FUEL & MINERAL RESOURCES, INC.

DOE/ET/12072-T17
(DE83003774)
Distribution Category UC-91

CRITICAL REVIEW, COMPARATIVE EVALUATION, COST UPDATE, AND BASELINE DATA DEVELOPMENT SERVICES IN OIL SHALE MINING, IN-SITU LIQUEFACTION, AND ABOVE GROUND RETORTING PROCESSES FROM THE ENVIRONMENTAL, PERMITTING, AND LICENSING VIEWPOINTS

VOLUME II

OIL SHALE INDUSTRY POLLUTANT CONTROL TECHNOLOGY

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CONTRACT NO. AC01-78ET12072

DOE CONTRACT ET-78-C-01-2628/16600-004-064
TASK 16600-004-064-E0109-02

JANUARY 28, 1981

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EXECUTIVE SUMMARY

The present volume is the second major deliverable of the title study. The first volume was dedicated to process engineering descriptions of six oil shale retorting technologies (or processes), namely: Paraho, Tosco II, Oxidental Modified In-Situ, Rio Blanco, Union Oil, and Superior Oil. The current volume provides brief, but comprehensive descriptions of the annotated state of the art of the most popular control technology options discussed today in the oil shale literature. All process engineering references listed in our Volume I - Oil Shale Retorting Process Engineering have been thoroughly studied. All Pollutant Control Technologies suggested in these studies as potential remedies to air pollutants, particulates, liquid effluents, sewage, and solid waste are qualitatively discussed in the present volume. Sources for these control technology descriptions are reference databooks in environmental engineering on file with the FMR library. Additional databooks, handbooks, and reference manuals were obtained from local libraries with which the FMR library maintains active interloan agreements. A partial list of the sources utilized in the present volume is provided in the reference section.

In a third volume of the present series, a quantitative record of pollutant emission levels and make-up in all key unit operations of the six process flowsheets will be compiled. The exact position of the controls to be instigated will be identified in a given flowsheet. In other words, Volume III will provide the analytic discussion as to where, how, and when the Control Technologies presented in Volume II will be installed on the processes described in Volume I.

The present second volume of the series is organized into three parts:

A. Gaseous Effluents Control Technology and Sewage Engineering
B. Liquid Effluents Control Technology and Sewage Engineering
C. Solid Waste Disposal Technology

In Part A of the present study the key types of gaseous effluents and particulates controls are qualitatively described. These types of controls are:

- Baghouses
- Cyclones
- Wet Collection Devices
- Water Sprays
- Electrostatic Precipitation

In addition to the above control technologies applicable in general to most gaseous effluents and particulates, specific treatment has been given to the control technologies particularly applicable to three specific gaseous pollutants of great concern to the oil shale industry. These pollutants are:

- Hydrocarbons
- NO_x
- Sulfur

A more comprehensive treatment of the pollution control technologies applicable to these three key types of pollutants is given in Volume III - Emission Source Identification and Source-Specific Pollution Control Applications. In this third volume all pollution control technologies potentially applicable to the oil shale industry are classified by specific key pollutant, i.e. H_2S, SO_2, Particulates, Arsenic, Mercury, Trace Metals, CO, NO_x, and Hydrocarbons.[2]

Part B of the present second volume of the series qualitatively describes the key types of control technologies applicable to liquid effluents. These technologies are:

- Ion Exchange
- Precipitation and Coagulation (Flocculation)
- Distillation
- Steam Stripping
- Sedimentation
- Filtration
- Adsorption
- Reverse Osmosis
- Flotation
- Air Stripping Ammonia Removal
- Stabilization Ponds
- Chemical Oxidation
- Biological (Trickling) Filtration
- Activated Sludge
- Nitrogen (Ammonia) Wastewater Controls

A systematic effort was made in the description of each technology to address two key issues:

- Operating Principles of the Controls Method
- Field of Applications of the Controls Method

Performance data based on actual tests of a subject controls technology on specific effluent flow streams are not provided in the present study. Comprehensive numerical performance data bases have been generated in another FMR study on behalf of the U.S. Department of Energy titled: "Computer Modeling of Oil Shale Environmental Controls".

The Part C of the present study focuses on technologies applicable to treatment of hazardous solid wastes. Again, operating principles and field of application are discussed, whereas numerical performance data are omitted.

A. GASEOUS EFFLUENTS AND PARTICULATES CONTROLS

1. BAGHOUSES

Suspended dust and fumes may be removed from an airstream by a number of different devices. For some time electrostatic precipitators have been used successfully by utilities to collect particulate emissions. But in recent years, air quality standards have been stiffened significantly; there has been a shift from high-sulfur to low-sulfur coals; and regulatory attention has begun to focus more and more on emissions of the fine particulates known to be most responsible for both health and visibility problems.

When high collection efficiency on small particle size is required, however, the most widely used method consists of separating the dust from the air by means of a fabric filter. The fabric is usually made into bags of tubular or envelope shape. The entire structure housing the bags is called a baghouse.

1.1 OPERATION

In understanding the mechanics of baghouse sizing and operation, there are two key parameters: air-to-cloth ratio and system pressure drop.

In simplest terms, pressure drop represents the energy required by a fan to pull flue gas through the system. Measured with a manometer in inches of water, a pressure drop reading of 4 in or less would typically be desired in a baghouse. Operation in excess of this level is expensive because of the amount of energy required to keep the system running.

Air-to-cloth ratio represents the most fundamental parameter of all because it determines the size (and thereby the cost) of the baghouse. It is calculated by dividing the volume flow of flue gas (ft^3/min; m^3/s) received by a baghouse by the total area (ft^2; m^2) of the filtering cloth. These ratios can and do vary among systems from about 1.6:1 upward to 3.4:1, a nominal ratio being 2:1. In the last instance, the baghouse would be constructed with 1 ft^2 (0.09 m^2) of bag area for every 2 ft^3/min (944 cm^3/s) of flue gas to be filtered.

It is important to note that baghouses can filter efficiently over a range of air-to-cloth ratios. The trade-off comes in the capital and operating costs involved. The higher the air-to-cloth ratio, the less fabric required and thereby the less structure and capital cost involved. But with the smaller amount of cloth, pressure drop may become more of a problem, forcing energy costs up. And more frequent cleaning may be required, meaning increased compartment downtime, additional flexing of bags, more opening and closing of valves, and the potential for reliability problems. Lower air-to-cloth ratios, on the other hand, produce more fabric area and therefore less resistance to gas flow, resulting in minimum maintenance and, it is hoped, lower pressure drops. Lower ratios, however, involve more equipment and higher capital costs.

Assuming a flow rate of 2 million ft^3/min (944 m^3/s) of flue gas to be filtered and an air-to-cloth ratio of 1.6:1, approximately 1.25 million ft^2

(116,250 m^2) of cloth would be called for. Inasmuch as one bag requires about 100 ft^2 (9.29 m^2) of material and costs about $100 installed, the capital cost for these bags alone would be approximately $1.25 million. Assuming a ratio of 3.4:1, the capital cost would be less than half that amount. Figure 1-1 shows a simple baghouse cut-away and Figure 1-2 diagrams a larger automatic baghouse design. Figure 1-3 shows a reverse-jet baghouse in cut-away.

In the filtering, a clean bag is not the most efficient collector. In fact, it is the collected dust on the inside of the bag, called the dust cake or the filter cake, that acts as the filtering medium.

Precoating with a relatively coarse dust is especially beneficial when a fine fume is being filtered. The precoat ensures a high efficiency immediately after the bags are cleaned, increases the capacity of the unit, and decreases the pressure loss. In many cases the additional expense of equipment for automatically precoating the bags would be repaid in additional usable life of the filter media, improved collection efficiency, and reduced draft loss.

The design of some simple baghouses may unintentionally result in automatically precoating the bags each time the unit is started. The inlet duct usually enters the baghouse through the dust-collecting hopper. At startup, some of the previously collected dust in the hopper is disturbed and serves as a precoat on the filter bags. Since the collected dust is usually agglomerated into relatively coarse particles, it is an effective precoat material. If, however, an excessive quantity of dust is deposited upon the filter media, the capacity of the unit is reduced and the resistance is increased unnecessarily.

Experience to date has shown that most emissions from baghouses occur after cleaning; less-frequent cleaning will prolong bag life and reduce maintenance; system pressure drop is intimately connected to how efficiently the bags are cleaned.

Baghouse cleaning is conducted in cycles on a regular, predetermined basis, with each compartment in a system sequentially shut down so that the filter cakes inside the bags can be cracked off. This cracking is accomplished in one of two basic ways, with a reverse gas system or a shaker.

In reverse gas cleaning, a gentle pulse of already filtered gas is turned back into the compartment and through the bags, causing the bags to partially collapse inward. This action knocks off the filter cake, which falls down through the thimble and cell plate into the hopper. In the shaker system, the bags are manipulated from the top so as to send a traveling wave down their length to dislodge the filter cake. Quite often a shaker system will also have reverse gas of deflate capabilities to assist in the cleaning.

An important aspect of efficient baghouse operation is the need to ensure a balanced distribution of particulates among baghouse compartments

