Kirk-Othmer Encyclopedia of Chemical Technology.

WASTE TREATMENT, HAZARDOUS WASTE

Hazardous waste treatment systems incorporate many different unit processes. For example, an activated sludge wastewater treatment system may include oil–water separation, neutralization, biological treatment, sedimentation, and sludge dewatering. Besides activated sludge, there are many other widely used, well-known technologies including incineration, carbon adsorption, air stripping, precipitation, ion exchange, reverse osmosis, and distillation. However, more stringent environmental regulation and an increasing knowledge of chemical hazards continually challenge the capabilities of waste treatment and monetary resources. These challenges have given rise to a keen interest in the development of new, innovative technologies. Many of these new technologies use familiar unit processes, but in innovative ways. Recycling technology, an important part of pollution prevention, incorporates both old and new unit processes.

The discussion of waste treatment technologies is divided into three principal technology groups: physical–chemical processes, biological processes, and thermal processes, and a fourth on the treatment of soil and ground water. To make it easy for the reader to locate a particular technology, technologies are listed alphabetically within each group. Table 1 provides a summary of the technologies described in this article.

1. Physical–Chemical Treatment

1.1. Air Stripping

Compounds that have relatively high volatilities and low water solubilities can be transferred (stripped) from aqueous streams into the air or an air stream. Examples of compounds that can be easily air-stripped include gasoline and jet fuels (with benzene [71-43-2], toluene [108-88-3], ethylbenzene [100-41-4], and xylenes [1330-20-7] as primary components of interest), solvents such as trichloroethylene [79-01-6] and tetrachloroethylene [127-18-4], and ammonia [7664-41-7]. The strippability of a compound is related to its Henry's coefficient which is the ratio of the vapor phase concentration of the chemical in equilibrium with its concentration in water. In general, the higher the Henry's coefficient, the more strippable is the compound. Similarly, since Henry's coefficient increases with temperature, higher temperatures generally improve air stripping efficiencies.

Types of air strippers include packed towers, tray towers, and spray towers. Packed towers are packed or filled with small forms made of polyethylene [9002-88-4], stainless steel, poly(vinyl chloride) (PVC) [9002-86-2], or ceramic that provide large surface area to volume ratios which increase transfer rates into the air stream. Packed towers operate in countercurrent mode, that is, the aqueous stream enters at the top of the tower while air is blown in from the bottom. An example of this type of unit is shown in Figure 1. Channeling or short circuiting of the aqueous stream is minimized by distribution plates placed at intervals throughout the column. Design criteria for packed towers include surface area provided by the packing forms, column height and diameter, and air to water flow rates. Tray towers also operate countercurrently, however, the aqueous stream contacts air as the liquid cascades from tray to tray to the bottom of the tower. Spray towers operate by spraying the aqueous stream into the top of the tower; air flows countercurrent to the liquid.

Table 1. Summary of Hazardous Waste Treatment Technologies

Physical–Chemical Treatment

air stripping
carbon adsorption
dissolved air flotation
distillation
evaporation
ion exchange
membrane filtration
neutralization
oil–water separation
oxidation/reduction
precipitation
sedimentation-clarification
solvent extraction
stabilization–solidification
steam stripping
supercritical fluid extraction
supercritical water oxidation
wet air oxidation

Biological Treatment: Activated Sludge

Thermal Treatment

catalytic oxidation
fluidized beds
liquid injection
multiple hearth furnaces
rotary kilns
thermal desorption

Soil and Ground Water Treatment

in situ air stripping
in situ and *ex situ* bioremediation
electrokinetics
pump and treat
soil flushing
soil leaching
soil vapor extraction
soil washing
vitrification

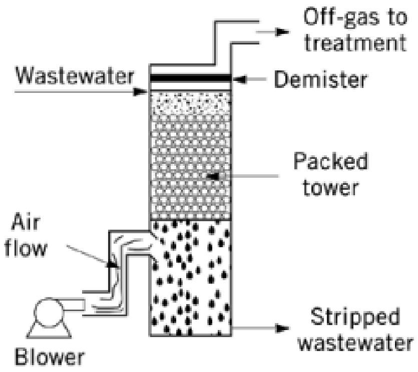

Fig. 1. Example of a countercurrent packed tower.

The air stream exiting a stripper may require some type of emissions control, depending on local and regulatory requirements. Carbon adsorption is often used; catalytic oxidation is another option.

1.2. Carbon Adsorption

Carbon adsorption is a well established and widely used technology for the removal of organics from wastewaters and gaseous streams. Carbon adsorption is a proven technology for potable water treatment and capable of reducing organic concentrations to very low or nondetectable levels.

In carbon adsorption, contaminants are physically attracted or adsorbed on the surface of the carbon. Adsorption capacities are high for carbon because its porous nature provides a large surface area relative to its volume. Activated carbon is prepared from lignite, bituminous coal, coke, wood, or other organic materials such as coconut shells.

Carbon adsorption is most effective at removing organic compounds that have low polarity, high molecular weight, low water solubility, and high boiling point. The Water Environment Federation (WEF) (1) lists some general guidelines for assessing carbon adsorption efficiency:

Branch-chain compounds are more sorbable than straight-chain compounds.
Compounds low in polarity and water solubility (less than 0.1 mg/L) are more sorbable.
For compounds that have similar chemical characteristics, larger ones are more sorbable.
There is a wide range in adsorption efficiency for inorganics.
A low pH promotes adsorption of organic acids.
A high pH promotes adsorption of organic bases.

Common examples of compounds that are amenable to carbon adsorption are aromatics (benzene, toluene) and chlorinated organics (trichloroethylene, trichloroethane [71-55-6, 79-00-5], tetrachloroethylene, polychlorinated biphenyls (PCBs), DDT [50-29-3], pentachlorophenol [87-86-5]. Compounds that are not adsorbed effectively by carbon include ethanol [64-17-5], diethylene glycol [111-46-6], and numerous amines (butylamine [109-73-9, 13952-84-6, 75-64-9], triethanolamine [102-71-6], cyclohexylamine [108-91-8], hexamethylenediamine [108-91-8] (1). Wastewater concentrations that are suitable for carbon adsorption are generally less than 5000 mg/L.

Most carbon adsorption units use granular activated carbon (GAC). The powdered form of activated carbon (PAC) typically is less than 100 microns in diameter and may be used to reduce dioxins in incinerator emissions (2) and in the treatment of drinking water and wastewater treatment (see the section on “Activated Sludge”).

GAC may be used in fixed or moving beds and in downflow or upflow mode. Fixed beds are operated in downflow mode and as such, provide some amount of solids filtration; however, influent solids concentration must be kept low (less than 5 mg/L suspended solids) to prevent rapid plugging of the bed. Filtered solids are periodically removed by backwashing. Upflow beds are more tolerant of solids because they are fluidized and expanded by the wastewater entering at the bottom. In moving beds, the flow is countercurrent and makeup, fresh carbon is added continuously at the top of the unit while an equal amount of spent carbon is removed from the bottom.

When the adsorption capacity of a carbon unit is exceeded, there is breakthrough of the contaminant in the treated stream. Fixed beds may be operated in series to allow continuous treatment while spent or exhausted units are replaced with fresh carbon. In series operation, there are two or more units. The majority of the contaminant is removed by the first unit in the series with the downstream units acting as polishing units. When breakthrough occurs in the first or primary unit, it is replaced with fresh carbon and becomes a polishing unit while the next unit in the series takes over and becomes the primary treatment unit. An example of this round-robin operation of a three-carbon bed is shown in Figure 2.

Spent carbon is usually regenerated, but if the quantity is small, it may be disposed instead. Regeneration can be done by several different methods and may actually be part of the treatment process. Regeneration technologies include steam or thermal desorption, incineration, acid and base washing, and solvent extraction. Organic-laden streams from the regeneration process are treated, recovered, or incinerated. Regeneration by incineration results in some loss of carbon and deterioration and loss of active surface area.

Design criteria for carbon adsorption include type and concentration of contaminant, hydraulic loading, bed depth, and contact time. Typical ranges are 1.4–6.8 L/s/m^2 for hydraulic loading, 1.5–9.1 m for bed depth, and 10–50 minutes for contact time (1). The adsorption capacity for a particular compound or mixed waste

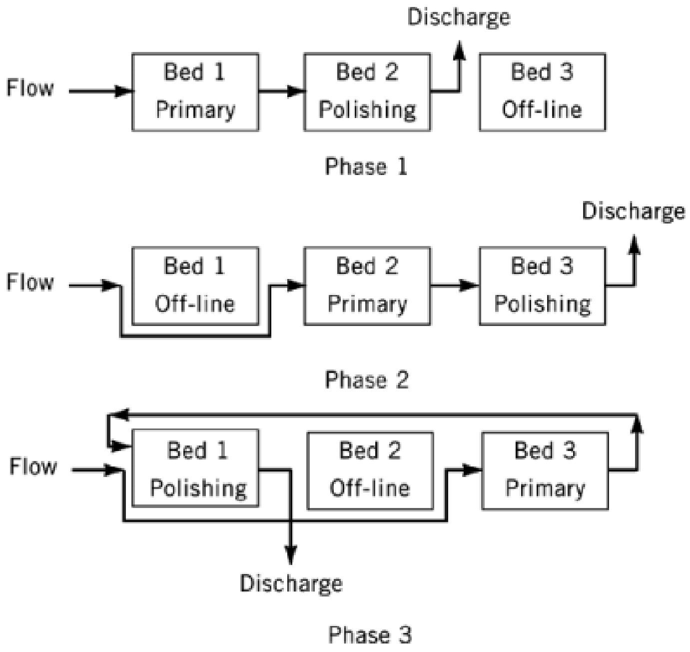

Fig. 2. Round robin operation of a three-bed carbon adsorption unit.

stream can be determined as an adsorption isotherm and pilot tested. The adsorption isotherm relates the observed effluent concentration to the amount of material adsorbed per mass of carbon.

New areas in adsorption technology include carbonaceous and polymeric resins (3). Based on synthetic organic polymer materials, these resins may find special uses where compound selectivity is important, low effluent concentrations are required, carbon regeneration is impractical, or the waste to be treated contains high levels of inorganic dissolved solids.

1.3. Dissolved Air Flotation

Dissolved air flotation (DAF) is used to separate suspended solids and oil and grease from aqueous streams and to concentrate or thicken sludges. Air bubbles carry or float these materials to the surface where they can be removed. The air bubbles are formed by pressurizing either the influent wastewater or a portion of the effluent in the presence of air. When the pressurized stream enters the flotation tank which is at atmospheric pressure, the dissolved air comes out of solution as tiny, microscopic bubbles. Dissolved air flotation is used in many wastewater treatment systems, but in the United States it is perhaps best known with respect to hazardous waste because it is associated with the listed waste, K048, DAF flotation solids from petroleum refining wastewaters. Of course, the process itself is not what is hazardous, but the materials it helps to remove from refining wastewaters.

1.4. Distillation

Distillation separates volatile components from a waste stream by taking advantage of differences in vapor pressures or boiling points among volatile fractions and water. There are two general types of distillation, batch or differential distillation and continuous fractional or multistage distillation (see also Distillation).

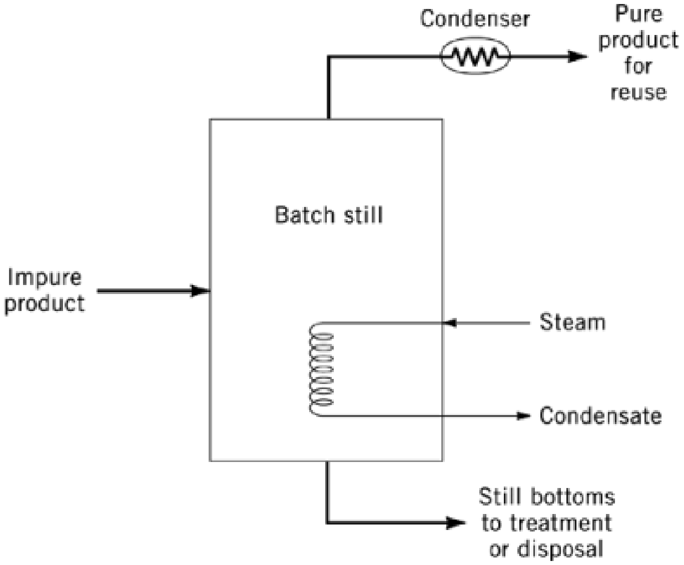

Fig. 3. Example of a batch distillation unit.

Batch distillation (see Fig. 3) typically is used for small amounts of solvent wastes that are concentrated and consist of very volatile components that are easily separated from the nonvolatile fraction. Batch distillation is amenable to small quantities of spent solvents which allows these wastes to be recovered onsite. With batch distillation, the waste is placed in the unit and volatile components are vaporized by applying heat through a steam jacket or boiler. The vapor stream is collected overhead, cooled, and condensed. As the waste's more volatile, high vapor pressure components are driven off, the boiling point temperature of the remaining material increases. Less volatile components begin to vaporize and once their concentration in the overhead vapors becomes excessive, the batch process is terminated. Alternatively, the process can be terminated when the boiling point temperature reaches a certain level. The residual materials that are not vaporized are called still bottoms.

