PDHonline Course C185 (2 PDH)

Chemical Treatment of Liquid Waste Streams

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Advantages	Disadvantages
Reduction can reduce the toxicity of some material	Reduction reactions usually require pH adjustment as pretreatment
Reduction can provide favorable conditions for precipitation of some metals	Can cause the precipitation of some metals

d. Data Requirements. Typical data requirements are listed below:

(1) Influent and peak flow rates.

(2) Variability of influent volumes and concentrations.

(3) pH conditions favorable to reduction reaction.

(4) Concentrations of chemical species that require reduction.

(5) Effectivness of the reducing agent to effect the desired reaction.

(6) Presence of interfering or competing chemicals in the waste.

e. Design Criteria.

(1) If wide fluctuations in flow and concentration are expected, equalization should precede this step.

(2) pH adjustment should be used as a pretreatment step to bring the solution to the desired pH.

(3) A stirred tank should be used to carry out the reduction. A chemical feed system is required to continuously charge the reducing agent. An oxidation reduction potential (ORP) control system may be used to control the quantity of reducing agent added.

(4) Detention time to accomplish chemical reduction will vary from 15 to 45 minutes and will be dictated by the particular reaction involved. Chromium reduction will require approximately 30 minutes but depends upon the pH and reducing agent used.

4-10. Precipitation.

a. Process Description.

(1) Precipitation is a widely used (in industrial practice), relatively low-cost physical chemical technique in which the chemical equilibrium of a waste is changed to reduce the solubility of the undesired components. These components precipitate out of solution as a solid phase, often in the form of small, colloidal particles, and are removed by one of

several possible solids removal techniques. Precipitation is most commonly used to treat heavy-metal-containing wastes.

(2) Precipitation can be induced by one of the following means:

(a) Adding a chemical that will react with the hazardous constituent in solution to form a sparingly soluble compound.

(b) Adding a chemical to cause a shift in solubility equilibrium, reducing the solubility of the hazardous substance.

(c) Changing the temperature of a saturated or nearly saturated solution in the direction of decreased solubility.

(3) Chemical additives are most commonly used. Typical reagents are:

(a) Sodium hydroxide, sodium sulfide.

(b) Hydrated lime ($Ca(OH)_2$).

(c) Iron salts such as iron sulfide, ferric sulfate.

(d) Phosphate salts (especially for heavy metals such as As, Cd, Cr, Zn, Cu, Pb, Hg, Ni).

(e) Alum ($Al_2(SO_4)_3$).

(4) The theoretical removal limit for many metal species is very low, particularly with sulfide precipitants. Figure 4-12 shows theoretical curves as a function of waste pH. Some organic species, for example, aromatic compounds and phthalates, can also be treated. Removal in practice often is one to two orders of magnitude less than the theoretical limit. Complexing agents, such as cyanide or ethylenediamine tetra-acetic acid (EDTA), may compete with the precipitant and hold the species in solution.

(5) Conventional precipitation processes are performed in the following three steps:

(a) Rapid mixing of precipitating chemicals and waste water.

(b) Slow mixing of treated waste water in a flocculation tank to allow settleable flocs to form.

(c) Sedimentation of solids in a clarification tank.

(6) The solids are removed by either:

(a) Sedimentation, which separates the phases by the gravitational settling of the precipitate to the bottom of the sedimentation tank.

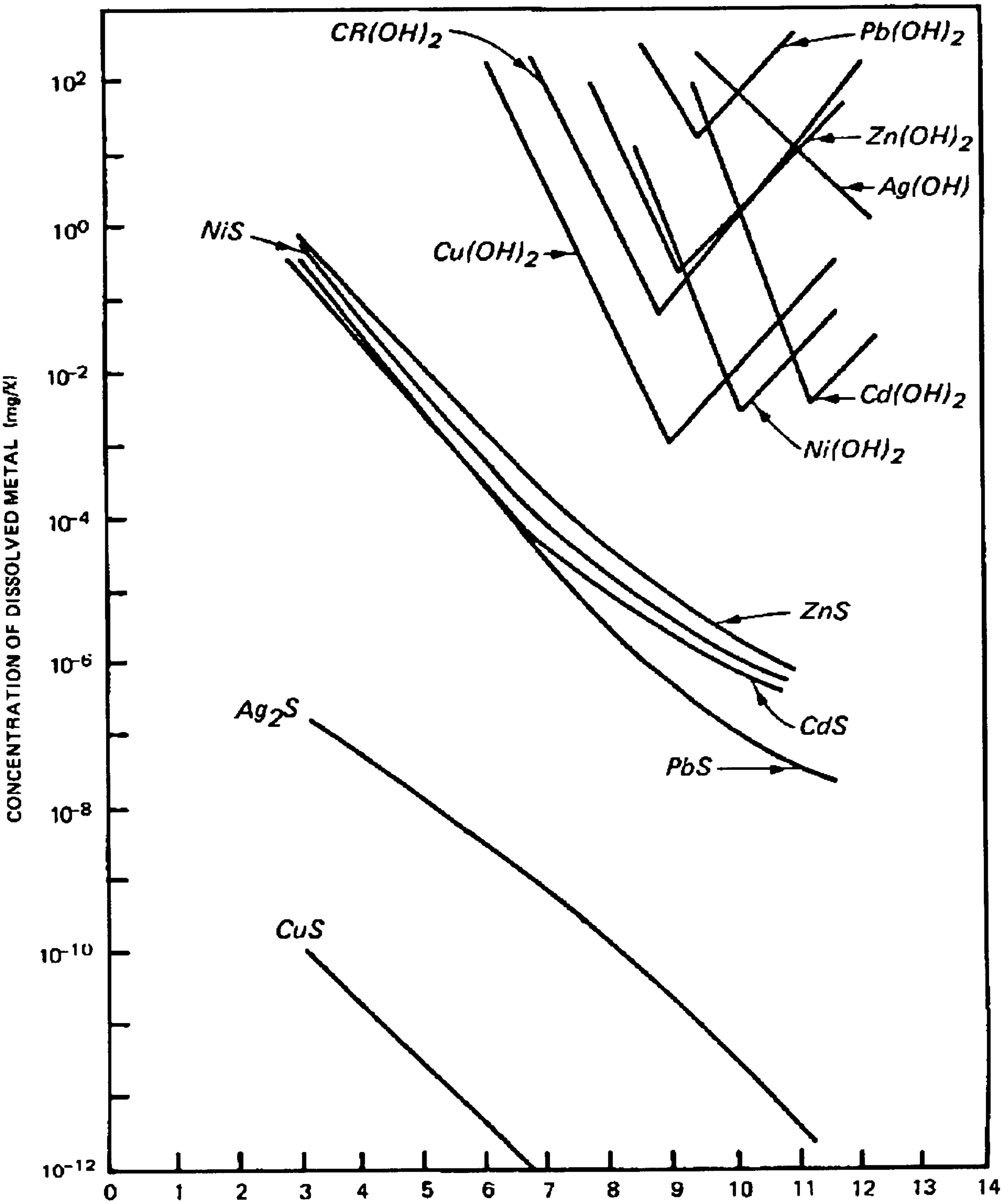

Figure 4-12. Solubility of Metal Hydroxides and Sulfides (Source: Ghassemi et al. 1981, EPA 1983)

(b) Filtration, which separates the phases by passing the precipitation effluent through a granular or cloth barrier, retaining the particles and allowing the clear effluent to pass through.

(c) Centrifugation, which separates the two phases in an enclosed vessel using centrifugal force to cause the solids to migrate through the liquid.

b. Applications.

(1) Precipitation is a process that finds its primary application in the area of metals removal. However, it may also be used to precipitate long chain or high molecular weight organic materials.

(2) Typically, metals are precipitated as the hydroxide and removed by sedimentation. Removals are limited by the physics of the system. Solubilities of metal sulfides and metal xanthates are much lower than the hydroxide and consequently may be used in situations where very low concentrations are required.

c. Advantages/Disadvantages. The technique of precipitation is widely used for treating waste containing metals. This concept enjoys a technology based upon thermodynamics which provides a theoretical base for the consideration of a multitude of operations. Limitations are also defined by thermodynamics.

(1) The extent of removal is governed by the physics of the system.

(2) High TDS reduces performance, requiring the use of activity coefficients.

(3) Chelating agents can drastically reduce performance.

(4) A variety of anions may be used to improve performance.

(5) Precipitate will usually require a coagulation and/or flocculation step.

d. Data Requirements. In most cases, data will be available in the literature for pure single component systems without interferences. These data should be adequate for planning level design. However, this should be confirmed by bench or pilot plant testing.

e. Design Criteria. Solubility relationships are generally much more complex than indicated in the preceding discussion. In natural waters or waste waters , several other factors must be considered in order to make a realistic solubility product calculation. The ionic strength of the solution affects ion activity and must be considered if more exact calculations are desired.

