host is much lower than the survival rate of coliforms. The combination of these factors suggests that, statistically speaking, the ratio of pathogens to coliforms should be sufficiently small that we can conclude that it is extremely unlikely that a sample of water would contain a pathogen without also containing numerous coliforms.

TABLE 6.3 CALCULATED VIRUS-COLIFORM RATIOS FOR SEWAGE AND POLLUTED SURFACE WATER

	Virus	Coliform	Virus/coliform ratio
Sewage	500/100 mL	46 × 10 ⁶ /100 mL	1:92,000
Polluted surface water	1/100 mL	5 × 10 ⁶ /100 mL	1:50,000

Source: Robeck et al. (1962).

This approach to testing for microbiological purity has been quite effective, but it is not an absolutely certain measure. There is considerable evidence, for example, that some nonbacterial pathogens, notably viruses and *Giardia* cysts, survive considerably longer outside of their hosts than coliform bacteria. This increases the probability of encountering pathogens without accompanying coliforms. However, as suggested by the approximations given in Table 6.3 for viruses, the risk of such an encounter is still considered to be acceptably small under normal circumstances.

The coliform test is also used to assess the safety of water-contact recreational activities, with many states recommending a limit of 1000 coliforms per 100 mL. However, proper interpretation of a coliform test made on surface water is complicated by the fact that fecal coliforms are discharged by animals as well as humans. Thus, a high fecal coliform count is not necessarily an indication of human contamination. When it is important to distinguish between human and animal contamination, more sophisticated testing can be performed. Such testing is based on the fact that the ratio of fecal coliform to fecal streptococci is different in human and animal discharges.

TABLE 6.4 SECONDARY STANDARD FOR DRINKING WATER

Contaminant	Level
Chloride	250 mg/L
Color	15 color units
Copper	1 mg/L
Corrosivity	Noncorrosive
Foaming agents	0.5 mg/L
Iron	0.3 mg/L
Manganese	0.05 mg/L
Odor	3 threshold odor number
pH	6.5–8.5
Sulfate	250 mg/L
Total dissolved solids	500 mg/L
Zinc	5 mg/L

6.2 WATER TREATMENT SYSTEMS

Secondary Standards

Secondary standards are nonenforceable, maximum contaminant levels based on aesthetic factors such as taste, color, and odor, rather than on health effects. The limits suggested in Table 6.4 for chloride, copper, total dissolved solids, and zinc are in large part based on taste. Excessive sulfate is undesirable because of its laxative effect; iron and manganese are objectionable because of taste and their ability to stain laundry and fixtures; foaming and color are visually upsetting; and odor from various dissolved gases may make water unacceptable to the drinker.

6.2 WATER TREATMENT SYSTEMS

The purpose of a water treatment system is to bring raw water up to drinking water quality. The particular type of treatment equipment required to meet these standards will depend to a large extent on the quality of the source water. Some water requires only simple disinfection. Surface water will usually need to be filtered and disinfected, while groundwater will often need to have hardness (calcium and magnesium) removed before disinfection.

As suggested in Figure 6.1, a typical treatment plant for surface water might include the following sequence of steps:

Screening to remove relatively large floating and suspended debris.

Mixing the water with chemicals that encourage suspended solids to coagulate into larger particles that will more easily settle.

Flocculation, which is the process of gently mixing the water and coagulant, allowing the formation of large particles of floc.

Sedimentation in which the flow is slowed enough so that gravity will cause the floc to settle.

Sludge processing where the mixture of solids and liquids collected from the settling tank are dewatered and disposed of.

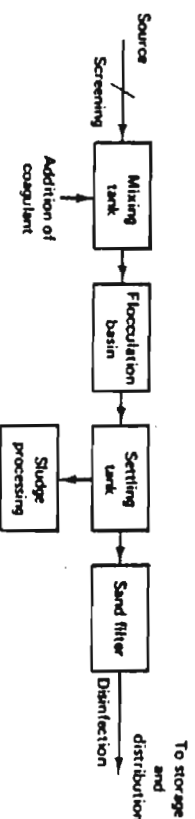


Figure 6.1 Schematic of a typical water treatment plant for surface water. Softening may be required as an additional step for groundwater.

Disinfection of the liquid effluent to ensure that the water is free of harmful pathogens.

Hardness removal can be added to this generalized flow diagram if needed.

Coagulation and Flocculation

Raw water may contain suspended particles of color, turbidity, and bacteria that are too small to settle in a reasonable time period, and cannot be removed by simple filtration. The object of coagulation is to alter these particles in such a way as to allow them to adhere to each other. Thus, they can grow to a size that will allow removal by sedimentation and filtration. Coagulation is considered to be a chemical treatment process that destabilizes colloidal particles (particles in the size range of about 0.001–1 μm), as opposed to the physical treatment operations of flocculation, sedimentation, and filtration that follow.

Most colloids of interest in water treatment remain suspended in solution because they have a net negative surface charge that causes the particles to repel each other. The intended action of the coagulant is to neutralize that charge, allowing the particles to come together to form larger particles that can be more easily removed from the raw water. The exact way that coagulants work is still not well understood, so past experience with similar treatment systems is invaluable to the design of new systems.

The usual coagulant is alum [$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$], though FeCl_3 , FeSO_4 , and other coagulants, such as polyelectrolytes, can be used. Since the intention here is simply to introduce the concepts of water treatment, leaving the complexities for more specialized books, let us just look at the reactions involving alum. Alum ionizes in water, producing Al^{3+} ions, some of which neutralize the negative charges on the colloids. Most of the aluminum ions, however, react with alkalinity in the water (bicarbonate) to form insoluble aluminum hydroxide [$\text{Al}(\text{OH})_3$]. The aluminum hydroxide adsorbs ions from solution and forms a precipitate of $\text{Al}(\text{OH})_3$ and adsorbed sulfates. The overall reaction is



If insufficient bicarbonate is available for this reaction to occur, the pH must be raised, usually by adding lime [$\text{Ca}(\text{OH})_2$] or sodium carbonate (Na_2CO_3).

Coagulants are added to the raw water in a chamber that has rapidly rotating paddles to mix the chemicals. Detention times in the rapid mix tank are typically on the order of one minute. Flocculation follows in a tank that provides gentle agitation for approximately one-half hour. During this time, the precipitating aluminum hydroxide attracts colloidal particles, forming a plainly visible floc. The mixing in the flocculation tank must be done very carefully. It must be sufficient to encourage particles to make contact with each other, enabling the floc to grow

in size, but it cannot be so vigorous that the fragile floc particles will break apart. Mixing also helps keep the floc from settling in this tank, rather than in the sedimentation tank that follows.

While Figure 6.1 suggests separate tanks for rapid mixing, flocculation, and sedimentation, the three physical processes can be combined into a single unit, as shown in Figure 6.2.

Sedimentation and Filtration

After flocculation, the water flows through a sedimentation basin, or clarifier. A sedimentation basin is a large circular, or rectangular, concrete tank designed to hold the water for a long enough time to allow most of the suspended solids to settle out. Typical detention times range from 1 to 10 hr. The longer the detention time the bigger and more expensive the tank must be, but, correspondingly, the better will be the tank's performance. Solids that collect on the bottom of the tank may be removed manually by periodically shutting down the tank and washing out the collected sludge, or the tank may be continuously and mechanically cleaned using a bottom scraper. The effluent from the tank is then filtered.

One of the most widely used filtration units is called a *rapid-sand filter*, which consists of a layer of carefully sieved sand on top of a bed of graded gravels. The pore openings between grains of sand are often greater than the size of the floc particles that are to be removed, so much of the filtration is accomplished by means other than simple straining. Adsorption, continued flocculation, and sedimentation in the pore spaces are also important removal mechanisms. When the filter becomes clogged with particles, which occurs roughly once a day, the filter is shut down for a short period of time and cleaned by forcing water backwards through the sand for 10–15 min. After cleaning, the sand settles back in place and operation resumes.

Disinfection

During coagulation, settling, and filtration, practically all of the suspended solids, most of the color, and all but a few percent of the bacteria, are removed. The final step is disinfection to kill any remaining pathogenic organisms.

Chlorination using chlorine gas (Cl_2), sodium hypochlorite (NaOCl), or calcium hypochlorite [$\text{Ca}(\text{OCl})_2$], is the most commonly used method of disinfection in this country. Chlorine is a powerful oxidizing agent that is easy to use, inexpensive, and reliable. The precise mechanism by which chlorine kills microorganisms is not well understood. It is thought that its strong oxidizing power destroys the enzymatic processes necessary for cell life. Though chlorination is completely effective against bacteria, its effectiveness is less certain with protozoal cysts, most notably those of *Giardia lamblia*, or with viruses. Complete treatment, including coagulation, sedimentation, filtration, as well as disinfection, is especially recommended where *Giardia lamblia* is problematic.

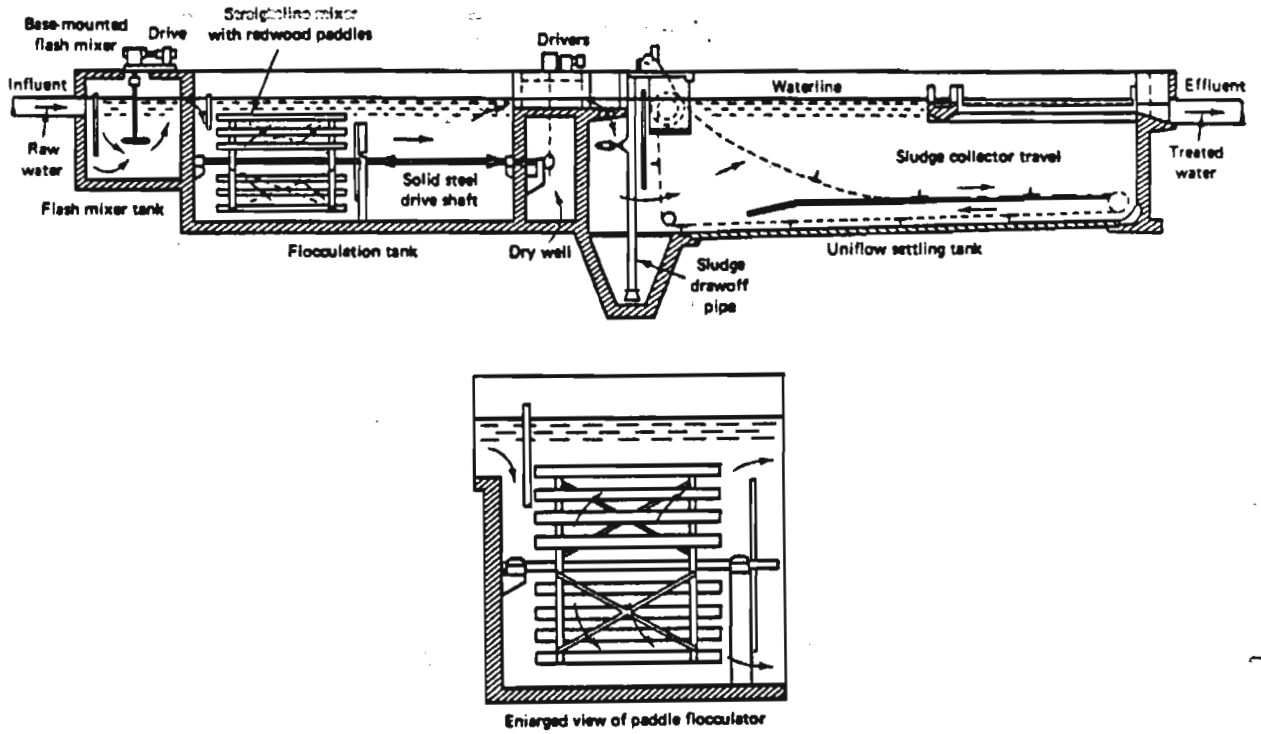


Figure 6.2 Cross section of a rapid mixing, flocculation, and sedimentation tank. (Source: Courtesy Materials Handling Systems Div., FMC Corp.).

Using chlorine gas to illustrate the chemical reactions occurring during chlorination, the key reaction is



The hypochlorous acid formed (HOCl) is the prime disinfecting agent. Its dissociation is pH dependent, yielding less effective hypochlorite (OCl^-) ions at higher pH values:



Together, HOCl and OCl^- are called the *free available chlorine*.

A principal advantage of chlorination over other forms of disinfection is that a chlorine residual is created that can protect the treated water after leaving the treatment plant. This guards against possible contamination that might occur in the water distribution system. To increase the lifetime of this residual, some systems add ammonia to the treated water, forming *chloramines* (NH_2Cl , NHCl_2 , NCl_3). Chloramines, although they are less effective as oxidants than HOCl, are more persistent. Residual chlorine that exists as chloramine is referred to as *combined available residual chlorine*.

A disadvantage of chlorination is the potential formation of trihalomethanes (THMs) such as the carcinogen chloroform (CHCl_3). THMs are created when chlorine combines with natural organic substances, such as decaying vegetation, that may be present in the water itself. One approach to reducing THMs is to remove more of the organics before any chlorination takes place. It was common practice in the past, for example, to chlorinate the incoming raw water before coagulation and filtration. This contributed to formation of THMs. By eliminating this step, and by increasing the organic removal during treatment before chlorination, some degree of control is achieved. In the future, the actual removal of THMs from the treated water, perhaps by aeration or adsorption on activated carbon, may become necessary.