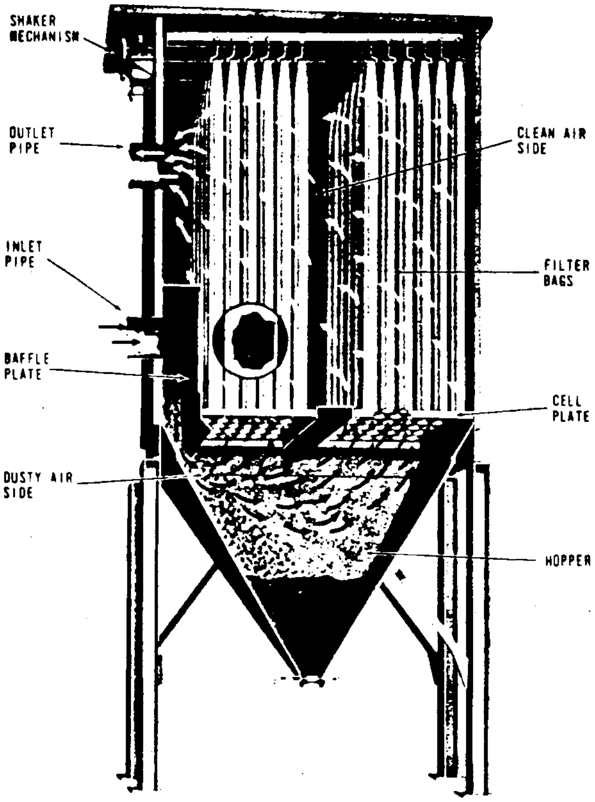

Figure 1-1 Typical Simple Baghouse with Mechanical Shaking

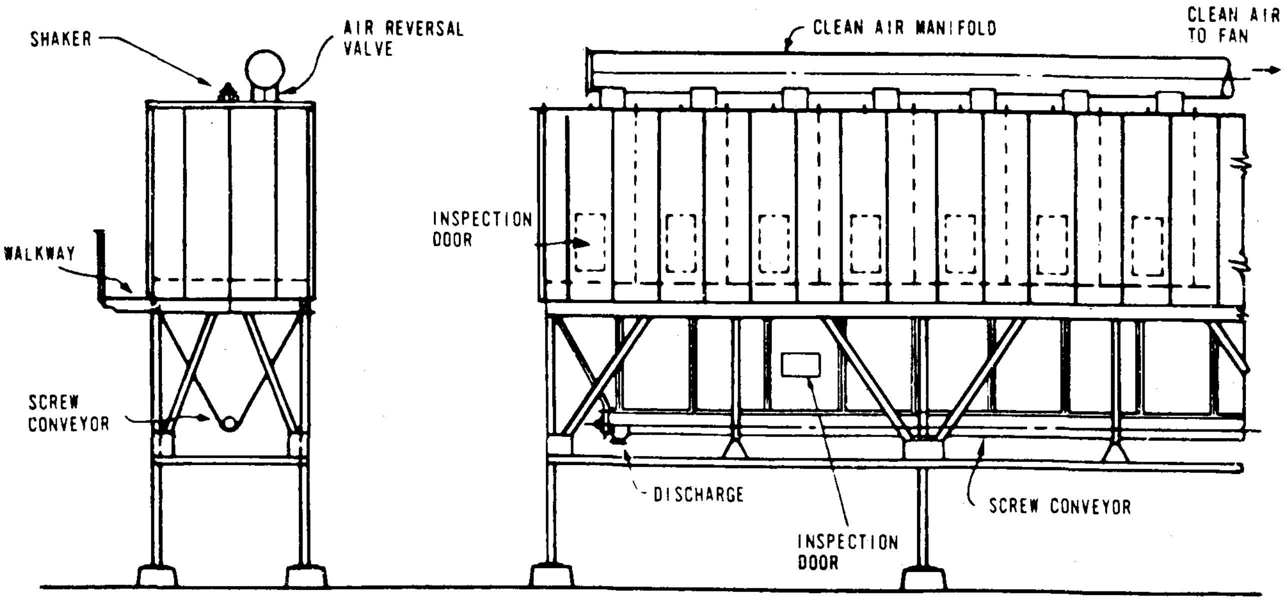

Figure 1-2 Fully Automatic Compartmented Baghouse with Hopper Discharge Screw Conveyor

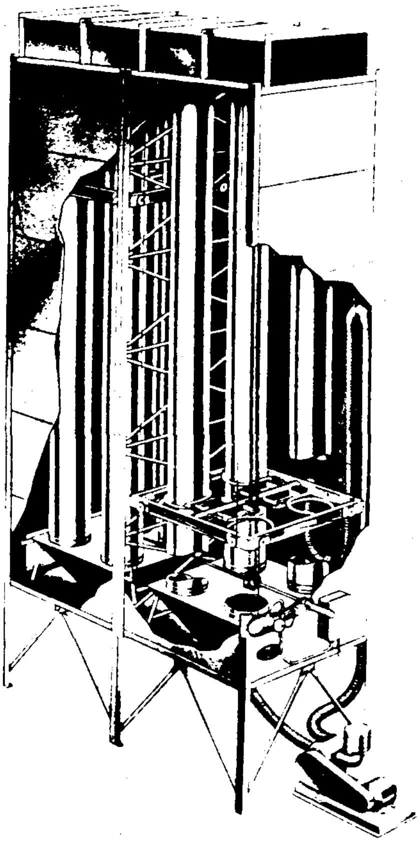

Figure 1-3 Reverse-Jet Baghouse

and among bags within those compartments. Without this balance, one or more bags or compartments could be overloaded, with consequent negative implications for overall system performance. To achieve a balance dust must be evently distributed within the gas flow. However, this task is difficult because particulates vary in size and density and an even gas flow does not necessarily mean an even dust distribution. Another difficulty is the tremendous quantities of gas the baghouses handle - as much as several million cubic feet a minute at speeds up to 50-60 ft/s (15-18 m/s).

Unequal dust distribution could occur, for example, because larger dust particles may not be able to negotiate ductwork turns as well as smaller ones, which would cause particles to segregate according to size in different regions of the baghouse. As a result, the whole character of the filter cake in those regions could be influenced. Excessive pressure drop represents yet another potential drawback of poor gas flow and duct design.

1.2 BAGHOUSE CONSTRUCTION

1.2.1 PUSHTHROUGH VERSUS PULLTHROUGH

The blower may be located on either side of the baghouse. If it is on the clean-air side, it is referred to as a pullthrough baghouse. This is desirable since it protects the blower from the dust or fume being handled. On the other hand, it does require a relatively airtight housing for the baghouse. The pushthrough type can be operated with open sides as long as protection from the weather is provided. This is advantageous when handling hot gases, since it permits a greater degree of cooling. Thus, a higher inlet gas temperature may be tolerated for the same temperature of the filtering media. For a pushthrough baghouse, however, the blower must handle the entire dust load. This frequently amounts to several hundred pounds of dust per hour, which may cause substantial wear to the blower. These blowers also require frequent dynamic balancing.

1.2.2 STRUCTURAL DESIGN

The gage of metal used to construct the baghouse walls, hoppers, and so forth must be adequate, and sufficient bracing must be provided to withstand the loads exerted. A pressure differential of 8 inches water column represents approximately 42 pounds per square foot. The total air pressure exerted on a side panel of a pullthrough baghouse may be in excess of 2 tons. Baghouses have been known to collapse as a result of this air pressure when inadequate bracing was provided. Pullthrough baghouses are more of a problem in this regard than the pushthrough type for two reasons. First, identical baghouse structures can withstand more internal pressure than external pressure without damage. Second, the pressure differential between the inside and outside of the baghouse housing is usually greater for a pullthrough installation than for an otherwise identical pushthrough type.

1.2.3 HOPPERS

1.2.3.1 SIZE

The size of the hoppers provided must be sufficient to hold the collected dust until it is removed for disposal. If the hopper is emptied once per day, it must be large enough to hold the total amount of dust collected in a full day's operation. Some reserve capacity should also be provided since the quantity of dust may vary from day to day depending upon variations in the basic process. If the hopper does not have adequate capacity, dust already collected becomes reentrained increasing the total dust load on the filter cloth and thereby the filter resistance. This is detrimental to the performance of the baghouse. Deflectors are often installed to minimize or prevent this reentrainment to some extent.

1.2.3.2 SLOPE OF HOPPER SIDES

The slope of the sides of the hopper must be sufficient to permit the dust to slide or flow freely. The design must also consider the possibility of bridging. Continuous emptying of hoppers will help to prevent bridging of material that has a strong tendency to do so. It will also prevent operating difficulties with materials that tend to become less fluid with time. For example, some materials have a tendency to cake if permitted to stand for a few hours or overnight. This is especially true of hygroscopic materials that absorb moisture from the air.

1.2.3.3 GAGE OF METAL

The gage of metal required for constructing hoppers depends upon the size of the hopper and the service. For small hoppers and light duty, 16-gage metal may be used. The gage should be increased as warranted by the size of the hopper and the total weight of the dust to be held at any one time. In addition, however, consideration should be given to the fact that workers frequently hammer on the sides of hoppers to assist the collected dust to flow freely from the discharge gate. If materials tend to stick or cake or are not freely flowing, some hammering on the sides of the hoppers will certainly result. Many hoppers have been badly dented as a result of rough treatment.

1.2.3.4 USE OF VIBRATORS AND RAPPERS

A much better solution than hammering on the sides of the hoppers is to provide mechanical rappers or vibrators. The most frequently used device is the electrically operated Syntron vibrator. Air-operated vibrators are also used extensively. A rapping device is highly desirable when a rotary discharge valve or screw conveyor is used. The rapper may be operated from a cam attached to the shaft of the rotary valve. In some cases the valve, rapper, and screw are all operated from a single electric motor.

1.2.3.5 DISCHARGE

Many baghouses, especially small, simple ones, use a slide gate at the bottom of the hopper to control the discharge of the collected dust from the hopper. The rotary valve is usually used on fully automatic units. The operation of the gravity trickle valve may be affected by the pressure in the baghouse. Figure 1-4 shows a baghouse hopper discharge valve.

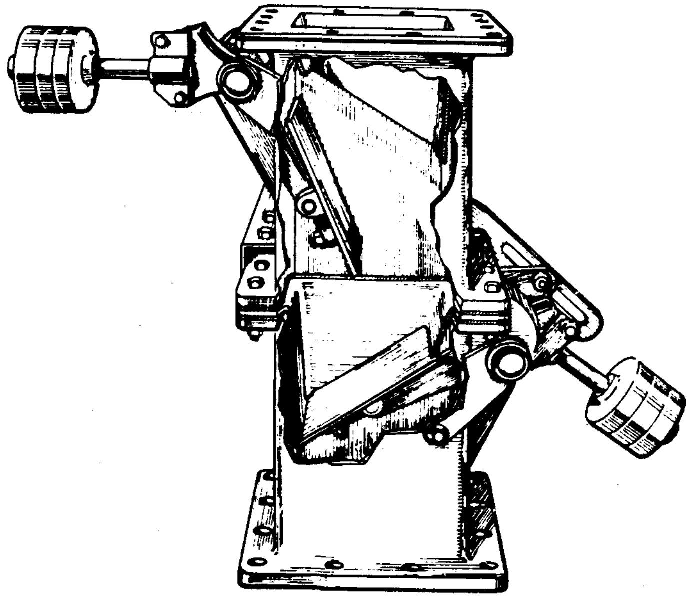

Figure 1-4 Baghouse Hopper Discharge Valve

1.3 FILTRATION PROCESS

Filter fabrics normally used to remove dust and fumes from airstreams are usually woven with relatively large open spaces, sometimes 100 microns or larger in size. Since collection efficiencies for dust particles of 1 micron or less may exceed 90 percent, the filtering process obviously cannot be simple sieving. Small particles are initially captured and retained on the fibers of the cloth by means of interception, impingement, diffusion, gravitational settling, and electrostatic attraction. Once a mat or cake of dust is accumulated, further collection is accomplished by sieving as well as by the previously mentioned mechanisms. The cloth then serves mainly as a supporting structure for the dust mat responsible for the high collection efficiency. Periodically the accumulated dust is removed for disposal. Some residual dust remains and serves as an aid to further filtering.

1.3.1 DIRECT INTERCEPTION

Under conditions normally existing in air filtration the flow is almost always laminar. For conditions of laminar flow, a small inertialess particle will remain on a single streamline. If the streamline passes close to an obstruction, such as a fiber of the filter fabric, and within a distance equal to the radius of the particle, the particle will contact the obstruction and will adhere because of the van der Waals forces. While no real particle is completely inertialess, small particles of 1 micron or less may be considered, without serious error, inertialess.

The shape of the streamlines is not affected by the airstream velocity in laminar flow, so that collection by direct interception is independent of velocity. The size of the obstruction is important since streamlines pass closer to small obstructions than they do to larger ones. Large particles are also collected more easily since the streamline need not pass as close, in the case of a larger particle, for the particle to contact the collecting surface. As the particle size increases, however, inertial forces rapidly increase and predominate.

1.3.2 IMPINGEMENT

When a particle has an appreciable inertia, it will not follow a streamline when the streamline is deflected from a straight path as it approaches an obstruction. Whether or not the particle contacts the surface of the obstruction and the size and inertia of the particle. As in the case of direct interception, smaller obstructions are more effective collectors for the mechanism of impingement or impaction and for the same reason. Other factors being equal, a particle with greater inertia is more likely to strike a collecting surface.

The inertia of a particle may be measured by its so-called stopping distance. This is the distance that the particle would travel before coming to rest if the streamline were to turn abruptly at 90 degrees.

Impaction is not a significant factor in collecting particles of 1 micron diameter or less. It is generally considered significant for collecting particles of 2-microns diameter or larger and becomes the predominant factor as particle size increases.