4-11. Flocculation and Sedimentation. Flocculation and sedimentation are well-developed waste-water treatment processes currently being applied to the full-scale treatment of many industrial waste waters containing particulates and/or soluble heavy metals. The operating parameters and economics associated with the application of flocculation and sedimentation to the treatment of specific industrial waste-water streams are well defined and well documented (refer to CAPDET for design considerations).

a. Process Description.

(1) Historically, the terms "flocculation" and "coagulation" have been used rather indiscriminately and interchangeably to describe the process by which small, unsettleable particles suspended in a liquid medium are made to agglomerate into larger, more settleable particles. For the purpose of this manual, the term "flocculation" shall be defined so as to encompass all of the mechanisms by which suspended particles agglomerate into larger particles. No distinction will be made between coagulation and flocculation.

(2) A variety of mechanisms are involved in the process of flocculation whereby small particles are made to form larger particles. Most of these mechanisms involve surface chemistry and particle charge phenomena. In simple terms, these various phenomena can be grouped into two sequential mechanisms:

(a) Chemically induced destabilization of the repulsive surface-related forces, thus allowing particles to stick together when contact between particles is made.

(b) Chemical bridging and physical enmeshment between the now nonrepelling particles allows for the formation of large particles.

(3) Typical chemicals used to cause flocculation include alum, lime, and various iron salts (ferric chloride, ferrous sulfate). Organic flocculating agents, often referred to as "polyelectrolytes," have come into widespread use. These materials generally consist of long-chain water-soluble polymers such as polyacrylamides. They are used either in conjunction with the inorganic flocculants such as alum or as the primary flocculating agent alone.

(4) The inorganic flocculants, such as alum, lime, or iron salts, make use of precipitation reactions. Alum (hydrated aluminum sulfate) is typically added to aqueous waste streams as a solution. Upon mixing, the slightly higher pH of the water causes the alum to hydrolyze and form fluffy, gelatinous precipitates of aluminum hydroxide. These precipitates, partially due to their large surface area, act to enmesh small particles and thereby cause larger particles. Lime and iron salts, as well as alum, are used as flocculants primarily because of this tendency to form large fluffy precipitates or "floc" particles. Many precipitation reactions, such as the precipitation of metals from solution by the addition of sulfide ions, do not readily form floc particles, but rather precipitate as very fine and relatively stable colloidal particles. In such cases, flocculating agents such as alum and/or polyelectrolytes must be added to cause flocculation of the metal sulfide precipitates.

(5) In the flocculation process, it is essential that the slow mixing step be very gentle and be given sufficient time, as newly agglomerated particles are quite fragile and can be broken apart by shear forces during mixing. Once suspended particles have been flocculated into larger particles, they can usually be removed from the liquid by sedimentation, provided, of course, that a sufficient density difference exists between the suspended matter and the liquid.

(6) Sedimentation is a purely physical process whereby particles suspended in a liquid are made to settle by means of gravitational and inertial forces acting on both the particles suspended in the liquid and the liquid itself. The fundamental elements of most sedimentation processes are:

(a) A basin or container of sufficient size to maintain the liquid to be treated in a relatively quiescent state for a specified period of time.

(b) A means of directing the liquid to be treated into the above basin in a manner which is conducive to settling.

(c) A means of physically removing the settled particles from the liquid (or the liquid from the settled particles, whichever the case may be).

(7) Clarifiers are gravity separation devices and are usually the type of equipment used in applications that involve precipitation and flocculation in addition to sedimentation. Very often, all three processes take place within the same piece of equipment (clariflocculator) since many clarifiers are equipped with separate zones for chemical mixing and precipitation, flocculation, and settling. Certain clarifiers are equipped with low lift turbines which mix a portion of the previously settled precipitates with the incoming feed, as this practice has been shown to enhance certain precipitation reactions and promote favorable particle growth. (This type of clarifier is often used in water-softening applications involving the precipitation of calcium as calcium carbonate.)

b. Applications. The processes of flocculation and sedimentation are suitable treatment methods whenever it is necessary to remove suspended particulates and/or soluble heavy metals. The most common applications suitable for hazardous waste sites will include:

(1) Settling of suspended solids from surface water run-off.

(2) Removal of soluble and insoluble toxic metals.

(3) Removal of soluble inorganics natural to ground-water supplies.

Many toxic metals, including cadmium, lead, arsenic, and chromium, are removed to some degree from waste waters by these processes. There is no upper limit on the concentrations that can be treated by these processes. The lower limit for removal of soluble species is generally governed by the solubility product of the particular ion, although this method of predicting removal efficiency is not very reliable.

c. Advantages/Disadvantages. The major advantages and disadvantages of flocculation and sedimentation as applied to hazardous waste sites are summarized below:

Advantages	Disadvantages
Can be economically applied to very large volumes of leachate or ground water	Often yields incomplete removal of many hazardous compounds
Widely used, equipment is relatively simple	Large quantities of hazardous sludges may be generated
Very low energy consumption	Equipment may be difficult to obtain for flows of less than 37.9 m^3/day (-10,000 gpd)
No upper limit to concentrations that can be treated	Because of continually changing leachate quality, required dosages of coagulants will continuously change

d. Data Requirements.

(1) The required dosage of coagulant depends upon pH, alkalinity, phosphate levels, and mode of mixing; dosage can be determined by jar tests and zeta potential tests. Typical chemical dosages used in industrial treatment processes are listed in Table 4-15. The hydraulic loading, also listed in Table 4-15, is used as a basis for determining suspended solids removal efficiencies. The hydraulic loadings shown are intended to achieve 80 to 90 percent suspended solids removal.

Table 4-15. Chemical Treatment of Industrial Waste Water by Coagulation

Criteria	$FeCl_3$	Alum	$Ca(OH)_2$
Dose, mg/ℓ	80-120	100-150	350-500
Hydraulic loading, $m^3/m/m^2$ (gpm/sq ft[1])	1.2×10^{-3} to 1.6×10^{-3} (0.3-0.4)	8.2×10^{-4} to 1.6×10^{-3} (0.2-0.4)	2×10^{-3} to 3.3×10^{-3} (0.5-0.8)
Chemical sludge production, mg/ℓ (lb/million gal)	42-84 (350-700)	30-60 (250-500)	480-839 (4,000-7,000)

[1] Without use of polyelectrolytes.

(2) Other data required to size the settling basins will include:

(a) Waste stream daily and peak flows.

(b) Settling velocity.

(c) Waste stream analysis for size distribution and solids and liquid specific gravity.

e. Design Criteria.

(1) The effectiveness of a particular flocculant varies in different applications, and in a given application each flocculant has an optimum concentration and pH range. The process of flocculation requires rapid mixing followed by a slow and gentle mixing to allow contact between small particles and agglomeration into larger particles. Rapid mixing for coagulants especially inorganic coagulants such as alum is required to completely disperse the coagulant into the water immediately. Rapid mixing is usually accomplished in 10 to 60 seconds. A mean temporal velocity gradient in excess of 91 m/s (300 feet per second per foot) is recommended. After achieving an effective mix, promotion of particle growth by flocculation during the slow mix step is next. Flocculation is accomplished in 15 to 30 minutes with a mean temporal velocity gradient of 40 to 80 meters per second per meter (40 to 80 feet per second per foot). The lower value is for fragile floc (aluminum or iron), and the higher value is for a lime floc (Azad 1976).

(2) Sedimentation may be carried out in a separate basin from flocculation or it may be carried out in the same basin with both flocculation and precipitation. Figures 4-13 and 4-14 present schematics of an "in-line" system and a sludge-blanket type unit in which all three processes are carried out in a single unit. Criteria for sizing settling basins are overflow rate (surface settling rate), tank depth at the side walls, detention time which usually averages 1 to 3 hours, and surface loading rates which average 1.5 to 2.5 $m^3/d/m^2$ (360 to 600 gallons per day per square foot) for alum floc, 2.2 to 4.9 $m^3/d/m^2$ (540 to 1,200 gallons per day per square foot) for lime floc, and 2.9 to 3.3 $m^3/d/m^2$ (700 to 800 gallons per day per square foot) for $FeCl_3$. In selecting the particular tank shape, proportions, equipment, etc., the designer should:

(a) Provide for even inlet flow distribution in a manner that minimizes inlet velocities and short-circuiting.

(b) Minimize outlet currents and their effects by limiting weir loadings and by proper weir placement.

(c) Provide sufficient sludge storage depths to permit desired thickening of sludge. Solids concentrations of two to seven percent should be obtained.

(d) Provide sufficient wall height to give a minimum of 457 mm (18 inches) of freeboard.

(e) Reduce wind effects on open tanks by providing wind screens and by limiting fetch of wind on tank surface with baffles, weirs, or launders.