The problem of THMs is helping spur interest in alternatives to chlorination as the preferred method of disinfection. Alternative disinfectants include chloramines, chlorine dioxide, and ozone. Each has the advantage of not creating THMs, but there are uncertainties and known disadvantages to each that have restricted their more widespread use. Chloramines, as mentioned above, are less certain disinfectants than free chlorine, so chloramination is usually used in combination with some other more effective method of disinfection. Chlorine dioxide (ClO_2), on the other hand, is a potent bactericide and viricide, and it does form a residual capable of protecting water in the distribution system. However, there is concern for certain toxic chlorate and chlorite substances that it may create, and it is a very costly method of disinfection. Ozonation involves the passage of ozone (O_3) through the water. Ozone is a very powerful disinfectant that is even more effective against cysts and viruses than chlorine, and it has the added advantage of leaving no taste or odor problems. Though ozonation is widely used in European

water treatment facilities, it has the disadvantages of not forming a protective residual in the treated water, and it is more expensive than chlorination.

Hardness and Alkalinity

The presence of multivalent cations, most notably calcium and magnesium ions, is referred to as water *hardness*. Groundwater is especially prone to excessive concentrations of these ions, leading to two distinct problems. First, the reaction between hardness and soap produces a sticky, gummy deposit called "soap curd" (the ring around the bathtub). Essentially all home cleaning activities, from bathing and grooming to dishwashing and laundering, are made more difficult with hard water.

While the introduction of synthetic detergents has decreased, but not eliminated, the impact of hardness on cleaning, the second problem, that of scaling, remains significant. When hard water is heated, calcium carbonate (CaCO_3) and magnesium hydroxide [$\text{Mg}(\text{OH})_2$] readily precipitate out of solution, forming a rock-like scale that clogs hot water pipes and reduces the efficiency of water heaters, boilers, and heat exchangers. Pipes filled with scale must ultimately be replaced, usually at great expense. Heating equipment that has scaled up not only transmits heat less readily, thus increasing fuel costs, but also is prone to failure at a much earlier time. For both of these reasons, if hardness is not controlled at the water treatment plant itself, many individuals and industrial facilities find it worth the expense to provide their own water softening.

Hardness is defined as the concentration of all multivalent metallic cations in solution. The principal ions causing hardness in natural water are calcium (Ca^{2+}) and magnesium (Mg^{2+}). Others, including iron (Fe^{2+}), manganese (Mn^{2+}), strontium (Sr^{2+}), and aluminum (Al^{3+}), may be present, though in much smaller quantities.

It is conventional practice in reporting hardness (as well as alkalinity) to measure the concentrations of these individual ions not in terms of mg/L, but in terms of *equivalents*. By noting, for example, that 8 g of oxygen combine with 1 g of hydrogen (forming H_2O), while 3 g of carbon combine with 1 g of hydrogen (forming CH_4), the idea of equivalents suggests that 8 g of oxygen ought to combine with 3 g of carbon (which it does in CO_2). In this example, the *equivalent weight* of oxygen would be 8 g, while that of carbon would be 3 g, and one equivalent weight of oxygen would combine with one equivalent weight of carbon (to form CO_2). This idea of equivalents, when first proposed in the 18th century, was not taken very seriously because it is complicated by the fact that individual elements can have more than one equivalent weight, depending on the reaction in question (e.g., carbon forms CO as well as CO_2). With the understanding of the structure of the atom that came later, however, it regained favor as a convenient method of handling certain chemical computations.

The *equivalent weight* of a substance is its atomic or molecular weight divided by a number n . For the reactions of interest in hardness and alkalinity

calculations, n is simply the ionic charge. For compounds, it is the number of hydrogen ions that would be required to replace the cation.

$$\text{Equivalent weight (EW)} = \frac{\text{Atomic (molecular) weight}}{n} \quad (6.4)$$

Thus, for example, CaCO_3 has $n = 2$ since it would take two hydrogen ions to replace the cation (Ca^{2+}). Its equivalent weight is therefore

$$\begin{aligned} \text{Equivalent weight of } \text{CaCO}_3 &= \frac{(40 + 12 + 3 \times 16)}{2} = \frac{100}{2} \\ &= 50 \text{ g/eq} = 50 \text{ mg/meq} \end{aligned}$$

where (mg/meq) are the units of milligrams per milliequivalent. For the calcium ion itself (Ca^{2+}), which has an atomic weight of 40.1 and a charge of 2, the equivalent weight is

$$\text{Equivalent weight of } \text{Ca}^{2+} = \frac{40.1}{2} = 20.05 \text{ mg/meq}$$

and for magnesium (Mg^{2+}) with atomic weight 24.3,

$$\text{Equivalent weight of } \text{Mg}^{2+} = \frac{24.3}{2} = 12.15 \text{ mg/meq}$$

In measuring hardness, the concentrations of the multivalent cations are converted to mg/L as CaCO_3 using the following expression

$$\begin{aligned} \text{mg/L of } X \text{ as } \text{CaCO}_3 &= \frac{\text{Concentration of } X \text{ (mg/L)} \times 50 \text{ mg } \text{CaCO}_3/\text{meq}}{\text{Equivalent weight of } X \text{ (mg/meq)}} \\ &\quad (6.5) \end{aligned}$$

The *total hardness* (TH) as CaCO_3 is the sum of each individual hardness:

$$\text{Total hardness} = \text{Ca}^{2+} + \text{Mg}^{2+} \quad (6.6)$$

where it has been assumed in (6.6) that calcium and magnesium are the only two multivalent cations with appreciable concentrations. The following example shows how to work with these units.

Example 6.1 Total Hardness as CaCO_3

A sample of groundwater has 100 mg/L of Ca^{2+} and 10 mg/L of Mg^{2+} . Express its hardness in units of meq/L and mg/L as CaCO_3 .

Solution The contribution of calcium in meq/L is

$$\frac{100 \text{ mg/L}}{20.05 \text{ mg/meq}} = 4.99 \text{ meq/L}$$

and in mg/L as CaCO_3 is

$$4.99 \text{ meq/L} \times 50 \text{ mg } \text{CaCO}_3/\text{meq} = 249.4 \text{ mg/L as } \text{CaCO}_3$$

For magnesium, the hardness is

$$\frac{10 \text{ mg/L}}{12.15 \text{ mg/meq}} = 0.82 \text{ meq/L}$$

or

$$0.82 \text{ meq/L} \times 50 \text{ mg CaCO}_3/\text{meq} = 41.0 \text{ mg/L as CaCO}_3$$

The total hardness is

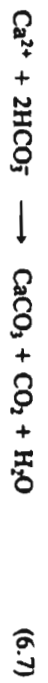
$$4.99 \text{ meq/L} + 0.82 \text{ meq/L} = 5.8 \text{ meq/L}$$

or

$$(249.4 + 41.0) \text{ mg/L} = 290.4 \text{ mg/L as CaCO}_3$$

While public acceptance of hardness is quite dependent on the past experiences of individual consumers, hardness above about 150 mg/L as CaCO₃ is noticed by most consumers. Though there are no absolute distinctions, the qualitative classification of hardness given in Table 6.5 is often used (Tchobanoglous and Schroeder, 1985).

It is useful at times to separate total hardness, which is almost entirely the combination of calcium and magnesium cations, into two components: *carbonate hardness* (CH), associated with the anions HCO₃⁻ and CO₃²⁻, and *noncarbonate hardness* (NCH) associated with other anions. If carbonate hardness exceeds the total hardness (TH), then CH is given the same value as TH. Carbonate hardness is especially important since it leads to scaling, as the following reaction suggests:



Carbonate hardness is sometimes referred to as temporary hardness because it can be removed by simply heating the water.

Another important characteristic of water is its *alkalinity*, which is a measure of the water's ability to absorb hydrogen ions without significant pH change. That is, alkalinity is a measure of the buffering capacity of water. In most natural water, the total amount of H⁺ that can be neutralized is dominated by the carbon-

TABLE 6.5 QUALITATIVE CLASSIFICATION OF WATERS ACCORDING TO HARDNESS

Description	Hardness	
	meq/L	mg/L as CaCO ₃
Soft	<1	<50
Moderately hard	1-3	50-150
Hard	3-6	150-300
Very hard	>6	>300

Source: Tchobanoglous and Schroeder (1985).

ate buffering system. Thus,

$$\text{Alkalinity (mol/L)} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (6.8)$$

Notice that the concentration of carbonate [CO₃²⁻] is multiplied by 2 since each ion can neutralize two H⁺ ions. This assumes that the concentrations are being measured in molarity units (mol/L). More often, the concentrations are measured in terms of equivalents, or in mg/L as CaCO₃, in which case the 2 is already accounted for in the conversions and concentrations are added directly:

$$\text{Alkalinity (meq/L)} = (\text{HCO}_3^-) + (\text{CO}_3^{2-}) + (\text{OH}^-) - (\text{H}^+) \quad (6.9)$$

where the quantities in parentheses are concentrations in meq/L or mg/L as CaCO₃.

The following example demonstrates these alkalinity calculations.

Example 6.2 Calculating Alkalinity

A sample of water at pH 10.0 has 32.0 mg/L of CO₃²⁻ and 56.0 mg/L of HCO₃⁻. Find the alkalinity as CaCO₃.

Solution The carbonate has a molecular weight of 12 + 3 × 16 = 60 and n = 2, so the equivalent weight is 60/2 = 30 mg/meq. Converting the given concentration into mg/L as CaCO₃ gives

$$\text{CO}_3^{2-} = 32.0 \text{ mg/L} \times \frac{1}{30 \text{ mg/meq}} \times 50 \text{ mg CaCO}_3/\text{meq} = 53.3 \text{ mg/L as CaCO}_3$$

The bicarbonate has molecular weight 61 with n = 1, so its equivalent weight is 61 mg/meq:

$$\text{HCO}_3^- = 56.0 \text{ mg/L} \times \frac{1}{61 \text{ mg/meq}} \times 50 \text{ mg CaCO}_3/\text{meq} = 45.9 \text{ mg/L as CaCO}_3$$

The pH is 10, so [H⁺] = 10⁻¹⁰ mol/L, and its EW is 1 mg/meq; expressed as CaCO₃ it becomes

$$\text{H}^+ = 10^{-10} \text{ mol/L} \times 1 \text{ g/mol} \times \frac{10^3 \text{ mg/g}}{1 \text{ mg/meq}} \times 50 \text{ mg CaCO}_3/\text{meq}$$

$$\text{H}^+ = 5.0 \times 10^{-4} \text{ mg/L as CaCO}_3$$

Since [H⁺][OH⁻] = 10⁻¹⁴, then [OH⁻] = 10⁻⁴ mol/L; its EW is 17 mg/meq.

$$\text{OH}^- = 10^{-4} \text{ mol/L} \times 17 \text{ g/mol} \times \frac{10^3 \text{ mg/g}}{17 \text{ mg/meq}} \times 50 \text{ mg CaCO}_3/\text{meq}$$

$$\text{OH}^- = 5.0 \text{ mg/L as CaCO}_3$$

Total alkalinity, then, is just (CO₃²⁻) + (HCO₃⁻) + (OH⁻) - (H⁺)

$$\text{Alkalinity} = 53.3 + 45.9 + 5.0 - 5.0 \times 10^{-4} = 104.2 \text{ mg/L as CaCO}_3$$

For nearly neutral water (pH around 6-8) the concentrations of H⁺ and OH⁻ are insignificant and alkalinity is determined entirely by the carbonates:

$$\text{Alkalinity (meq/L)} = (\text{HCO}_3^-) + (\text{CO}_3^{2-}) \quad (6.10)$$

An analysis of a sample of water with pH 7.5 has produced the following concentrations (mg/L):

Cations		Anions	
Ca ²⁺	80	Cl ⁻	100
Mg ²⁺	30	SO ₄ ²⁻	201
Na ⁺	72	HCO ₃ ⁻	165
K ⁺	6		

Find the total hardness, the carbonate hardness, the noncarbonate hardness, and the alkalinity, all expressed as CaCO₃. Find the total dissolved solids (TDS) in mg/L.