If a waste contains a mixture of volatile components that have similar vapor pressures, it is more difficult to separate these components and continuous fractional distillation is required. In this type of distillation unit (Fig. 4), a packed tower or tray column is used. Steam is introduced at the bottom of the column while the waste stream is introduced above and flows downward, countercurrent to the steam. As the steam vaporizes the volatile components and rises, it passes through a rectification section above the waste feed. In this section, vapors that have been condensed from the process are refluxed to the column, contacting the rising vapors and enriching them with the more volatile components. The vapors are then collected and condensed. Organics in the condensate may be separated from the aqueous stream after which the aqueous stream can be recycled to the stripper.

Factors affecting distillation include the vapor pressures of the volatile components; column temperature, pressure, and internal structure (packing or trays); and concentrations of oil and grease, total dissolved solids, and total dissolved volatile solids. The higher the vapor pressure of a volatile component, the more easily it can be distilled or stripped from solution. Column pressure influences the boiling point of the liquid stream. Column temperature can be reduced by operating the column under a vacuum. Trays used in columns (bubble cap, sieve, valve, and turbo-grid) do not plug as easily with solids and can be used with a wider range of liquid and vapor flow rates. Packed columns have lower pressure drops per stage, are more corrosion resistant, and

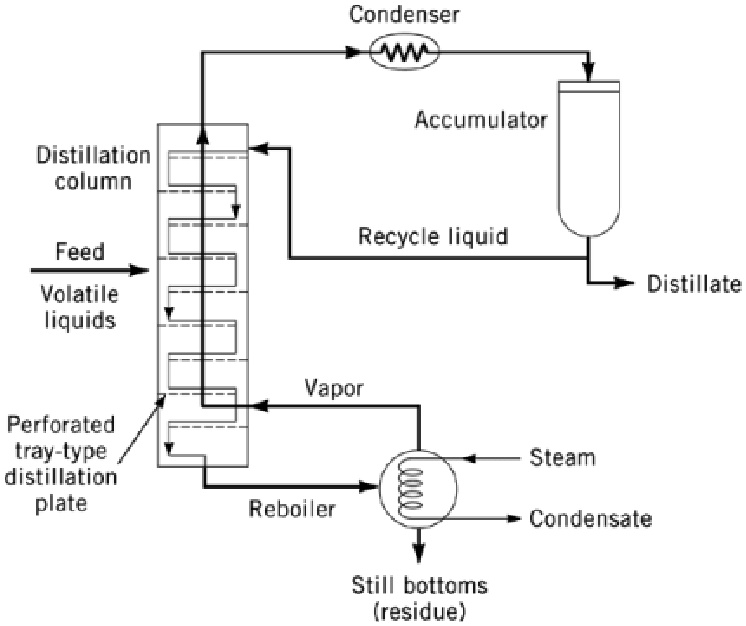

Fig. 4. Example of a continuous fractional distillation system.

reduce foam by distributing the liquid flow more uniformly. Oil and grease, total dissolved solids, and total dissolved volatile solids affect the partial pressures and solubilities of volatile components.

1.5. Evaporation

Evaporation can be used to separate volatile compounds from nonvolatile components and often is used to remove residual moisture or solvents from solids or semisolids. Thin-film evaporators and dryers are examples of evaporation equipment used for this type of application. Some evaporators are also appropriate for aqueous solutions.

1.5.1. Thin-Film Evaporators

There are two types of thin-film evaporators commonly used in industrial applications. The first type introduces feed material into the center of a rotating heated conical receiver. Centrifugal force causes the feed to travel to the outer edge of the conical receiver where it is collected and drawn off as residue. During the process, the heat causes the volatile components to be driven from the feed. These volatile components are condensed on a chilled surface of the evaporator and collected as distillate.

The second type of thin-film evaporator, termed a wiped-film evaporator, introduces feed material on a heated wall of a cylinder. Rotating wiper blades continuously spread the feed along the inner wall of the cylinder to maintain uniformity of thickness and to ensure contact with the heated surface. The volatile components are driven off and collected on an internal chilled condenser surface. The condensate or distillate is removed continuously. At the end of the process, the residual becomes dry and heavy and drops to the bottom of the unit for removal. The wiped-film evaporator is best suited for treatment of viscous or high-solids content feed.

1.5.2. Dryers

Drying, another type of evaporation technique, is suited for waste streams of very high solids content. Several common types of dryers are vacuum rotary dryers, drum dryers, tray and compartment dryers, and pneumatic conveying dryers.

The vacuum rotary dryer is a batch system that uses a cylindrical rotating unit and agitator blades to mix or agitate the waste stream during the drying process. A vacuum is applied and maintained during the process to remove liquids during agitation. The process is terminated when the solids are dried to a specified moisture content.

The drum dryer is a continuously operated unit that uses rotating heated drums for the evaporation contact area. This method of drying can be used with materials high in volatiles. In several designs, the volatiles can be withdrawn and collected for reuse, as appropriate.

A tray and compartment dryer is a batch unit that uses a stationary tray or compartment to dry the waste, generally before transport for disposal or further treatment. Some units can be mounted on removable trucks.

A continuously operating pneumatic conveying dryer is used for applications similar to the tray and compartment dryer. In this case, however, drying is performed in conjunction with grinding, as the solids are conveyed and dried within the unit.

1.5.3. Aqueous Evaporation

Aqueous evaporation for hazardous waste treatment can be accomplished in a closed process vessel that uses steam to evaporate the liquid into a water vapor, which is ultimately condensed and may be reused, as shown in Figure 5. The concentrated liquid is collected for further treatment or disposal.

1.6. Ion Exchange

Ion exchange is an adsorption process where ionic species are adsorbed from solution by exchanging places with a similarly charged ion on the exchange media. Ion exchange is used primarily to remove metals, although nonmetallic inorganic and organic ions can also be removed. Metals that can be removed by ion exchange include barium [7440-39-3], cadmium [7440-43-9], hexavalent chromium [7440-47-3], copper [7440-50-8], lead [7439-92-1], mercury [7439-97-6], nickel [7440-02-0], selenium [7782-49-2], silver [7440-22-4], uranium [7440-61-1], and zinc [7440-66-6]. Nonmetallic ions that may be removed by ion exchange include nitrate, sulfate, cyanide (when complexed with iron), and some organic acids, phenols, and amines under special conditions.

The adsorptive materials used for ion exchange are called zeolites. Naturally occurring zeolites belong to a group of hydrous aluminum silicate minerals. Synthetic zeolites or resins are based on organic polymers and are in more common usage today. Ion-exchange resins that adsorb positively charged ions are cationic and those that adsorb negatively charged ions are anionic. These resins can be designed to remove certain ions with greater specificity than other ions; however, ions with the same charge (positive, negative) can still compete for exchange sites and adversely affect the removal efficiency of the targeted ion if they are present in high enough concentrations.

Ion-exchange units can be operated in parallel or series and in downflow or upflow (fluidized) mode. A unit is regenerated when the target ion appears in the effluent (breakthrough). Ion-exchange resins are regenerated by washing with a concentrated solution containing the original exchangeable ion. This results in the desorption of the target ion from the resin with replacement by the original ion. Hydrogen-based cationic resins are regenerated with acid solutions such as sulfuric [7664-93-9], nitric [7697-37-2], or hydrochloric [7647-01-0] acid. Anionic resins that are hydroxide-based are regenerated with caustic solutions such as sodium hydroxide [1310-73-2]. Sodium chloride [7647-14-5] solution is used to regenerate sodium-based cationic and chloride-based anionic resins. Concurrent regeneration is when the regenerant solution flows through the unit

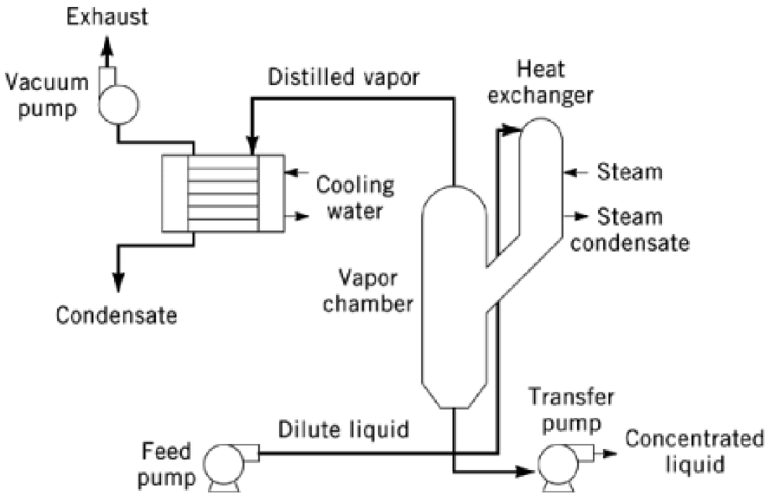

Fig. 5. Example of an aqueous evaporation unit.

in the same direction as does the wastewater, countercurrent regeneration flows in the opposite direction and requires less solution.

Pretreatment of aqueous streams may be required prior to using ion exchange. Suspended solids that can plug an ion-exchange unit should be reduced to the 10 μm level. Organics that can foul resins can be removed by carbon adsorption. Iron [7439-89-6] and manganese [7439-96-5], commonly present in ground waters, should be removed because they precipitate on the resin.

1.7. Membrane Filtration

Membrane filtration describes a number of well-known processes including reverse osmosis, ultrafiltration, nanofiltration, microfiltration, and electrodialysis. The basic principle behind this technology is the use of a driving force (electricity or pressure) to filter particles, ions, and organic molecules through a membrane, producing a clean stream on one side and a concentrated stream on the other. Although membrane filtration is discussed in this section in relation to waste treatment, this technology also has many industrial applications such as water desalination and softening, product concentration and purification, and metal recovery. Applications in waste treatment include metals removal–recovery, oil–water separation, and removal of toxic organic compounds.

The individual membrane filtration processes are defined chiefly by pore size although there is some overlap. The smallest membrane pore size is used in reverse osmosis (0.0005–0.002 microns), followed by nanofiltration (0.001–0.01 microns), ultrafiltration (0.002–0.1 microns), and microfiltration (0.1–1.0 microns). Electrodialysis uses electric current to transport ionic species across a membrane. Micro- and ultrafiltration rely on pore size for material separation, reverse osmosis on pore size and diffusion, and electrodialysis on diffusion. Separation efficiency does not reach 100% for any of these membrane processes. For example, when used to desalinate–soften water for industrial processes, the concentrated salt stream (reject) from reverse osmosis can be 20% of the total flow. These concentrated, yet still dilute streams, may require additional treatment or special disposal methods.

Reverse osmosis and electrodialysis are used to separate metals from electroplating bath rinse waters in the metal finishing industry. Ultrafiltration is used for oils–solids–water separation, metals recovery, and paint recovery from anodic paint processes. It has also been tested as an innovative technology for removal of solids and residual organics following biological treatment of contaminated ground water (4). Microfiltration is used for oil–solids–water separation and metals removal–recovery. Although nanofiltration has been used successfully for water treatment (removal of hardness, organic compounds, and viruses), it has not been used much for waste treatment. Testing has also been conducted with another type of membrane filtration process, pervaporation, that uses a vacuum to induce transfer of volatile organics from a liquid across the membrane (5). Membrane filtration of gaseous streams, which is used on industrial process streams to recover volatile organics, has been tested as posttreatment for air stripping and soil venting gases.

Membranes are subject to fouling which can be caused by metal oxides, precipitating salts, colloids, and biological growth. Cleaning agents include acids, alkalines, oxidizers, detergents, and organic solvents. Pretreatment prior to membrane filtration is required to reduce heavy solids and remove free oil.

1.8. Neutralization

Neutralization is pH adjustment of an acidic or caustic waste to a more neutral range. Neutralization is a very common treatment step for wastewaters and gases; it is used less frequently with solid wastes because the pH is less of a problem with these wastes. The most commonly used neutralizing agents are lime or calcium hydroxide [1305-62-0] for acidic wastewaters and sulfuric acid for caustic wastewaters. Other chemicals used for wastewater neutralization include sodium hydroxide and magnesium hydroxide [1309-42-8] for acidic streams and hydrochloric acid and carbon dioxide [124-38-9] for caustic streams. At facilities where both acidic and caustic streams are generated, commingling these streams helps reduce the amount of neutralizing chemicals that would otherwise be required. These acid–caustic waste streams can only be commingled, however, where they are compatible, that is, where the mixture will not generate unwanted precipitants or chemical reactions. Neutralization of acid gases with liquid caustic solutions (wet scrubbing) is very common. For example, the flue gas from an incinerator may be scrubbed with a soda ash [497-19-8] solution to remove acid gases. Wet scrubbing is normally done in a packed tower; the packing referred to is usually small plastic forms that provide a high degree of surface area per unit volume in order to maximize the contact of the gas with the scrubbing solution. There are also dry scrubbing systems for acid gases where the neutralizing agent, for example, lime, is sprayed into the gas stream.

1.9. Oil–Water Separation

Gravity separation of oil and water is a very simple process, often used as a pretreatment step in an overall wastewater treatment system. Under quiescent conditions, free oil floats to the surface where it can be skimmed off. Water emulsions may be broken for separation by using coagulants, acids, pH adjustment, heat, centrifuging, or high-potential alternating current. The API separator and corrugated plate interceptor (CPI) are common types of oil–water separators. In the United States, API separator sludge from petroleum refining wastewaters is listed as a hazardous waste, K051. As in the DAF process discussed earlier in this section, it is not the API separator itself that makes K051 hazardous, but the hazardous materials it contains.