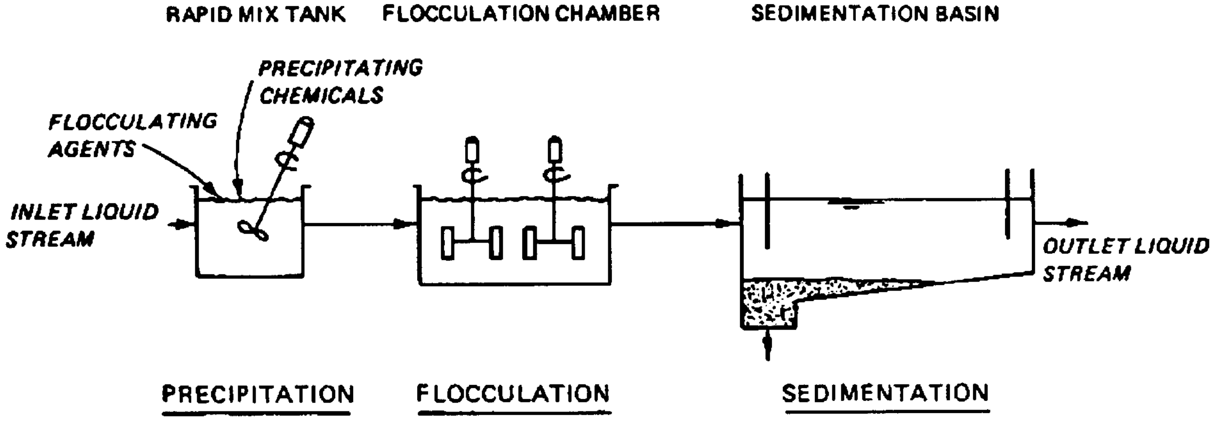

Figure 4-13. Representative Configuration Employing Precipitation, Flocculation, and Sedimentation

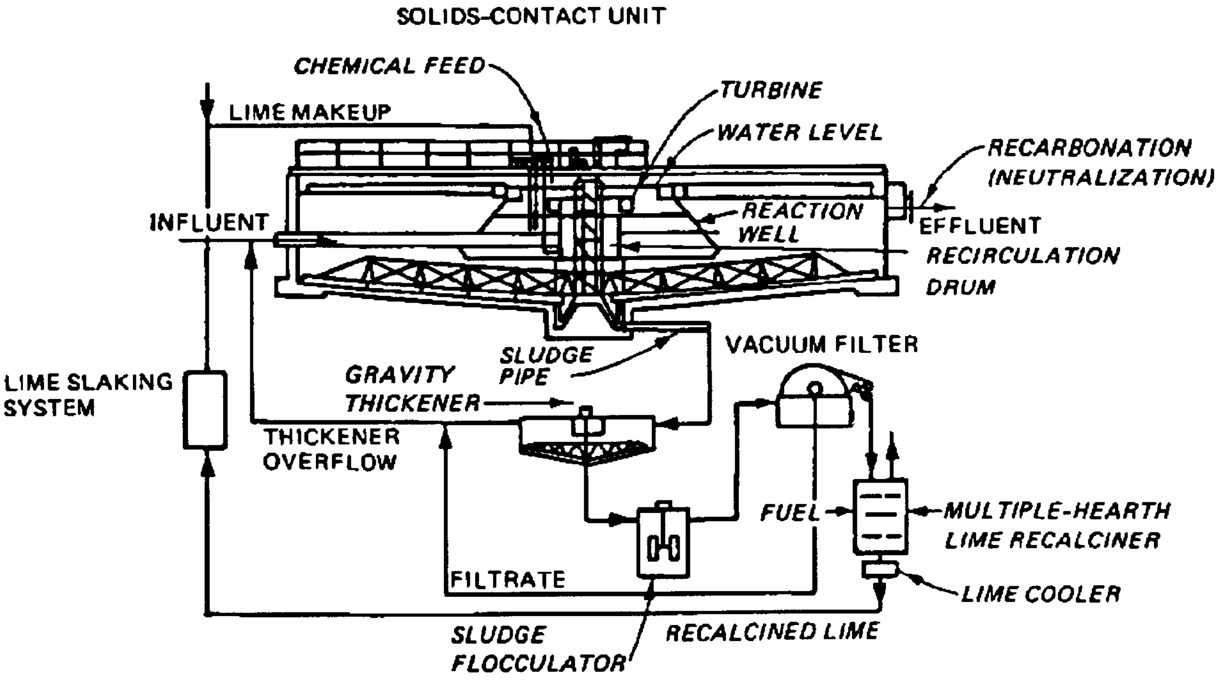

Figure 4-14. Typical Solids Contact Chemical Treatment System

(f) Consider economy of alternative layouts that can be expected to provide equivalent performance.

(g) Maintain equal flow to parallel units. This is most important and often forgotten. Equal flow distribution between settling units is generally obtained by designing equal resistances into parallel inlet flow ports or by flow splitting in symmetrical weir chambers.

4-12. Neutralization.

a. Process Description.

(1) The neutralization process described herein is intended for use in two different ways. The word "neutralization" implies a neutral pH of 7.0. However, in the present context, the process will be used to describe the adjustment and control of pH at a specified level.

(2) Many manufacturing processes generate waste streams that are acidic or alkaline in nature. Before such wastes can be discharged to the environment, the pH must be adjusted to be within the EPA-specified range, usually 6 to 9.

(3) Adjustment of pH may also be desirable to control chemical reaction rates and to effect precipitation. For example, in the reduction of chromium (VI) to chromium (III), the pH must be lowered to 3.0 or less in order for the reaction to proceed at a satisfactory rate. In order to precipitate the chromium (III), the pH must be raised to between 8 to 8.5.

(4) The basic principle behind the process is simple: the mixing of an acid or a base with a process stream to bring about the desired pH. Typically, the process is carried out in a completely stirred reactor (CSTR).

(5) The addition of appropriate quantities of neutralizing agent is monitored and adjusted by pH measurements and control. Generally, these systems are of a continuous flow variety and use automatic pH monitors to check the acidity or alkalinity and control the feeding of neutralizing agent. The number of neutralization units and the location of pH sensors are determined by the stability of the waste stream pH. Where widely varying pH levels are experienced, several reaction units plus additional monitoring equipment may be required. A stream with large fluctuations in pH might also be preceded by an equilization basin which would yield a more consistent feed with a limited pH range.

(6) The choice of a neutralizing agent is dictated by a number of factors such as economics, availability, and process compatibility. Commonly, the choice of an acid for neutralizing alkaline waste is sulfuric acid, whereas the choice for an acid stream may be lime or caustic.

b. Applications. Neutralization is a treatment process of demonstrated technical and economic feasibility industry wide. Two primary applications are intended here and are as follows:

(1) Neutralize a waste stream to a suitable level such that it can be discharged to the environment.

(2) Adjust pH of a waste stream to a specified level that would be suitable for carrying out chemical reactions or further treatment.

c. Advantages/Disadvantages. Advantages and disadvantages of neutralization are summarized below:

Advantages	Disadvantages
Proven and simple process	Does not remove or degrade pollutants, rather adds them
Some waste may be discharged directly following neutralization	pH controllers require frequent maintenance
Can provide favorable conditions for oxidation/reduction reactions	May require equilization as pretreatment
Can provide conditions favorable to precipitation of metals	May generate large amounts of heat

d. Data Requirements. Data requirements include:

(1) Average daily flow; peak flow.

(2) pH range of influent stream.

(3) Desired control pH.

(4) Equivalents per liter of alkalinity or acidity to be neutralized.

e. Design Criteria.

(1) If the influent hydraulic flow is expected to vary significantly, equalization should be considered for pretreatment. This approach is also true for wide fluctuations in the influent pH.

(2) A CSTR with 10 to 20 minutes residence time should suffice in most cases. Neutralization reactions are typically very fast. There may be, however, extenuating circumstances that would make it desirable to increase or decrease this time. A larger volume would tend to stabilize the control system. On the other hand, if pH adjustment is being carried out in a number of stages, retention time may be reduced to a minimum.

(3) Feed systems and storage tanks must be provided for acid and/or base for neutralization. If lime is used, a slurry tank may be required.

(4) If strong acids require neutralization with strong bases, care must be exercised to consider the potential for a violent exothermic reaction. This situation should be avoided if at all possible.

4-13. Oil-Water Separation.

a. Process Description.

(1) Oil-water separators may be of several different types that utilize either gravity or mechanical acceleration to separate phases of varying density. Gravity separators are more commonly called API (American Petroleum Institute) separators. This terminology stems from a hydrometer scale in °API that is used by the petroleum industry to specify the specific gravity of petroleum products.