Solution It is helpful to set up a table in which each of the concentrations can be expressed in terms of CaCO₃. Equation 6.5 and the approach used in Example 6.1 will be followed. For example, for Ca²⁺

$$\text{Ca}^{2+} = 80 \text{ mg/L} \times \frac{1}{20.05 \text{ mg/meq}} \times 50 \text{ mg CaCO}_3/\text{meq} \\ = 199.5 \text{ mg/L as CaCO}_3$$

Ion	mg/L	MW	n	mg/meq	meq/L	mg/L as CaCO ₃
Ca ²⁺	80	40.1	2	20.05	3.99	199.5
Mg ²⁺	30	24.3	2	12.15	2.47	123.5
Na ⁺	72	23.0	1	23.0	3.13	156.5
K ⁺	6	39.1	1	39.1	0.15	7.7
Cl ⁻	100	35.5	1	35.5	2.82	140.8
SO ₄ ²⁻	201	96.1	2	48.05	4.18	209.2
HCO ₃ ⁻	165	61.0	1	61.0	2.70	135.2

As a first check on the chemical analysis, we can compare the sum of the concentrations of cations and anions as CaCO₃ or as meq/L to see if they are nearly equal.

$$\Sigma \text{ cations} = 199.5 + 123.5 + 156.5 + 7.7 = 487.2 \text{ mg/L as CaCO}_3$$

$$\Sigma \text{ anions} = 140.8 + 209.2 + 135.2 = 485.2 \text{ mg/L as CaCO}_3$$

which is quite close. The difference would probably be associated with small concentrations of other ions as well as measurement error.

a. The total hardness is the sum of the multivalent cations, Ca²⁺ and Mg²⁺:

$$\text{TH} = 199.5 + 123.5 = 323.0 \text{ mg/L as CaCO}_3$$

b. The carbonate hardness is that portion of total hardness associated with carbonates, which in this case is just bicarbonate HCO₃⁻:

$$\text{CH} = 135.2 \text{ mg/L as CaCO}_3$$

c. The noncarbonate hardness is the difference between the total hardness and the carbonate hardness:

$$\text{NCH} = \text{TH} - \text{CH} = 323.0 - 135.2 = 187.8 \text{ mg/L as CaCO}_3$$

d. Since the pH is nearly neutral, the concentrations of H⁺ and OH⁻ are negligible, so the alkalinity is given by just the bicarbonate:

$$\text{Alkalinity} = (\text{HCO}_3^-) = 135.2 \text{ mg/L as CaCO}_3$$

e. The total dissolved solids is simply the sum of the cation and anion concentrations expressed in mg/L:

$$\text{TDS} = 80 + 30 + 72 + 6 + 100 + 201 + 165 = 654 \text{ mg/L}$$

It is sometimes helpful to display the ionic constituents of water using a bar graph such as that shown in Figure 6.3.

Softening

Surface waters seldom have hardness levels above 200 mg/L as CaCO₃, so softening is not usually part of the water treatment process. For groundwater, however, where hardness levels are often over 1000 mg/L, it is quite common. There are two common approaches to softening water: the *lime-soda* process and the *ion-exchange* process. Either may be used in a central treatment plant prior to distribution, but individual home units use the ion-exchange process.

In the lime-soda process, either quick lime (CaO) or hydrated lime [Ca(OH)₂] is added to the water, raising the pH to about 10.3 and converting soluble bicarbonate ions (HCO₃⁻) into insoluble carbonate (CO₃²⁻). The carbonate

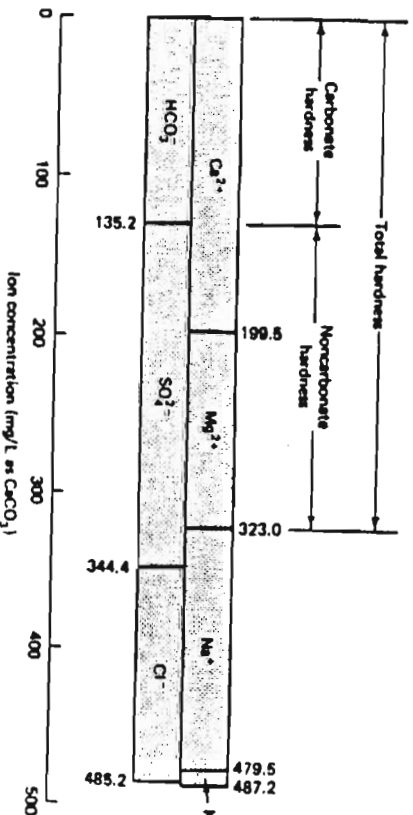


Figure 6.3 Bar graph illustrating the ionic constituents of Example 6.3.

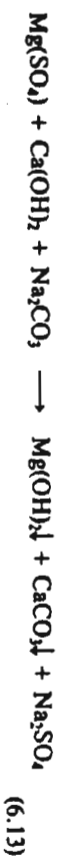
then precipitates out as CaCO_3 , as is suggested in the following reaction:



Similarly, magnesium ions can be removed by forming the precipitate $\text{Mg}(\text{OH})_2$:



If insufficient natural bicarbonate alkalinity (HCO_3^-) is available to cause reaction (6.11) or (6.12), it may be necessary to add carbonate in the form of soda ash (Na_2CO_3). The reaction for magnesium would then be



The additional carbonate required makes the process of noncarbonate hardness removal more expensive than the removal of carbonate hardness.

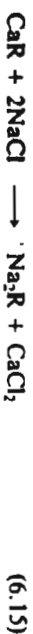
Most of the precipitates formed are removed in a sedimentation basin. Particles too finely divided to settle can later contribute to the clogging of filters and distribution piping, so the water is often recarbonated with CO_2 to convert those carbonate particles into soluble bicarbonates.

The alternate softening process uses ion exchange whereby hard water is forced through a column containing solid resin beads made of naturally occurring clays called *zeolites*, or synthetic resins. In an ion-exchange unit, the resin removes Ca^{2+} and Mg^{2+} ions from the water and replaces them with sodium ions, which form soluble salts. Using $\text{Ca}(\text{HCO}_3)_2$ as an example, the reaction can be represented as follows:



where R represents the solid ion-exchange resin. The calcium reacts with the resin and is removed from the water as CaR. The alkalinity (HCO_3^-) remains unchanged. The sodium salts that are formed do not cause hardness, but the dissolved sodium ions remain in the treated water and may be harmful to individuals with heart problems.

The hardness removal is essentially 100 percent effective as long as the ion-exchange medium has sodium remaining. When the sodium is depleted, the ion-exchange bed must be regenerated by removing it from service and backwashing it with a solution of NaCl, forming new Na_2R . The wastewater produced during regeneration must be properly disposed of, since it contains a high concentration of chlorides. The regeneration reaction involving Ca can be represented as



The ion-exchange process can be used in waste treatment as well as water treatment. In such cases, the process can enable recovery of valuable chemicals for reuse, or harmful ones for disposal. It is, for example, often used to recover chromic acid from metal finishing waste, for reuse in chrome-plating baths. It is even used for the removal of radioactivity.

6.3 WASTEWATER TREATMENT

Municipal wastewater is typically over 99.9 percent water. The characteristics of the remaining portion vary somewhat from city to city, with the variation depending primarily on inputs from industrial facilities that mix with the somewhat predictable residential flows. Given the almost limitless combinations of chemicals found in wastewater, it is too difficult to list them individually. Instead, they are often described by a few general categories, as has been done in Table 6.6.

In Table 6.6, a distinction is made between total dissolved solids and *suspended solids* (SS). The sum of the two is *total solids* (TS). The suspended solids portion is, by definition, the portion of total solids that can be removed by a membrane filter (having a pore size of about $1.2 \mu\text{m}$). The remainder (TDS) that cannot be filtered includes dissolved solids, colloidal solids, and very small suspended particles.

Wastewater treatment plants are usually designated as providing either *primary*, *secondary*, or *advanced* treatment, depending on the degree of purification. Primary treatment plants utilize physical processes, such as screening and sedimentation, to remove a portion of the pollutants that will settle, float, or that are too large to pass through simple screening devices. This is followed by disinfection. Primary treatment typically removes about 35 percent of the BOD and 60 percent of the suspended solids. In the early 1970s, the sewage of about 50 million people in the United States was receiving no better treatment than this. While the most visibly objectionable substances are removed in primary treatment, and some degree of safety is provided by the disinfection, the effluent still has enough BOD to cause oxygen depletion problems and enough nutrients, such as nitrogen and phosphorus, to accelerate eutrophication.

The *Clean Water Act* (CWA) of 1977, in essence, requires at least secondary treatment for all publicly owned treatment works (POTWs) by stipulating that such facilities provide at least 85 percent BOD removal (with possible case-by-case variances that allow lower percentages for marine discharges). This translates into an effluent requirement of 30 mg/L for both 5-day BOD and suspended

TABLE 6.6 TYPICAL RANGE OF COMPOSITION OF UNTREATED DOMESTIC WASTEWATER

Constituent	Abbreviation	Concentration (mg/L)
5-day biochemical oxygen demand	BOD ₅	100–300
Chemical oxygen demand	COD	250–1000
Total dissolved solids	TDS	200–1000
Suspended solids	SS	100–350
Total Kjeldahl nitrogen	TKN	20–80
Total phosphorus (as P)	TP	5–20

Source: Adapted from Davis and Cornwell (1983).

solids (monthly average). In secondary treatment plants, the physical processes that make up primary treatment are augmented with processes that involve the microbial oxidation of wastes. Such biological treatment mimics nature by utilizing microorganisms to oxidize the organics, with the advantage being that the oxidation can be done under controlled conditions in the treatment plant itself, rather than in the receiving body of water. When properly designed and operated, secondary treatment plants remove about 90 percent of the BOD and 90 percent of the suspended solids.

While the main purpose of primary treatment (in addition to disinfecting the wastes) is to remove objectionable solids, and the principal goal of secondary treatment is to remove most of the BOD, neither is effective at removing nutrients, dissolved material, or biologically resistant (refractory) substances. For example, typically no more than half of the nitrogen and one-third of the phosphorus are removed during secondary treatment. This means the effluent can still be a major contributor to eutrophication problems. In circumstances where either the raw sewage has particular pollutants of concern or the receiving body of water is especially sensitive, so-called advanced treatment (previously called *tertiary treatment*) may be required. Advanced treatment processes are varied and specialized, depending on the nature of the pollutants that must be removed. In most circumstances, advanced treatment follows primary and secondary treatment, although in some cases, especially in the treatment of industrial waste, it may completely replace those conventional processes.

An example wastewater treatment plant that provides primary and secondary treatment is illustrated in Figure 6.4.

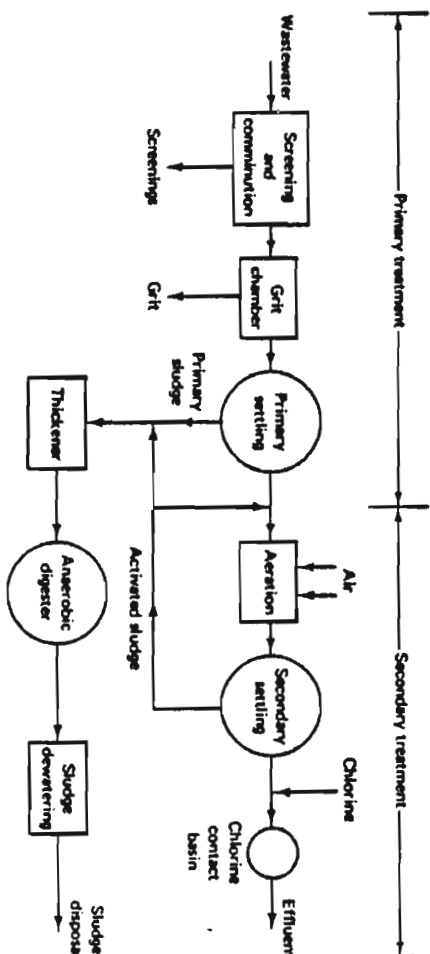


Figure 6.4 Schematic of an example wastewater treatment facility providing primary and secondary treatment using the activated sludge process.

Primary Treatment

As suggested in Figure 6.4, primary treatment begins with simple screening. Screening removes large floating objects such as rags, sticks, old shoes, and whatever else that might damage the pumps or clog small pipes. Screens vary, but typically consist of parallel steel bars spaced anywhere from 2 to 7 cm apart, perhaps followed by a wire mesh screen with smaller openings. One way to avoid the problem of disposal of materials collected on screens is to use a device called a comminuter, which grinds those coarse materials into small enough pieces that they can be left right in the wastewater flow.

After screening, the wastewater passes into a grit chamber where it is held for a few minutes. The *detention time* (the tank volume divided by the flow rate) is chosen to be long enough to allow sand, grit, and other heavy material to settle out but is too short to allow lighter, organic materials to settle. By collecting only these heavier materials, the disposal problem is simplified since those materials are usually nonoffensive and, after washing, can be easily disposed of in a landfill.

From the grit chamber, the sewage passes to a primary settling tank (also known as a "sedimentation basin" or a "clarifier") where the flow speed is reduced sufficiently to allow most of the suspended solids to settle out by gravity. Detention times of approximately 2–3 hr are typical, resulting in the removal of from 50 to 65 percent of the suspended solids and 25 to 40 percent of the BOD. Primary settling tanks are either round or rectangular and their behavior is similar to that of the clarifiers already described for water treatment facilities. The solids that settle, called *primary sludge* or raw sludge, are removed for further processing, as is the grease and scum that floats to the top of the tank.

If this is just a primary treatment plant, the effluent at this point is chlorinated to destroy bacteria and help control odors. Then it is released.