1.10. Oxidation and Reduction

Oxidation and reduction (redox) reactions are used for both partial and complete degradation of many organic and inorganic compounds. A substance is oxidized when its oxidation state is increased, likewise it is reduced when its oxidation state is reduced. For inorganic compounds, oxidation involves the loss of electrons, reduction is a gain in electrons. Redox reactions for organics are more complicated and may include the transfer of electrons, a hydrogen atom, an oxygen atom, a hydroxyl radical, a chlorine atom, a chlorinium ion (Cl_+), or similar species (6). Examples of compounds that are treated by redox processes include alcohols, phenols, and cyanide. Common chemical oxidants for waste treatment include chlorine [7782-50-5], ozone [10028-15-6], and hydrogen peroxide [7722-84-1].

Oxidizers do not discriminate among compounds and are capable of reacting with any oxidizable compounds in a waste stream. Oxidation is used either to degrade a compound completely or quite often, to degrade a compound partially to a less toxic form or intermediate that can be discharged or if needed, treated further by another process.

Factors affecting oxidation processes include pH, the type and quantity of oxidizable compounds in the waste, and metals that can react with the oxidizing agent. The pH affects the oxidation rate by changing the free energy of the overall reaction, changing the reactivity of the reactants, and/or affecting specific OH^- ion or H_3O^+ ion catalysis (6). The presence of oxidizable compounds in addition to the target compound increases the amount of oxidant required. Metal salts, especially those of lead and silver, can also react with the oxidizer and increase the required dosage or interfere with the treatment process.

1.10.1. Chlorine

Chlorine is a well known disinfectant for water and wastewater treatment, however, it can react with organics to form toxic chlorinated compounds such as the trihalomethanes bromodichloromethane, dibromochloromethane, chloroform [67-66-3], and bromoform [75-25-2]. Chlorine dioxide [10049-04-4] may be used instead since it does not produce the troublesome chlorinated by-products as does chlorine. In addition, by-products formed by chlorine dioxide oxidation tend to be more readily biodegradable than those of chlorine, however, chlorine dioxide is not suitable for waste streams containing cyanide.

Cyanide destruction by alkaline chlorination is a widely used process. With alkaline chlorination, cyanide is first converted to cyanate with hypochlorite [7681-52-9] at a pH greater than 10. A high pH is required to prevent the formation of cyanogen chloride [506-77-4] which is toxic and may evolve in gaseous form at a lower pH. With additional hypochlorite, cyanate is then oxidized to bicarbonate, nitrogen gas, and chloride. The pH for this second stage is 7–9.5 (6).

1.10.2. Ozone

A primary advantage of oxidation with ozone is the avoidance of chlorinated by-products of the reaction. Excess ozone that is not consumed in the reaction decomposes to oxygen [7782-44-7]. The main disadvantage is the high electrical cost of producing ozone which is generated onsite from dry air or oxygen by high voltage electric discharge.

Ozone can be used to completely oxidize low concentrations of organics in aqueous streams or partially degrade compounds that are refractory or difficult to treat by other methods. Compounds that can be treated with ozone include alkanes, alcohols, ketones, aldehydes, phenols, benzene and its derivatives, and cyanide. Ozone readily oxidizes cyanide to cyanate, however, further oxidation of the cyanate by ozone proceeds rather slowly and may require other oxidation treatment like alkaline chlorination to complete the degradation process.

Ozone is only slightly soluble in water. Thus, factors that affect the mass transfer between the gas and liquid phases are important and include temperature, pressure, contact time, contact surface area (bubble size), and pH.

Ozonation can be enhanced by the addition of ultraviolet (uv) radiation. This combination can be effective in degrading chlorinated organic compounds and pesticides. In addition, metal ions such as iron, nickel, chromium, and titanium [7440-32-6], can act as catalysts, as can ultrasonic mixing.

1.10.3. Hydrogen Peroxide

Hydrogen peroxide is typically used as an oxidizer in combination with uv light, ozone, and/or metal catalysts. Fenton's reagent is hydrogen peroxide with iron as a catalyst. Hydrogen peroxide/uv light has been shown to be

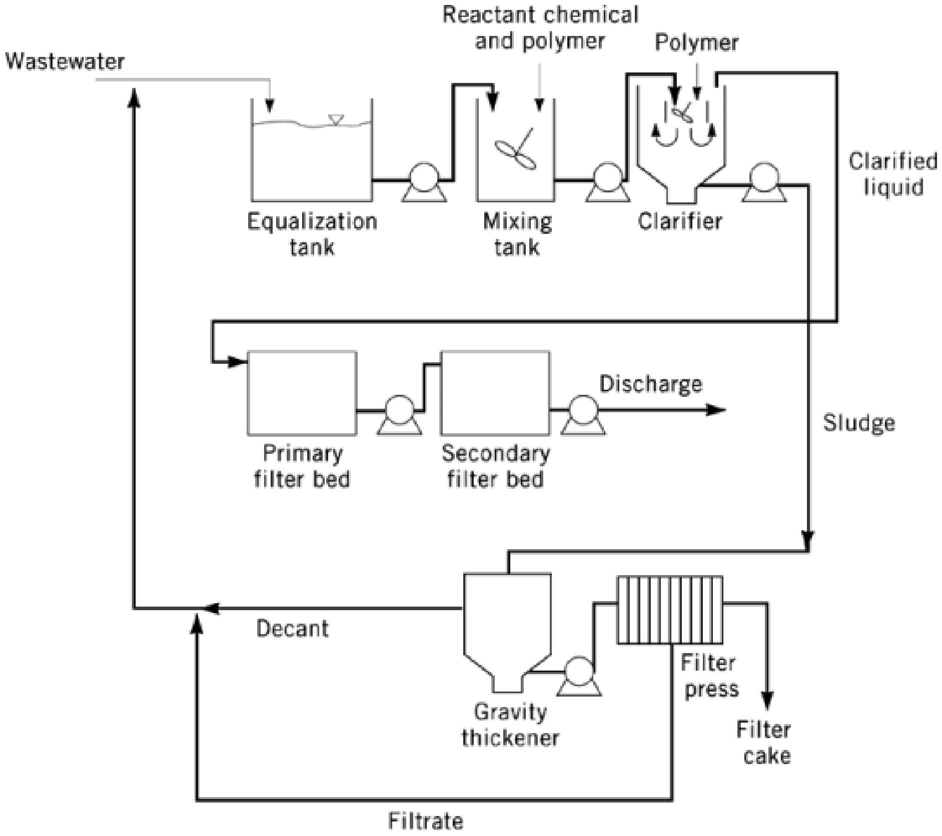

Fig. 6. Example of a chemical precipitation system.

effective in oxidizing benzene, chlorobenzene [108-90-7], chloroform, chlorophenol, 1,1-dichloroethane [75-34-3], dichloroethene [540-59-0, 75-35-4], phenol [108-95-2], tetrachloroethylene, 1,1,1-trichloroethane [71-55-6], trichloroethylene, toluene, xylenes (7–10) and many other organic compounds.

1.11. Precipitation

Precipitation processes have been used for many years to remove metals from aqueous streams. An example of this process is shown in Figure 6. Metals precipitation is accomplished by pH adjustment and the addition of a chemical reagent that forms a precipitant with the metal that can be settled out and separated from the aqueous stream. Chemical reagents such as calcium hydroxide (lime), sodium hydroxide (caustic), magnesium oxide [1309-48-4], and magnesium hydroxide can be used to precipitate arsenic [7440-38-2], cadmium, trivalent chromium, copper, iron, lead, manganese, nickel, and zinc. Hydroxide precipitation, particularly with lime, is the most common precipitation process because the chemical reagents are readily available, relatively inexpensive, easy to handle, and form sludges that dewater easily. Sulfide precipitation with reagents such as sodium sulfide [1313-82-2] and ferrous sulfide [1317-37-9] can be used with cadmium, cobalt [7440-48-4], copper, iron, mercury, manganese, nickel, silver, tin, and zinc. Carbonate precipitation with reagents such as sodium carbonate (soda ash) and calcium carbonate [471-34-1] can be used with cadmium, lead, nickel, and zinc. Because the sulfide forms of metals are much less soluble than their hydroxide counterparts, sulfide

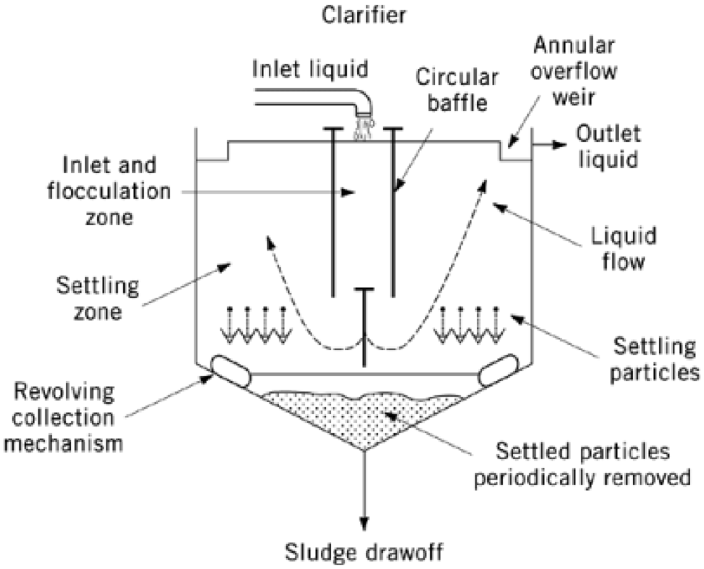

Fig. 7. Example of a sedimentation–clarification system.

precipitation can treat metals to lower concentrations. Although very insoluble, metal sulfides form very fine, hard to settle particles and generate large quantities of sludge.

The typical precipitation process takes place in a series of tanks beginning with chemical addition, followed by flocculation and coagulation of precipitated solids, sludge thickening, and finally, sludge dewatering. Sand filtration of the wastewater effluent to remove residual solids may be used as a final polishing step. Chemicals may be added to aid flocculation and coagulation and to produce a more dense and easily dewatered sludge. Typical chemical aids are alum (aluminum sulfate [10043-01-3], ferric chloride [7705-08-0], and proprietary polyelectrolytes. Precipitation of arsenic first requires oxidation of the arsenite form to arsenate. Hexavalent chromium requires reduction to the trivalent form.

Precipitation is affected by pH, solubility product of the precipitant, ionic strength and temperature of the aqueous stream, and the presence of metal complexes. For each metal precipitant, there is an optimum pH where its solubility is lowest and hence, the highest removals may be achieved. When an aqueous stream contains various metals, the precipitation process cannot be optimized for each metal, sometimes making it difficult to achieve effluent targets for each. Solubility products depend on the form of the metal compound and are lowest for metal sulfides, reflecting the relative insolubility of these compounds. For example, the solubility product for lead sulfide [1314-87-0] is on the order of 10^{-45} compared to 10^{-13} for lead carbonate. Metal sulfides and hydroxides are more soluble at higher temperatures, whereas carbonates are less soluble. When metals are complexed or chelated with other ions or molecules (for example, cyanide and ethylenediaminetetraacetic acid (EDTA) [60-00-4], they are more soluble, may not precipitate easily, and require additional or alternative forms of treatment.

1.12. Sedimentation–Clarification

Sedimentation–clarification is a process by which hazardous and nonhazardous grits, fines, and other suspended solids are removed from the waste stream through gravity settling. The process typically is used as a pretreatment step or in conjunction with another treatment process such as chemical or biological treatment. Usually, sedimentation–clarification is performed in a gravity settling clarifier, as shown in Figure 7. A settling system provides enough residence time to allow the heavier suspended solids to gravitationally settle to the bottom of the system. These solids are removed and thickened periodically prior to disposal.

Flocculation, commonly used in clarifiers to enhance sedimentation, is a physical–chemical process in which small particles agglomerate to form larger particles. The large particles, because they are heavier than the smaller particles, settle more effectively in the clarifier or sedimentation basin. Flocculation of certain types of particles can be induced by slow agitation of the wastewater, without the addition of a flocculating agent. However, a flocculating chemical usually is added to the wastewater to promote flocculation of the smaller particles. The flocculants adhere readily to suspended solids and to each other to form larger particles with greater density, which settle better. The settled solids thicken at the bottom of the clarifier and, in some clarifier designs, are used to form a sludge blanket that becomes a filtration mechanism within the clarifier.

Clarifiers typically are used in chemical precipitation and biological treatment processes to remove precipitated metal solids and suspended biological solids. To prevent the sludge blanket from becoming too thick or heavy, part of the sludge blanket is removed continuously or intermittently from the system and thickened prior to disposal.

1.13. Solvent Extraction

With solvent extraction, organics are separated from a waste by mixing the waste with a solvent capable of dissolving or extracting the organics. The extraction process can have multiple stages and be operated where the solvent and waste pass concurrently or countercurrently.

After mixing, the solvent and waste are separated. The solvent with dissolved organics is called the extract. The waste remaining after extraction is called the raffinate. The extract may be sent to a distillation or steam stripping unit to separate the dissolved organics from the solvent and the solvent can be recycled back to the extraction process. The raffinate may require additional treatment or may be disposed or incinerated.

Factors affecting solvent extraction include type of solvent and the relative solubilities of the organic components in the solvent, selectivity value (the ratio of the equilibrium concentrations of the organic in the solvent and in the waste), temperature, pH, mixing, and settling time for separation. Temperature and pH affect equilibrium conditions. The type and quantity of mixing affects the degree of contact and transfer efficiency between solvent and waste. Sufficient time must be allowed for settling to separate the extract and raffinate.