For effective collection of particles by inertial forces, the direction of the aerosol stream must change abruptly within a distance from the collector or obstacle approximately equal to or less than the stopping distance. Effectively, this requires a collector with a dimension perpendicular to the aerosol stream of the same magnitude as the stopping distance. Theoretical considerations indicate that the collection efficiency for a given size particle decreases as the collector size increases. Observations have shown that large fibers do not collect small particles well. In fact, for a given size fiber and airstream velocity, there is a minimum particle size below which virtually no collection by inertial forces occurs. On the other hand, as fibers are made smaller, collection continues to improve down to the practical limits of fiber size.

The velocity of the airstream is important in impaction. Collection efficiency increases with increasing velocity since the stopping distance also increases with velocity. The underlying assumption is that the particle velocity is the same as that of the airstream, which is approximately true. If the velocity becomes excessive, however, the drag forces increase rapidly and may exceed the adhesive forces so that collected particles are blown off and collection efficiency decreases.

The fibers of filter fabrics are in general relatively large compared with the size of the particles to be collected. Fibers of cotton and wool, for example, are about 10 to 20 microns in diameter. Fibers such as these are too large to be effective collectors for particles a few microns or less in diameter. Collection efficiency for fine dusts and fumes can, therefore, be expected to be poor until a dust mat is built up on the filter fabric. This has been verified by many field observations. For a short time after new bags are installed or immediately after the bags have been thoroughly cleaned, visible emissions bleed through the fabric. In most cases, bleeding ceases in a few seconds or several minutes at the most. In some cases where bleeding has been a problem after each cleaning cycle, reducing the cleaning effectiveness has been found helpful.

Filter fabrics are sometimes woven from a mixture of asbestos and wool fibers to take advantage of the smaller diameter of the asbestos fibers and to improve collection efficiency on fine dusts and metallurigical fumes. Another method reported successful is the use of a relatively coarse dust as a precoat on the filter, which then becomes highly efficient on very fine dusts and fumes.

1.3.3 DIFFUSION

When particles are very small, of a dimension about equal to the intermolecular distance, or less than about 0.1 to 0.2 micron in diameter, diffusion becomes the predominant mechanism of deposition. Particles as small as these no longer follow the streamlines because collisions with gas molecules occur, resulting in a random Brownian motion that increases the chance of contact between the particles and the collecting surfaces. Once a few particles are collected, a concentration gradient is established that acts as a driving force to increase the rate of deposition. Lower air velocity increases efficiency by increasing the time available and hence the chance of contacting a collecting surface. Smaller collectors or obstructions also increase collection efficiency.

1.4 MAINTENANCE

1.4.1 SERVICE

Every mechanical device, no matter how well designed and constructed, must be serviced periodically if it is to continue to operate properly. A baghouse, even the simplest, is no exception to this rule. Maintenance is usually adequate when the collected dust has sufficient economic value. The self-interest of the operator then requires that the equipment be kept in optimum operating condition. In many cases, however, baghouses are installed because local air pollution regulations require it. When the baghouse is nonproductive, the operator has little motivation to maintain it in optimum condition; however, this is a foolish and shortsighted attitude. Unless the baghouse is properly maintained, the investment, large or small, is wasted. In many cases the additional expense required to recondition equipment, which has long been neglected, is as much or more than the expense of continually maintaining the equipment in optimum condition would have been.

A proper maintenance program requires establishing a schedule for the various operations that must be performed periodically. The hoppers should be emptied and the collected dust disposed of at least once a day. Depending upon the nature of the dust, the quantity collected, and the general severity of the service, the equipment should be thoroughly inspected at intervals of a week, a month, or quarterly. Moving parts such as the shaking mechanisms must be greased and oiled at intervals specified by the manufacturer. For baghouses in daily use, all bags should be examined at least once a week to determine whether any are showing wear. Bags having holes or rips should be replaced immediately. Frequently, trouble can be detected before it becomes fullblown. Large baghouses benefit by the maintenance of a chart on which the history of each bag is recorded. If bags in one area show a history of more frequent replacement than those in other areas, this should be investigated.

1.4.2 BAG REPLACEMENT

Some operators find it more economical to replace all the bags periodically before serious trouble begins to develop. If an individual bag develops a hole or a rip or shows any sign of wear, it is replaced when detected. The advantage of this maintenance schedule is that the overall cost may be lower compared with replacing bags only when they fail. In this particular case, experience with other, similar equipment indicates that bag failures generally occur between 1 and 2 years after installation, with an average life of 18 months. Thus, after a year, frequent replacements would be required. The labor required to replace a bag when one bag is replaced at a time can be estimated to be approximately ½ to 1 man-hour. If an entire section (375 bags) is replaced at one time, the greater efficiency reduces the labor required to about 0.086 man-hour per bag. While the labor and material cost of group replacement is not necessarily less, there are many other advantages. The baghouse in Figure 4-1 serves a furnace operated 24 hours per day, 7 days per week. When a bag failure occurs, the baghouse must be shut down while the bag is replaced. This means that the furnace must shut down or a citation will be received for excessive emissions. Obviously, lost production time is expensive. When group replacement is used, service is scheduled to coincide with furnace shutdown for relining without loss of production.

Each operator must decide which method is best in respect to his own operating experience, the anticipated bag life, and the material and labor cost. Also to be considered is whether or not the equipment can easily be shut down when trouble develops.

Replacement of one or several bags in a large baghouse is not usually desirable though it is sometimes unavoidable if an individual bag becomes defective. In this case, the resistance of the new bags during the initial startup will be very low compared with that of the older bags. As a result, the filtering velocity through the new bags will be many times in excess of the normal rate. This could result in blinding of a new bag during the first few minutes of operation. It would be desirable to take the precaution of returning the equipment to service gradually in such cases, but baghouses are not normally designed and constructed in a manner that permits this to be done.

1.5 DISPOSAL OF COLLECTED DUST

Once the dust is collected in a baghouse, it must be disposed of without creating a new dust problem. Occasionally one sees dust dropped on the ground from the collecting hopper of a baghouse. The wind then picks it up and blows it around the neighborhood. The result is substantially the same as if the dust had not been collected in the first place.

The most common means of disposing of the collected dust is to transfer it from the hopper of the baghouse into a truck and then to a dump. In order to minimize dust emissions during transfer from the hopper to the truck, a sleeve or sock of canvas is frequently installed on the outlet of the hopper. The sleeve should be sufficiently long to reach the floor of the truck body. The dust must then be thoroughly wetted with water before it is transported to the dump. This method is suitable for installations wherein the quantity of dust collected is such that emptying the hopper once a day is sufficient. When the quantity of dust collected is greater, the hoppers must be emptied more frequently. Some type of automatic or semiautomatic method is then advisable.

1.6 FUTURE DEVELOPMENT

Research is being done toward applying baghouse technology to provide a one-step process for eliminating both particulate and SO_2 emissions from flue gases. Combining the SO_2 removal and baghouse technologies a spray-drying unit is being developed to begin operations in mid-1981.

As flue gas enters the facility, it will be sprayed with an alkaline reagent in a slurry; this will convert the SO_2 into a dry, solid product that can be filtered out with the fly ash particulates in the baghouse.

A second system, capable of performing the same function and favored for its simplicity is now scheduled for testing. Because chemical reaction with the SO_2 is thought to occur principally in the region of the filter cake inside the bag, a 100% dry sodium-based reagent is injected into the flue gas by sprinkling it in the ductwork upstream of the baghouse. If the system proves to be technically and economically feasible, it would help to reduce materials handling problems associated with wet sludge, and eliminate water consumption in flue gas desulfurization.

2. CYCLONES

Cyclones are the most widely used devices for collecting medium- and course-sized particulates. The construction of inertial separators is usually relatively simple, and initial costs and maintenance costs are generally lower than for most other types of dust collectors. Collection efficiencies, however, are usually not high. Although suitable for medium-sized particulates (15 to 40), ordinary inertial separators are generally unsuitable for fine dusts or metallurgical fumes. Dusts with a particle size ranging from 5 to 10 microns are normally too fine to be collected efficiently. In some cases, however, small-diameter, high-efficiency cyclones can be effective in collecting particles in the 5-micron range.

Inertial separators operate by the principle of imparting centrifugal force to the particle to be removed from the carrier gas stream. This force is produced by directing the gas in a circular path or effecting an abrupt change in direction.

2.1 OPERATION

Cyclonic collectors are round conically shaped vessels in which the gas stream enters tangentially and follows a spiral path to the outlet. The spiral motion produces the centrifugal forces that cause the particulate matter to move toward the periphery of the vessel and collect on the walls and fall to the bottom of the vessel. The centrifugal force is the major force causing separation of the particulate in a cyclone separator. This force (F_c) is equal to the product of the particulate mass (M_p) and centrifugal acceleration (V_p^2/R), where V_p is the particle velocity and R is the radius of motion (curvature).

$$F_c = (M_p)\left(\frac{V_p^2}{R}\right)$$

The centrifugal forces cause the particles to move outward the wall of the cyclone. However, this movement of the particle through the gas stream is opposed by fractional drag on the particle caused by the relative motion of the particle and gas. The frictional drag (F_f) is directly proportional to the product of (C_f), a drag coefficient, the projected cross-sectional area of the particle (A_p), particle density (p), the square of the particle velocity relative to the gas stream (V_r^2), and an inverse function of the acceleration due to gravity (g).

$$F_f = (C_f)\ (A_p)\ (p)\ (V_r^2)/2g$$

The centrifugal and frictional forces, plus the force of gravity, combine to determine the collection efficiency. This collection efficiency increases with:

(1) dust particle size
(2) particle density
(3) gas velocity
(4) cyclone body length
(5) smoothness of cyclone wall

Although efficiency increases with increasing gas velocity, this is at a lower rate than that at which the pressure drop increases. For a given cyclone and dust combination, an optimum velocity exists, beyond which turbulence increases more rapidly than separation efficiency, and efficiency decreases.

The cyclonic collectors are generally of two types: the large diameter, lower efficiency cyclones, and the small diameter, multitube high-efficiency units. The larger cyclones have lower efficiencies especially on particles less than 50μ. However, they have low initial cost and usually operate at pressure drops of 1 to 3 in. of water. The multitube cyclones are capable of efficiencies exceeding 90% but the cost is higher and their pressure drop is usually 3 to 5 in. of water. They are also more susceptible to plugging and erosion.

Cyclones can be designed to handle a wider range of chemical and physical conditions of operation than most other types of collection equipment can handle. Any conditions for which structural materials are available can be met by a cyclone, if the degree of collection falls within the operating range of the cyclone, and physical characteristics of the particulates are such that no fouling of the cyclone or excessive wall buildup occurs.

In the oil shale industry cyclones have potential application to these oil shale gaseous effluent streams: (1) grinding off-gases; (2) screening off-gases; (3) mining dusts; (4) retorting off-gases.

2.1.1 SEPARATION EFFICIENCY

The centrifugal force applied to particulates varies as the square of the inlet velocity and inversely as the radius of the cyclone. These factors have been combined into a dimensionless quantity called the separation factor:

$$S = \frac{V^2}{rg}$$

where

S = separation factor
V = inlet velocity, ft/sec
r = cyclone cylinder radius, ft
g = gravitational constant, 32.2 ft/sec^2.

It has not been possible to establish a definite correlation between separation factor and collection efficiency; yet, for cyclones of similar design and use, collection efficiency generally varies directly as a function of the separation factor.