Secondary (Biological) Treatment

The main purpose of secondary treatment is to provide BOD removal beyond what is achievable by simple sedimentation. There are three commonly used approaches, all of which take advantage of the ability of microorganisms to convert organic wastes into stabilized, low-energy compounds. Two of these approaches, the *trickling filter* (and its variations) and the *activated sludge* process, sequentially follow normal primary treatment. The third, *oxidation ponds* (or lagoons), however, can provide equivalent results without preliminary treatment.

Trickling Filters

A trickling filter consists of a rotating distribution arm that sprays liquid wastewater over a circular bed of "first size" rocks or other coarse materials (Figure 6.5). The spaces between the rocks allow air to circulate easily so that

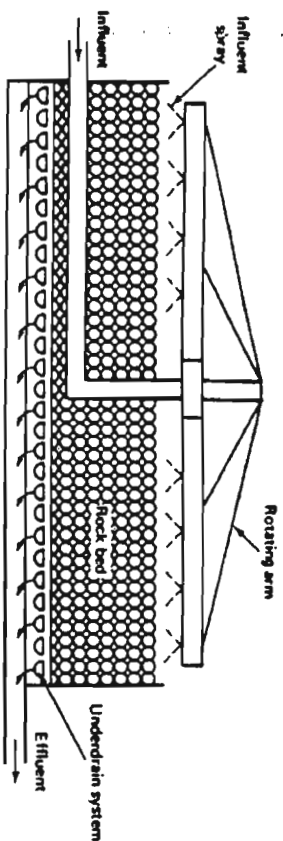


Figure 6.5 Sketch of the cross section of a trickling filter.

aerobic conditions can be maintained. Of course, the size of the openings is such that there is no actual filtering taking place, so the name trickling filter is somewhat of a misnomer. Instead, the individual rocks in the bed are covered by a layer of biological slime that adsorbs and consumes the wastes trickling through the bed. This slime consists mainly of bacteria, but it may also include fungi, algae, protozoa, worms, insect larvae, and snails. The accumulating slime periodically slides off individual rocks and is collected at the bottom of the filter, along with the treated wastewater, and passed on to the secondary settling tank where it is removed. Not shown is a provision for returning some of the effluent from the filter back into the incoming flow. Such recycling not only enables more effluent organic removal, it also provides a way to keep the biological slimes from drying out and dying during low flow conditions.

If ordinary rocks are used in the bed of a trickling filter, structural problems caused by their weight tend to restrict the bed depth to about 3 m. This makes it necessary for the beds to be quite large. Diameters as great as 60 m are not unusual. However, plastic media are becoming increasingly popular as a replacement for rocks, since in the same volume they can be designed to achieve greater surface areas for slime growth, and their lightness allows much deeper beds. The combination allows equivalent treatment to rock beds, but with much smaller land area requirements. They can also be designed to be less prone to plugging by the accumulating slime, and modestly higher rates of BOD removal are possible. These filters, made with plastic media, are sometimes referred to as *biological towers*.

Rotating Biological Contactor

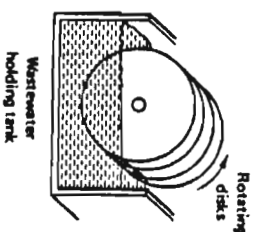
Trickling filters (and biological towers) are examples of devices that rely on microorganisms that grow on the surface of rocks, plastic, or other media. A variation on this *attached growth* idea is provided by the *rotating biological contactor* (RBC). An RBC consists of a series of closely spaced, circular, plastic disks, that are typically 3.6 m in diameter and attached to a rotating horizontal shaft. The bottom 40 percent of each disk is submerged in a tank containing the

wastewater to be treated. The biomass film that grows on the surface of the disks moves into and out of the wastewater as the RBC rotates. While the microorganisms are submerged in the wastewater, they adsorb organics; while they are rotated out of the wastewater, treatment levels that exceed conventional secondary treatment can be achieved (Figure 6.6). These devices have been used in the United States only since 1969, and, although early units suffered from assorted mechanical problems, they are now generally accepted. They are easier to operate under varying load conditions than trickling filters, since it is easier to keep the solid medium wet at all times.

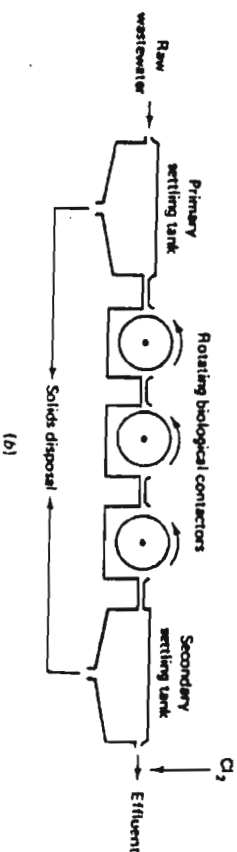
Activated Sludge

Trickling filters were first used in 1893 and they have been successfully used ever since, but they do cost more to build, are more temperature sensitive, and remove less BOD than the activated sludge plants that were later developed.

The example wastewater treatment plant flow diagram given in Figure 6.4 was drawn to illustrate the activated sludge process. As indicated there, the key biological unit in the process is the aeration tank, which receives effluent from the primary clarifier. It also receives a mass of recycled biological organisms from the



(a)



(b)

Figure 6.6 Rotating biological contactor cross section and treatment system: (a) RBC cross section; (b) RBC treatment system.

secondary settling tank, known as *activated sludge*. To maintain aerobic conditions, air or oxygen is pumped into the tank and the mixture is kept thoroughly agitated. After about 6–8 hr of agitation, the wastewater (now referred to as the "mixed liquor") flows into the secondary settling tank where the solids, mostly bacterial masses, are separated from the liquid by subsidence. A portion of those solids is returned to the aeration tank to maintain the proper bacterial population there, while the remainder must be processed and disposed of.

Figure 6.7 illustrates several variations of the basic activated sludge process (after primary settling). The earliest aeration tanks were designed so that the mixture of influent and recycled sludge was introduced at one end of a long, narrow tank, so that it tended to move uniformly from one end of the tank to the other (so-called "plug flow"). With such designs, the oxygen demand is exerted mostly at the entrance to the tank, with relatively little oxygen required at the

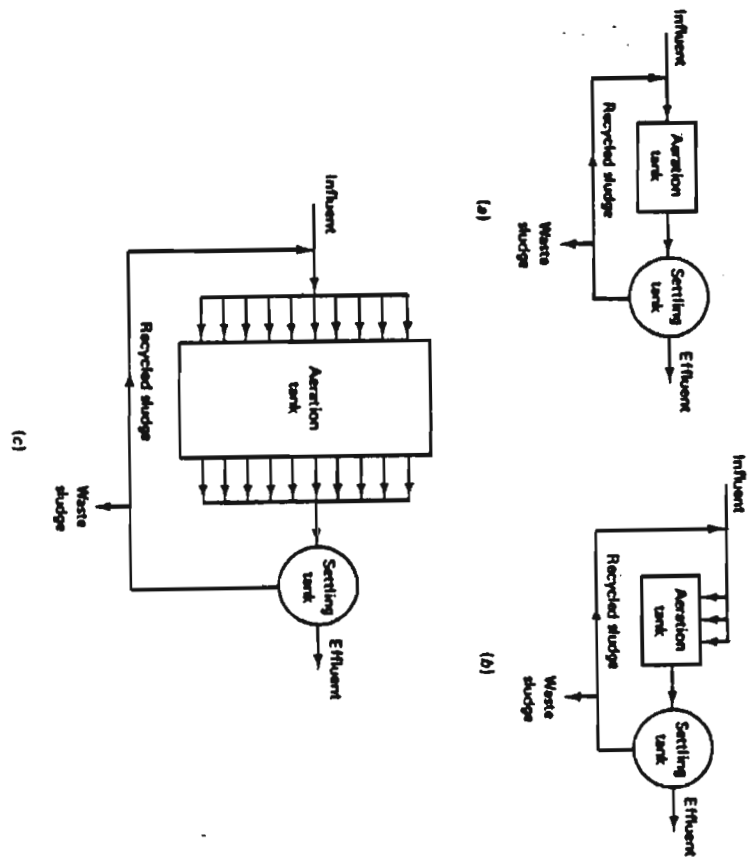


Figure 6.7 Modifications of the activated sludge process: (a) simple plug flow, (b) complete mix, and (c) complete mix. (Source: After Linsley, R. K., and Franzini, J. B. *Water-Resources Engineering*, 3d ed. Copyright © 1979 by McGraw-Hill, Inc. Used with permission of the publisher.)

exit. This nonuniformity of demand requires careful control by the plant operators to maintain aerobic conditions throughout, especially under variations in load. By introducing the mixture of wastes and recycled sludge at several points along the tank, as is shown in Figure 6.7b, or continuously along the edge of the tank, as is shown in Figure 6.7c, the stability of the process is increased, thus reducing the likelihood of biological upsets that can render the plants useless.

By allowing greater contact between microorganisms and wastewater in a given volume of space, activated sludge tanks can take up considerably less land area than trickling filters with equivalent performance. They are also less expensive to construct than trickling filters, have fewer problems with flies and odors, and can achieve higher rates of BOD removal. They do, however, require more energy for pumps and blowers, and hence have higher operating costs.

Sludge Treatment

The processes described thus far have the purpose of removing solids and BOD from the wastewater before the liquid effluent is released to a convenient, nearby body of water. What remains to be disposed of is a mixture of solids and water, called sludge. The collection, processing, and disposal of sludge can be the most costly and complex aspect of wastewater treatment.

The quantity of sludge produced may be as high as 2 percent of the original volume of wastewater, depending somewhat on the treatment process being used. Since sludge can be as much as 97 percent water, and since the cost of disposal will be related to the volume of sludge being processed, one of the primary goals of sludge treatment is to separate as much of the water from the solids as possible. The other goal is to stabilize the solids so that they are no longer objectionable or environmentally damaging.

The traditional method of sludge processing utilizes anaerobic digestion. That is, it involves bacteria that thrive in the absence of oxygen. Anaerobic digestion is slower than aerobic digestion, but has the advantage that only a small percentage of the wastes are converted into new bacterial cells. Instead, most of the organics are converted into carbon dioxide and methane gas. The digestion process is complex, but can be summarized by the two steps shown in Figure 6.8. In the first phase, complex organics such as fats, proteins, and carbohydrates are biologically converted into simpler organic materials, mostly organic fatty acids. The bacteria that perform this conversion are commonly referred to as *acid form-*

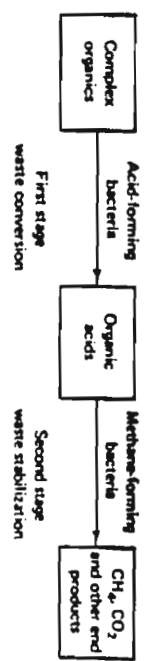


Figure 6.8 The two phases of anaerobic digestion.

ers. They are relatively tolerant to changes in temperature and pH, and they grow much faster than the *methane formers* that carry out the second stage of digestion.

Methane-forming bacteria slowly convert the organic acids into CO_2 , CH_4 , and other stable end products. These bacteria are very sensitive to temperature, pH, toxins, and oxygen. If their environmental conditions are not just right, the rate at which they convert organic acids to methane slows, and organic acids begin to accumulate, dropping the pH. A positive feedback loop can be established where the acid formers continue to produce acid, while the methane formers, experiencing lower and lower pH, become more and more inhibited. When this occurs, the digester is said to have gone sour, and massive doses of lime may be required to bring it back to operational status.

Most treatment plants utilizing anaerobic digestion for sludge stabilization use a two-stage digester as shown in Figure 6.9. Sludge in the first stage is thoroughly mixed and heated to increase the rate of digestion. Typical retention times are between 10 and 15 days. The second stage tank is neither heated nor mixed and is likely to have a floating cover to accommodate the varying amount of gas being stored. Stratification occurs in the second stage, which allows a certain amount of separation of liquids (called supernatant) and solids, as well as the accumulation of gas. The supernatant is returned to the main treatment plant for further BOD removal, and the settled sludge is removed, dewatered, and disposed of. The gas produced in the digester is about 60 percent methane, which is a valuable fuel with many potential uses within the treatment plant. The methane may be used to heat the first stage of the digester, and it can run in an engine/generator set to power pumps, compressors, and other electrical equipment.

Digested sludge removed from the second stage of the anaerobic digester is still mostly liquid. The solids have been well digested, so there is little odor. The most popular way of dewatering has been to pump the sludge onto large sludge drying beds where evaporation and seepage remove the water. Other methods include use of vacuum filters, filter presses, centrifuges, or incinerators. The

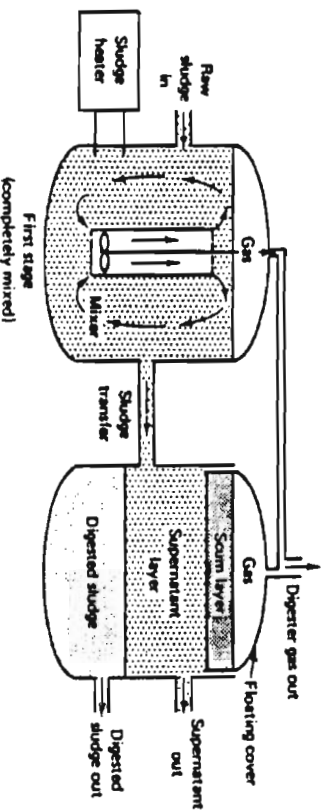


Figure 6.9 Schematic of a two-stage anaerobic digester.

digested and dewatered sludge is potentially useful as a soil conditioner, but most often it is simply trucked away and disposed of in a landfill.