1.14. Stabilization–Solidification

Stabilization and solidification are technologies that are often used together to improve or strengthen the physical nature of a waste and to bind, immobilize, or otherwise prevent the migration of toxic constituents contained in the waste. Stabilization generally refers to processes that reduce the toxicity, leaching, or mobility of toxic constituents, perhaps through chemical reactions, but the physical form of the waste is not necessarily changed or improved. Solidification generally refers to processes that change the physical nature of the waste to make it more manageable, increase its structural strength and load-bearing capacity, or reduce its permeability, but not necessarily by chemical reaction. Many treatment technologies involve characteristics of both stabilization and solidification, making distinctions between the two processes unclear at times such that the two terms are often used together. Applying the correct definition to a particular treatment process is not important, rather it is in the changes in the waste characteristics that are important. Are toxic constituents rendered less toxic or mobile and can the waste be handled easily and withstand the physical stresses during and after disposal?

Some of the most common stabilization–solidification processes are those using cement, lime, and pozzolanic materials. These materials are popular because they are very effective, plentiful, and relatively inexpensive. Other stabilization–solidification technologies include thermoplastics, thermosetting reactive polymers, polymerization, and vitrification. Vitrification is discussed in the thermal treatment section of this article and the other stabilization–solidification processes are discussed below.

1.14.1. Cement, Lime, and Pozzolanic Materials

Cement is the chemical binder used in making concrete, a chemically cured mixture of cement, water, and aggregate (usually sand and gravel). With sufficient water for hydration, cement forms a calcium alumino–silicate crystalline structure that can physically and/or chemically bind with toxic constituents such as metal hydroxides and carbonates. Use of lime (calcium hydroxide) involves similar reactions where alumino–silicates are supplied by the waste or treatment additives. Pozzolans are siliceous materials that can combine with lime to form cementitious materials (Pozzolans derive their name from Pozzuoli, Italy, near Mt. Vesuvius where a siliceous ash is found). Common pozzolanic materials are fly ash, blast furnace slags, and cement kiln dust. The high pH of cementitious binders protects against acid conditions that can result in metal leaching. Organics interfere with hydration and the formation of the crystalline structure binding the waste. This interference can be minimized by treatment additives such as clays (natural and organically modified), vermiculite, or organically modified silicates. Other waste constituents that can reduce the effectiveness of cementitious processes include sulfates, chlorides, borates, and silt.

1.14.2. Thermoplastics

Wastes containing heavy metals and/or radioactive materials may be mixed with thermoplastics. In this process, the waste is mixed with a molten thermoplastic material such as bitumen, asphalt, polyethylene [9002-88-4], or polypropylene [9003-07-0]. Wastes are normally dried, heated, mixed with the thermoplastic, cooled, and finally placed in containers for disposal. The process is not suitable for organic wastes unless air emission controls are installed because the high temperatures will drive off volatile components. It is also not suitable for hygroscopic wastes which absorb water, expanding and cracking the thermoplastic. Likewise, strongly oxidizing constituents, anhydrous inorganic salts, and aluminum salts are unsuitable for thermoplastics.

1.14.3. Thermosetting Reactive Polymers

Materials used as thermosetting polymers include reactive monomers such as urea–formaldehyde, phenolics, polyesters, epoxides, and vinyls, which form a polymerized material when mixed with a catalyst. The treated waste forms a sponge-like material which traps the solid particles, but not the liquid fraction; the waste must usually be dried and placed in containers for disposal. Because the urea–formaldehyde catalysts are strongly acidic, urea-based materials are generally not suitable for metals that can leach in the untrapped liquid fractions. Thermosetting processes have greater utility for radioactive materials and acid wastes.

1.14.4. Polymerization

Spills of chemicals that are monomers or low-order polymers can be polymerized by adding a catalyst. Compounds that may be treated by polymerization include aromatics, aliphatics, and other oxygenated monomers such as vinyl chloride and acrylonitrile [107-13-1].

1.15. Steam Stripping

Steam stripping is used to separate volatile components from wastewater. Steam stripping is very similar to distillation which has been discussed earlier. Steam stripping differs from distillation, however, in that there is no rectifying section and the waste steam is introduced at the top of the column (packed or tray). Steam is introduced at the bottom and as it rises countercurrent to the downflowing wastewater, it vaporizes the volatile components. The vapor stream is collected overhead and condensed. Steam stripping is amenable to volatile components that phase separate from water. The organic and aqueous phases are separated after condensation; the organics may be recovered or disposed and the aqueous stream can be recycled to the stripper. A column with rectification (ie, distillation) is required if the volatile components are not phase-separable in order to obtain a high concentration of volatiles in the overhead stream.

1.16. Supercritical Fluid Extraction

Supercritical fluid extraction takes advantage of the enhanced solvent power of compounds at supercritical temperature and pressure conditions to extract organics from oily and/or organic liquids and sludges. Carbon dioxide [124-38-9] is a particularly attractive solvent at supercritical conditions (greater than 7400 kPa and 31°C) because it is nontoxic and leaves no residue when it is reverted to gaseous form during the recovery step. Carbon dioxide is not suitable for wastes with high alkalinity, however, because excessive amounts of the supercritical solvent will be consumed in the formation of carbonates and bicarbonates. Applications using carbon dioxide have been developed to clean products and equipment to replace toxic organic solvents.

1.17. Supercritical Water Oxidation

Supercritical water oxidation is similar to wet air oxidation in that it uses high temperature and high pressure conditions to oxidize organics. Temperature and pressure conditions, however, are higher (greater than 22,000 kPa and 374°C) such that water is at supercritical conditions where it has properties between those of a liquid and a gas. Organics are easily solubilized in supercritical water and once solubilized, they are completely oxidized at the high temperature and pressure conditions. Reaction times are very short (a few seconds to less than a minute) and treatment efficiencies very high (essentially 100%). Supercritical water oxidation has the capability of treating many different kinds of organics including polycyclic aromatic hydrocarbons, chlorinated hydrocarbons, PCBs, paint, oil, dyes, pulp and paper wastes, chemical warfare agents, and missile propellants (11). Wastes must be either aqueous or in slurry form.

Reaction vessels for supercritical water oxidation must be highly corrosion resistant because of the aggressive nature of supercritical water and oxidation reaction products at extreme temperatures and pressures. Supercritical oxidation of PCBs and some chlorinated hydrocarbons can be difficult because acids are formed that are highly corrosive to almost any materials used for reactor components (11). Inorganic salts can be a problem because they are sparingly soluble under these conditions and will precipitate on the vessel walls and components.

1.18. Wet Air Oxidation

With wet air oxidation, increased temperature and pressure are used to oxidize dilute concentrations of organics and some inorganics, such as cyanide, in aqueous wastes that contain too much water to be incinerated, but are too toxic to be treated biologically. In general, wet air oxidation provides primary treatment for wastewaters that are subsequently treated by conventional methods. This technology can be used with wastes that are pumpable (slurries and liquids).

Waste streams that are treated by wet air oxidation generally are those having dissolved or suspended organic concentrations from 500 to 50,000 mg/L. Below 500 mg/L, oxidation rates are too slow and above 50,000 mg/L, incineration may be more feasible.

Operating parameters include temperature, pressure, oxygen concentration, and residence time. Materials of construction include stainless steel, nickel, and titanium alloys (the latter for extremely corrosive wastes containing heavy metals). Vented gases from the process may require scrubbing or other emission controls.

Because of high energy input, wet air oxidation is relatively expensive. To reduce energy demand, the incoming wastewater can be preheated by heat exchange with the treated effluent. Operating temperatures may be lowered by using a catalyst. Typically, removal of the catalyst from the effluent is needed to avoid contamination and to minimize operating costs.

2. Biological Treatment

2.1. Biodegradability of Compounds

Biological processes are effective in treating a wide variety of organic and inorganic compounds. Most biological processes are aerobic and use the oxygen available in supplied air or pure oxygen. The chief products of aerobic biodegradation of carbonaceous and nitrogenous compounds are carbon dioxide, ammonia, water, and biomass (cell growth of the microorganisms). The ease with which a compound is degraded is related to its chemical structure. Some compounds are not degraded completely, but are instead broken down into simpler compounds.

The biodegradability of hazardous compounds according to general structure has been summarized in Ref. 12 from a number of studies. They have found that the biodegradability of hydrocarbons generally decreases in the following order: alkanes and alkenes with straight alkyl chains, mono- and dicycloalkanes, and aromatic hydrocarbons, including polycyclic ones. Mono- and dicyclic aromatic hydrocarbons are usually more biodegradable than cycloalkanes. Chain branching in alkanes and alkenes decreases biodegradability, although biodegradability of alkanes and alkenes are essentially the same if they have identical chain configurations. Monocycloalkanes are usually readily biodegradable, although exceptions have been noted with specific compounds. Polycycloalkanes are less biodegradable, especially tetra- and higher polycycloalkanes. Naphthalene [91-20-3], lower alkylbenzenes, and phenanthrene [85-01-8] are aromatic hydrocarbons that are biodegraded relatively easily. The biodegradability of alkylbenzenes depends on the number and position of the alkyl groups. Polyalkylation of aromatic hydrocarbons usually decreases biodegradability. With phenylalkanes, biodegradability depends on the branching of long alkyl chains and those phenylalkanes with a quaternary carbon atom, particularly in the terminal position, are quite resistant to biodegradation. Polycyclic aromatic hydrocarbons (except for naphthalene) are relatively slow to biodegrade, particularly tetra- and higher aromatics.

General guidelines for biodegradability have been developed by others. Ref. 13 gives the following general guidelines for the biological treatment of industrial wastewaters:

Nontoxic aliphatic compounds containing carboxyl, ester, or hydroxyl groups are readily biodegradable. Those with dicarboxylic groups require longer acclimation times than those with a single carboxyl group.

Compounds with carbonyl groups or double bonds are moderately degradable and slow to acclimate.

Compounds with amino or hydroxyl groups decrease in biodegradability relative to degree of saturation, in the following order: primary, secondary, then tertiary carbon atom of attachment.

Biodegradability decreases with increasing degree of halogenation.

Ref. 14 contains a more general and simplistic order of decreasing biodegradability: straight-chain compounds, aromatic compounds, chlorinated straight-chain compounds, and chlorinated aromatic compounds.

Many different factors influence the performance of biological treatment systems. Although each specific biological process has special requirements, factors common to biological processes, besides biodegradability, include: organic concentration, temperature, pH, nutrients, and oxygen (aerobic or anaerobic).

2.2. Activated Sludge

Activated sludge is widely used to treat both municipal and industrial wastewater. Used in a variety of process configurations and operating modes, the activated sludge process contains three basic elements: an aeration basin, clarification, and sludge recycle. The aeration basic contains a suspension of *activated* microorganisms, primarily bacteria and protozoa, that biodegrade the wastewater under aerobic conditions. Aerators supply oxygen for the microorganisms and mixing energy to keep them in suspension and in contact with the waste. The microorganisms are separated from the treated wastewater by clarification and a portion of this biological

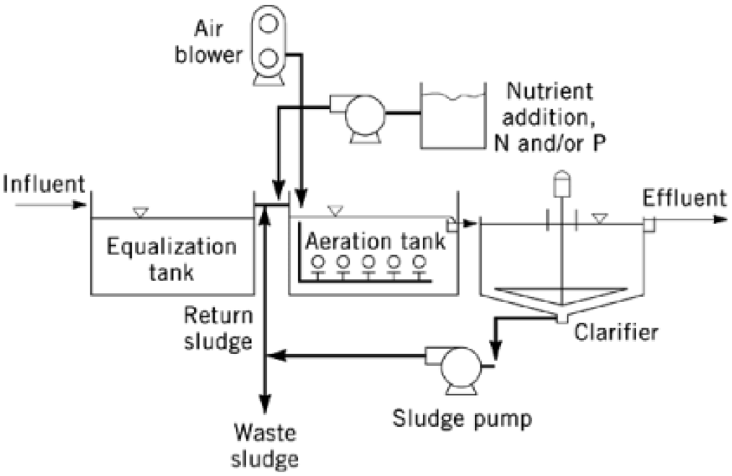

Fig. 8. Example of an activated sludge process.

sludge is recycled back to the aeration basin to maintain the microbial population and begin a new treatment cycle.

Although the activated sludge process is relatively robust and able to handle variable wasteloads and operating conditions, it must be protected from shock loadings that are toxic or excessively high in concentration. Influent variability, both in flow and quality, can be reduced through equalization prior to the aeration basin. Other pretreatment steps that may be needed to protect the aeration basin are neutralization, oil–water separation, and grit or solids removal. An example of an activated sludge process is shown in Figure 8.

The microorganisms grow in response to the food source supplied in the wastewater and produce more biological sludge than is needed to maintain the process. This excess sludge must be wasted from the process and is usually treated by dewatering and aerobic or anaerobic digestion.

Aeration basins can be constructed as concrete or steel tanks or earthen impoundments, although tanks are more common in the United States now because of ground water problems with leakage from impoundments and stringent regulation of impoundments for the treatment of hazardous waste.