(2) An API separator consists of a settling chamber that allows oil to separate from an aqueous phase and rise to the surface, a baffle and oil skimming device that prevents the loss of the oil phase to the effluent while continuously removing the surface oil, and a holding basin that collects and stores the oil until final disposal is desired.

(3) Gravity separators should be used only for gross oil-water separators. They are not intended for removals to low parts per million levels. Also, they should not be used for emulsified oil and grease.

(4) Low-level oil removal may require a membrane process, centrifugation, chemical coagulation, or carbon adsorption. One or more of these processes may be used after the API separator. A flow diagram for an API separator is presented in Figure 4-15.

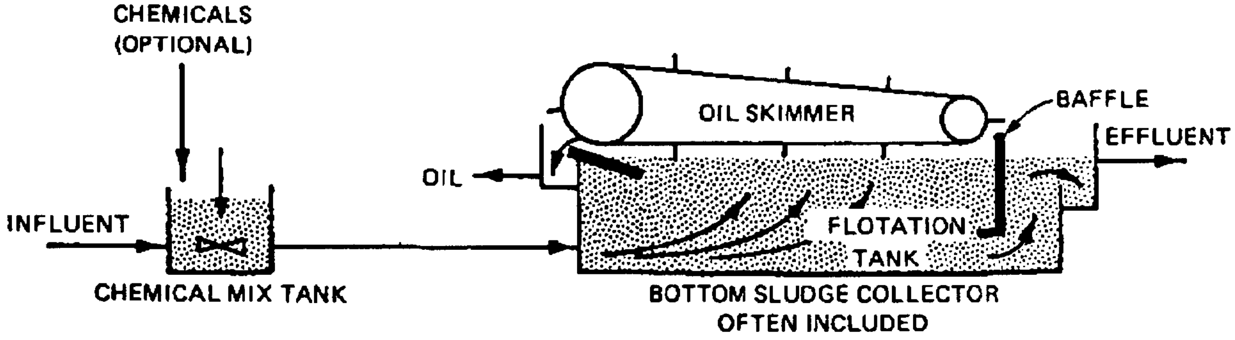

Figure 4-15. Flow Diagram for API Separator

b. Application.

(1) API are gravity separators which are technically simple oil-water separators that have found wide usage at manufacturing facilities. They are used to separate residual oil from washing down floors, equipment, parts, compressor blowdown, and spillage.

(2) Gravity separators are typically used as a pretreatment step before further processing of the waste water. Oil is automatically skimmed and collected in a holding basin where it is held for final disposition. Residual oil in the effluent may be removed in subsequent treatment steps, or specific processes may be required in the process train for total removal, perhaps carbon adsorption.

c. Advantages/Disadvantages. Advantages and disadvantages of oil/water separators are summarized below:

Advantages	Disadvantages
Provide excellent gross oil removal	Cannot treat emulsified oil or oil droplets smaller than 0.015 centimeters
Proven, inexpensive technology	Separated oil requires disposal and water phase may requre futher treatment
Variety of proprietary units are readily available	Short-circuiting may be a problem
	Sensitive to shock loadings

d. Data Requirements. Data requirements are as follows:

(1) Hydraulic flow, average and peak.

(2) Size of oil droplet to be removed.

(3) API or density of oil.

(4) API or density of water phase.

(5) Viscosity of fluid.

(6) Expected operating temperature.

e. Design Criteria.

(1) Gravity separators are based upon the rise rate of oil droplets of a specified size and density. These droplets rise to the surface or to a baffle and then to the surface within the retention time provided. A skimming device then physically removes the oil to a holding facility.

(2) Rise rates are amenable to theoretical considerations through a rather simple force balance on the system. These forces include drag, buoyant, and gravitation forces. The design of oil separators as developed by the American Petroleum Institute is based upon removing oil droplets that are larger than 0.015 centimeter in diameter. The Reynolds number for this situation can be shown to be less than 0.5. This says that, for spherical

particles, laminar flow can be assumed with little error and Stoke*s law is applicable.

(3) Stoke*s law describes the terminal settling velocity of a particle as a function of the particle and medium density, particle diameter, and drag characteristics. Stokes equation is as follows:

$$V_t = \frac{(P_s - P)\, gD_p^2}{18u} \qquad (4\text{-}5)$$

where

V_t = terminal settling velocity, cm/sec

P_s = density of particle, g/cm^3

P = density of fluid, g/cm^3

g = gravitational constant, cm/sec^2

D_p = diameter of particle, cm

u = viscosity of fluid, dyne-sec/cm^2

(4) The API design procedure must consider short-circuiting and turbulence for best performance.

4-14. Dissolved Air Flotation.

a. Process Description.

(1) Flotation is a solid-liquid separation process. Separation is artificially induced by introducing fine gas bubbles (usually air) into the system. The gas-solid aggregate has an overall bulk density less than the density of the liquid; thus, these aggregates rise to the surface of the fluid. Once the solid particles have been floated to the surface, they can be collected by a skimming operation.

(2) Air flotation systems may be classified as dispersed air flotation or dissolved air flotation. In dispersed air flotation, air bubbles are generated by introducing air through a revolving impeller or porous media. This type of flotation system is usually ineffective and finds very limited application in waste-water treatment. Dissolved air flotation may be subclassified as pressure flotation or vacuum flotation. Pressure flotation involves air being dissolved into the waste water under elevated pressures and later released at atmospheric pressure. Vacuum flotation consists of applying a vacuum to waste water aerated at atmospheric pressure. Dissolved air-pressure flotation considered herein is the most commonly used in waste-water treatment.

(3) The principal components of a dissolved air-pressure flotation system are a pressurizing pump, air injection facilities, a retention tank, a back-pressure regulating device, and a flotation unit. The primary variables for flotation design are pressure, recycle ratio, feed solid concentration, detention period, air-to-solids ratio, use of polymers, and solids and hydraulic loadings. Optimum design parameters must be obtained from bench scale or pilot plant studies. A flow diagram for a dissolved air flotation system is presented in Figure 4-16.

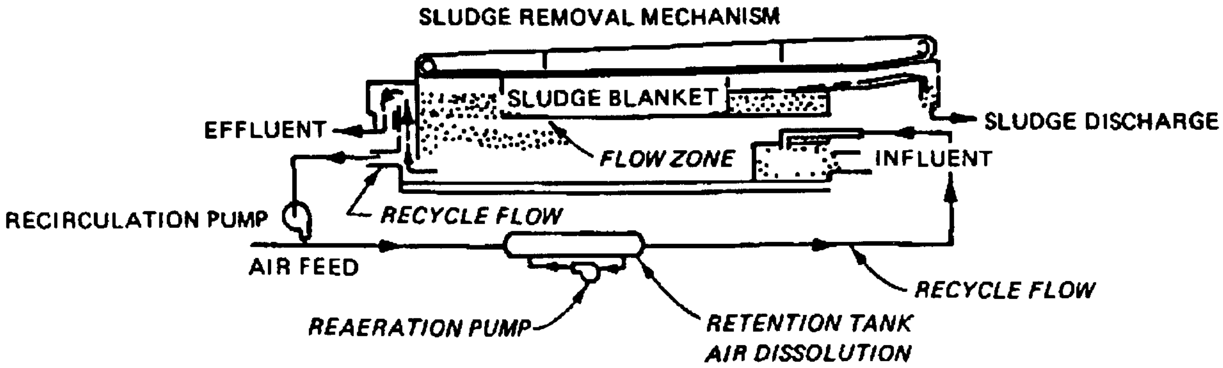

Figure 4-16. Flow Diagram for Dissolved Air Flotation System

b. Applications. In waste-water treatment, flotation is used as a clarification process to remove suspended solids and as a thickening process to concentrate various types of sludges. However, high operating costs of the process generally limit its use to clarification of certain industrial wastes and for concentration of waste-activated sludge. In industrial practice, with wastes containing total suspended solids (TSS) and oil and grease levels up to 900 milligrams per liter, removal efficiency of 90 percent has been recorded.

c. Advantages/Disadvantages. Advantages and disadvantages of dissolved air flotation are summarized below:

Advantages	Disadvantages
Requires very little land area	Only effective on particles with densities near that of water
Well documented and available technology	Varying influent will affect performance
	Sludge generated will require disposal
Air released in unit unlikely to strip volatile organics	

d. Data Requirements. Required design information includes:

(1) Waste stream daily average flow.

(2) Waste stream temperature.

(3) Waste stream oil/grease or suspended solids concentration.

(4) Treatability tests to determine air requirements and pressure.

e. Design Criteria.