Oxidation Ponds

Oxidation ponds are large, shallow ponds, typically 1–2 m deep, where raw or partially treated sewage is decomposed by microorganisms. The conditions are similar to those that prevail in a eutrophic lake. The ponds can be designed to maintain aerobic conditions throughout, but more often the decomposition taking place near the surface is aerobic, while that near the bottom is anaerobic. Such ponds, having a mix of aerobic and anaerobic conditions, are called *facultative ponds*. In ponds, the oxygen required for aerobic decomposition is derived from surface aeration and algal photosynthesis; deeper ponds, called *lagoons*, are mechanically aerated. A schematic diagram of the reactions taking place in a facultative pond is given in Figure 6.10.

Oxidation ponds can be designed to provide complete treatment to raw sewage, but they require a good deal of space. These ponds have been used extensively in small communities where land constraints are not so critical. The amount of pond surface area required is considerable, with 1 hectare per 240 people (1 acre per 100 people) often being recommended, although in areas with warm climates and mild winters, such as in the southwestern United States, about half that area is often used (Viessman and Hammer, 1985).

Ponds are easy to build and manage, they accommodate large fluctuations in flow, and they can provide treatment that approaches that of conventional biological systems but at a much lower cost. The effluent, however, may contain undesirable concentrations of algae and, especially in the winter when less oxygen is

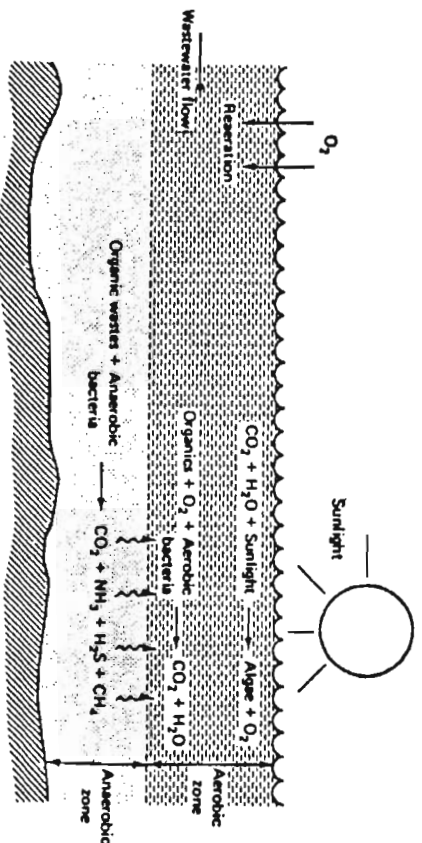


Figure 6.10 Schematic of an oxidation pond.

liberated by photosynthesis, they may produce unpleasant odors. Used alone, they also have the disadvantage that the effluent may not meet the EPA secondary treatment requirement of 30 mg/L BOD₅ and suspended solids. Their simplicity and effectiveness in destroying pathogenic organisms, however, make these ponds especially useful in developing countries.

Oxidation ponds are also used to augment secondary treatment, in which case they are often called *polishing ponds*.

Advanced Wastewater Treatment

Anything that follows conventional primary and biological treatment is considered to be advanced treatment. Many of the early advanced treatment facilities were designed with the primary purpose of removing nitrogen and phosphorus (the principal nutrients responsible for eutrophication), as well as to more completely reduce BOD. Very often now, advanced treatment is designed with the additional goal of removing various toxic substances, such as metals. Treatment technologies that can be used for hazardous wastes will be described in the next section.

Nitrogen Removal

Nitrogen exists in a variety of forms in wastewater. As bacteria decompose waste, nitrogen that was bound up in complex organic molecules is released as ammonia nitrogen. Ammonia, in turn, exists in water in two forms: as ammonium ion (NH₄⁺), which is highly soluble, and as ammonia gas (NH₃), which is not. As pH increases, the equilibrium relationship between these two forms is driven toward the less soluble ammonia gas (see Example 2.5):



One method of nitrogen removal, *ammonia stripping*, is based on this reaction. In this process, the pH of treated wastewater is raised to at least 10, typically with quick lime (CaO), to form dissolved ammonia gas. The ammonia can then be liberated in a stripping tower of the sort illustrated in Figure 6.11. Unfortunately, these systems have been plagued by a number of problems that have limited the usefulness of this approach. For one, the lime reacts with CO₂ to form a calcium carbonate scale, which must be removed periodically from the stripping surfaces. This scaling can be so severe, as was the case at the tertiary treatment plant in South Lake Tahoe, that the tower may eventually cease to function. Ammonia stripping is also less effective in cold weather, in part because ammonia is more soluble in cold water, making it harder to strip, but also because towers can ice up. The process also has been criticized because it simply transfers the pollution problem from one medium to another, in this case from water to air, creating an additional burden on the atmosphere.

A second approach to nitrogen control utilizes aerobic bacteria to convert ammonia (NH₄⁺) to (NO₃⁻), which is nitrification, followed by an anaerobic stage

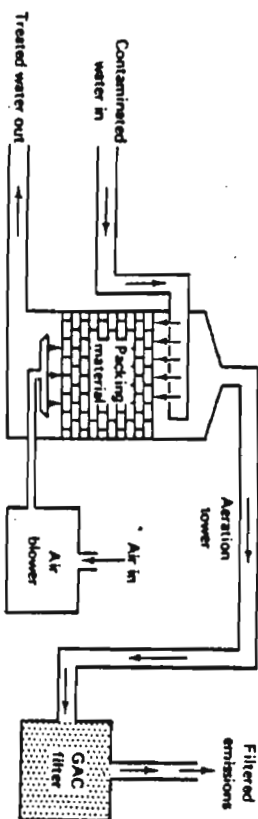


Figure 6.11 An air stripping tower followed by a granular activated carbon filter provides effective removal of VOCs. To remove nonvolatiles, the treated water coming out of the tower may be pumped through other carbon adsorbers.

where different bacteria convert nitrates to nitrogen gas (N₂), which is denitrification. The overall process then is referred to as *nitrification/denitrification*.

The nitrification step actually occurs in two stages. Ammonia is converted to nitrites (NO₂⁻) by *Nitrosomonas*, while *Nitrobacter* oxidize nitrites to nitrates, as was described in Section 4.4. The combination of steps can be summarized by



Nitrification does not begin to be important until domestic wastewater is at least 5–8 days old. Thus, if this method of nitrogen control is to be used, the wastewater must be kept in the treatment plant for a much longer time than would normally be the case. Detention times of 15 days or more are typically required. If reaction (6.17) takes place in the treatment plant rather than in the receiving body of water, at least the oxygen demand for nitrification is satisfied. The nitrogen, however, remains in the effluent, and if the process were to stop here, that nitrification could go on to contribute to unwanted algal growth. To avoid this, the denitrification step is required.

The second phase of the nitrification/denitrification process is anaerobic denitrification:



which releases harmless, elemental nitrogen gas. The energy to drive this reaction comes from the organic matter indicated in (6.18). Since this denitrification process occurs after waste treatment, there may not be enough organic material left in the waste stream to supply the necessary energy and an additional source, usually methanol (CH₃OH), must be provided.

Phosphorus Removal

Only about 30 percent of the phosphorus in municipal wastewater is removed during conventional primary and biological treatment. Since phosphorus is very often the limiting nutrient, its removal from the waste stream is especially important when eutrophication is a problem.

Phosphorus in wastewater exists in many forms, but all of it ends up as orthophosphate (H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-}). Removing phosphates is most often accomplished by adding a coagulant, usually alum [$\text{Al}_2(\text{SO}_4)_3$] or lime [$\text{Ca}(\text{OH})_2$]. The pertinent reaction involving alum is



Alum is sometimes added to the aeration tank when the activated sludge process is being used, thus minimizing the need for additional equipment.

The reaction for precipitation with lime can be represented as



where the precipitate formed is called calcium hydroxyphosphate, or, hydroxylapatite. When lime is used as the coagulant, it is often used after biological treatment, especially when ammonia stripping is also part of the treatment process. The lime not only causes the phosphate to precipitate out of solution, it also raises the pH of the waste stream so that soluble ammonium ions are converted to ammonia gas.

6.4 HAZARDOUS WASTE TREATMENT TECHNOLOGIES

Even with a much more vigorous hazardous waste reduction program, as RCRA requires, there will still be large quantities of hazardous wastes that will require treatment and disposal. In the past, there was little treatment, and disposal was most often on land. In both SARA (Superfund) and the 1984 Hazardous and Solid Waste Amendments of RCRA, emphasis is on the development and use of alternative and innovative treatment technologies that result in permanent destruction of wastes or a reduction in toxicity, mobility, and volume. Land disposal is greatly restricted under the 1984 RCRA amendments.

Treatment technologies are often categorized as being physical, chemical, biological, thermal, or stabilization/fixation. These categories are reasonably well defined, though there is room for confusion when technologies have overlapping characteristics.

Chemical, biological, and physical wastewater treatment processes are currently the most commonly used methods of treating aqueous hazardous waste. Chemical treatment transforms waste into less hazardous substances using such techniques as pH neutralization, oxidation or reduction, and precipitation. Biological treatment uses microorganisms to degrade organic compounds in the waste stream. Physical treatment processes include gravity separation, phase change systems, such as air and steam stripping of volatiles from liquid wastes, and various filtering operations, including carbon adsorption.

Thermal destruction processes include incineration, which is increasingly becoming a preferred option for the treatment of hazardous wastes, and pyrolysis, which is the chemical decomposition of waste brought about by heating the material in the absence of oxygen.

Fixation/stabilization techniques involve removal of excess water from a waste and solidifying the remainder either by mixing it with a stabilizing agent, such as Portland cement, or vitrifying it to create a glassy substance. Solidification is most often used on inorganic sludges.

Choosing an appropriate technology to use in any given situation is obviously beyond the scope of this text. Not only are there many different kinds of hazardous wastes, in terms of their chemical makeup, but the treatability of the wastes depends on their form. A technology suitable for treating PCBs in sludges, for example, may not be appropriate for treating the same contaminant in dry soil. Table 6.7 gives a partial listing of available treatment technologies appropriate for a variety of types of hazardous waste streams along with the applicable form of waste (liquid, gaseous, solids/sludges.) For a more complete list, as well as detailed descriptions of each technology, see for example Freeman (1989).

Physical Treatment

Sedimentation. The simplest physical treatment systems that separate solids from liquids take advantage of gravity settling and natural flotation. Special sedimentation tanks and clarification tanks are designed to encourage solids to settle so they can be collected as a sludge from the bottom of the tank. Some solids will float naturally to the surface and they can be removed with a skimming device. It is also possible to encourage flotation by introducing finely divided bubbles into the waste stream. The bubbles collect particles as they rise and the combination can be skimmed from the surface. Separated sludges can then be further concentrated by evaporation, filtration, or centrifugation.

Adsorption. Physical treatment can also be used to remove small concentrations of hazardous substances dissolved in water that would never settle out. One of the most commonly used techniques for removing organics involves the process of *adsorption*, which is the physical adhesion of chemicals onto the surface of a solid. The effectiveness of the adsorbent is directly related to the amount of surface area available to attract the molecules or particles of contaminant. The most commonly used adsorbent is a very porous matrix of *granular activated carbon* (GAC), which has an enormous surface area (on the order of 1000 m^2/g). A single handful of GAC has an internal surface area of about one acre.

Granular activated carbon treatment systems usually consist of a series of large vessels partially filled with adsorbent. Contaminated water enters the top of each vessel, trickles down through the GAC, and is released at the bottom. After a period of time, the carbon filter becomes clogged with adsorbed contaminants

TABLE 6.7 A PARTIAL LIST OF TREATMENT TECHNOLOGIES FOR VARIOUS HAZARDOUS WASTE STREAMS

Treatment process	Hazardous waste streams											Form of waste			
	Corrosives	Cyanides	Halogenated solvents	Nonhalogenated organics	Chlorinated organics	Other organics	Oily wastes	PCBs	Aqueous with metals	Aqueous with organics	Reactives	Contaminated soils	Liquids	Solids/sludges	Gases
Separation/filtration		x	x	x	x	x			x	x			x		
Carbon adsorption									x	x	x		x		x
Air and steam stripping			x	x	x	x				x			x		
Electrolytic recovery									x				x		
Ion exchange	x								x	x			x		
Membranes									x	x			x		
Chemical precipitation	x								x				x		
Chemical oxidation/reduction		x								x			x		
Ozonation			x			x					x		x		x
Evaporation				x	x	x	x						x	x	
Solidification	x	x											x	x	
Liquid injection incineration			x	x	x	x	x						x		x
Rotary kilns			x	x	x	x	x	x					x	x	x
Fluidized bed incineration			x	x	x	x	x	x					x	x	x
Pyrolysis			x	x	x	x						x	x	x	
Molten glass			x	x	x	x	x			x			x	x	x

Source: Based on Freeman (1989).

and must be either replaced or regenerated. Regeneration can be an expensive, energy-intensive process, usually done off-site. During regeneration, the contaminants are usually burned from the surface of the carbon granules, though in some cases a solvent is used to remove them. Carbon filters that cannot be regenerated due to their contaminant composition must be properly managed for disposal.