The degree of collection efficiency is most dependent upon the horsepower expended. Hence, cyclones with high inlet velocities, small diameters, and long cylinders are generally found most efficient.

For high efficiency, the separating forces should be large and the dust removal effective so that separated dust is not reentrained. In general, cyclone efficiency increases with an increase in the following: (1) Density of the particulate matter, (2) inlet velocity into the cyclone, (3) cyclone body length, (4) number of gas revolutions (experiments indicate that the number of revolutions made by the gas stream in a typical simple cyclone ranges from 0.5 to 3 and averages 1.5 for cyclones of normal configuration), (5) ratio of cyclone body diameter to cyclone outlet diameter, (6) particle diameter, (7) amount of dust entrained in carrier gas, and (8) smoothness of inner cyclone wall.

An increase in the following will decrease the overall efficiency: (1) Carrier gas viscosity, (2) cyclone diameter, (3) gas outlet diameter, (4) gas inlet duct width, (5) inlet area, and (6) gas density.

A common cause of poor cyclone performance is leakage of air into the dust outlet. A small air leak at this point can result in an appreciable decrease in collection efficiency, particularly with fine dusts.

For continuous withdrawal of collected dust a rotary star valve, a double-lock valve, or a screw conveyor with a spring-loaded choke should be used.

Collection efficiency is noticeably reduced by the installation of inlet vanes, probably because of interference with the normal flow pattern. In general, all sorts of guide vanes, straightening vanes, baffles, and so forth placed inside an otherwise well-designed cyclone have been found of little value or actually detrimental. In some instances, for poorly designed cyclones, these devices have improved performance. Baffles designed to reduce leakage of air into the dust outlet are sometimes helpful. These consist of a horizontal, circular device installed on the cyclone axis near the dust outlet.

In practice, extensive agglomeration may be expected for dust concentrations greater than 100 grains per cubic foot and may be present at much smaller concentrations, depending upon the physical properties of the particulates being collected. Fibrous or tacky particles are especially apt to agglomerate. Agglomeration produces a larger effective particle size and thereby increases the efficiency of separation. Nevertheless, extremely sticky, hygroscopic, or similar material that could possibly plug the dust outlet or accumulate on the cyclone walls adversely affects cyclone operation. In addition, the agglomeration effect is reduced sharply when high inlet velocities are used. In some cases where agglomeration was significant, an increase in cyclone inlet velocity actually reduced the collection efficiency. Conversely, the efficiency was improved by reducing the inlet velocity.

Many investigations attempt to correlate cyclone performance with various parameters. Lapple (1951, 1963) treats the subject at length in several publications, introducing the concept of cut size (D_{pc}), which is defined as the diameter of those particles collected with 50% efficiency. Collection efficiency for particles larger than the cut size will be greater than 50% while that for smaller particles will be less. Another term used is the average particle size (D_p), which is simply the average of the size range. For example, if the size range is 10 to 15 microns, D_p = 12.5 microns.

2.2 TYPES OF CYCLONE SEPARATORS

2.2.1 SINGLE-CYCLONE SEPARATORS

A cyclone, which is an inertial separator without moving parts, separates particulate matter from a carrier gas by transforming the velocity of an inlet stream into a double vortex confined within the cyclone. In the double vortex the entering gas spirals downward at the outside and spirals upward at the inside of the cyclone outlet. This double-vortex is shown in Figure 2-1.

Because of its versatility and low cost, the single cyclone separator is probably the most widely used of the dry centrifugal separators. These cyclones are made in a wide variety of configurations.

As shown in Figure 2-2, this cyclone consists of a cylinder with a tangential gas inlet, an axial gas outlet, and a conical lower section with an axial dust outlet. The gas inlet is a rectangular opening, with the height of the opening equal to twice the width. The gas outlet is a tube approximately one half the diameter of the major cylinder, concentric with and extending inside the major cylinder to slightly below the lower edge of the gas inlet. The tangential, high-velocity gas entry imparts a circular motion to the gas stream; the particulates, because of their greater inertia, tend to concentrate on the wall of the cyclone. The inlet gas follows a double vortex path, spiraling downward at the outside and spiraling upward at the inside to the gas outlet. The downward spiral, assisted by gravity, carries the particulates downward to the dust outlet where they drop into a dusttight bin, or are removed by a rotary valve or screw conveyor.

The dimension ratios for the single cyclone shown in Figure 2-2 are given below:

Major cylinder diameter	D_c
Major cylinder length	$L_c = 2\ D_c$
Cone length	$Z_c = 2\ D_c$
Gas outlet diameter	$D_e = \frac{D_c}{2}$
Gas outlet length	$H_c + S_c = 5/8\ D_c$

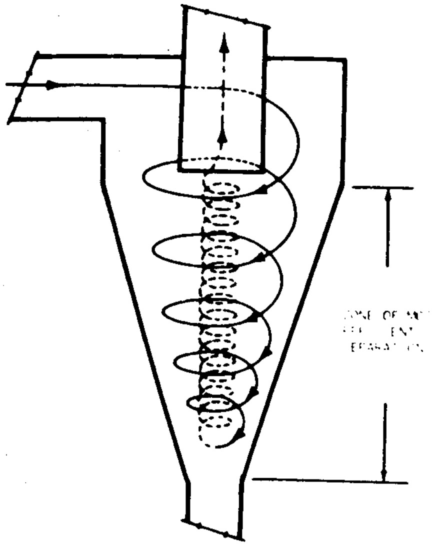

Figure 2-1 Double-Vortex Path of the Gas Stream in a Cyclone

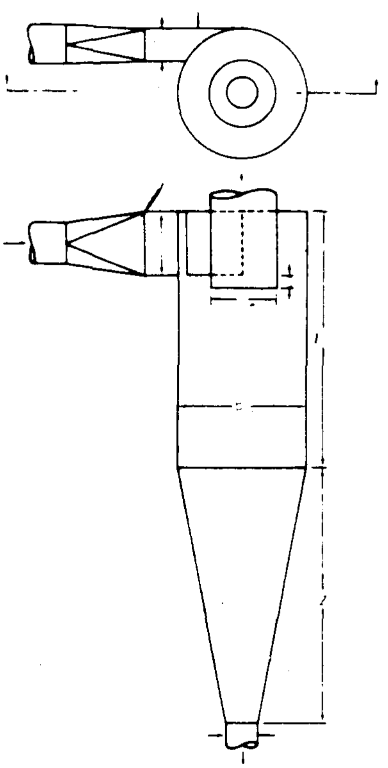

Figure 2-2 Single High-Efficiency Cyclone with Typical Dimension Ratios

Gas inlet height $H_c = \frac{D_c}{2}$

Gas inlet width $B_c = \frac{D_c}{4}$

Dust outlet $J_c = \frac{D_c}{4}$

2.2.2 MULTIPLE-CYCLONE SEPARATORS

A multiple-cyclone separator consists of a number of small-diameter cyclones operating in parallel, having a common gas inlet and outlet . The flow pattern differs from that in a conventional cyclone in that the gas, instead of entering at the side to initiate the swirling action, enters at the top of the collecting tube and has a swirling action imparted to it by a stationary vane positioned in its path. The diameters of the collecting tubes usually range from 1 foot to as small as 2 inches. Properly designed units can be constructed that have a collection efficiency as high as 90% for particulates in the 5- to 10-micron range.

Figure 2-3 diagrams a patented multiple cyclone separator. There is shown a first stage centrifugal particle separator unit (1) having a gas inlet opening (2) leading into gas-particle distributing chamber (3) which is defined by a lower horizontal tube sheet (4) and an upper sloping tube sheet (5). The horizontal tube sheet (4) supports the upper ends of a plurality of centrifugal separator tubes (6) which in turn are provided at their inlet ends with a plurality of sloping or spiral shaped vanes (7). These vanes are spaced peripherally around the inside upper wall portions of the separator tubes (6) and externally around the mid portions of axially positioned gas off-take tubes (8). The cleaned gas stream rising from the tubular members (8) and from an outlet plenum section (9) is discharged by way of outlet port (10). Within each of the separator tubes (6), the centrifugal flow of the gas stream, as provided by the spiral vanes (7), effects the usual outward spin-off of particles to the inner walls of each of the tubular members (6). The particles then fall on through the lower ends of each of the tubes to the lower discharge end of a bin or particle collection hopper (11). The latter is provided as the lower portion of the separator (1) in order to support tube sheet (4) and to enclose the area around the plurality of separator tubes (6). Collected particles are continuously discharged from the hopper (11) by way of outlet (12) to suitable conveyor means not shown in the drawing.

In accordance with one embodiment of the device, a removable or adjustable open-ended aspirator tube (13), with a flared lower end section (14) is positioned within the upper portion of the bin section (11) whereby a gaseous stream carrying the more finely divided particles may be pulled from the bin zone and carried to a secondary fine particle collector section, indicated as (15). Aspirator tube (13) is shown as being slidable within an upper tube section (16) extending through the plenum sections (3) and (9) and connective with an upper transfer conduit (17). The latter in turn connects with the inlet section (21) of the second stage collector (15) whereby fine particles may

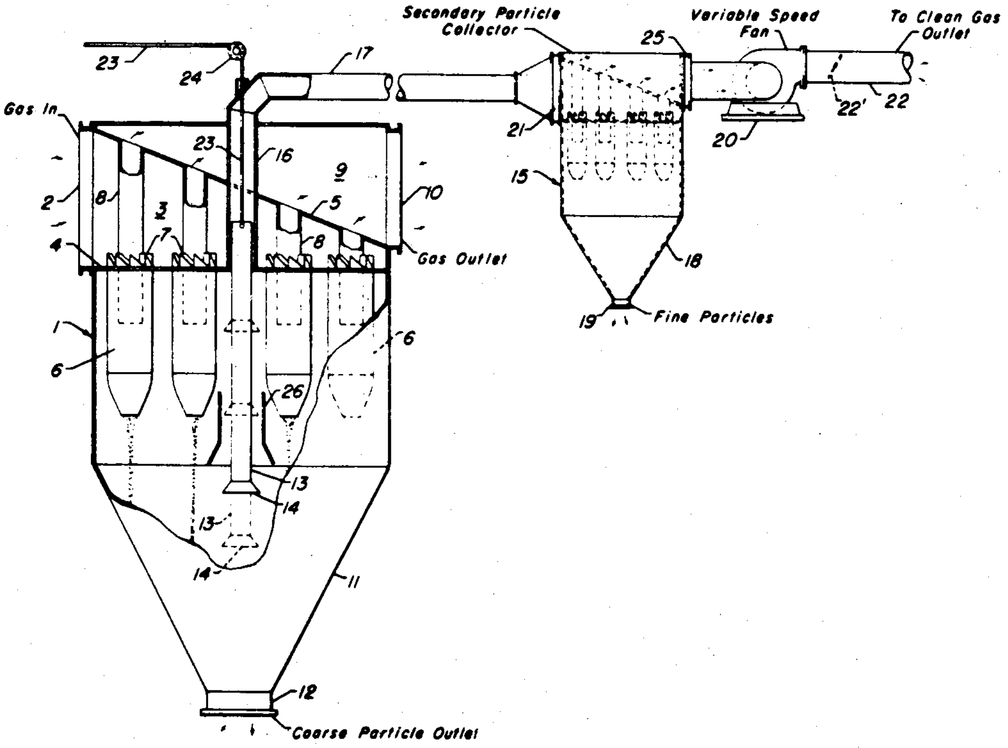

Figure 2-3 Multiple Cyclone Separator Device for Separation and Classification of Particles. (Source: A. A. Peterson; U.S. Patent #3,365,058; Jan. 23, 1968)

be collected in a hopper section (18) and discharged by way of outlet (19) for disposal or for reuse in a particular processing operation. A suction fan (20), which in turn is operated by a motor with adjustable speed driving means is shown connecting with the outlet section (25) of separator (15) to provide suction through the collector (15) and to the aspirator tube (13). The suction fan (20) is also shown as discharging a cleaned gas stream to suitable outlet duct means (22) with a flow control valve means (22).