(1) Major design variables and corresponding operating conditions are:

(a) System pressure, 276-413 kPa (40-60 psig) (pounds per square inch, gage).

$$\frac{A}{S} = \frac{1.3s_a(fP - 1)}{S_a}$$

Temp., °C	0	10	20	30
s_a, mℓ/ℓ	29.2	22.8	18.7	15.7

where

A/S = air to solids ratio, mℓ (air)/mg (solids)

S_a = air solubility, mℓ/ℓ

f = fraction of air dissolved at pressure P, usually 0.5

P = pressure, atm

$$= \frac{p + 14.7}{14.7} \quad \text{(U.S. customary units)}$$

$$= \frac{p + 101.35}{101.35} \quad \text{(SI units)}$$

p = gage pressure, lb/in^2 gage (kPa)

S_a = sludge solids, mg/ℓ

The corresponding equation for a system with only pressurized recycle is

$$\frac{A}{S} = \frac{1.3s_a(fP - 1)R}{S_aQ}$$

where

R = pressurized recycle, Mgal/d (m^3/d)
Q = mixed-liquor flow, Mgal/d (m^3/d)

In both equations, the numerator represents the weight of air and the denominator the weight of the solids. The factor 1.3 is the weight in milligrams of 1 mℓ of air, and the term (-1) within the brackets accounts for the fact that the system is to be operated at atmospheric conditions. The required area of the thickener is determined from a consideration of the rise velocity of the solids, 0.2 to 4.0 gal/m • ft^2 (8 to 160 ℓ/m^2 • min), depending on the solids concentration, the degree of thickening to be achieved, and the solids-loading rate.

(b) Hydraulic loading, $4.1 \times 10^{-3} - 1.6 \times 10^{-2}$ $m^3/min/m^2$ (1-4 gpm/ft^2).

(c) Retention period, 20-40 mm.

(2) It is common engineering practice to triple the calculated A to provide a safety factor and excess air for high dissolution efficiency.

(3) The hydraulic loading rate (referred to as surface loading rate (SLR)) is determined by plotting laboratory experimental values of effluent pollutant concentrations versus surface loading rates. The rate which is sufficient to achieve effluent water quality goals is identified from the graph.

(4) The retention time equation is

$$t = \frac{d}{SLR} \qquad (4\text{-}7)$$

where a depth of 1.2 to 2.7 m (4 to 9 feet) is typically chosen (EPA 1980).

4-15. Reverse Osmosis.

a. Process Description.

(1) Osmosis is the movement of a solvent through a membrane which is impermeable to a solute. If a salt solution is separated from water by means of a semipermeable membrane, there will be a net transport of water in the direction of the salt solution. This phenomenon develops a hydrostatic pressure known as "osmotic pressure." It may also be defined as the excess pressure that must be applied to the solution to produce equilibrium.

(2) Reverse osmosis removes contaminants from aqueous wastes by passing the waste stream, at high pressure, through a semipermeable membrane. At sufficiently high pressure, usually in the range of 1378 to 2756 kPa (200 to 400 pounds per square inch), pure water passes out through the membrane leaving a more concentrated waste stream. As the waste stream becomes more concentrated, the osmotic pressure increases and consequently requires addi-

tional external pressure to maintain the flow in the proper direction, hence the name reverse osmosis.

(3) The semipermeable membrane itself is perhaps the most critical part of reverse osmosis (RO). At present, commercial RO membranes are made from two types of polymers. The first membranes developed were cellulose acetate. The second type of membranes were developed from cellulose triacetate. Both membranes can be prepared in sheet form with water fluxes of 4.1×10^{-2} -8.2×10^{-2} $m^3/day/m^2$ (10 to 20 gallons per day per square foot) at 2756 kPa (400 pounds per square inch). Polyamine membranes are being developed but, at present, they have no resistance to chlorine.

(4) The design of the modules containing the RO membranes is crucial to the efficient operation of the process. As solute is rejected by the membranes, it concentrates at the membrane surface and results in a situation known as "concentration polarization," where the concentration at the membrane surface is many times higher than in the bulk feed solution. Since the driving force for water transport decreases with increasing concentration, polarization can have a very deleterious effect on water flux.

(5) Concentration polarization can be minimized by high fluid shear at the membrane surface to aid the back-transport of polarized solute into the bulk of the process stream. This is accomplished by flowing the feed stream at high velocities in thin channels to promote laminar shear, or in wide channels to produce turbulence. RO membranes can be spiral wound, hollow fine fiber, tubular, or flat membrane.

(6) One of the difficulties with RO membranes is their susceptibility to fouling by film-forming organics or insoluble salts. It is common practice to preprocess feed water as necessary to remove oxidizing materials, iron, and magnesium salts; to filter out particulates; and to remove oils, greases, and other film-formers. If there is likelihood of fouling by living organisms, chlorination or UV treatment may be employed as well to ensure that maximum flux rates may be obtained. A typical flow sheet for an RO plant is shown in Figure 4-17.

b. Applications.

(1) RO systems are in extensive use throughout the world in generating potable water. Over 2.27×10^5 m^3/day (60,000,000 gallons per day) in capacity is now in operation.

(2) The number of plants in use to treat industrial waste water is not clearly defined but appears to be significant. Specific applications include:

(a) Preparation of pure water and process feed water.

(b) Preparation of rinse water in semiconductor and electronic manufacturing.

(c) Purification of water for hospital use.

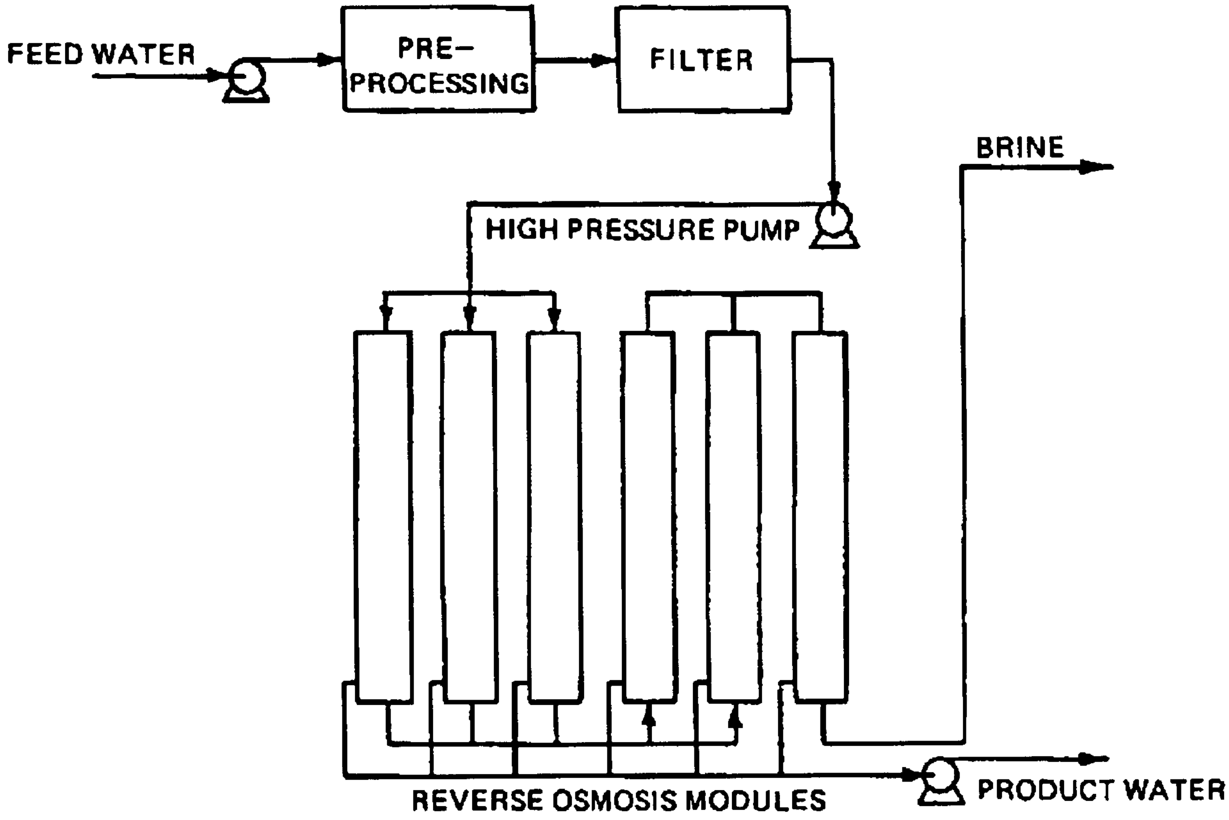

Figure 4-17. Reverse Osmosis Plant Flow Sheet

(d) Reclamation of electroplating chemicals.

(e) Recovery of sugar wastes by candy manufacturers.

(3) Industrial waste treatment offers a great potential for RO. This process should be considered when it is desirable or necessary to accomplish:

(a) A reduction in the waste volume.

(b) Recovery of valuable or reusable materials.

(c) Water conservation and recovery.