Aeration. For chemicals that are relatively volatile, another physical process, *aeration*, can be used to drive the contaminants out of solution. These stripping systems typically use air, though in some circumstances steam is used. In the most commonly used air stripper, contaminated water is sprayed downward through packing material in a tower, while air is blown upward carrying away the volatiles with it. Such a *packed-tower* can easily remove over 95 percent of the volatile organic compounds (VOCs), including such frequently encountered ones as trichloroethylene, tetrachloroethylene, trichloroethane, benzene, toluene, and other common organics derived from solvents. There is another type of stripper, called an *induced-draft stripper*, which does not use a blower or packing material. In the induced-draft tower, a carefully engineered series of nozzles spray contaminated water horizontally through the sides of a chamber. Air passing through the chamber draws off the volatiles. Induced-draft strippers are cheaper to build and operate, but their performance is much lower than a packed-tower. By combining air stripping with GAC, many volatile and nonvolatile organic compounds can be removed from water to nondetectable levels. By passing contaminated water first through the air stripper, most of the volatile organics are removed before reaching the GAC system, which extends the life of the carbon before regeneration or replacement is required.

The volatiles removed in an air stripper are, in some circumstances, released directly to the atmosphere. When discharge into the atmosphere is unacceptable, a GAC treatment system can be added to the exhaust air, as shown in Figure 6.11.

Other Physical Processes. Other physical processes that are sometimes used to treat hazardous wastes include reverse osmosis, ion exchange, and electro dialysis. *Reverse osmosis* devices use pressure to force contaminated water against a semipermeable membrane. The membrane acts as a filter, allowing the water to be pushed through its pores, but restricting the passage of larger molecules that are to be removed. *Ion exchange* is a process wherein ions to be removed from the wastewater are exchanged with ions associated with a special exchange resin. Ion exchange has already been mentioned in the context of water softening where calcium and magnesium ions are replaced with sodium ions from the exchange resin. In the context of hazardous wastes, ion exchange is often used to remove toxic metal ions from solution. *Electrodialysis* uses ion-selective membranes and an electric field to separate anions and cations in solution. In the past, electrodialysis was most often used for purifying brackish water, but it is now finding a role in hazardous waste treatment. Metal salts from plating rinses are sometimes removed in this way, for example.

Chemical Treatment

Chemically treating hazardous waste not only has the potential advantage of converting it to less hazardous forms, but can also produce useful by-products in some circumstances. By encouraging resource recovery, the treatment cost can sometimes be partially offset by the value of the end products produced.

Neutralization. There are many chemical processes that can be used to treat hazardous wastes, and the process decision depends primarily upon the characteristic of the waste. For example, recall that one of RCRA's categories of hazardous waste is anything corrosive, that is, anything having a pH of less than 2 or more than 12.5. Such wastes can be chemically neutralized. Acidic wastewaters are usually neutralized with slaked lime $[\text{Ca}(\text{OH})_2]$ in a continuously stirred chemical reactor. The rate of addition of lime is controlled with a feedback control system that monitors pH and adjusts the feed rate accordingly.

Alkaline wastewaters may be neutralized by adding acid directly or by bubbling in gaseous CO_2 , forming carbonic acid (H_2CO_3). The advantage of CO_2 is that it is quite often readily available in the exhaust gas from any combustion process at the treatment site. Simultaneous neutralization of acid and caustic waste can be accomplished in the same vessel, as is suggested by Figure 6.12.

Chemical Precipitation. The ability to adjust pH is important not only for waste neutralization, but also because it facilitates other chemical processes that actually remove undesirable substances from the waste stream. For example, a common method for removing heavy metals from a liquid waste is via *chemical precipitation*, which is pH dependent. By properly adjusting pH, the solubility of toxic metals can be decreased, leading to formation of a precipitate that can be removed by settling and filtration.

Frequently, the precipitation involves the use of lime, $\text{Ca}(\text{OH})_2$, or caustic (NaOH) to form metal hydroxides. For example, the following reaction suggests the use of lime to form the hydroxide of a divalent metal (M^{2+}):



Metal hydroxides are relatively insoluble in basic solutions, and, as shown in Figure 6.13, they are *amphoteric*; that is, they have some pH at which their solubility is a minimum. Since each metal has its own optimum pH, it is tricky to control precipitation of a mix of different metals in the same waste. For a waste containing several metals, it may be necessary to use more than one stage of

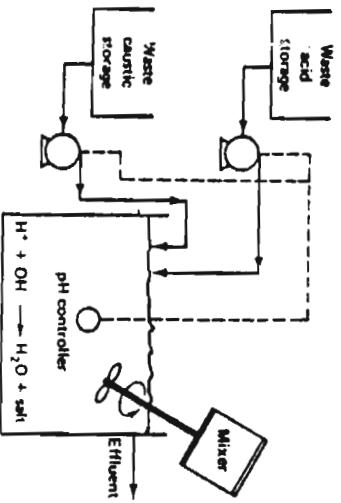


Figure 6.12 Simultaneous neutralization of acid and caustic waste (USEPA, 1987b).

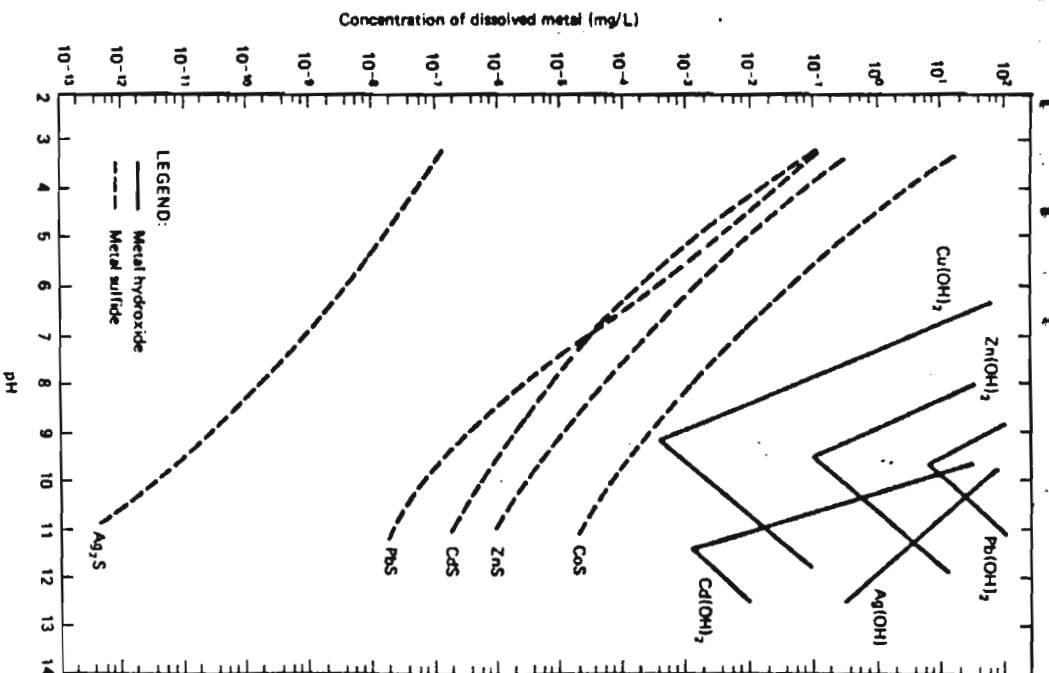


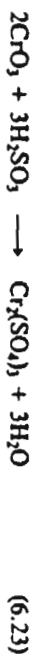
Figure 6.13 Chemical precipitation of metals can be controlled by pH. Metal sulfides are less soluble than metal hydroxides (USEPA, 1980).

precipitation to allow different values of pH to control the removal of different metals.

While hydroxide precipitation using lime is the most common metal removal process, even lower concentrations of metals in the effluent can be obtained by precipitating the metals as sulfides. As can be seen in Figure 6.13, metal sulfides

are considerably less soluble than metal hydroxides. A disadvantage of sulfide precipitation is the potential formation of odorous and toxic hydrogen sulfide gas.

Chemical Reduction-Oxidation. Reduction-oxidation (redox) reactions provide another important chemical treatment alternative for hazardous wastes. When electrons are removed from an ion, atom, or molecule, the substance is *oxidized*; when electrons are added, it is *reduced*. Both oxidation and reduction occur in the same reaction; hence the abbreviation redox. One of the most important redox treatment processes is the reduction of hexavalent chromium (CrVI) to trivalent chromium (CrIII) in large electroplating operations. Sulfur dioxide is often used as the reducing agent, as shown in the following reactions:



The trivalent chromium formed in reaction (6.23) is much less toxic and more easily precipitated than the original hexavalent chromium. Notice that the chromium in reaction (6.23) is reduced from an oxidation state of +6 to +3, while the sulfur is oxidized from +4 to +6.

Another important redox treatment involves the oxidation of cyanide wastes, which are also common in the metal finishing industry. In the following reactions, cyanide is first converted to a less toxic cyanate using alkaline chlorination (pH above 10); further chlorination oxidizes the cyanate to simple carbon dioxide and nitrogen gas. Nearly complete destruction of cyanide results:



Wastes that can be treated via redox oxidation include benzene, phenols, most organics, cyanide, arsenic, iron, and manganese; those that can be successfully treated using reduction treatment include chromium (VI), mercury, lead, silver, chlorinated organics like PCBs, and unsaturated hydrocarbons (USEPA, 1988a).

Biological Treatment

Virtually all municipal wastewater treatment plants in the United States and a large number of industrial systems rely on biological treatment processes to decompose organic wastes. Biological treatment systems use microorganisms, mainly bacteria, to metabolize organic material, converting it to carbon dioxide, water, and new bacterial cells. Since biological systems rely on living organisms to transform wastes, considerable care must be exercised to assure conditions are conducive to life. Microbes need a source of carbon and energy, which they can get from the organics that they consume, as well as nutrients such as nitrogen and phosphorus. They are sensitive to pH and temperature and some need oxygen.

As living organisms, they are susceptible to toxic substances, which at first glance makes biological treatment of hazardous wastes seem an unlikely choice.

Surprisingly, though, most hazardous organics are amenable to biological treatment, provided that the proper distribution of organisms can be established and maintained. For any given organic substance, there may be some organisms that will find that substance to be an acceptable food supply, while others may find it toxic. Moreover, organisms that flourish with the substance at one concentration may die when the concentration is increased beyond some critical level. Finally, even though a microbial population may have been established that can handle a particular kind of organic waste, it may be destroyed if the characteristics of the waste are changed too rapidly. If changes are made slowly enough, however, selection pressures may allow the microbial consortium to adjust to the new conditions and thereby remain effective.

Aqueous Waste Treatment. It is convenient to consider biological treatment of various sorts of wastewaters, including leachates from hazardous waste landfills, separately from in situ biological treatment of soils and groundwater. When liquid hazardous wastes can be conveyed to the treatment facility, it is possible to carefully control the characteristics of the waste that reach the biological portion of the facility, increasing the likelihood of a successful degradation process (Figure 6.14).

Biological treatment is just one step in an overall treatment system. An example system would include a chemical treatment stage to oxidize and precipitate some of the toxics, followed by physical treatment to separate the resulting solids from the waste stream. The effluent from the physical treatment step may

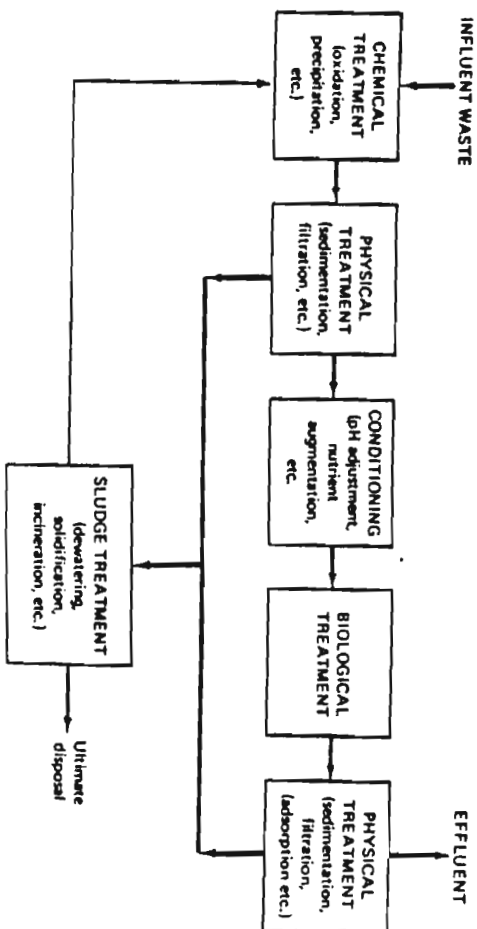


Figure 6.14 General flow diagram for treatment of liquid hazardous waste.

then be conditioned to give it the right pH and nutrient supply needed by the microorganisms in the biological treatment step.