2.2.1. Process Variations

There are many variations of the activated sludge process which have been developed in response to different wastewater characteristics and process requirements. The mixing regime of the process may be plug flow, completely mixed, or more often, something between the two. In a plug flow system, influent wastewater and return activated sludge are mixed at the head of the aeration basin and travel as a *plug* along the length of the basin. Therefore, the organic concentration is greatest at the head of the basin and diminishes as the wastewater travels towards the basin outlet. In a completely mixed activated sludge system, the influent wastewater and return activated sludge are uniformly or completely mixed in the aeration basin. Mixing the influent wastewater with the larger volume of the aeration basin allows high organic loads and toxic or inhibitory compounds to be diluted to protect the system from shock, an advantage over plug flow systems. In general, complete mix systems have higher mixed liquor concentrations than plug flow systems and consequently can treat high organic loads. However, complete mix systems tend to produce a sludge that is less dense and may be more difficult to settle. In reality, pure plug flow and complete mixing do not exist as the process operates somewhere in between. Some of the most common process variations of activated sludge systems are described in the following sections.

2.2.1.1. Tapered Aeration. In this process, aeration is provided in a tapered or stepped fashion to match oxygen requirements in a plug flow system. Oxygen requirements are highest at the head of the aeration basin where the organic-laden influent enters. Aeration is decreased along the basin as the organics are degraded. Toward the end of the basin, it may be necessary to maintain a certain level of aeration in excess of oxygen requirements in order to provide enough mixing energy to keep the microorganisms in suspension.

2.2.1.2. Contact Stabilization. This process takes advantage of the ability of the activated sludge to quickly adsorb organics. Contact stabilization is operated either as a two-unit system or as two zones within a single aeration basin. In the two-unit system, the influent wastewater is first mixed with return activated sludge in a contact basin. Contact time is short, 30–90 min, but sufficient for the sludge to adsorb the organics. The mixture then flows to a clarifier where the sludge and adsorbed material are settled out. The treated effluent is discharged from the clarifier. A portion of the settled sludge is wasted as excess biomass and the remainder enters the stabilization basin where the adsorbed organics are biodegraded over a period of 3–6 h, thereby reactivating the sludge. In the two-zone system, the aeration basin is operated as plug flow. The contact zone for the influent wastewater is near the end of the aeration basin where organic concentrations are lowest and the sludge is ready to adsorb additional organics. The stabilization zone begins at the head of the aeration basin where the settled sludge with its adsorbed organic load enters. Contact stabilization requires about 50% less aeration basin capacity than conventional systems and produces less biomass which settles better. On the down side, effluents are poorly nitrified and the process is better suited to wastewaters that contain high proportions of biochemical oxygen demand (BOD) as colloidal or suspended matter.

2.2.1.3. Extended Aeration. As its name implies, extended aeration operates with a long aeration period. With a long sludge age and low food-to-microorganism ratio, sludge production is low and the sludge settles well. Because aeration and basin volume requirements are high, extended aeration is normally used for small flows and small communities. The oxidation ditch is a common form of the extended aeration process. Viewed from above, an oxidation ditch looks like a racetrack around which the wastewater flows. Aeration is provided by rotors or brushes which also provide the energy to keep the water flowing around the track Influent wastewater usually enters upstream of the aerator. Anoxic zones can be set up in oxidation ditches, allowing nitrogen removal through denitrification. In addition to the racetrack design, oxidation ditches can be of the carrousel type which resembles a long racetrack folded in half. The carrousel has two aerators that allow larger flows to be treated.

2.2.1.4. Pure Oxygen. Activated sludge systems can be designed to use pure oxygen instead of air to increase oxygen transfer rates. Advantages of pure oxygen systems are increased BOD removal rates, smaller aeration basin volumes, lower sludge production, and improved sludge settling. The aeration basin is covered and divided into a series of stages. Influent wastewater, return activated sludge, and oxygen are introduced into the first stage. In each progressive stage, both the BOD and oxygen content decrease, acting like a tapered aeration plug-flow system. Operating parameters for pure oxygen systems, such as mixed liquor suspended solids, mixed liquor oxygen levels, and food-to-microorganism (F/M) loading rate, are higher than for conventional activated sludge. Disadvantages of pure oxygen systems include the high cost of oxygen production and the need for safety precautions and monitoring with combustible hydrocarbons in high oxygen environments.

2.2.1.5. PACT System. Powdered activated carbon treatment, or PACT (is a registered trademark of Du Pont), is the simple addition of powdered activated carbon to an activated sludge system. This process is used to prevent inhibitory effects of toxic compounds, remove refractory organics or color, or remove effluent toxicity. Other benefits of the process are reduced emissions of volatile compounds from wastewaters and improved sludge settling. Carbon dosage rates depend on the given situation, but usually range from 50 to 3000 mg/L.

2.2.2. Process Control

There are many different process control variables that determine the efficiency of the activated sludge process. Effluent quality depends primarily on wastewater characteristics, plant loading (organics and flow), residence time in the system, temperature, type and concentration of microorganisms degrading the waste, oxygen supply, and degree of mixing. The main process control variables are described below.

2.2.2.1. Hydraulic Retention Time. The hydraulic retention time (HRT) is a measure of the average time the wastewater spends in the aeration basin. It is calculated by dividing the volume of the aeration basin by the influent wastewater flow rate. Since the flow rate of recycle sludge is not included in the calculation, the actual retention time is less. The HRT depends on the type of activated sludge process being used. Conventional systems have HRTs at 4–8 h. Extended aeration systems can have much longer HRTs: 18 h to as much as 72 h.

2.2.2.2. Organic Loading. Organic loading is the mass of influent BOD per volume of aeration basin. Typical values for conventional systems are 0.32–0.64 kg/1000 L. Loading for extended aeration systems are lower whereas loadings for most other process configurations are higher.

2.2.2.3. MLSS/MLVSS. The concentration of microorganisms in the aeration basin determines the organic loading and the efficiency of the process. The contents of the aeration basin, the mixture of wastewater and microorganisms, is referred to as mixed liquor. The mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) are both used as measures of the microorganism concentration in the aeration basin. The MLVSS more closely approximates the biologically active portion of the solids in the mixed liquor because microbial cellular material is organic and volatilizes or burns at 500°C (the temperature for volatile solids analysis). The MLSS includes both the volatile and inert solids in the mixed liquor. It is often used or at least monitored more frequently than the MLVSS because the analytical test for suspended solids is quicker than for volatile suspended solids. The volatile fraction representing the MLVSS varies, but a typical value is 0.8. The MLSS concentration for conventional systems ranges from 1500 to 3500 mg/L. MLSS concentrations will be higher in other process configurations. For example, pure oxygen systems may have MLSS concentrations from 5000 to 8000 mg/L. Specially acclimated systems may have MLSS concentrations of 10,000 mg/L and higher. MLSS concentrations are limited by the availability of oxygen in the aeration basin, and recycle sludge flow rates.

2.2.2.4. F/M Ratio. The food-to-microorganism ratio (F/M) is a measure of the organic loading on the biological population. The F/M ratio is calculated as the mass of BOD per day divided by the mass of MLSS or MLVSS in the aeration basin. Thus, the F/M ratio has units of day^{-1}. The F/M ratio can be controlled by adjusting both the flow rate and concentration of the sludge recycled to the aeration basin. When based on MLVSS, typical values for the F/M ratio for conventional systems range from 0.2 to 0.4 day^{-1}. The F/M ratio is higher for contact stabilization (0.2 to 0.6 day^{-1}) and pure oxygen systems (0.4 to 1.0 day^{-1}), and lower for extended aeration systems (0.03 to 0.15 day^{-1}).

2.2.2.5. Mean Cell Residence Time. The mean cell residence time (MCRT) is a measure of the average length of time (in days) spent in the system by the microorganisms and relates to the overall growth phase of the microbial population. It is calculated as the mass of microoganisms in the aeration basin, as represented by the MLSS or MLVSS, divided by the mass of microorganisms removed from the system through sludge wastage and in the effluent discharge. The MCRT may also be referred to as the solids retention time or sludge residence time (SRT) or sludge age. The MCRT in conventional systems typically ranges from 3 to 5 days. Pure oxygen systems have higher MCRTs (8 to 20 days) as do extended aeration systems (6 to 40 days).

2.2.2.6. Sludge Recirculation. The concentration of microorganisms in the aeration basin is achieved by recirculating settled sludge from the clarifier. Both the flow rate and concentration of the return activated sludge determine the solids in the aeration basin. The recirculation rate is the ratio of the flow rate of the return activated sludge to the flow rate of the influent wastewater. Typical ratios for conventional systems are 0.25 to 0.5. Pure oxygen systems have similar rates, whereas the recirculation rates are higher for both contact stabilization (0.25 to 1.0) and extended aeration (0.75 to 1.5).

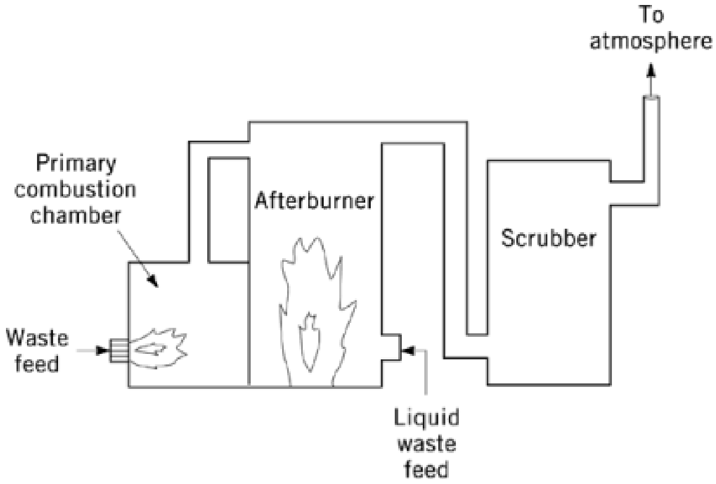

Fig. 9. Typical configuration of an incinerator.

2.2.2.7. Aeration. Aeration not only delivers oxygen to the activated sludge system, but provides mixing energy to keep the microorganisms in suspension and in contact with the wastewater. Aeration is provided by mechanical aeration using surface aerators or by diffusers on the bottom of the aeration basin. Both types of aeration equipment are common in conventional and pure oxygen systems, whereas horizontal surface aerator brushes are used in oxidation ditches. In activated sludge systems using air, oxygen concentrations in the aeration basin are usually maintained between 0.5 and 2.0 mg/L. In pure oxygen systems, the concentrations are much higher (4 to 8 mg/L).

3. Thermal Treatment

Thermal treatment is used to destroy, break down, or aid in the desorption of contaminants in gases, vapors, liquids, sludges, and solids. There are a variety of thermal processes that destroy contaminants, most of which are classified as incineration. Incineration literally means to become ash (from Medieval Latin, *incinerare*, in or into ashes). With respect to the incineration of hazardous wastes regulated in the United States, however, there is a strict legal definition of what constitutes an incinerator. The Resource Conservation and Recovery Act (RCRA) definition of incinerator at 40 *CFR* §260.10 is

> any enclosed device that: (*1*) uses controlled flame combustion and neither meets the criteria for classification as a boiler, sludge dryer, or carbon regeneration unit, nor is listed as an industrial furnace; or (*2*) meets the definition of infrared incinerator or plasma arc incinerator.

A more simplified description is a unit that combusts materials in the presence of oxygen at temperatures normally ranging from 800 to 1650°C. A typical configuration of an incinerator is shown in Figure 9. Typical types of incineration units that are discussed herein are catalytic oxidation, fluidized beds, liquid injection, multiple hearth furnaces, and rotary kiln. Thermal desorption is also discussed. However, an overview of the main factors affecting incinerator performance is presented first, below.

3.1. Factors Affecting Performance

There are many factors that affect both the choice of a particular thermal treatment and its performance. Chief among these are waste characteristics, temperature, residence time, mixing or turbulence, and air supply.

3.1.1. Waste Characteristics

The physical form of the waste restricts the applicability of some thermal technologies. A convenient summary of physical characteristics and thermal processes has been presented by Cheremisinoff (15). Those processes that can treat the widest range in physical form are incineration, pyrolysis, calcination, and microwave discharge. These processes are capable of treating wastes in essentially any form: containerized, solid, sludge, slurry, liquid, or fume. Molten salt reactors and plasma technology can be used with any of these types of wastes, except fumes. Evaporative processes are amenable to solids, sludges, slurries, and liquids. Wet air oxidation can be used for slurries and liquids. Distillation (with and without steam) and steam stripping are limited to liquid treatment. Catalytic incineration is limited to fume treatment.

Other waste characteristics that affect the choice of thermal treatment and its operation include heating value, contaminant boiling points, metal content, heterogeneity, moisture content, decomposition products and by-products, and the presence of explosive constituents. The heating value and moisture content of the waste determine if combustion is self-supporting or if auxiliary fuel will be required. Elemental constituents in the waste may be carried in the exhaust gases and must be removed. Problem metals are antimony [7440-36-0], arsenic, cadmium, lead, and mercury. Acid gases containing chlorine, sulfur [7704-34-9], fluorine [7782-41-4], or bromine [7726-95-6] that are generated must be neutralized and scrubbed from the flue gases. The heterogeneity of the waste is determined by the distribution and concentration of combustible organics; localized concentrated materials can produce hot spots in the combustion chamber. Heterogeneity is also defined by the type and amount of debris that may be included in excavated wastes. These materials can interfere with the process by shielding the waste, fouling equipment, or slagging in the reactor. Undesirable decomposition products and byproducts include nitrogen oxides and dioxins.