(d) The concentration of pollutants for further processing.

c. <u>Advantages/Disadvantages</u>. Advantages and disadvantages of reverse osmosis are listed below:

Advantages	Disadvantages
Capable of high salt rejection	Requires high operating pressure and extensive pretreatment
Produces high purity solvent	Subject to membrane fouling and compression
Applicable to small installations	Cannot be used for fractionation
Provides for water conservation and use	Proportion of reject water may be too high to be acceptable

d. Data Requirements.

(1) A variety of proprietary designs for RO units are available from numerous manufacturers. These suppliers will usually supply the following pertinent information with regard to their particular system and for a variety of membranes:

(a) Packing density, m^2/m^3 (ft^2/ft^3).

(b) Water flux at a specified pressure and temperature.

(c) Sodium chloride rejection.

(d) Acceptable pH ranges.

(e) Recommended operating pressure.

(2) Data with regard to specific waste are also required that must be determined experimentally from bench scale studies. Manufacturers and suppliers are usually eager to be of help in this area.

(3) One important piece of information that must be determined for any specific application is pretreatment requirements. In general, pretreatment will always be required and should be carried out to:

(a) Remove excess turbidity and suspended solids.

(b) Adjust pH to desirable level.

(c) Adjust temperature of feed.

(d) Control the formation of components that tend to precipitate.

(e) Disinfect to prevent slime growth.

(f) Remove oil and grease that may be present.

(4) Data regarding flux rates must be determined experimentally. Flux decline is a serious operational problem that must be given the proper attention. Membrane compaction and membrane fouling are responsible for reductions in flux. Membrane compaction is a function of membrane type, operating temperature, pressure, and time.

e. Design Criteria.

(1) The design of an RO system is based upon the feed water composition, variability, temperature, and osmotic pressure. Rejection of various components in the feed stream by a specific membrane flow rate usually dictates the number of units or size of the plant. Product quality is difficult to predict but can be varied by adjusting product recovery.

(2) When plant capacity and energy requirements are established, the membrane requirements must be set. Membrane considerations include the expectancy, compaction, fouling, and operating net pressure. If, for example, data are available for a certain membrane that would suggest a flux of 10 gallons per square foot per day at 70°F at 500 pounds per square inch is applicable, the membrane requirement for a 100,000 gallons-per-day facility would be 10,000 square feet of membrane. It is common design practice to base the design flux upon the expected volume after 1 year of operation which may reduce flux rate by 10-15 percent. Membrane lifetime is critical.

(3) Minimization of concentration polarization is another design consideration. This is done by regulating the brine flow rate through the RO units. Since product is continuously being taken out, the brine flow is reduced. To compensate for this, units are staged in a series-parallel arrangement that is similar to an inverted pyramid.

4-16. Solidification/Stabilization. Solidification/stabilization technology as applied to wastes uses physical and chemical processes to produce chemically stable solids with improved contaminant containment and handling characteristics. Waste solidification is the term used to describe the process of sorbing a liquid or semiliquid waste onto a solid medium, such as fly ash, cement, kiln dust, or clay, or otherwise incorporating the waste in a solid matrix. This partial treatment eliminates any free liquid and reduces the risk of spillage or escape of contaminants in any liquid phase. This technology is discussed in detail in paragraph 4-21.

4-17. Ultrafiltration.

a. Process Description.

(1) Ultrafiltration and RO are similar processes and some confusion exists about their distinction. Both involve the transport of a solution under a pressure gradient through a semipermeable membrane to achieve at least partial separation of solvent molecules from solute molecules. In addition, both require a velocity vector parallel to the plane of filtration. The two processes differ because ultrafiltration is not impeded by osmotic pressure and can be effected at low pressure differences of 34.5 to 689 kPa (5 to 100 pounds per square inch). Ultrafiltration is usually applicable for separation

of solutes above a molecular weight of 500, which have very small osmotic pressures at moderate concentrations. These include such materials as bacteria, viruses, starches, gums, proteins, clays, and paint pigments. The upper molecular weight limit for ultrafiltration is usually defined as 500,000. Above that molecular weight size, separation occurs by conventional microporous filtrations.

(2) Concentration polarization effects in ultrafiltration are similar to those in RO except more severe. Since micromolecular diffusion constants are two to three orders of magnitude smaller than those of salts, back-diffusion to the bulk of the liquid is much slower. Figure 4-18 illustrates the impact of concentration polarization.

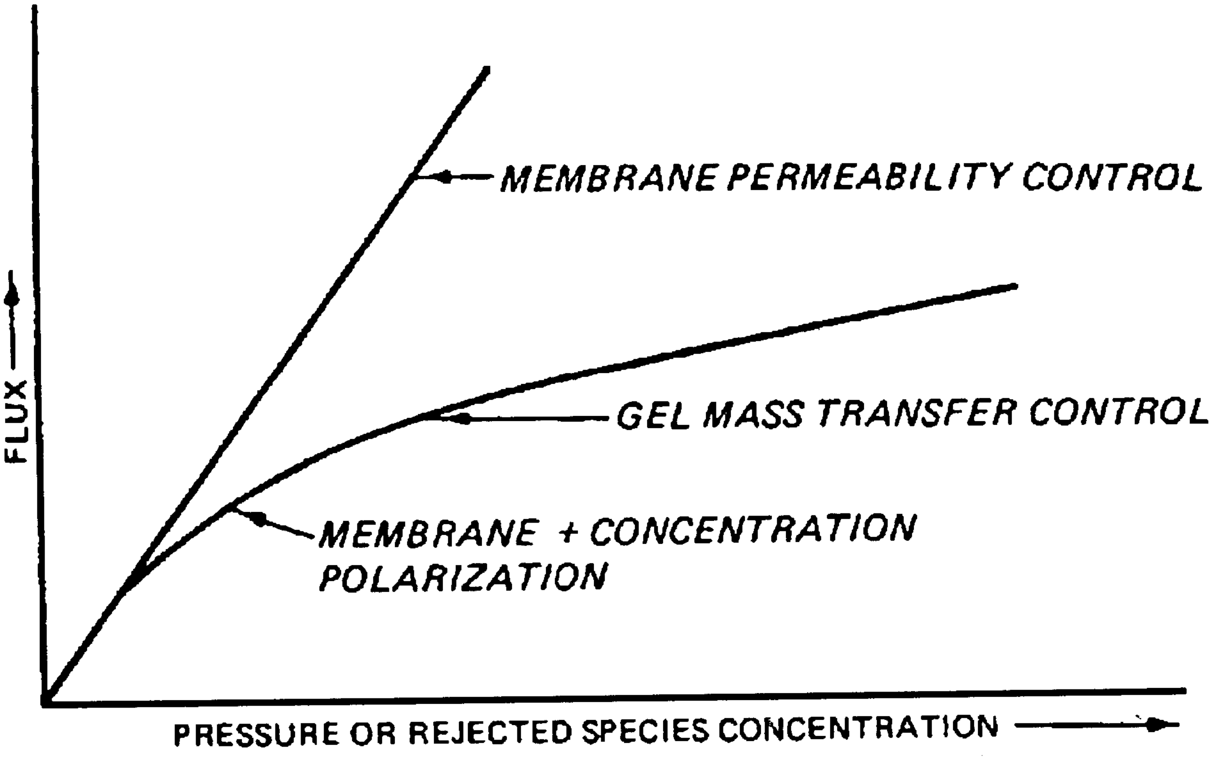

Figure 4-18. Effect of Concentration Polarization Upon Membrane Flux in Ultrafiltration

b. Applications.

(1) The properties of ultrafiltration membranes lead to a range of applications quite distinct from those of conventional filtrations. Where solutes are being separated from solution, ultrafiltration can serve as a concentration or fractionation process for single-phase liquid streams. Thus, ultrafiltration competes with adsorptive and evaporative separation processes and has the potential for broader applicability than conventional filtration. Usually, it will not perform the entire task because it produces a concentrate

rather than a solvent-free product, and the concentrate requires further processing if a pure solute is to be recovered.

(2) Application of ultrafiltration may fall into one of three categories:

(a) Concentration, where the desired component is rejected by the membrane and taken off as a fluid concentrate.

(b) Fractionation, for systems where more than one solute is to be recovered, and products are taken from both the rejected concentrate and permeate.

(c) Purification, where the desired product is purified solvent.

(3) Table 4-16 summarizes major existing ultrafiltration applications. Also shown is the function of ultrafiltration processing for the specific application.

(4) Table 4-17 summarizes developmental applications of ultrafiltration. These represent areas which are likely to be commercial within the next 5 years. Table 4-16 indicates commercial applications and the nature of their technology.