In order that there may be adjustability for the lower gas intake end of the aspirator tube (13) and varying classifications in particle sizes for the particles being separated by centrifugal separator tubes (6) and fed into the hopper (11), there is indicated a cable means (23) connected to the upper end of the aspirator tube (13) and working over pulley means (24) that is connective with a winch or other adjustment means not shown. Thus, any desired gas intake level may be obtained by the adjustment of cable (23) causing the intake end (14) of aspirator tube (13) to be positioned at any desired level within bin (11). A dust shield (26) is shown positioned between the aspirator tube (13) and the nearest of the particle separator tubes (6) such that there is no strong interference of particle flow from these separator tubes.

Although not shown in the drawing, there also may be varying types of other baffle means or grids spaced below the outlet ends of the collector tubes in order to preclude the effects of eddy action from interfering with particle classification. In the operation of the classifier-collector system, as hereinbefore noted, there will be a greater withdrawal of particles, including some of the heavier particles, where the aspirator nozzle (13) is lowered to a lowermost level in bin (11) such that the aspirated gas stream will have a greater proportion of heavier particles. Conversely, where the aspiration tube (13) is raised to a high level in bin (11), there will be a greater percentage of fine particles and a minimum of the heavier of coarse particles such that the aspirated gas stream from the upper portion of bin (11) will carry primarily ultra-fine particulates to the secondary particle collection zone (15).

It is to be understood that the secondary particle collector means need not be of any particular type but may comprise the centrifugal form, the electrostatic type or bag filtering means, depending upon the type of efficiencies desired in the collection of such fine particles or depending upon the degree of atmospheric pollution which may be permissible in a particular area. It may also be noted, that variations in the speed of fan (20) may be effected by adjustable drive means in combination with adjustments in the level of the gas intake for the aspirator tube (13) so as to provide still greater control of the particle classification being carried out between the first stage of collection in bin (11) and that being effected in the secondary stage (15). Still further, it should be pointed out that a similar type of adjustable level aspirator tube construction may be used in combination with a single large centrifugal separator being used for the first stage unit in lieu of the use of the multiple separator tube construction.

2.2.3 MECHANICAL, CENTRIFUGAL SEPARATORS

Several types of collectors are readily available in which centrifugal force is supplied by a rotating vane. Figure 2-4 illustrates this type of collector, in which the unit serves both as exhaust fan and dust collector. In operation, the rotating fan blade exerts a large centrifugal force on the particulates, ejecting them from the tip of the blades to a skimmer bypass leading into a dust hopper.

Efficiencies of mechanical, centrifugal separators are somewhat higher than those obtainable with simple cyclones. Mechanical, centrifugal separators are compact and are particularly useful where a large number of individual collectors are required. These units cannot, however, be generally used to collect particulates that cake or tend to accumulate on the rotor blades since these particulates cause clogging and unbalancing of the impellor blades with resultant high maintenance costs and shutdowns.

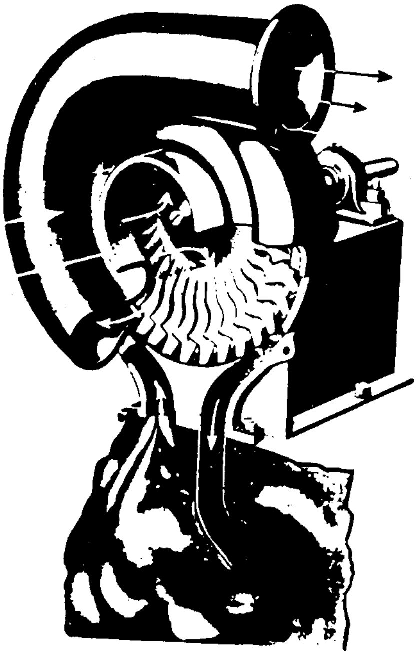

Figure 2-4 Mechanical, Centrifugal Separator

3. WET COLLECTION DEVICES

Wet collection devices use a variety of methods to wet the contaminant particles in order to remove them from the gas stream. There is also a wide range in their cost, their collection efficiency, and the amount of power they expend.

Wet collectors have the following advantages: They have a constant pressure drop (at constant volume), they present no secondary dust problem in disposing of the collected dust, and they can handle high-temperature or moisture-laden gases. They can also handle corrosive gases or aerosols, but corrosion-resistant construction may add materially to their cost. Space requirements are reasonably small. Disposal of the waste water or its clarification for reuse may, however, be difficult or expensive.

For collection of dusts and fumes, the baghouse is to be preferred over a scrubber. The positive collection mechanism of the baghouse ensures virtually complete collection of almost any dust or fume, whereas only the best scrubbers ensure good collection of very fine dusts and fumes. If, however, mists or hygroscopic particles are present in the effluent, a baghouse cannot be used. In many cases, a scrubber is the only choice. Mists that form freerunning liquids when collected can be successfully collected in an electrical precipitator. If, however, sticky or gummy materials are formed, removing the collected material is very difficult, and an electrical precipitator is then impractical.

Wet collectors use water "sprays" to collect and remove particulate matter. There are many variations of wet collectors but they may generally be classified as low or high energy scrubbers. Low energy scrubbers of 1 to 6 in. of pressure drop may consist of simple spray towers, packed towers or impingement plate towers. The water requirements may run 3 to 6 gal./1,000 cu. ft. of gas and collection efficiencies can exceed 90 to 95%. The lower energy scrubber finds frequent application in incinerators, fertilizer manufacturing, lime kilns, and iron foundries.

The high energy scrubber, or Venturi, imparts high velocity to the gas stream by means of converging-diverging duct section, and contacts the stream with injected water. The high velocities provide increased collection efficiency, up to 99.5%, but the pressure drop may range from 10 to 60 in. of water. This requires a draft fan with high power imput.

The wet scrubbers can provide high collection efficiency but may involve treatment of liquid wastes with settling ponds. They also saturate the gas stream and produce a resultant steam plume. The principal mechanisms involved in wet scrubbing are: (1) increasing the size of the particles by combination with liquid droplets thereby increasing their size so they may be collected more easily, and/or (2) trapping them in a liquid film and washing them away.

The particles can be wetted by the following mechanisms:

- Impingement by spray droplets. A spray directed across the path of the dust particles impinges upon them with an efficiency proportional to the number of droplets and to the force imparted to them. Johnstone and Roberts (1949) states that the optimum droplet particle size is about 100 microns. Above 100 microns there are too few droplets and below 100 microns, the droplets do not have sufficient force. Fine spray is effective by another mechanism, diffusion.

- Diffusion. When liquid droplets are dispersed among dust particles, the dust particles are deposited on the droplets by Brownian movement or diffusion. This is the principal mechanism in the collection of submicron particles. Diffusion as the result of fluid turbulence may also be an appreciable mechanism in the deposition of dust particles on spray droplets.

- Condensation (Lapple, 1963). If a gas is cooled below the dewpoint in passing through a wet collector, then condensation of moisture occurs, the dust particles acting as condensation nuclei. This effective increase in the particle size makes subsequent collection easier. Condensation is an important mechanism only for gases that are initially hot. Condensation alone can remove only relatively small amounts of dust, since the amount of condensation required to remove large concentrations is greater than can be achieved.

- Humidification and electrostatic precipitation have been suggested as mechanisms that facilitate collection of particles by causing them to agglomerate. These effects are not, however, well understood and cannot be relied upon to play any significant role in the collection mechanisms.

Several investigators have used wetting agents for scrubbing water in an effort to improve collection efficiency. In most cases, little or no improvement has been found (Friedlander et al., 1952). In order to be wetted, a particle must either make contact with a spray droplet or impinge upon a wetter surface. When either of these occurs, the particle is apparently wetted as adequately without the use of wetting agents as it is with their use.

Particles that have been wetted must reach a collection surface if the collecting process is to be completed. They may be impinged against surfaces placed in the path of the gas flow; or centrifugal action may be used to throw them to the outer walls of the collector; or simple gravity settling may be employed.

Dust collection efficiency is believed by some investigators to be directly related to contacting power and the properties of the particulate matter. Contacting power is that portion of useful energy expended in producing contact of the particulate matter with the scrubbing liquid, as well as in producing turbulence and mixing in the scrubber device. The contacting power represents the kinetic energy or pressure head loss across the scrubber, kinetic energy or pressure head drop of the scrubbing liquid, and other forms of energy dissipated in the gas stream such as sonic energy or energy supplied by a mechanical rotor. This means that the higher the power input, the higher is the efficiency. However, the efficiency is also a function of the particulate matter properties and the smaller particles require higher power input than larger particles.

3.1 TYPES OF WET COLLECTION DEVICES

3.1.1 Spray Chambers

The simplest type of scrubber is a chamber in which spray nozzles are placed. The gas stream velocity decreases as it enters the chamber, and the wetted particles settle and are collected at the bottom of the chamber. The outlet of the chamber is sometimes equipped with eliminator plates to help prevent the liquid from being discharged with the clean air stream. The spray chamber is extensively used as a gas cooler. Its efficiency as a dust collector is low except for coarse dust. Efficiency can be improved by baffle plates upon which particles can be impinged. Water rates range from 3 to 8 gallons per minute (gpm) 1,000 cfm.

3.1.2 Cyclone-Type Scrubbers

Cyclone-type scrubbers range from simple dry cyclones with spray nozzles to specially constructed multistage devices. All feature a tangential inlet to a cylindrical body, and many feature additional vanes that accentuate the cyclonic action and also act as impingement and collection surfaces.

Some investigators disagree on the most effective placement of spray nozzles; however, the principal benefit is derived from the wetted walls in preventing reentrainment of separated material. The gas enters tangentially at the bottom of the scrubber and pursues a spiral path upwards. Liquid spray is introduced into the rotating gas from an axially located manifold in the lower part of the unit. The atomized fine-spray droplets are caught in the rotating gas stream, and are, by centrifugal force, swept across to the walls of the cylinder, colliding with, absorbing, and collecting the dust or fume particles en route. The scrubbing liquid and particles run down the walls and out of the bottom of the unit; the clean gas leaves through the top.

Since centrifugal force is the principal collecting mechanism, efficiency is promoted by comparatively high gas velocities. Pressure drop varies from 2 to 8 inches water gage, and water rates vary from 4 to 10 gpm per 1,000 cfm gas handled.

A scrubber developed by L.C. Hardison, E.H.R. Pegg, D.E. Reedy and J.M. Barr; U.S. Patent 3,546,851; December 15, 1970; assigned to Universal Oil Products Company is a two-stage scrubber unit combining a cyclone and liquid mixing and spray means in the inlet thereof with a frusto-conical tube having

360° of slotted passageways for upward flow through an axially positioned diverging frusto-conical path so as to obtain the effects of further gas-liquid mixing. Separated entrained particles and liquid are returned to the lower end of the unit and a liquid level is maintained therein to be at the lower end of the center cone section and adjacent to the slotted gas inlet openings thereto around the periphery of the cone.