3.1.2. Temperature

The temperature for combustion processes must be balanced between the minimum temperature required to combust the original contaminants and any intermediate by-products completely and the maximum temperature at which the ash becomes molten. Typical operating temperatures for thermal processes are: incineration (750–1650°C), catalytic incineration (315–550°C), pyrolysis (475–815°C), and wet air oxidation (150–260°C at 10,350 kPa) (15). Pyrolysis is thermal decomposition in the absence of oxygen or with less than the stoichiometric amount of oxygen required. Because exhaust gases from pyrolytic operations are somewhat “dirty” with particulate matter and organics, pyrolysis is not often used for hazardous wastes.

3.1.3. Residence Time

For cost efficiency, residence time in the reactor should be minimized, but long enough to achieve complete combustion. Typical residence times for various thermal processes are incineration (0.1 s to 1.5 h), catalytic incineration (1 s), pyrolysis (12–15 min), and wet air oxidation (10– 30 min) (15).

3.1.4. Turbulence

Turbulence is important to achieve efficient mixing of the waste, oxygen, and heat. Effective turbulence is achieved by liquid atomization (in liquid injection incinerators), solids agitation, gas velocity, physical configuration of the reactor interior (baffles, mixing chambers), and cyclonic flow (by design and location of waste and fuel burners).

3.1.5. Air Supply

Oxygen in excess of stoichiometric requirements for complete combustion is needed because incineration processes are not 100% efficient and excess air is needed to absorb a portion of the combustion heat to control the operating temperature. In general, units that have higher degrees of turbulence such as liquid injection incinerators require less excess air (20 to 60%) while units with less mixing such as hearth incinerators require more (30 to 100%).

3.2. Catalytic Oxidation

Catalytic oxidation is used only for gaseous streams because combustion reactions take place on the surface of the catalyst which otherwise would be covered by solid material. Common catalysts are palladium [7440-05-3] and platinum [7440-06-4]. Because of the catalytic boost, operating temperatures and residence times are much lower which reduce operating costs. Catalysts in any treatment system are susceptible to poisoning (masking of or interference with the active sites). Catalysts can be poisoned or deactivated by sulfur, bismuth [7440-69-9], phosphorus [7723-14-0], arsenic, antimony, mercury, lead, zinc, tin [7440-31-5], or halogens (notably chlorine); platinum catalysts can tolerate sulfur compounds, but can be poisoned by chlorine.

3.3. Fluidized Beds

In this type of incinerator, the waste and an inert bed material, sand normally, or alumina (aluminum oxide) [1344-28-1], are fluidized by blowing heated air through a distributor plate at the bottom of the bed. Fluidization results in good mixing and uniform distribution of materials within the bed which results in lower operating temperatures (450–710°C) and lower excess air requirements. Fluidized beds can be used to incinerate gases, liquids, or solids, although the each type of waste is introduced into the bed differently. Fluidized beds are susceptible to seizing or binding up or agglomeration on individual bed particles which can lead to seizing up. Bed seizure can occur with wastes containing clays, inorganics (salts), or high concentrations of lime.

3.4. Liquid Injection

Liquid injection units are the most common type of incinerator today for the destruction of liquid hazardous wastes such as solvents. Atomizers break the liquid into fine droplets (100–150 microns) which allows the residence time to be extremely short (0.5–2.5 s). The viscosity of the waste is very important; the waste must be both pumpable and capable of being atomized into fine droplets. Both gases and liquids can be incinerated in liquid injection units. Gases include organic streams from process vents and those from other thermal processes; in the latter case, the liquid injection incinerator operates as an afterburner. Aqueous wastes containing less than 75% water can be incinerated in liquid injection units.

3.5. Multiple Hearth Furnaces

Although well-suited for combustion of wet sludges, particularly municipal biological wastewater sludges, multiple hearth incinerators are not often used for hazardous wastes because operating temperatures (800–1000°C) of this type of incinerator are too low for many hazardous compounds. The multiple hearths are stacked vertically and sludges are introduced unto the top hearth. A series of “rabble” arms extending from a center rotating shaft mix and move the waste along the circular hearth until the waste falls through holes unto the hearth below. For incineration, usually a minimum of six hearths is required; more hearths are required for pyrolysis. Liquid wastes may be incinerated along with sludges when injected through burner nozzles.

3.6. Rotary Kiln

A rotary kiln is a long, cylindrical incinerator that is sloped a few degrees from horizontal. Waste is introduced at the upper end. The gentle slope and slow rotation of the kiln continually mix and re-expose the waste to the hot refractory walls, moving the waste toward the exit point. Rotary kilns operate in continuous or batch mode, although continuous operation is more cost-efficient and less wearing on the refractory material. Operating temperatures range from about 800 to 1650°C. They can be operated in either ashing or slagging mode; the former is common in the United States. Rotary kilns are relatively large incinerators, but because of their versatility in treating a wide range of wastes and their treatment efficiency, they are often used for incinerating hazardous wastes. Rotary kilns can be used to incinerate gases, liquids, sludges, and solids. However, highly aqueous organic sludges tend to form a ring on the walls of the kiln that prevent the discharge of ash and they can also form sludge balls that are not completely incinerated.

3.7. Thermal Desorption

Thermal desorption is an innovative treatment that has been applied primarily to soils. Wastes are heated to temperatures of 200 to 600°C to increase the volatilization of organic contaminants. Volatilized organics in the gas stream are removed by a variety of methods including incineration, carbon adsorption, and chemical reduction.

4. Soil and Ground Water Treatment

Contaminated soil and ground water present special challenges because the contamination is often diffuse and difficult to access. *In situ* processes, those that leave both soil and ground water in place during treatment, are often favored because they are less disruptive; they take advantage of natural, existing conditions; and they preserve the existing subsurface environment. *Ex situ* and pump and treat processes remove soil and ground water for treatment. They may be favored over *in situ* treatment where they will reduce cleanup times, their operation and capabilities are considered more reliable or better understood, or they can achieve lower cleanup levels. Both *in situ* and *ex situ* treatment for soil and ground water rely on a combination of unit processes, which often include biological degradation of organics.

Nonaqueous phase liquids (NAPLs) present special problems for soil and ground water cleanup. Contaminant transport through ground water depends in part on the water solubility of the compound. Because NAPLs cling to subsurface particles and are slow to dissolve in ground water, they hinder cleanups and prolong cleanup times. Dense nonaqueous phase liquids (DNAPLs) migrate downward in the aquifer and can collect in pools or pockets of the substructure. Examples of DNAPLs are the common solvents tetrachloroethylene (PCE) and trichloroethylene (TCE) which were used extensively at many facilities before the extent of subsurface contamination problems was realized.

Today, strict regulation of hazardous waste and material management promises to minimize future soil and ground water contamination, however, past practices have left the environment with a large legacy of contaminated sites that are often difficult and costly to remediate. This is the driving force behind the development of innovative technologies for soil and ground water cleanup. The United States Environmental Protection Agency (U.S. EPA) strongly supports the development of innovative technologies and maintains a Vendor Information System for Innovative Treatment Technologies (VISITT) database to provide information on availability, performance, and cost of these technologies.

In this section, soil and ground water cleanup technologies are divided into five subsections. Many of the unit processes for soil and ground water treatment are general waste treatment technologies, but are discussed here in the context of soil and ground water cleanup. A more general discussion of these technologies are found elsewhere in this article.

4.1. Plume Containment

Wells can be placed at a contaminated site to prevent the contamination from spreading further or migrating offsite. In the past, containment efforts often relied on physical methods such as bentonite slurry trenches, grout curtains, sheet pilings, well points, and fixative injections. Containment by judiciously placed wells generally costs less, takes less time to install, and is more flexible because pumping rates and locations can be varied.

Four typical well patterns for contaminant plume containment are described in Ref. 16. The first is a pair of injection-production wells. The second is a line of downgradient pumping wells. The third is a pattern of injection-production wells around the boundary of a plume. The fourth, the *double-cell* system, uses an inner cell and outer recirculation cell, with four cells along a line bisecting the plume in the direction of flow. Two other methods of plume containment are biofilters and a funnel-and-gate system, which are described in the *in situ* bioremediation section.

4.2. Bioremediation

Bioremediation has great appeal. It is a natural process that degrades hazardous organic chemicals into innocuous carbon dioxide and water or nonhazardous byproducts and it is often less expensive and more effective than pump and treat methods. Articles on bioremediation appear regularly in environmental journals and the U.S. EPA has its own regular series of reports on current activities called “Bioremediation in the Field.”

On the down side, there is lot that is not known or completely understood about the process that makes it difficult to design and prove up in field applications. It is a relatively slow process and complete remediation of a site can take several years. The efficiency of the bioremediation cannot always meet target cleanup levels. Bioremediation has been very successful in cleaning up sites contaminated with gasoline and other fuels because the primary contaminants, benzene, toluene, ethylbenzene, and xylenes (BTEX), are relatively easy to extract and degrade. Other compounds have been biodegraded successfully, however, there are many compounds that are still subjects of bioremediation research. Nevertheless, what is known and has been done so far with bioremediation is very encouraging and points to the great potential that bioremediation has in the future of contaminated ground water and soil.

4.2.1. Biodegradation Principles

Microorganisms degrade organic compounds to synthesize cellular materials and to obtain the energy to grow and reproduce. Anabolism results in the synthesis of new cellular material and catabolism (degradation) produces chemicals with lower free energy, and in the case of aerobic biodegradation, often results in complete decomposition of a hydrocarbon to carbon dioxide and water. The principal microorganisms that are involved in the degradation of organic chemicals in water and soil are bacteria and fungi.

Microorganisms can degrade compounds under aerobic or anaerobic conditions, although the types of microorganisms and compounds and degradation process and products may differ. In aerobic environments, free oxygen is present. In anaerobic conditions, free oxygen is not present although oxygen may be present in the form of compounds such as nitrates, sulfates, and iron oxide.

Respiration, or biological oxidation, is the use of oxygen as an electron receptor in the catabolic degradation of an organic and can occur either aerobically or anaerobically. Aerobic respiration uses free oxygen as an electron receptor whereas anaerobic respiration uses inorganic oxygen. In both cases, however, water and carbon dioxide are the principal end products.

Fermentation is an anaerobic catabolic process that uses organics as electron receptors. Since fermentation produces organic products that have lower free energy than their precursors, it is useful in remediation. The lowest free energy form of carbon produced is methane [74-82-8].

Although both fermentation and respiration degrade organics, microorganisms that use respiration to meet their energy requirements for synthesis and reproduction generally grow much more quickly. This, and the fact that respiration completely oxidizes organics to carbon dioxide and water, usually make aerobic biodegradation the treatment of choice. However, because certain synthetic organics do not or are difficult to degrade aerobically, there is much interest in anaerobic processes.

Cometabolism refers to situations where a compound cannot be biodegraded effectively unless another food source is available. The recalcitrant compound, such as TCE, does not provide the energy to allow the microorganisms to grow and thrive. When another food source is available such as methane, energy is produced for growth and enzymes are produced to metabolize the energy-providing food source and cometabolize the recalcitrant compounds.

4.2.2. Types of Treatment

Bioremediation can be conducted either *ex situ* or *in situ*. *Ex situ* is where ground water is pumped to the surface or soil is excavated for treatment. Pump and treat refers to the *ex situ* removal and treatment of ground water. After treatment, the ground water can either be reinjected or discharged; treated soils can be redeposited, landfilled, or recycled. *In situ* bioremediation takes place in the ground; neither ground water or soil is extracted although ground water may be pumped to the surface for oxygen and nutrient addition. *In situ* bioremediation has become very popular because the process takes full advantage of natural conditions (microorganisms, soil, water) as a bioreactor, little site disturbance is necessary, and it is less equipment intensive than *ex situ* treatment.

Ex situ bioremediation may use various biological wastewater treatment processes, soil piles, or land application. With *in situ* bioremediation, the basic process is the same: microbes, soil, and water working together as a bioreactor. Where the *in situ* techniques differ are in how contaminants and microbes are brought in contact and how oxygen, nutrients, and other chemical supplements are distributed in the soil–water–air matrix. Typical *in situ* bioremediation techniques include natural or intrinsic attenuation, air sparging, and bioventing.

4.3. *In Situ* Bioremediation

In situ bioremediation can be an aerobic or anaerobic process, or a combination of the two. In designing an *in situ* bioremediation system, one should consider the types of microorganisms available (naturally in place or added), the structural and chemical makeup of the soil matrix, types of contaminants, oxygen and nutrient addition and distribution, and temperature. These factors are discussed prior to introducing the individual techniques for *in situ* bioremediation.

4.3.1. Aerobic, Anaerobic, and Combined Systems

The vast majority of *in situ* bioremediations are conducted under aerobic conditions because most organics can be degraded aerobically and more rapidly than under anaerobic conditions. Some synthetic chemicals are highly resistant to aerobic biodegradation, such as highly oxidized, chlorinated hydrocarbons and polynuclear aromatic hydrocarbons (PAHs). Examples of such compounds are tetrachloroethylene, TCE, benzo(a)pyrene [50-32-8], PCBs, and pesticides.

Besides being slower, anaerobic treatment is more difficult to manage and can generate by-products that are more mobile or toxic than the original compound, for example, the daughter products of TCE, ie, dichloroethenes and vinyl chloride. It requires a longer acclimation period which means slower startup times in the field. The microbial processes are less well understood, and hence, are less controlled than for aerobic systems.