Table 4-16. Commercial Applications of Ultrafiltration

Application	Function
Electrocoat	Fractionation
Paint rejuvenation and rinse water	Concentration and fractionation
Protein recovery from cheese whey	Concentration and fractionation
Metal machining, rolling, and drawing--oil	Purification
Emulsion treatment	Purification
Textile sizing (PVA) waste	Fractionation
Electronics component manufacturing washwater treatment	Purification
Pharmaceuticals manufacturing sterile water production	Purification

c. Advantages/Disadvantages. Ultrafiltration is a concentration process that is in competition with other membrane processes as well as evaporation processes. Its advantages and disadvantages are summarized below:

Advantages	Disadvantages
Operates at lower pressure than RO	Requires membranes that are subject to fouling
Can be used for fractionation	Limited range of particle sizes for for which it is effective
Does not require pretreatment as RO, but can be used as pretreatment for RO	
Requires less capital than RO or evaporative processes	
Highly suitable for small flows and small installations	

Table 4-17. Development Applications of Ultrafiltration

Application	Function
Dye waste treatment	Concentration and purification
Pulp mill waste treatment	Concentration and purification
Industrial laundry waste treatment	Purification and fractionation
Protein recovery from soy whey	Concentration
Hot alkaline cleaner treatment	Fractionation and purification
Power plant boiler feedwater treatment	Purification
Sugar recovery from orange juice pulp	Fractionation
Product recovery in pharmaceutical and fermentation industries	Concentration
Colloid-free water pollution for beverages	Purification

d. Data Requirements.

(1) A variety of proprietary designs for ultrafiltration units are available from numerous manufacturers. These suppliers will usually supply the following pertinent information with regard to their particular system and for a variety of membranes:

(a) Packing density, 1.5 m^2/m^3 (5 ft^2/ft^3).

(b) Water flux at a specified pressure and temperature.

(c) Molecular weight cutoff or rejection.

(d) Acceptable pH ranges.

(e) Recommended operating pressure.

(2) Data with regard to specific waste are also required that must be determined or verified experimentally. Manufacturers and suppliers will usually provide assistance in this area. Flux rates and rejection should be determined experimentally.

e. Design Criteria.

(1) The approach to the design of an ultrafiltration system is similar to that for RO. In ultrafiltration design, concentration polarization effects are magnified, and care must be exercised to alleviate this problem. Typically, channels are designed for minimum height, and the unit is operated at a high parallel surface velocity.

(2) Operating pressures for ultrafiltration systems are in the range of 68.9 to 689 kPa (10 to 100 pounds per square inch) with 413 to 551 kPa (60 to 80 pounds per square inch) being typical. As is the case with RO, temperature plays a significant role in the flux rate of ultrafiltration membranes. Fluxes are expected to double for a 15° to 25°C rise in temperature. Operating temperatures are limited by economics and the material from which the membrane is constructed. Membranes produced from cellulose are limited to the 50° to 60°C range, while other membranes may be operated at temperatures as high as 100°C.

(3) Ultrafiltration membranes are specified in terms of molecular weight cutoff or a rejection of a specific molecular weight compound. This is not an absolute measure of rejection. In actuality, rejection is a function of molecular shape, size, and flexibility as well as the operating conditions.

Section II. Treatment of Sludges and Soils

4-18. Biological Treatment.

a. Bioslurry Reactors.

(1) Process description.

(a) Bioslurry reactors (BSRs) (also referred to as liquid/solids reactors) are an innovative biological technology for rapid treatment of sludges and excavated soils. BSRs offer treatment conditions that are conducive to the optimal biotreatment of contaminated soils by slurrying contaminated soils in water using liquid-to-solid ratios ranging from 20 to 50 percent. The soil/water slurries are usually kept in suspension using mechanical mixers,

4-21. Solidification/Stabilization.

a. Process Description.

(1) Solidification/stabilization technology as applied to wastes uses physical and chemical processes to produce chemically stable solids with improved contaminant containment and handling characteristics (Figure 4-23). Waste solidification is the term used to describe the process of sorbing a liquid or semiliquid waste onto a solid medium, such as fly ash, cement, kiln dust, or clay, or otherwise incorporating the waste in a solid matrix. This partial treatment eliminates any free liquid and reduces the risk of spillage or escape of contaminants in any liquid phase.

(2) Solidification may involve the addition of cementing agents so that the solid material (with the sorbed liquid) can be formed into a free-standing impermeable monolith. This part of the waste treatment process reduces the surface area across which transfer or loss of pollutants can occur. Stabilization of waste refers to chemical alteration of the waste so as to reduce the potential for escape of contaminants or to lower the toxicity of specific waste components. Both solidification and chemical stabilization result in transformation of liquid or semisolid wastes to an environmentally safer form. For example, metal-rich sludge would be considered solidified if it were mixed with a dry absorber such as fly ash or dry soil. The benefits of solidification could be carried further if the sorbent and waste were cemented into a permeable, monolithic block. The waste would be considered chemically stabilized if the chemical composition of the sludge were altered by the addition of lime ($Ca(OH)_2$) to raise the pH **so** that the potential contaminants (toxic metals) were less soluble and hence less easily leached. An absorbing medium can be formulated to take up free liquid and maintain conditions of lowered solubility for the potential contaminants. Cementing agents (organic polymers, pozzolanic materials, or portland cement) can be added to bind the stable, solid waste into a free-standing, relatively impermeable monolith that represents a substantially reduced environmental threat.

(3) Waste solidification/stabilization systems that have potentially useful application in remedial action activities discussed in this paragraph are: sorption, lime-fly ash pozzolan, and pozzolan-portland cement systems. Encapsulation processes such as thermoplastic microencapsulation and macroencapsulation were addressed in paragraph 4-19.

(a) Sorption. Most waste materials considered for solidification/ stabilization are liquids or sludges (semisolids). In order to prevent the loss of drainable liquid and improve the handling characteristics of the waste, a dry, solid sorbent is generally added to the waste. The sorbent may interact chemically with waste or may simply be wetted by the liquid part of the waste (usually water) and retain the liquid as part of the capillary liquid. The most common sorbents used with waste include soil and waste products such as bottom ash, fly ash, or kiln dust from cement manufacture.