The biological treatment stage itself utilizes processes already described for municipal wastewater treatment plants. After biological treatment, further sedimentation and clarification followed by carbon adsorption can be used to polish the effluent. Inorganic sludges produced during chemical processing and organic sludges from the biotreatment stage are separated from the liquid wastestream and treated. These sludges must be dewatered and disposed of in accordance with RCRA regulations since they are likely to be hazardous themselves.

In Situ Biodegradation. One way to clean a contaminated aquifer is to pump out the groundwater, treat it, and then either reinject it back into the ground, find some acceptable way to reuse it, or simply "dispose" of the water while gaining minimal environmental or economic benefit from the treated effluent. The latter "pump and dump" schemes have been used extensively in many Superfund sites. Not only does "pump and dump" remediation waste a valuable resource, other problems such as salt water intrusion into the freshwater aquifer (for coastal sites) and land subsidence can result.

Similarly, treatment of contaminated soils above an aquifer has often been accomplished by removing huge quantities of soil from the site, then treating and disposing of them elsewhere.

A promising alternative to moving water or soil to a treatment facility is to, in essence, reverse the process and move the treatment facility to the contaminated water and soil. *In situ biodegradation* is such a process wherein bacteria are used to degrade organic compounds in the soil and groundwater on site. An obvious advantage to *in situ* biodegradation is that soils and groundwater do not have to be removed, so there is less land disturbance, less wasted water, less risk associated with hazardous waste transportation, and potentially decreased costs. Moreover, there is the potential for aquifer restoration to be more complete since contaminants tend to adsorb onto soil particles, making it difficult to ever completely remove them by pumping.

The technology requires creating conditions underground that will stimulate growth of indigenous, or newly introduced bacteria that have the capability of degrading the organic contaminants of concern. There are basically two approaches to *in situ* biodegradation. First, the environment of existing microbial populations can be enhanced by adding nutrients and/or oxygen. Nutrients that may be called for include nitrogen, phosphorus, and inorganic salts such as ammonium sulfate, magnesium sulfate, sodium carbonate, and calcium chloride. Significant quantities of these nutrients may have to be added to the affected aquifer before treatment is complete. The supply of oxygen can be enhanced by injecting an oxidant such as hydrogen peroxide or by forcing air through wells with diffusers.

The second approach to *in situ* biodegradation involves altering the underground microbial population by seeding with new microorganisms that have al-

ready been acclimated to the pollutants to be degraded. These new microbes can be picked based on laboratory studies of their effectiveness against the wastes in question. There is also the possibility of genetically altering microorganisms to get strains that will work even better.

In situ biodegradation is a relatively new technique that has been used most frequently to treat soil contaminated with gasoline and diesel. It shows great promise as a way to treat chlorinated solvents such as trichloroethylene (TCE), tetrachloroethylene (PCE), and 1,2-dichloroethylene (DCE), which are among the most commonly found contaminants in underground water supplies. Figure 6.15 shows one version of an *in situ* bioremediation system.

Waste Incineration

Waste incineration is being strongly advocated by the EPA as its technology of choice for many types of hazardous wastes. Incineration is particularly effective with organic wastes, not only in soils but in other solids, gases, liquids, and slurries (thin mixtures of liquids and solids) and sludges (thick mixtures). Carcinogens, mutagens, teratogens, as well as pathological wastes can all be completely detoxified in a properly operated incinerator. Incinerators are not, however, capable of destroying inorganic compounds, although they can concentrate them in ash, making transportation and disposal more efficient. In addition, metals that volatilize at temperatures below 2000 °F pose a particular problem since, once vaporized, they are difficult to remove using conventional air pollution control equipment.

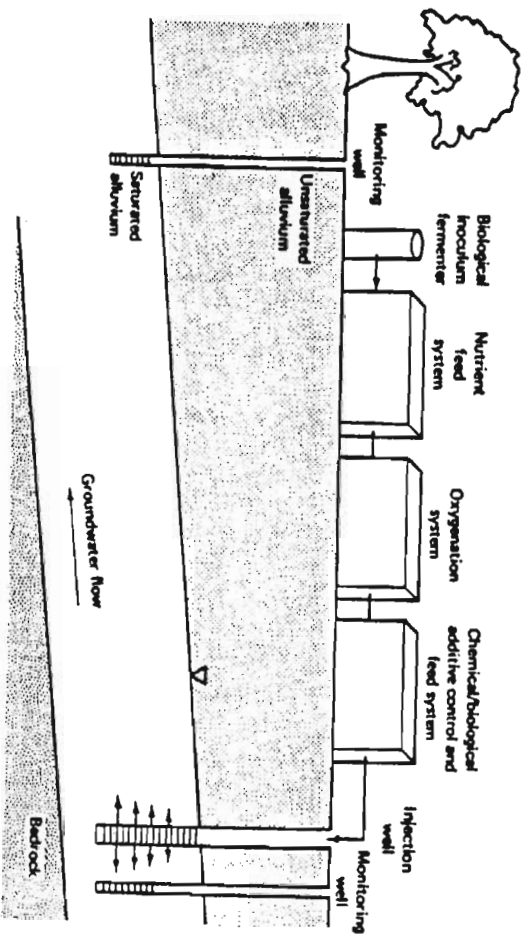


Figure 6.15 In situ bioremediation (USEPA, 1988a).

The principal measure of an incinerator's performance is known as the *destruction and removal efficiency* (DRE). A DRE of 99.99 percent, for example, (commonly called "four nines DRE") means that one molecule of an organic compound is released to the air for every 10 000 molecules entering the incinerator. RCRA requires a minimum DRE of 99.99 percent for most organic compounds, and a DRE of 99.9999 percent (six nines) for dioxins and dibenzofurans. The Toxic Substances Control Act regulations cover thermal destruction of PCBs, and although they are written somewhat differently from RCRA, they in essence require a 99.9999-percent DRE. Incinerator standards also have been written for hydrogen chloride emissions and particulates.

As is the case for all combustion processes, the most critical factors that determine combustion completeness are (1) the temperature in the combustion chamber, (2) the length of time that combustion takes place, (3) the amount of turbulence, or degree of mixing, and (4) the amount of oxygen available for combustion. Controlling these factors, which is crucial to obtaining the high levels of performance required by law, is made especially difficult in hazardous waste incinerators because of the variability of the wastes being burned. In addition to combustion controls, stack gas cleaning systems similar to those that will be described in Chapter 7 are a necessary part of the system. Proper operation and maintenance of these complex incineration systems requires highly trained personnel, diligent and qualified supervisory staff, and an alert governmental agency to assure compliance with all regulations.

While there are a number of types of hazardous waste incinerators, there are only two principal designs that account for most of the existing units in operation: the *liquid injection incinerator* and the *rotary kiln incinerator*. Liquid injection incinerators are the most common, even though they are usable only for gases, liquids, and slurries thin enough to be pumped through an atomizing nozzle. The nozzle emits tiny droplets of waste that are mixed with air and an auxiliary fuel such as natural gas or fuel oil. The resulting gaseous mixture is burned at a very high temperature. The atomizing nozzle used in a liquid injection incinerator must be designed to accommodate the particular characteristics of the expected waste stream, which limits the types of waste that any given incinerator can treat.

The rotary kiln incinerator is more versatile than the liquid injection type, being capable of handling gases, liquids, sludges, and solids of all sorts, including drummed wastes. Figure 6.16 shows a diagram of such an incinerator. The main unit consists of a slightly inclined, rotating cylinder perhaps 2–5 m in diameter and 3–10 m long. Wastes and auxiliary fuel are introduced into the high end of the kiln and combustion takes place while the cylinder slowly rotates. The rotation helps increase turbulence, which improves combustion efficiency. Partially combusted waste gases are passed to a secondary combustion chamber for further oxidation. Rotary kiln incinerators are commercially available as mobile units and fixed installations.

In spite of numerous controls, hazardous waste incinerators have the potential to emit amounts of noxious gases that may be unacceptable to neighbors.

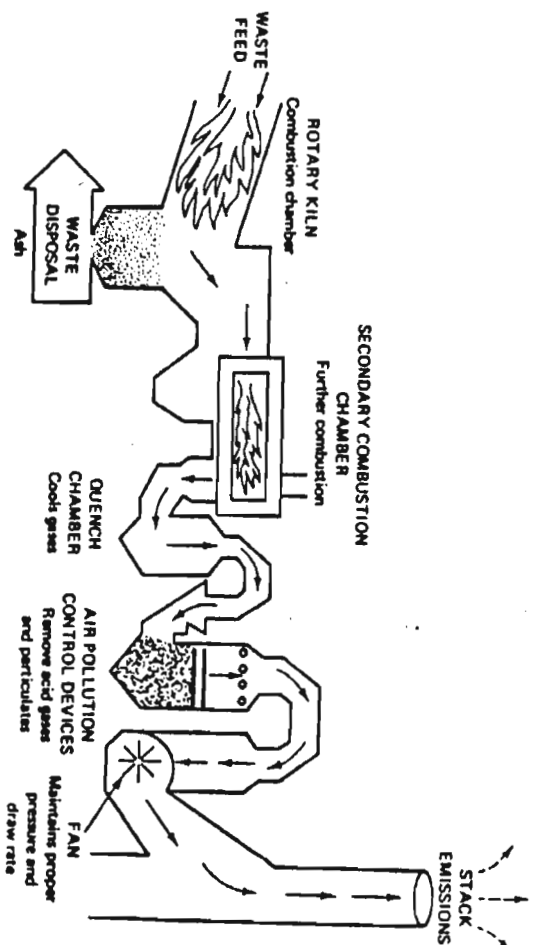


Figure 6.16 A rotary kiln hazardous waste incinerator (USEPA, 1988b).

Emissions may include unburned organic compounds from the original waste, various products of *incomplete combustion* (PICs) formed in the incinerator itself, odors, carbon monoxide, nitrogen and sulfur oxides, hydrogen chloride, and particulates. The unburned ash and sludge from the air pollution control devices are considered hazardous wastes themselves and must be treated as such. If they are transported off-site, then not only are there hazardous materials transported into the facility, but there are some leaving as well. The perception of potentially adverse impacts associated with incineration has made the siting of these facilities an extremely difficult task.

Liquid injection incinerators have been built into two ships, the Vulcanus I and the Vulcanus II, for hazardous waste incineration at sea, but public opposition has prevented their use. Proponents of incineration at sea point out the advantages of incineration, the difficulties associated with land-based siting, and the reductions in human risk that would come with incineration far from any centers of population. Opposition has focused on the chances of hazardous waste spills and the near impossibility of controlling such a spill should it occur. Also, the small amounts of unburned wastes routinely released, as well as those that might be released should the incinerator ever be improperly operated, could have unknown implications for marine life.

A stalemate has developed between the EPA, which is advocating incineration as a way to avoid land disposal (with its almost invariable toxic leakage into the groundwater) and the public, which has, with good reason, learned to be suspicious of any complex and potentially dangerous technology.

Land Disposal

Land disposal techniques include landfills, surface impoundments, underground injection wells, and waste piles. About 5 percent of the hazardous waste that we dispose of on land in the United States is placed in specially designed landfills. About 35 percent is disposed of in diked surface impoundments such as pits, ponds, lagoons, and basins. About 60 percent is disposed of deep underground in underground injection wells. Waste piles, which are noncontainment accumulations of solid hazardous waste typically used for temporary storage, account for less than 1 percent of our disposal volume (USEPA, 1986b).

Historically, land disposal has been the traditional method of getting rid of hazardous wastes in this country. Unfortunately, many of these disposal sites have been poorly engineered and monitored and the results have sometimes been tragic, as was the case at Love Canal, New York. They have been used extensively in the past because they were the most convenient and inexpensive method of disposal. However, remediation at older sites that have leaked toxics into the soil and groundwater has proven to be tremendously costly and the originally perceived economic advantage of land disposal is now seen to have been short-sighted.

As was mentioned in Chapter 5, the 1984 amendments to RCRA ban unsafe, untreated wastes from land disposal. The amendments require that the EPA assess all hazardous wastes to determine whether they should be banned. If they are banned, the EPA must determine the level of treatment that would be required before land disposal could be allowed. RCRA goes on to provide new restrictions and standards for those land disposal facilities that will be allowed to accept hazardous substances, including (USEPA, 1986b):

- Banning liquids from landfills.
- Banning underground injection of hazardous waste within 1/4-mile of a drinking water well.
- Requiring more stringent structural and design conditions for landfills and surface impoundments, including two or more liners, leachate collection systems above and between the liners, and groundwater monitoring.
- Requiring cleanup or corrective action if hazardous waste leaks from a facility.
- Requiring information from disposal facilities on pathways of potential human exposure to hazardous substances.
- Requiring location standards that are protective of human health and the environment; for example, allowing disposal facilities to be constructed only in suitable hydrogeologic settings.