Figure 3-1 shows sectional plan and elevation views of such a scrubber design. There is indicated a vertically oriented housing section (1) having a tangential laden gas inlet (2) and an upper cleaned gas outlet (3). The lower end of the housing, above a bottom plate (4) is provided with a sloping interior plate section (5) which in turn provides for a sloping bottom to a liquid retaining section (6).

Positioned axially within the central portion of the housing (1) is a frusto-conical section (7) which is open at each end thereof and arranged to diverge upwardly to an enlarged upper and portion (8). The lower end of the cone section (7) is provided with a plurality of slots (9) that extend around the entire periphery thereof so as to permit 360° of inward flow of an entire gas stream from the interior of the housing (1). Positioned adjacent the top portion of cone (7) and extending transversely across the entire interior of the housing (1) is a sloping transverse partition member (10) which, in turn, is provided with an opening (11) leading into a depending pipe (12). The latter preferably extends downwardly into the lower end portion of the housing to a level slightly below the lower end of the cone section (7) such that its open lower end is within the liquid 6 maintained in the lower end of the housing. The provision for recirculating the scrubbing liquor from above partition (10) into the liquid retaining section (6) is, of course, of desirable economic advantage.

Within the upper portion of the housing (1) and spaced above the open end (8) of the cone section (7) there is a deflector plate or cone member (13) which will serve to preclude the direct outward flow of the scrubbed gas stream from the cone section (7) to outlet (3). In other words, the gas flow will be channeled laterally by deflector cone (13) into a gas-liquid separation zone (14) and thence permitted to enter the outlet section (3). Any liquid droplets which are entrained with the gas stream from the top of cone section (7) will impinge upon the lower side of the plate (13) and then drop therefrom into a liquid collection zone (15) provided above the top of transverse plate (10) and below the top level of cone section (7). In the combination with the laden gas inlet (2) there will be provided a suitable spray means (16) which is supplied with water, or other scrubbing liquid, from line (17) with control valve (18). Thus, as noted hereinbefore, there will be the provision for effecting the initial spraying and wetting of entrained particulates in the gas stream entering the tangential gas inlet (2). As the liquid sprayed gas stream enters the interior of housing (1) there will preferably be a wetting of the entire cross-section of the stream and then a resulting centrifugal flow of the entire gas stream at high velocity so as to centrifuge wetted particulates to the interior wall of the housing (1) where they are permitted to descend into the liquid retaining zone (6). The gas stream, with at least a substantial portion of all of the larger particulates removed, will then be forced to

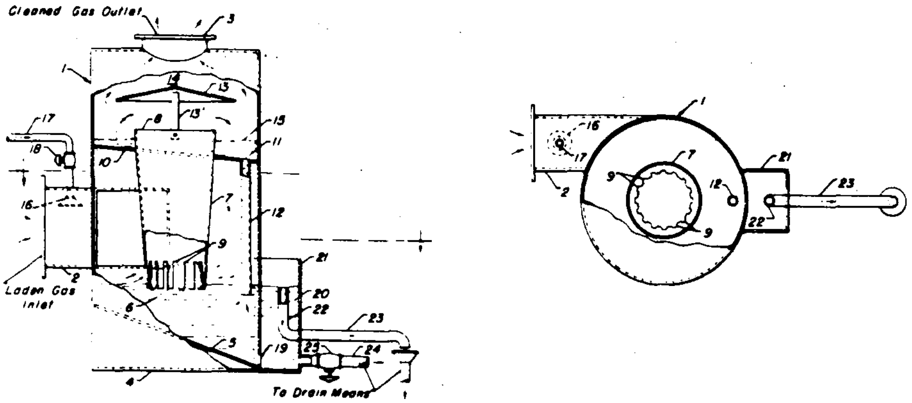

Figure 3-1 Two Stage Scrubber Design Combining Wet Spray and Cyclone. (Source: L.C. Hardison, E.H.R. Pegg, D.E. Reedy and J.M. Barr; U.S. Patent #3,546,851; December 15, 1970)

flow through the slot means (9) around the lower end of the cone section (7) and then carry upwardly through the diverging cone to the separation section (14) prior to being discharged by way of outlet (3). Generally, the vertical height or length of the cone section (7) will be such as to permit a loss in velocity of the entrained liquid droplets and particulates so that a large portion of the liquid will be maintained within the interior height of the cone (7) and fall downwardly along the interior wall thereof to reach the zone of the slots (9). However, some portion of entrained liquid will carry to the under side of baffle plate (13) and drip from the edges thereof to the designed collection area (15).

Thus, in the actual operation of the unit, the high velocity entrance of the gas stream through the plurality of the narrow slots (9) will be for the full 360° of the cone and through wetted-wall slots such that there is again a high energy mixing of liquid with the gas stream to insure the wetting of all of the remaining particulates that may be entrained therein. The high energy and high velocity of the gas stream may also be such that it tends to entrain some additional liquid from the top surface of the liquid resevoir maintained with the lower zone (6) in the housing. It is thus obvious that there is provided by the design and arrangement an efficient two-stage liquid contacting of the gaseous stream. First, there is the initial liquid spray distribution in to the gas stream at the tangential gas inlet opening and a subsequent redistribution and wetting of the gas stream as it passes through the plurality of spaced slots (9). Such additional wetting of the redistributed stream results from the downward wetted wall flow in the cone section (7) and from the high level of liquid (6) maintained in the lower portion of the scrubbing chamber. The liquid discharge means from the reservoir zone (6) will be slightly above the level of the lower end of cone section (7) and slots (9); however, the level should not be so high as to block the gas flow area provided by the plurality of slots (9) and preclude proper gas flow into the interior of cone section (7).

Liquid flow with recovered and settled particulates will pass from the lower portion of liquid retaining section 6 by way of opening means (19) into an outer liquid discharge section (20) maintained within an outlet box means (21). The latter is preferably open-topped and shall carry to a height sufficient to be above the normal liquid level maintained in the liquid reservoir zones (6) and (20). The open top arrangement for the outlet box (21) will permit easy access into section (20) for removing undesired sediment or large sized debris that may tend to block normal liquid flow outwardly by way of stand pipe section (22) and pipe (23). Also, as a safety arrangement, there may be provided an overflow drain or funnel arrangement for receiving flow from pipe outlet (23) so that in the event of donwstream blockage, there can be overflow into a floor drain in other auxiliary drain means. The top of pipe (22) is carefully set so as to maintain the proper desired liquid level in zone (6) and at slots (9). In order to remove sludge or settled particles, there will be a separate lower outlet pipe (24) with valve means (25), to regulate the flow therefrom as may be required. The water addition rate through line (17) to nozzle (16) will be an amount that is in excess of that required for humidification of the laden gas stream and, in addition, sufficient to insure a free flow of liquid from the lower end of the unit to preclude clogging from solids concentration. The outlet means have at least one access opening which will permit the manual, or auxiliary pump, removal of settled particulates and the cleaning of any pipe slugging debris carrying to the lower outlet portion of the housing. Also, there shall be an overflow weir or other secondary drainage means to insure the removal of liquid from the bottom of the chamber where the liquid level rises above normal, but will spill over a predetermined height, so as to permit gas flow to continue inwardly through the slot means (9).

The entire gas scrubbing unit may be fabricated to be of varying sizes in order to accommodate varying quantities of particle laden gas flow, as well as of different materials to suit varying types of scrubbing liquid being utilized. Generally, water will be utilized as the scrubbing liquid except in those instances where the contaminated gas stream has fumes or particulates that indicates an advantage to having a particular type of scrubbing liquor. For example, an alkaline liquid may be used in order to assist in neutralizing the effects of an acidic contaminated gas stream. Also, although not shown in the drawing, there may be the addition of a suitable mist extraction means within the interior upper portion of the unit adjacent the gas outlet means.

The size of the interior axially positioned cone section (7) will vary in accordance with the gas flow quantity and its velocity, while the height of the housing (1) will normally vary in accordance with the desired height of the cone section (7). Generally, the cone will be of sufficient length and have sufficient length and have sufficient slope or upward divergence, to provide for a substantially complete de-entrainment of liquid from the gaseous stream as it carries upwardly for the full height of the cone section (7). Although, as noted hereinbefore, by providing the deflector plate (13) at a spaced distance above the cone section (7) there may be insured further adequate removal of entrained liquid and particulates and a baffling of the gas flow prior to its reaching the outlet zone (3). In this embodiment, the deflector cone (13) is indicated as being supported from spaced support members (13) carrying to the top section of the cone section (7); however, other suitable support means may be provided.

3.1.3 Venturi Scrubbers

In the venturi scrubber, the gases are passed through a venturi tube to which low-pressure water is added at the throat. Gas velocities at the throat are from 15,000 to 20,000 fpm, and pressure drops are from 10 to 0 inches water gage. Recirculation of water is feasible. The predominating mechanism is believed to be impaction. In spite of the relatively short contact time, the extreme turbulence in the venturi promotes very intimate contact. The wetted particles and droplets are collected in a cyclone spray separator, as shown in Figure 3-2. Water rates are about 3 gpm per 1,000 cfm gas. Very high collection efficiencies have been reported for very fine dusts.

A scrubber developed by I.S. Shah and A. Kirschner; U.S. Patent 3,567,194; March 2, 1971; assigned to Chemical Construction Corporation is a venturi-type gas scrubber which features a liquid projection lip in the approach section of the venturi. Scrubbing liquid is passed downwards on the wall of the approach section and is projected into the accelerated gas stream by the lip,

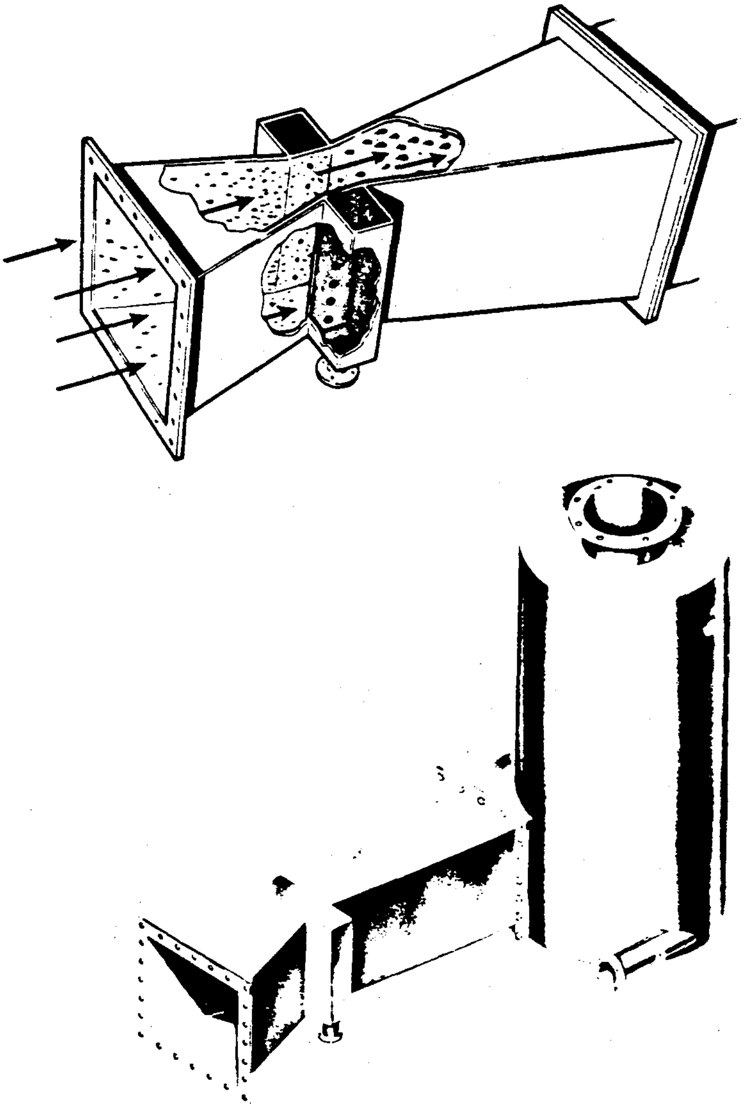

Figure 3-2 Venturi Scrubber

which terminates outside of the dimension of the throat section, so that the scrubbing liquid penetrates the gas stream through the entire throat section. In a preferred embodiment, the lip is removable and is disposed on a ring, with an additional frusto-conical baffle depending downwards from the lower surface of the lip adjacent to the ring and terminating inside the inner dimension of the lip. A central conical baffle may be provided, to define an annular venturi scrubbing passage.