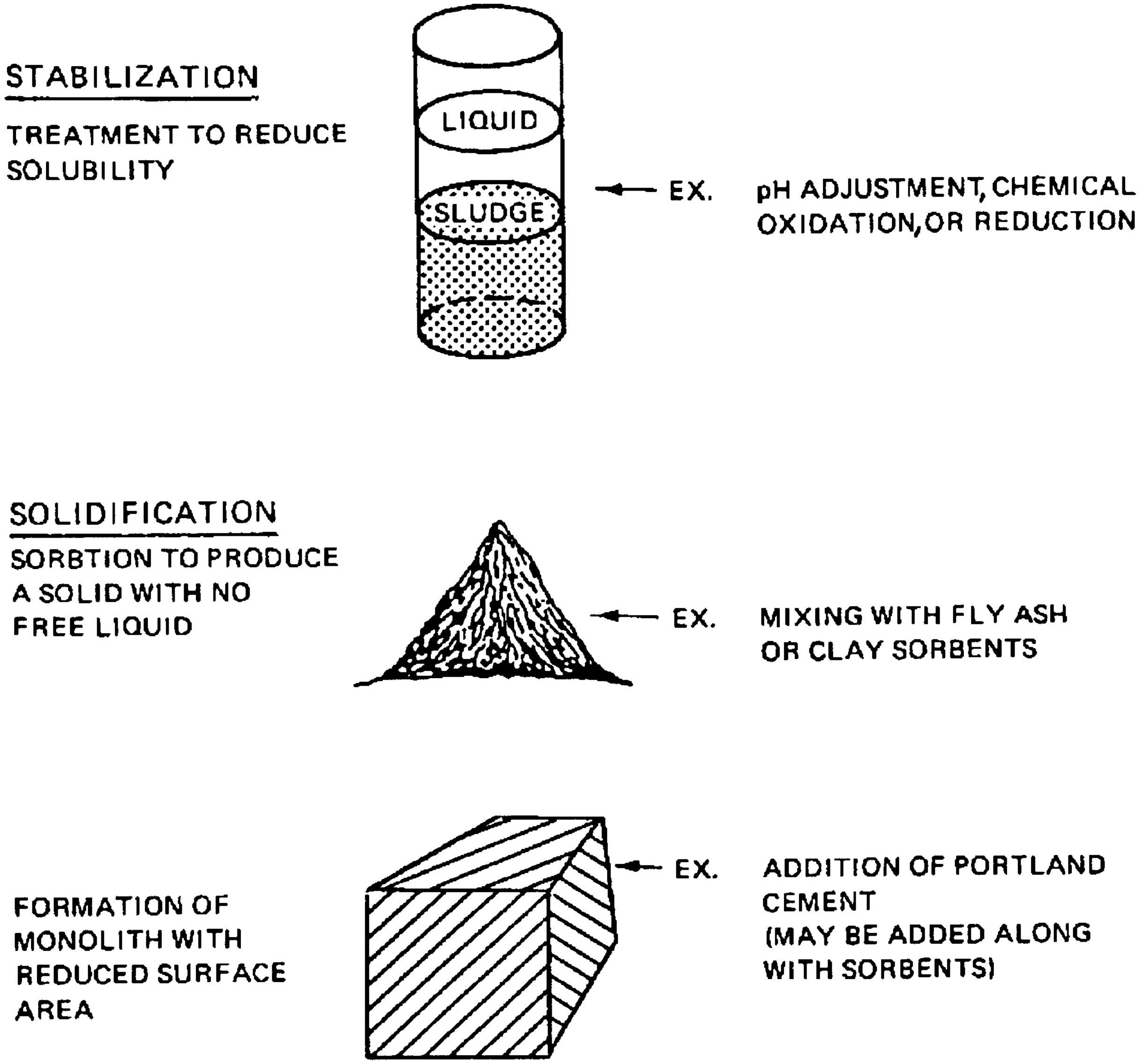

Figure 4-23. Steps in Stabilization/Solidification of Hazardous Wastes

In general, selection of sorbent materials involves tradeoffs between chemical effects, costs, and amounts required to produce a solid product suitable for burial. Table 4-18 summarizes chemical binding properties of natural sorbents for selected waste leach liquids. Where the ability of a sorbent to bind particular contaminants is important to containment, sorbents with specific chemical affinities can be selected. The pH of the waste strongly affects sorption/waste interactions, and pH control is an important part of any sorption process.

Table 4-18. Natural Sorbents and their Capacity for Removal of Specific Contaminants from Liquid Phases of Neutral, Basic, and Acidic Wastes

Contaminant	Neutral waste (calcium fluoride)		Basic waste (metal finishing sludge)		Acidic waste (petroleum sludge)	
Ca	Zeolite	(5054)*	Illite	(1280)	Zeolite	(1390)
	Kaolinite	(857)	Zeolite	(1240)	Illite	(721)
			Kaolinite	(733)	Kaolinite	(10.5)
Cu	Zeolite	(8.2)	Zeolite	(85)	Zeolite	(5.2)
	Kaolinite	(6.7)	Kaolinite	(24)	Acidic F.A.	(2.4)
	Acidic F.A.**	(2.1)	Acidic F.A.	(13)	Kaolinite	(0)
Mg	Basic F.A.	(155)	Zeolite	(1328)	Zeolite	(746)
			Illite	(1122)	Illite	(110)
			Basic F.A.	(176)	Basic F.A.	(1.7)
Zn					Zeolite	(10.8)
					Vermiculite	(4.5)
					Basic F.A.	(1.7)
Ni			Zeolite	(13.5)		
			Illite	(5.1)		
			Acidic F.A.	(3.8)		
F	Illite	(175)	Kaolinite	(2.6)	Illite	(9.3)
	Kaolinite	(132)	Illite	(2.2)	Acidic F.A.	(8.7)
	Acidic F.A.	(102)			Kaolinite	(3.5)
Total CN					Illite	(12.1)
					Vermiculite	(7.6)
					Acidic F.A.	(2.7)
COD	Acidic F.A.	(690)	Illite	(1744)	Vermiculite	(6654)
	Illite	(180)	Acidic F.A.	(1080)	Illite	(4807)
			Vermiculite	(244)	Acidic F.A.	(3818)

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* Values represent sorbent capacity in micrograms of contaminant removed per gram of sorbent used.

** F. A. = fly ash. Acidic F.A. = Class F; Basic F.A. = Class C.

(b) Lime-fly ash pozzolan. Solidification/stabilization of waste using lime and pozzolanic material requires that the waste be mixed with a carefully selected, reactive fly ash (or other pozzolanic material) to a pasty consistency. Lime (calcium hydroxide) is blended into the waste-fly ash mixture. Typically 20 to 30 percent lime is needed to produce a strong pozzolan. The resulting moist material is packed or compressed into a mold to cure or is placed in the landfill and compacted.

(c) Pozzolan-portland cement. There are a wide variety of treatment processes that incorporate portland cement as a binding agent. Pozzolanic products (materials with fine-grained, noncrystalline, reactive silica) are frequently added to portland cement to react with any free calcium hydroxide and thus improve the strength and chemical resistance of the concrete-like product. In waste solidification, the pozzolanic materials (such as fly ash) are often used as sorbents. Much of the pozzolan in waste processing may be waste coated and relatively unreactive. Any reaction that does occur between the portland cement and free silica from the pozzolan adds to the product strength and durability. Waste solidifying formulations based on portland and pozzolan-portland systems vary widely, and a variety of materials have been added to change performance characteristics. These include soluble silicates, hydrated silica gels, and clays such as, bentonite, illite, or attapulgite. Approximate reagent requirements for some example applications are given in Table 4-19.

Table 4-19. Approximate Reagent Requirements for Various Waste Types Using a Portland Cement/Fly Ash Solidification[1]

Waste	Kilograms of reagent per liter of waste
Spent brine	3.8
Metal hydroxide sludge	2.4
Copper pickle liquor sludge	1.9
$FeCl_2$ pickle liquor sludge (1.5 percent HCl)	3.5
Sulfuric acid plating waste (15 percent (H_2SO_4)	3.8
Oily metal sludge	0.96

[1] After Stanczyk, Senefelder, and Clarke (1982). The proportion of portland cement to fly ash was not given.

b. Applications.

(1) Most large, hazardous waste landfills are currently employing sorption to satisfy requirements prohibiting burial of liquids. Nineteen million liters (five million gallons) of oil sludge from a former refinery site was landfilled onsite after treatment with cement kiln dust. The process required 3.71×10^7 kg (40,939 tons) of kiln dust.

(2) Lime-fly ash solidification/stabilization systems have been successfully used in managing hazardous waste, but generally the containment performance is such that a hazardous waste after processing would still be classed as hazardous. Lime-fly-ash-pozzolan-based landfills have been established using liner and monitoring systems to ensure safe disposal. There have been cases where lead wastes were judged nonhazardous after treatment, but in most cases a pozzolan-treated waste is not delisted.

(3) Pozzolan-portland-cement-based systems are among the most versatile. They can neutralize and seal acids and can handle strong oxidizers such as chlorates and nitrates. These methods are also good for solidifying many toxic metals, since at the pH of the cement (pH 9-11), many metals are insoluble carbonates and hydroxides.

c. Advantages/Disadvantages.

(1) Sorption has been widely used to eliminate free water and improve handling. Some sorbents have been employed to limit the escape of volatile organic compounds. Sorbents may also be useful in waste containment when they modify the chemical environment and maintain the pH and redox potential to limit the solubility of the waste. Although sorption eliminates the bulk flow of wastes from the site, in many cases leaching of waste constituents from the sorbent can be a significant source of pollution.

(2) The major advantages of the lime-fly ash solidification/stabilization technique include the ready availability and low cost of materials, and the familiarity of commonly used equipment. A disadvantage is that the solid mass resulting from lime-based solidification is porous. As such, it must either be sealed or placed in a secure landfill to prevent leaching of contained wastes. Another major disadvantage is that sludge or wastes containing organics cannot be treated.

(3) Provided pozzolan-portland cement based systems are used on compatible wastes, the short-term effectiveness can be expected to be quite good. The equipment for cement mixing is commonplace and the process is quite tolerant of chemical variations. However, because cement is a porous solid, contaminants can be leached out of the matrix over time and, therefore, these systems are usually not effective for organic wastes. Although it is possible to seal the outside of a block of cement-solidified wastes using styrene, vinyl, or asphalt to prevent leaching, no commercial systems are available to do this.

d. Data Requirements. The principal data requirements for solidification/stabilization techniques include:

(1) Waste characteristics (binding agent selection).

(a) pH.

(b) Buffer capacity.

(c) Water content.

(d) Total organic carbon.

(e) Inorganic and organic constituents.

(2) Treatability tests (cure time, mix).

(a) Leachability.

(b) Strength.

e. Design Criteria. The key design parameters for solidification/stabilization techniques include:

(1) Solidification mixing ratios.

(2) Curing time.

(3) Volume increase of solidified product.

f. Evaluation. The evaluation of these factors is dependent on the solidification technology and the specific waste being treated.

4-22. Thermal Destruction.

a. Process Description. Incineration combusts or oxidizes organic material at very high temperatures. The end products of complete incineration are CO_2, H_2O, SO_2, NO_1, and HCl gases. Emission control equipment (scrubbers, electrostatic precipitators) for particulates, SO^2, NO_x, and products of incomplete oxidation are needed to control emissions of regulated air pollutants. Common types of incinerators most applicable to hazardous waste include:

(1) Rotary kilns.

(2) Multiple hearth.

(3) Fluidized bed.

(4) Liquid injection.

The key features of incineration methods cited previously are summarized in Table 4-20.