Nevertheless, an anaerobic system may be the method of choice under certain conditions: (*1*) contamination with compounds that degrade only or better under anaerobic conditions, (*2*) low yield aquifers that make pump and treat methods or oxygen and nutrient distribution impractical, (*3*) mixed waste contamination where oxidizable compounds drive reductive dehalogenation of chlorinated compounds, or (*4*) deep aquifers that make oxygen and nutrient distribution more difficult and costly.

Anaerobic respiration can degrade organics by using nitrate or sulfate as oxygen sources. Compounds that have been shown to be biodegraded by nitrate-respiring microorganisms are methanes, carbon tetrachloride [56-23-5], *m*-xylene, and some phenols, cresols, and PAHs. Chloroform and stable chlorinated ethanes and ethenes are not degraded by nitrate respiration. Reductive dehalogenation, not degradation, has been observed of naturally occurring aromatics where sulfate respiration was occurring. Sulfate respiration can be inhibited by the accumulation of its byproduct, hydrogen sulfide [7783-06-4].

Combined aerobic–anaerobic systems use sequenced aerobic and anaerobic conditions to degrade compounds that are resistant to aerobic biodegradation. Ground water passes through the anaerobic zone first which partially degrades the resistant compounds. These degradation products are then further degraded in an aerobic zone. A two-zone, plume interception approach was tested under the U.S. EPA's Superfund Innovative Technology Evaluation (SITE) Emerging Technologies Program to degrade chlorinated compounds (17). The first zone was anaerobic where methanogenic (methane producing) microorganisms were expected to promote reductive dechlorination of chlorinated solvents. The second zone was aerobic where the partially dechlorinated products were to be biodegraded. Combined systems do not necessarily have to be separate zones in the aquifer. Aerobic and anaerobic conditions can be alternated by eliminating the oxygen source at timed intervals.

In one study, a coarse-grained sand aquifer was injected with methane and oxygen to stimulate the production of methane monooxygenase (MMO) enzyme which is capable of degrading TCE (18). TCE, added at 60–100 μg/L, was degraded by 20–30%. Injected concentrations of methane and oxygen were approximately 20 mg/L and 32 mg/L, respectively.

4.3.2. Design Considerations

The effectiveness of *in situ* bioremediation is influenced by many factors, including: microorganisms, soils, oxygen, pH, temperature, type and quantity of contaminants, and nutrients.

4.3.2.1. Microorganisms. A large number of naturally occurring bacteria and fungi can use hydrocarbons for growth. The most commonly found genera of bacteria and fungi that are capable of hydrocarbon biodegradation are (*1*) bacteria: *Pseudomonas*, *Arthrobacter*, *Alcaligenes*, *Corynebacterium*, *Flavobacterium*, *Achromobacter*, *Micrococcus*, *Nocardia*, and *Mycobacterium* and (*2*) fungi: *Thricoderma*, *Penicillium*, *Aspergillus*, and *Mortierella* (19).

Soils contain a diverse culture of microorganisms, with the number and type present being a function of local environmental conditions. Usually, the limiting factor on the microbial population at an uncontaminated site is the amount of type of carbonaceous material available for biodegradation (19). However, there are almost always some microorganisms present in every soil environment that will take advantage of a new or different carbon source when it becomes available and will rapidly increase their populations to metabolize it. Addition of more or especially cultured microbes has been studied and applied in the field, however, some people believe that all that is needed in most cases is simply to optimize environmental conditions for the naturally occurring microbes. But for recalcitrant compounds or for more rapid biodegradation, specialized microbes may have potential. For example, the U.S. EPA has agreed to license specialized microbes that degrade chlorinated aromatic and chlorinated aliphatic compounds such as TCE under aerobic conditions which avoids the generation of vinyl chloride as a byproduct (20).

4.3.2.2. Soils. Soils with hydraulic conductivities greater than 10^{-4} centimeters per second (cm/s) are good candidates for *in situ* bioremediation because they are permeable enough to allow the transport of oxygen and nutrients through the aquifer. The degree of homogeneity of the soil is important in order to predict ground water flow patterns for plume containment and distribution of oxygen and nutrients.

4.3.2.3. Contaminants. The type and concentration of contaminants in an aquifer dictate what type of *in situ* bioremediation system, aerobic, anaerobic, or combination, are the most effective.

4.3.2.4. Oxygen. Many microorganisms require either free oxygen or inorganic oxygen for growth. Some bacteria can use either free oxygen or inorganic oxygen for respiration, thus, these are called facultative bacteria. Many bacteria, however, require free oxygen for growth.

A rule of thumb used in wastewater treatment is that at least 1.5 mg/L of dissolved oxygen is needed to prevent oxygen from being a growth limiting factor. Ref. 21 documents a threshold dissolved oxygen concentration of 0.5 mg/L in ground water. Below 0.5 mg/L, it was found that the biodegradation rates of benzene, toluene, and xylene were retarded. It was also shown that biodegradation rates increased until the ground water dissolved oxygen concentration reached 2 mg/L at which point no further increase was observed. Thus, it appears that a target of 1.5 to 2.0 mg/L dissolved oxygen maximizes biodegradation rates and put an upper limit on the cost to supply the oxygen.

Field data collected from ground water in spill areas have shown that dissolved oxygen concentrations are typically reduced below 1 mg/L due to biodegradation. For example, at the site of a gasoline spill where gasoline-degrading bacteria had been identified, dissolved oxygen in the contaminated ground water ranged from 0 to 0.5 mg/L while in the uncontaminated areas, levels were from 2.3 to 4 mg/L (22). In another study of an aquifer contaminated with chlorinated solvents, dissolved oxygen was always less than 0.2 mg/L (18). These studies demonstrate that biological growth and biodegradation of hydrocarbons is oxygen-limited, a fact which stimulates a continuing interest in developing effective oxygen sources and the means of distributing oxygen in ground water and soil.

4.3.2.5. Hydrogen Peroxide. Hydrogen peroxide is an effective means of getting more oxygen into the ground water for bioremediation and has many advantages over air or pure oxygen. Hydrogen peroxide has been demonstrated to not only boost dissolved oxygen levels, but it also stimulates microbial activity. It also has the advantage of chemically degrading contaminants partially or fully. Hydrogen peroxide mixes intimately with ground water for better distribution in the aquifer and can prevent injection well plugging caused by bacterial growth.

On the downside, various studies (23–25) have shown that hydrogen peroxide decomposes rapidly after soil contact, it is cytotoxic at a 3% solution and unless stabilized, oxygen bubbles can escape prematurely through the unsaturated zone before they have a chance to disperse well in the ground water. Catalase enzymes generated by aerobic bacteria near the injection wells appear to be the main cause of hydrogen peroxide decomposition and oxygen off-gassing. Others have noted that hydrogen peroxide also reacts with dissolved iron, manganese, and other inorganics to produce oxides which can plug wells and formations (26, 27). Precipitation of inorganic compounds during bioremediation has been studied in more detail (28). Concentrated solutions of hydrogen peroxide (30%) used in bioremediation must be handled carefully to avoid skin burns.

Reports of ground water remediation studies using hydrogen peroxide are found frequently in the literature. Hydrogen peroxide reactions as an oxidant during bioremediation have been reviewed in Ref. 29. A field-scale study of an area contaminated by an aviation gasoline fuel spill showed that hydrogen peroxide did increase the concentration of oxygen downgradient of the injection well (24). Hydrogen peroxide was used to remediate ground water after a jet fuel leak at Eglin Air Force Base in Florida (25). Field applications using hydrogen peroxide for ground water cleanup are continuously reported by the U.S. EPA in its “Bioremediation in the Field” series. Treatment conditions common to these studies are the use of hydrogen peroxide and nutrient addition to stimulate biodegradation by the indigenous microorganisms.

Most reports citing hydrogen peroxide do not specify dosage rates. Concentrations as high as 500 mg/L have been shown to be nontoxic to most microorganisms (26). Other studies report dosage rates of 100 to 500 mg/L. Unpublished reports of rates as high as 1000 to 10,000 mg/L are not uncommon (24). Research studies have shown that a 0.05% solution (500 mg/L) was the maximum tolerated by a mixed culture of microorganisms capable of degrading gasoline. Concentrations up to 2000 mg/L could be tolerated if the dosage was stepped up incrementally; however, most toxicity studies showing no toxicity at relatively high concentrations are usually based on bacteria counts. Other studies have shown that concentrations greater than 100 mg/L decrease the *oxygen utilization rate* by microorganisms which is counterproductive to biodegradation, and therefore, increases the time needed for remediation.

Premature decomposition of hydrogen peroxide can be inhibited by adding monobasic potassium phosphate [7778-77-0] as a stabilizer (24). The phosphorus in the solution has the added benefit as a nutrient for the microorganisms. The concentration of 190 mg/L potassium phosphate was used in Huling's field study of ground water contaminated with aviation gasoline. The phosphate is added ahead of the hydrogen peroxide until breakthrough occurs in the downgradient wells. By adding the phosphate first, the phosphate binds with the inorganics in the soils and allows the hydrogen peroxide to be distributed further. Other chemicals have been used or studied to increase the stability of hydrogen peroxide are polyphosphates, stannate or phosphate, sodium pyrophosphate, citrate, and sodium silicate [1344-09-8] (30).

Hydrogen peroxide is also used as a treatment to clean wells of biological growth. One treatment is to pour a 0.5% solution into the well and allow it to sit for four hours after which pumping is resumed (31). Some treatments use solution concentrations as high as 10% to remove biofouling from wells (16).

4.3.2.6. Pure Oxygen. By increasing the oxygen level in soils and ground water, pure oxygen or oxygen-enriched streams stimulate bacterial activity. Using bottled oxygen, 35 to 40 mg/L of dissolved oxygen can be supplied at most field temperatures (31), which is less stable than hydrogen peroxide, a disadvantage with oxygen is that it may not distribute as well in the aquifer, although surfactants can promote highly stable microbubbles that are better able to travel throughout the ground water. Unlike hydrogen peroxide, oxygen does not aid in keeping the injection well free from biological growth that can plug the well.

4.3.2.7. Nitrates and Sulfates. There is much less information on actual applications of nitrate or sulfates as oxygen sources. Advantages of nitrate are that it is more soluble than oxygen, less costly, and less toxic than hydrogen peroxide. Regulatory agencies are less inclined to approve the use of nitrates in ground water cleanup as an oxygen or nutrient supplement because it can potentially contaminate drinking water supplies and plug the aquifer with biological growth. If nitrate is used, dosages must be carefully calculated and controlled to avoid these problems. In one study (32), nitrate was used as the oxygen source for microbial respiration in the cleanup of a drinking water aquifer contaminated with jet fuel and concentrations of benzene, toluene, ethylbenzene, and xylenes were treated below 5 μg/L. There is less literature on sulfate as an oxygen source than nitrate. Most references merely state that sulfate can be used as an oxygen source for anaerobic respiration.

4.3.2.8. Solid Phase Oxygen. Solid phase oxygen in the form of peroxides (calcium peroxide [1305-79-9], magnesium peroxide [1335-26-8]) has been investigated as a slow, continuous release system that avoids problems associated with the transient nature of molecular oxygen and hydrogen peroxide (33, 34). Calcium peroxide releases oxygen into the system by first breaking down into hydrogen peroxide and calcium hydroxide; the hydrogen peroxide then decomposes to oxygen and water. Cages or socks of the material are suspended directly in the ground water well and the material can be blended into the soil for *ex situ* treatment and landfarming. For ground water treatment, this form of oxygen has the most potential for containment or remediation of low concentrations of dissolved organics.

4.3.2.9. Iron Oxides. Chelated iron oxide, using nitrilotriacetic acid [139-13-9] and EDTA, has been studied as an alternative oxygen source (35). Iron oxide which is often difficult for the microbes to access, is made more available by chelating agents.

4.3.2.10. Nutrients. In addition to carbon and oxygen, other nutrients are needed for microbial growth. Nitrogen, phosphorus, potassium [7440-09-7], calcium [7440-70-2], magnesium [7439-95-4], sodium [7440-23-5], sulfur [7704-34-9], chlorine, iron, manganese, cobalt, copper, boron [7440-42-8], zinc, molybdenum [7439-98-7], and aluminum [7429-90-5] are all present in the microbial cellular material (36). With the possible exceptions of nitrogen and phosphorus, which are present in the cell in relatively large amounts, these nutrients are needed at only trace levels and there is almost always enough in the natural environment to prevent growth-limiting conditions.

In the presence of large amounts of degradable carbon, the naturally available nitrogen and phosphorus could potentially limit growth and thus biodegradation rates. Based on a literature review (19) typical aerobic soil microorganisms contain 5 to 15 parts of carbon per part of nitrogen, with 10 parts being an acceptable average. This is about twice the 5:1 ratio of carbon to nitrogen that is usually assumed to represent the composition of the biomass in wastewater treatment processes (37). If this difference is real, it may be due to the specific environmental conditions in a particular location, since such conditions are known to influence the amount of nitrogen accumulated with cellular material (37). Phosphorus requirements are about one-fifth that of nitrogen (19, 37).