In Figure 3-3 which shows a typical application of the device to the scrubbing of a waste gas derived from a steam power boiler or the like, fuel stream (1) which may consist of any suitable gaseous, liquid or solid fuel such as a fluid hydrocarbon or coal, is passed together with combustion air stream (2) into stream power boiler (3) for the generation of high pressure steam for electricity production. Solid ash is removed from unit (3) via stream (4) and the generated combustion flue gas containing entrained solid fly ash and sulfur dioxide is also removed from unit (3) via outlet stack (5) which in typical prior art practice discharges the flue gas to the atmosphere with resultant air pollution. In this process, the flue gas passes from unit (5) via stream (6) which flows downwards through the vertically oriented conduit (7) and into the apparatus.

Conduit (7) extends downwards and connects with the annular collar or trough (8) which connects conduit (7) with the inverted frusto-conical approach or converging baffle (9) which defines the converging section of the venturi passage. The annular tangential nozzles (10) are provided in the collar (8) and serve to pass scrubbing liquid streams such as stream (11) onto the inner surface of baffle (9) so that the scrubbing liquid flows downwards on the inner surface of baffle (9) in a whirling spiral flow path. Stream 11 may consist of water or a suitable aqueous alkaline solution which dissolves sulfur dioxide, in addition to scrubbing fly ash from the gas stream.

The scrubbing liquid film or layer which flows downwards on the inner surface of baffle (9) is projected by lip (12) into the accelerated gas stream, which flows at high velocity through the lower portion of the venturi passage defined by baffle (9) and the cylindrical throat section baffle (13) which depends downwards from baffle (9). The lip (12) is a generally horizontal ring-shaped annular member, which extends inwards from the inner surface of baffle (9) and terminates at a circular inner perimeter which is of greater diameter than the diameter of baffle (13) so that a convergence of a gas flow passage takes place between lip (12) and baffle (13). The liquid which is projected into the gas stream by lip (12) is dispersed into small droplets above and at the entry into the throat section defined by baffle (13) and effective scrubbing of the highly accelerated gas stream takes place within the throat section.

The resulting mixture of dispersed liquid droplets in the gas stream next flows downwards through the frusto-conical baffle (14) which depends downwards from baffle (13) and is provided to promote recover of gas pressure head without turbulence, thus providing a minimum overall loss of gas pressure or pressure drop through the device. The gas-liquid mixture next flows through cylindrical conduit (15) which depends from baffle (14) and conducts the mixture via stream (16) to

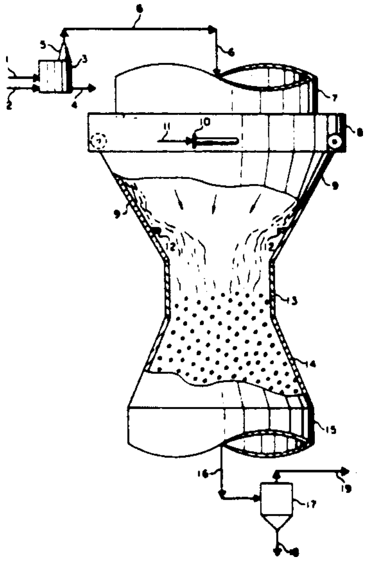

Figure 3-3 Wet Approach Venturi Scrubber Design (Chemico Design) (Source: I.S. Shah and A. Kirschner; U.S. Patent #3,567,194; March 2, 1971)

the gas liquid separator (17) which is a baffled or cyclonic vessel for the separation of scrubbed gas from the entrained liquid phase. The separated scrubbing liquid, now containing fly ash and sulfur dioxide removed from the flue gas, is removed from separator (17) via stream (18) which is discharged to waste or processed for recovery of dissolved sulfur dioxide or sulfites. The scrubbed flue gas is discharged from unit (17) via stream (19) which may now be safely discharged to the atmosphere without causing air pollution.

4. HYDROCARBONS

Except for hydrocarbon (HC) vapor losses during periods of abnormal operation, i.e. process vessel and equipment leaks, normal operations of the conceptual shale oil processes are expected to produce very low HC emission rates. Four basic approaches to hydrocarbon and carbon monoxide control that will be discussed here include: destruction, recovery and recycle, containment, and conversion.

Use is made of afterburners (direct flame incineration and catalytic incineration) for HC control by destruction. This control technique is applicable for combustible hydrocarbons which do not have a high recovered product market value, or which are too dilute to be economically recovered. The recovery and recycle control technologies include compression-condensation, condensation, and absorption systems. Each of these systems allows recovery of the controlled hydrocarbons and are most economical for hydrocarbons having a high market value. The third approach to hydrocarbon control is vapor containment, the principle behind adsorption systems. In adsorption systems, hydrocarbon emissions are trapped on the surface of an adsorbent such as activated carbon. These adsorbed hydrocarbons must later be removed or recovered by one of the other hydrocarbon emission control technologies. The last approach, conversion, involves utilizing the shift conversion process to react carbon monoxide with steam to form carbon dioxide and hydrogen.

4.1 AFTERBURNERS

Afterburners are gas cleaning devices which use furnace for the combustion of gaseous and particulate matter. Combustion is accomplished either by direct flame incineration or by catalytic combustion. The disposal of particulate matter by combustion is limited to residue-free vapors, mists and particulate matter which is readily combustible, as well as to particle sizes which require short furnace retention time and small furnace size. Afterburners are usually used to dispose of fumes, vapors, and odors when relatively small volumes of gases and low concentrations of particulate matter are involved.

4.1.1 DIRECT FLAME INCINERATION

Emission control by direct flame incineration (also termed thermal combustion) is widely used to control combustible gaseous materials such as hydrocarbon vapors, aerosols, and particulates. These systems are also used extensively in removing odors and in reducing the opacity of visible plumes from ovens, dryers, stills, cookers, and refuse incinerators. The principle of operation consists of ducting the exhaust process gases to a combination chamber which employs direct-fired burners to combust the process gases to their appropriate oxides. A well-designed plant flare system is a good example of control by direct incineration.

In direct flame incinerators, the combustible process gases are delivered to a refractory-lined incinerator by either the process exhaust system or by a self-contained blower. If the process gases do not have a sufficient heating value to sustain combustion, a metered fuel stream is combined with a portion of the process gases in the burner and then allowed to combust in the combustion zone. If the process gases have a high heating value, air must often be introduced at the burner instead of fuel. The remaining process gases are then introduced into the mixing zone where they are combusted. For maximum destruction of contaminants, the combusted gases are retained briefly in a reaction zone where additional oxidation occurs before being vented to the atmosphere. When sized and operating properly, most direct-flame incinerators will obtain 99+% destruction of hydrocarbon compounds. Most units are sized to operate at efficiencies between 95 and 99%.

Many components in the process gas stream form hazardous combustion products, such as: nitrogen oxides, sulfur oxides, hydrogen chloride, hydrogen fluoride, trace elements, and particulates. When required, the most common means of controlling these secondary pollutants is aqueous solution scrubbing. Noise can also be a problem in high turbulence incinerators, and is normally reduced through the application of standard acoustical technology.

Advantages of the direct flame incineration afterburner include: high removal efficiency of submicron odor-causing particulate matter; simultaneous disposal of combustible gaseous and particulate matter; compatibility with existing combustion equipment; relatively small space requirements; simple construction; and low maintenance. Disadvantages include: high operational costs including fuel and instrumentation; fire hazards; and excessive weight.

An incinerator developed by L.C. Hardison and W.L. Hable; U.S. Patent 3,189; December 16, 1969; assigned to Universal Oil Products Company for contaminated air streams uses the air content of said streams to provide all the oxygen requirements for the burning of the fuel. In this way handling and heating the primary air for the burner is eliminated. Figure 4-1 shows an elevation and transverse section of such an incinerator. There is provided a scroll of volute shaped contaminated air inlet section (1) which encompasses an internally positioned perforate frusto-conically shaped member 2. The latter is located within the eye portion of the inlet chamber (1) and encompasses a fuel inlet area or mixing zone (3) that is directly downstream from a fuel inlet nozzle (4). Downstream from the end of the perforate conically shaped member (2) and connective with the wall of the air stream inlet section (1) is an elongated housing section (5) which provides for an internal combustion zone (6) leading to a treated gas outlet port (7). The inner peripheral wall of the housing (5) is indicated as having a suitable insulating material (8) such that the combustion zone may withstand high temperature conditions, generally above 800°F. and up to 1500°F. or more. At the same time there is indicated a suitable annular passageway space (9) around the downstream end of the conical member (2) and within the upstream inner face of the liner (8) such that the major portion of the air stream entering scroll housing (1), but not entering the fuel inlet zone (3), can mix with the resulting flame and hot combustion gases being discharged from the latter.

The particular embodiments illustrated utilize a multiplicity of spaced holes (10) over the entire wall area of conical section (2) which will result in a corresponding multiplicity at small jet-like air streams entering the mixing zone

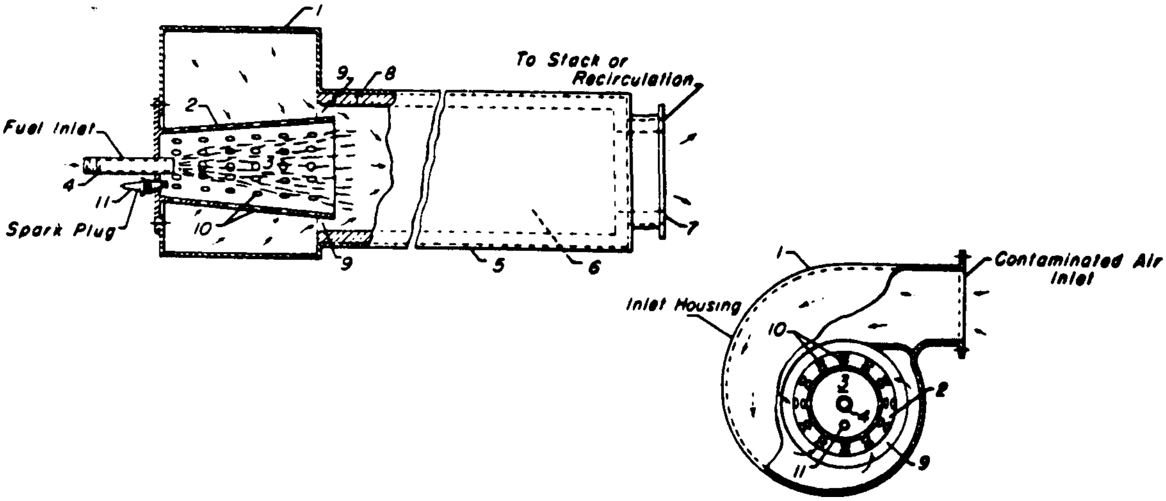

Figure 4-1 Thermal Incinerator Design (Source: L.C. Hardison and W.L. Hable; U.S. Patent #3,484,189; December 16, 1969)

(3) for admixture with the fuel from inlet (4) as secondary air. There shall be sufficient apertures (10) to insure an excess of oxygen into the mixing zone (3) and into admixture with the fuel stream to sustain a highly complete burning of all of the fuel being introduced to the unit. The fuel introduction will, of course, be predetermined to provide sufficient Btu output to in turn effect complete oxidation of the fumes or other components being entrained with the air stream entering housing (1). In order to insure jet-like streams of air through the apertures (10), the latter may be designed, for example, to provide from 2" to 3" of water column pressure drop. Also, in order to have initial combustion of fuel and air, a spark plug or other suitable ignitor means (11) is shown adjacent the burner nozzle (4) and within the confines of the inlet to mixing section (3). During normal or continuous incinerator operation, the spark plug means (11) need not be energized.