Landfills. In accordance with these new, more stringent RCRA requirements, the design and operation of hazardous waste landfills has become much

more sophisticated. A hazardous waste landfill is now designed as a modular series of three-dimensional control cells. By incorporating separate cells it becomes possible to segregate wastes so that only compatible wastes are disposed of together. Arriving wastes are placed in an appropriate cell and covered at the end of each working day with a layer of cover soil.

Beneath the hazardous wastes there must be a double-liner system to stop the flow of liquids, called *leachate*, from entering the soil and groundwater beneath the site. The upper liner must be a *flexible-membrane lining* (FML), usually made of sheets of plastic or rubber. Commonly used plastics include polyvinyl chloride (PVC), high-density polyethylene (HDPE), and chlorinated polyethylene (CPE). Rubber FMLs include chlorosulfonated polyethylene (CSPE) and ethylene propylene diene monomer (EPDM). Depending on the material chosen for the FML, the thickness is typically anywhere from 0.25 mm (10 mils) to over 2.5 mm (100 mils). The lower liner is usually an FML, but recompressed clay at least 3 ft thick is also considered acceptable.

Leachate that accumulates above each liner is collected in a series of perforated drainage pipes and pumped to the surface for treatment. To help reduce the amount of leachate formed by precipitation seeping into the landfill, a low permeability cap is placed over completed cells. When the landfill is finally closed, a cap that may consist of an FML along with a layer of compacted clay is placed over the entire top, with enough slope to assure drainage away from the wastes.

The landfill must also include monitoring facilities. The groundwater flowing beneath the site should be tested with monitoring wells placed upgradient and downgradient from the site. There may need to be only one upgradient well to test the "natural" quality of the groundwater before it flows under the site, but there should be at least three or more monitoring wells placed downgradient to assure detection of any leakage from the site. In addition, the soil under the site, above the water table, should be tested using devices called a suction lysimeters.

A cross section of a completed hazardous waste landfill is shown in Figure 6.17.

Surface Impoundments. Surface impoundments are excavated or diked areas used to store liquid hazardous wastes. Usually storage is temporary unless the impoundment has been designed to eventually be closed as a landfill. Impoundments have been popular because they have been cheap and because wastes remain accessible, allowing some treatment to take place during storage. Typical treatment technologies used in surface impoundments include neutralization, precipitation, settling, and biodegradation.

Historically, surface impoundments have typically been poorly constructed and monitored. In a survey of 180,000 surface impoundments, the EPA estimated that prior to 1980 only about one-fourth were lined and fewer than 10 percent had monitoring programs (USEPA, 1984). The same survey also found that surface impoundments were usually poorly sited. More than half were located over very thin or very permeable soils that would allow easy transport of leachate to ground-

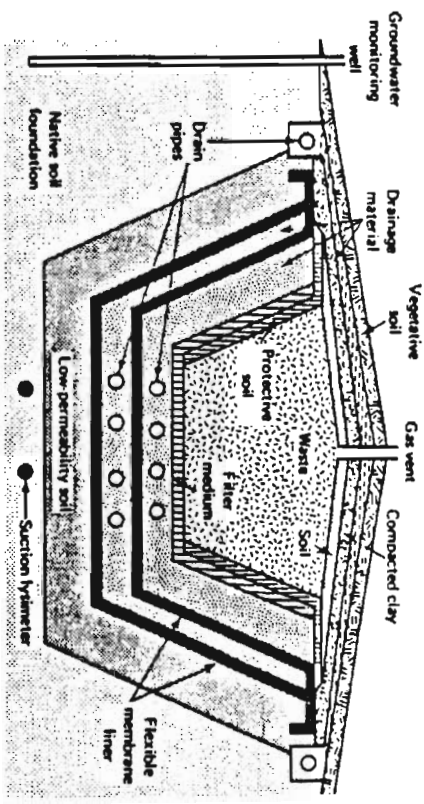


Figure 6.17 Schematic of a hazardous waste landfill.

water. Over three-fourths of the impoundments were located over very thick and permeable aquifers that would allow relatively rapid dispersion of contaminants should they reach the water table. Moreover, about 98 percent of the surface impoundments were located less than one mile from sources of high-quality drinking water.

As a result of these poor siting, construction, and management problems, surface impoundments are the principal source of contamination in a large number of Superfund sites. Recent EPA regulations require new surface impoundments, or expansions to existing impoundments, to have two or more liners, a leachate-collection system, and monitoring programs similar to those required for landfills. However, the legacy of past practices will undoubtedly take billions of dollars and decades of time to remediate.

Underground Injection. The most popular way to dispose of liquid hazardous wastes has been to force them underground through deep injection wells (Figure 6.18). To help assure that underground drinking water supplies will not become contaminated, injection wells used to dispose of hazardous industrial wastes are required to extend below the lowest formation containing underground sources of drinking water. Typical injection depths are more than 700 m below the surface. Since the main concern with underground injection is the potential for contaminating underground drinking water supplies, the regulation of such systems has come under the Safe Drinking Water Act of 1974.

Unfortunately, a number of hazardous waste injection wells have had leakage problems, so such wells cannot be considered entirely safe. Regulations covering construction, operation, and monitoring of injection wells are becoming more stringent, and, as is the case for all land disposal options, continued reliance on this technology is being discouraged.

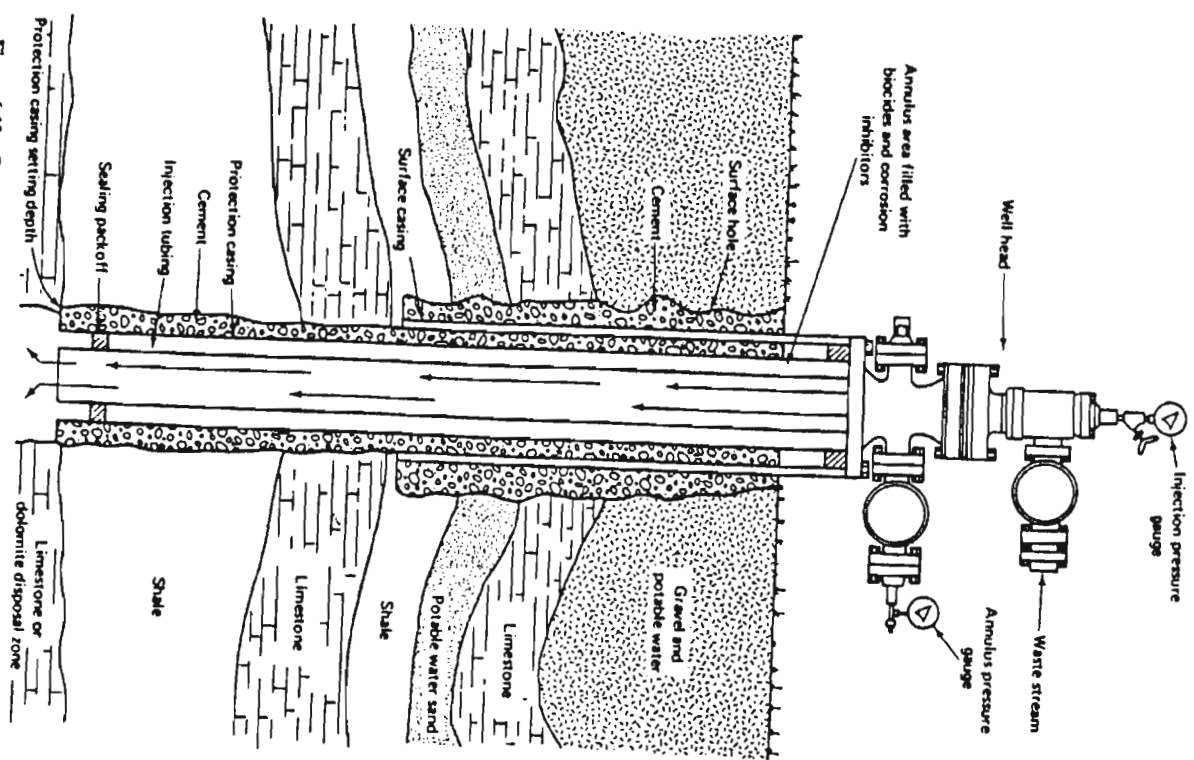


Figure 6.18 Cross section of a hazardous waste disposal well. (Source: Wentz, C. A. *Hazardous Waste Management*. Copyright © 1989 by McGraw-Hill, Inc. Used with permission of the publisher.)

PROBLEMS

- 6.1. A sample of groundwater has 150 mg/L of Ca^{2+} and 60 mg/L of Mg^{2+} . Find the total hardness expressed in milliequivalents per liter (meq/L) and mg/L as CaCO_3 . Using Table 6.5, how would this water be classified (e.g., soft, hard, ...)?
- 6.2. For a solution with pH equal to 9.0, express the concentrations of H^+ and OH^- in meq/L and mg/L as CaCO_3 .
- 6.3. A sample of water at pH 10.5 has 39.0 mg/L of CO_3^{2-} and 24.5 mg/L of HCO_3^- .
 - a. Ignoring the contribution of $[\text{H}^+]$ and $[\text{OH}^-]$ to alkalinity, what is the alkalinity as CaCO_3 ?
 - b. Including the contribution of $[\text{H}^+]$ and $[\text{OH}^-]$, find the alkalinity as CaCO_3 .
- 6.4. A sample of water has the following concentrations of ions (and the pH is near neutral):

Cations	mg/L	Anions	mg/L
Ca^{2+}	95.0	HCO_3^-	160.0
Mg^{2+}	26.0	SO_4^{2-}	135.0
Na^+	15.0	Cl^-	73.0

- a. What is the total hardness (TH)?
 - b. What is the carbonate hardness (CH)?
 - c. What is the noncarbonate hardness (NCH)?
 - d. What is the alkalinity?
 - e. What is the total dissolved solids concentration?
 - f. Draw an ion concentration bar graph.
- 6.5. A sample of water has the following concentrations of ions:

Cations	mg/L	Anions	mg/L
Ca^{2+}	40.0	HCO_3^-	110.0
Mg^{2+}	10.0	SO_4^{2-}	67.2
Na^+	?	Cl^-	11.0
K^+	7.0		

- a. Assuming no other constituents are missing, use an anion-cation balance to estimate the concentration of Na^+ .
- b. What is the total hardness (TH)?
- c. Draw an ion concentration bar graph.

REFERENCES

DAVIS, M. L., and D. A. CORNWELL, 1985, *Introduction to Environmental Engineering*, PWS Engineering, Boston, MA.

- FREEMAN, H. M. (ed.), 1989, *Standard Handbook of Hazardous Waste Treatment and Disposal*, McGraw Hill, New York.
- LEVINE, R. L., and P. A. WILDERER, 1989, Aerobic processes, in *Standard Handbook of Hazardous Waste Treatment and Disposal*, H. M. Freeman (ed.), McGraw Hill, New York.
- LINSLEY, R. K., and J. B. FRANZINI, 1979, *Water-Resources Engineering*, 3d ed., McGraw Hill, New York.
- MORRISON, A., 1983, In third world villages, a simple handpump saves lives, *Civil Engineering/ASCE* October: 68-72.
- ROBECK, G. G., N. A. CLARKE, and K. A. DOSTAL, 1962, Effectiveness of water treatment processes in virus removal, *Journal American Water Works Association*, 54:1275-1290.
- TCHOBANOGLOUS, G., and E. D. SCHROEDER, 1985, *Water Quality*, Addison-Wesley, Reading, MA.
- USEPA, 1976, *National Interim Primary Drinking Water Regulations*, Office of Water Supply, EPA-570/9-76-003, Washington, DC.
- USEPA, 1980, *Summary Report, Control and Treatment Technology for Metal Finishing Industry*, EPA 625/R-80-003, Washington, DC.
- USEPA, 1984, *Surface and Impoundment Assessment National Report*, EPA-570/9-84-002, Washington, DC.
- USEPA, 1986a, *Drinking water in America: An overview*, *EPA Journal*, September.
- USEPA, 1986b, *Solving the Hazardous Waste Problem: EPA's RCRA Program*, Office of Solid Waste, Washington, DC.
- USEPA, 1987a, *The Hazardous Waste System*, Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.
- USEPA, 1987b, *A Compendium of Technologies Used in the Treatment of Hazardous Wastes*, Center for Environmental Research Information, EPA/625/R-87/014, Washington, DC.
- USEPA, 1988a, *Technology Screening Guide for Treatment of CERCLA Soils and Sludges*, Office of Solid Waste and Emergency Response, EPA/502/2-88/004, Washington, DC.
- USEPA, 1988b, *Hazardous Waste Incineration: Questions and Answers*, Office of Solid Waste, EPA/530-SW-88-018, Washington DC.
- VISSMAN, W., Jr., and M. J. HAMMER, 1985, *Water Supply and Pollution Control*, 4th ed., Harper & Row, New York.
- WENTZ, C. A., 1989, *Hazardous Waste Management*, McGraw Hill, New York.