These estimates of nitrogen and phosphorus do not consider that which is reintroduced by biological recycling. Bacterial growth and death continually recycle some fraction of the synthesized nitrogen and phosphorus. Ref. 19 cites an optimum carbon to nitrogen to phosphorus ratio of 250:10:3 for biodegradation of carbon compounds in soil, which accounts for the carbon oxidized to carbon dioxide and that assimilated into cellular material. Assuming that one part of carbon is incorporated into cellular material for every two parts of carbon that are used for energy and are converted to carbon dioxide, the ratio of carbon to nitrogen in the cell is about 8.3 to 1, a reasonably conservative estimate. A C:N:P ratio of 300:10:1 should be adequate for biodegradation, assuming no recycle (19).

Nutrients are usually added at concentrations ranging from 0.005 to 0.02% by weight (16). In a field application using hydrogen peroxide, nutrients were added to the injected water at the following concentrations: 380 mg/L ammonium chloride; 190 mg/L disodium phosphate, and 190 mg/L potassium phosphate, the latter used primarily to complex with iron in the formation to prevent decomposition of hydrogen peroxide (24).

4.3.2.11. Temperature. Ambient temperature is a key factor to successful biodegradation. In the range of 15 to 35°C, bacterial growth rates double for every 10°C rise in temperature. For most soil microorganisms, the optimal temperature for maximum growth is 30–35°C (19). Since vadose zone and ground water temperatures are typically in the range of 10 to 25°C (38), microbial growth will not be prevented, but will be at less than the maximum possible rates.

4.3.2.12. pH. A pH between 6 and 8 should be maintained for *in situ* bioremediation. Since most soil pHs are within this range, pH should not be a controlling factor for biodegradation of hydrocarbons, unless the soil has also been contaminated with acidic or caustic substances.

4.3.3. Air Sparging

With this technique, air is injected in the saturated zone to volatilize organics and to deliver oxygen for biodegradation. Soil vapor extraction may be used in conjunction with air sparging to capture the volatilized organics. Air sparging is used frequently at sites that have been contaminated with volatile compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX), common hazardous components of gasoline and other fuels. However, performance data are lacking and difficult to measure.

4.3.4. Biosparging

Biosparging is a form of air sparging, but the difference is that the primary purpose of biosparging is to deliver just enough air to meet oxygen requirements for bioremediation. Volatilization of organics may be an added benefit, but it is secondary to oxygen delivery. An enhancement is to sparge ozone in place of air. Besides providing oxygen for biodegradation, ozone aids in breaking down recalcitrant compounds such as chlorinated ethenes, polycyclic aromatic hydrocarbons, and pentachlorophenol [87-86-5].

4.3.5. Biofilters

Biofilters, also known as biobarriers or microbial fences, are used to hinder migration of a contaminant plume. A biofilter is essentially a zone of biological activity that treats the contaminant as the ground water flows through the area. The biofilter zone can be established by installing a line of air sparging wells perpendicular to the direction of ground water flow.

4.3.6. Bioventing

Bioventing is soil venting that enhances biodegradation while extracting volatile compounds from the unsaturated zone.

4.3.7. Funnel-and-Gate

This *in situ* bioremediation method is so-named because ground water is funneled through openings or gates in an impermeable sheet piling or slurry wall. Zones of biological activity are created at the gates through air sparging. Contaminants are biodegraded as ground water is forced to pass through the gates. The funnel-and-gate method (also known as flume-and-gate) is used where ground water gradients are small. Because smaller treatment zones are created, operating expenses can be reduced and there is better process control.

4.3.8. Phytoremediation

Phytoremediation is a developing technology that uses plants, trees, and grasses to biodegrade, extract, or stabilize organic and metal contaminants in soil and ground water. Engineered wetlands is a well-known form of phytoremediation. Phytoremediation is likely to be used in conjunction with other treatment processes, primarily as a polishing step (39). As reported, this method has potential in the cleanup of residual contamination in soil micropores, hydraulic control (poplars and weeping willows pump 190 to 1325 L per day per tree, alternative landfill caps for leachate control, leachate treatment, and buffer zones for plume containment.

4.4. *Ex Situ* Bioremediation

4.4.1. Biological Wastewater Treatment

Ground water and leachate can be treated in a biological wastewater treatment system such as rotating biological contactors (RBCs), trickling filters, sequencing batch reactors, fluidized bed reactors, activated sludge, or aerated impoundments. For biological treatment to be feasible, the ground water or leachate must contain sufficient organics to support microbial growth; otherwise, dilute streams should be treated by physical–chemical means or combined with higher strength wastewaters for biological treatment in a larger wastewater treatment system (for example, in an onsite wastewater plant treating process wastewaters at a manufacturing facility). A sequencing batch reactor is similar to activated sludge except that treatment takes place in one tank in batch mode, ie, biodegradation with mixing, followed by quiescent settling and sludge withdrawal. A fluidized bed reactor uses granular activated carbon or sand as the support media for microbial growth. The ground water to be treated is introduced through the bottom of the reactor which serves to fluidize or suspend the support media. Pretreatment to remove solids is required to avoid plugging the reactor.

4.4.2. Slurry-Phase Soil Treatment

Contaminated soil can be treated biologically in slurry form, not unlike biological treatment of wastewater. However, one important difference with contaminated soil is that the contaminants preferentially adsorb unto the soil particles and must be desorbed before the microorganisms can effectively degrade the compounds. Contaminated soil may be pretreated prior to the bioreactor, for example, by soil washing to separate the fine particles which normally contain the majority of the contamination. Contaminated soil can be slurried by mixing with water, wastewater, or contaminated ground water. The solids concentration of the slurry can be fairly high, upwards to 50%, which makes mixing to keep the soil in suspension an important design parameter.

4.4.3. Soil Heaps, Piles, Beds, and Windrows

Contaminated soil can be excavated and placed in heaps, piles, beds, or windrows. Other organic or bulking agents such as wood chips or straw, may be added to aid in composting, mixing, and aerating the soil. In a windrow system, the soil is placed in long rows and turned periodically to mix and aerate the soil. Soil piles and heaps differ in size, heaps being larger and used where large volumes of contaminated soil must be treated. Piles and heaps may be covered or uncovered, depending on the volatility of the contaminants and air emissions requirements and whether a vacuum is drawn through or air is blown into the soil. With treatment beds, contaminated soil is placed on top of a liner system consisting of a synthetic liner, sand, and leachate drainage pipe. The bed may be covered or enclosed. In any of these treatment systems, volatilized contaminants that are removed by vacuum may be treated by incineration, carbon adsorption, or vapor-phase biodegradation. Leachate may be treated biologically in a wastewater treatment system.

5. Physical–Chemical–Thermal *In Situ* Treatment Related Specifically to Soils and Ground Water

5.1. Electrokinetics

Electrokinetics is a tested technology that has been used for over half a century to dewater and stabilize soils, and has recently been investigated for in situ use at hazardous waste sites (23). Primarily used for metals removal, the technology utilizes an electrical field to generate a flow and concentration gradient in porous and semiporous soils.

An innovative technology called the "lasagna" process is based on the electrokinetic phenomenon called electroosmosis. The lasagna process was created to treat difficult wastes in low permeability, silt- and clay-laden soils (40). The lasagna process is so named because it consists of a number of layered subsurface electrodes and treatment zones. These layers can be constructed either horizontally where contaminants are forced to more upward or in vertical position where lateral contaminant movement is desired.

A low voltage electric current is applied by subsurface electrodes which forces the migration of contaminants from low permeable soils into high permeable treatment zones. These treatment zones that may be created by hydrofracturing (injecting a slurry to create porous pancake-shaped zones), directional drilling, or sheet piling. Treatment in these zones may include physical, chemical, or biological processes such as adsorption by activated carbon which would then serve as a biodegradation matrix.

5.2. *In Situ* Air Stripping

An innovation to conventional pump and treat air stripping is *in situ* air stripping. Two horizontal wells are installed, one below the water table and one in the vadose zone. Air is injected in the lower well while contaminated soil vapor is extracted by vacuum through the upper well.

5.3. Soil Flushing

Soil flushing is similar to soil washing of excavated soils except flushing is done *in situ* below the ground surface. With soil flushing, the contaminated area is flooded with water. Surfactants or detergents may be added to the water to enhance removal of organics.

5.4. Soil Vapor Extraction

Volatile compounds can be extracted from subsurface soils by applying a vacuum. An added benefit is that the vacuum pulls in air from the ground surface that stimulates biodegradation through increased oxygen transport. The ground water below the vadose zone can also be aerated to volatilize contaminants in the ground water (air sparging) which then move into the vadose zone where they are removed along with the soil vapors.

A U.S. EPA study (41) showed that soil vapor extraction (SVE) is an effective treatment for removing volatile contaminants from the vadose zone. Sandy soils are more effectively treated than clay or soils with higher organic content because higher air flows are possible in sand and clays–organic soils tend to adsorb or retain more contaminants. Removal of volatiles is rapid in the initial phase of treatment and thereafter decreases rapidly thereafter-an important consideration in the design of air emissions control over the life of the project.

An innovative companion technology to SVE is radio frequency heating of the soil (42, 43). Heating the soil increases the volatilization of the containments which are removed by SVE. Antennae are installed near the center of the contaminated area; the radio frequency energy applied through the antennae heat the soil to target levels of 100 to 150°C.

5.5. Vitrification

Vitrification is an innovative treatment that turns contaminated soils into a glasslike monolithic mass. Heat is applied through electrodes placed in the ground, the soil reaching temperatures of 1600 to 2000°C. A layer of graphite [7782-42-5] and glass frit is first placed on the surface of the ground between the electrodes to act as the initial conductive starter path. The conductive layer and adjacent soils become a molten mass that becomes the primary electrical conductor and heat transfer medium. As heat continues to be supplied by the electrodes, the molten mass moves both outward and downward. As organic contaminants in the soil are heated, they begin to vaporize and eventually pyrolize with the rising temperature. Inorganic contaminants are immobilized in the molten material. Off-gases, which include vaporized organics and the by-products of organic and inorganic pyrolysis, are captured above the site and treated to meet air emissions standards. Once cooled, the vitrified mass is very stable with low leaching potential.

Vitrification is effective at destroying and immobilizing hazardous materials, but it is very energy intensive and thus expensive. Consequently, it is used primarily where wastes are difficult to treat or destruction–immobilization of contaminants is very important such as with radionuclides.

6. Pump and Treat

In the early years of ground water and soil remediation, pump and treat was the conventional technology. Contaminated ground water is pumped to the surface where it is treated and reinjected or discharged to surface waters or wastewater treatment plants. Reinjection may be used to stimulate *in situ* bioremediation, where the treated ground water is enriched with oxygen and nutrients prior to reinjection. Many years of experience with pump and treat methods have brought to light certain limitations, as well as improvements and enhancements. Therefore, pump and treat technology must be reviewed for its applicability to a particular site.

Pump and treat technology is inherently slow because it depends on ground water for transport of the contaminant to the extraction well. This characteristic is particularly troublesome when the contaminant is only slightly water soluble, adheres to the soil, or collects in pools within the aquifer.

There are many cases of contamination by dense nonaqueous phase liquids (DNAPLs) that have frustrated pump and treat efforts. The general consensus is that pump and treat can reduce contamination or keep it from spreading, but it has failed in many cases to remediate aquifers to stringent cleanup goals.

Common technologies for surface treatment of contaminated ground water are air stripping, carbon adsorption, biodegradation, and ion exchange. If cleanup goals are in the μg/L range, then typically pump and treat options are limited to air stripping and carbon adsorption. Conventional biological treatment is usually not suitable for the relatively low levels of contaminants found in ground water. Biological treatment of extracted ground water is discussed under "Bioremediation." Air stripping, carbon adsorption, and ion exchange are discussed under "Physical/Chemical Treatment Technologies."

7. Extraction Techniques

Two-phase vacuum extraction (TPVE) is a way of pumping both contaminated air and ground water through a single well. A vacuum is applied through a well that is screened both through the vadose and ground water zones. Both air and ground water are pumped to the surface where they are separated for treatment. Advantages of this system are that it does not require separate wells for air extraction and ground water pumping and that water pumping rates can be greatly increased.

8. *Ex Situ* Soil Nonbiological Treatment

8.1. Soil Leaching

Soil leaching or acid extraction uses acid to solubilize metals for removal from soils, a technique akin to that in the mining industry. After extraction with an acid such as hydrochloric, sulfuric, or nitric, the soil is separated from the acid, rinsed with water to remove excess acid and metals, dewatered, and neutralized. The acid is regenerated and recycled back to the process. The extracted metals can be precipitated and recovered.

8.2. Soil Washing

Soil washing is as simple a process as the name implies. Soil is excavated, physically broken up, washed with a water-based solution, and separated into size fractions (sand–gravel and silt–clay). The goal of soil washing is to transfer pollutants to the wash water and to isolate the finer soil fraction that preferentially adsorbs organics and metals. Various surfactants, extractants, or detergents are added to the wash water to enhance removal of organic contaminants from the soil particles. Soil fines and contaminants are removed from the wash water which is then recycled back to the process.

The finer soil fraction contains adsorbed organics, small metallic particles, and bound ionic metals. This fraction may be treated further to remove the contaminants, or it may be incinerated or landfilled. The "clean" coarse fraction may contain some residual metallic fragments. With metal contamination, both the fine and coarse soil fractions may be leached with an acid solution to remove the metals.

8.3. Other Techniques

Other methods, more conventional in type, are employed for *ex-situ* treatment. These include solvent extraction and thermal desorption, which are detailed under the "Physical/Chemical Treatment" and "Thermal Treatment" sections, respectively.

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