After ignition takes place between the fuel being introduced by way of nozzle (4) and a part of the air through openings (10), there will be sustained high temperature luminous flame and hot combustion gases which will be discharged from the downstream end of the mixing section (3) and into the combustion section (6). The annular passageway (9) to the latter also provides for the main portion of the contaminated air stream to spirally mix with the hot combustion gases and flame from section (3) for continued flow down through the elongated zone (6) to outlet (7).

4.1.2 CATALYTIC INCINERATION

Catalytic incineration is a widely used alternative to direct flame combustion for the control of combustible gaseous materials such as hydrocarbon vapors and aerosols. These systems are also used extensively in removing odors and in reducing the opacity of visible plumes from ovens, dryers, stills, cookers, and refuse incinerators. The principle of operation consists of ducting exiting process gases to an incineration chamber filled with a catalyst. Upon contact with the catalyst, the selected components of the process gases are oxidized. The use of a catalyst allows more complete combustion at lower temperature, resulting in lower fuel costs and more economic materials of construction. However, catalysts are generally selective and may not destroy as many components of the process gases as direct flame incineration. In addition, because of catalyst fouling and poisoning, pollutants must be free of smoke, particulates, and heavy metals and other catalyst poisons.

When sized and operated properly, catalytic incinerators will obtain 95% to 99+% destruction of selected compounds. Many catalysts are highly selective as to the reactions they promote. Although relatively reliable and simple to operate, catalytic incinerators are more complex than direct flame incinerators. Accurate, dependable fuel and/or air controllers are required to maintain close control of catalyst bed temperature in the midst of highly variable process gas heating values and flow rates. Catalyst beds are also highly susceptible to fouling and poisoning by halogens, heavy metals, and sulfur species. As a result, catalyst beds must be routinely cleaned and eventually replaced.

As in direct incineration, aqueous scrubbing may be required to remove secondary pollutants resulting from combustion. Likewise, standard acoustical technology may be required in high turbulence incineration.

Advantages of the catalytic afterburner include: reduced fuel requirements; and reduced temperature, insulation requirements and fire hazards. Disadvantages of catalytic afterburners include: high initial cost; sensitivity to catalytic poisoning; inorganic particles must be removed and organic droplets must be vaporized before combustion to prevent damage and plugging of the catalyst; and catalysts may require frequent reactivation.

4.2 COMPRESSION CONDENSATION

Compression-condensation systems are desirable for recovering concentrated hydrocarbon vapors from relatively small gas streams. The compression-refrigeration-absorption (CRA) recovery system is based on the absorption and condensation of compressed hydrocarbon vapors with cool liquid from storage. Compression-refrigeration-condensation (CRC) vapor recovery systems are based on the condensation of hydrocarbon vapors by compression and refrigeration.

In both systems, incoming vapors are first passed through a saturator where they are sprayed with fuel to insure that the hydrocarbon concentration of the vapors is above the explosive limit. This is performed as a safety measure to reduce the hazards of compressing hydrocarbon vapors. The saturated vapors are then compressed and passed through a condenser or heat exchanger. In the CRC system, most of the hydrocarbons are condensed in a condenser. Essentially hydrocarbon-free air is vented from the top of the condenser. In the CRA system, the compressed vapors are cooled in a heat exchanger prior to entering an absorber. In the absorber, the cooled vapors are contacted with chilled liquid product drawn from storage and are condensed and absorbed into the liquid. The remaining air, containing only a small amount of hydrocarbons, is vented from the top of the absorber.

The vapor collection efficiencies of both CRA and CRC systems are dependent on the inlet hydrocarbon concentration. Current CRA systems can surpass 90 percent recovery for inlet hydrocarbon concentrations of greater than 20 percent by volume. CRC units can recover 96 percent of the hydrocarbons in saturated gasoline vapors and 88 percent to 90 percent in subsaturated gasoline vapors.

No secondary pollutants are generated, but vent streams from a compression-condensation system may require incineration.

4.3 CONDENSATION

Condensation is usually applied in combination with other air pollution control systems. Condensers located upstream of afterburners, carbon beds, or absorbers can reduce the total load entering the more expensive control equipment. When used alone, condensation often requires costly refrigeration to achieve the low temperatures needed for adequate control.

Condensers employ several methods for cooling the vapor. In surface condensers, the coolant does not contact the vapor or condensate; condensation occurs on a wall separating the coolant and the vapor. Most surface condensers are common shell-and-tube heat exchangers. The coolant normally flows through the tubes and the vapor condenses on the outside tube surface. The condensed vapor forms a film on the cool tube and drains away to storage or disposal.

Contact condensers usually cool the vapor by spraying a liquid at ambient temperature or slightly cooler directly into the gas stream. Contact condensers also act as scrubbers in removing vapors which normally do not condense. The use of quench water as the cooling medium results in a waste stream which must be contained and treated before discharge.

Equipment used for contact condensation includes simple spray towers, high velocity jets, and barometric condensers. Contact condensers are, in general, less expensive, more flexible, and more efficient in removing organic vapors than surface condensers. On the other hand, surface condensers recover marketable condensate and present no waste disposal problem. Surface condensers require more auxiliary equipment and have greater maintenance requirements.

Condensers have been widely used (usually with additional control equipment) in controlling organic emissions from petroleum refining, petrochemical manufacturing, dry cleaning, degreasing, and tar dipping. Condensation processes with significant refrigeration requirements are being used for the recovery of gasoline vapors at bulk gasoline terminals and service stations.

Control effectiveness depends on hydrocarbon contaminants and condenser operating parameters. In the removal of gasoline from saturated vapors, removals of about 99% can be obtained. Efficiencies for recovering heavy hydrocarbons with nonrefrigerated condensers can exceed 99%.

Secondary environmental problems include the disposal of noncondensibles, and the treatment of the liquid effluent from contact condensers. The noncondensible gas effluent can be vented to the atmosphere or further processed (e.g., incinerated), depending on the effluent composition. The liquid effluent from contact condensers must be treated or separated before disposal or reuse.

4.4 ABSORPTION

Absorption is the process in which certain constitutents of a gas stream are selectively transferred to a liquid solvent. Absorption may be purely physical, in which the solute simply dissolves in the absorbent, or it may be chemical, in which the solute chemically reacts with the absorbent or with reagents dissolved in the absorbent. Typical absorption equipment includes plate towers, packed towers, spray towers, and venturi scrubbers. After absorption, the vapor-laden absorbent may be regenerated, used as make-up to nearby processes, or disposed. The most common absorbents used for the removal of hydrocarbons are nonvolatile petroleum liquids ("lean oils"). Other commonly-used absorbents are water, and aqueous solutions of oxidizing agents, sodium carbonate, or sodium hydroxide.

Several lean oil absorption systems are in service at pipeline terminals for the control of loading emissions. These systems treat gas flows of less than 0.5 m^3/sec (1000 scfm). Absorption is quite common in petroleum and petrochemical operations for treating gas streams with relatively high concentrations of organic vapors. Organic vapors removed include alcohols, ketones, amines, glycols, aldehydes, phenols, organic acids, and light hydrocarbons.

Control effectiveness depends on inlet hydrocarbon concentration. Lean oil absorption systems routinely achieve removal efficiencies in excess of 95% for inlet hydrocarbon concentrations of 24% or greater. Lean oil absorbers have little impact on methane. Higher removal efficiencies are achieved with larger oil flow rates attained at greater cost.

Secondary emissions are dependent on the fate of the solute-laden absorbent. If the absorbent is regenerated, a regeneration gas is produced that consists of the stripped solute and the stripping gas (usually steam or air). If this regeneration gas stream is incinerated, hazardous combustion products may be produced. If the stripped vapors are condensed, the condensate may pose a liquid disposal problem. If the solute-laden absorbent is simply disposed, further treatment or neutralization is required. Another secondary pollutant is absorbent carried into the "clean" exit gas.

4.5 ADSORPTION

Adsorption is the process by which components of a gas are retained on the surface of granular solids. The solid adsorbent particles are highly porous and have a very large surface-to-volume ratio. Gas molecules penetrate pores of the material and contact the large surface area available for adsorption. Vapors retained on the adsorbent are subsequently desorbed. Both the vapors and the adsorbent can be recovered for re-use.

Activated carbon is the most widely used adsorbent because it can selectively adsorb hydrocarbons from gases even in the presence of water. Because of their strong affinity for water, other adsorbents such as silica gel, activated alumina, and molecular sieves are better suited for the treatment of "dry" gases. Soda lime alone or combined with activated carbon has also been used to adsorb certain hydrocarbon vapors.

After completion of the adsorption cycle, the used adsorption may be either regenerated or replaced. Regenerative systems reactivate the adsorbent by desorbing the adsorbed vapors. The desorbed vapors may then be reused or disposed. Nonregenerative systems usually return the used adsorbent to the vendor for regeneration. The adsorbent is most commonly regenerated by steam stripping, although air stripping and vacuum stripping are also used. The steam and pollutant vapors may then be directly incinerated or routed to a condenser, after which they can be separated by gravity decantation or by distillation. Although two-unit adsorber systems have been proven efficient, a third unit may be desirable to allow a freshly regenerated bed to cool after steam stripping.

Adsorption is highly efficient (in excess of 99%) in removing hydrocarbons. The process is technically feasible for controlling hydrocarbon emissions from: (1) tail gases from sulfur recovery processes; (2) streams produced in the regeneration of acid gas removal systems; or (3) other waste streams containing hydrocarbons. However, it is normally used for treating streams of low hydrocarbon concentrations. Particulates and condensables must be removed in a pretreatment step.

Secondary pollutants arise during gas pretreatment and regeneration. Particulates and condensibles in the inlet gas to the adsorber must be removed in a pretreatment step; the removed particulates and condensibles must then be safely disposed. Regeneration gases typically consist of steam, nitrogen, oxygen, and desorbed vapors. If the regeneration gas stream is incinerated, hazardous combustion products may be produced. If the steam and vapors are recovered by condensation and separation, the water stream may require further treatment due to presence of soluble hydrocarbons.

4.6 SHIFT CONVERSION

In the shift conversion process, steam is reacted with carbon monoxide to form carbon dioxide and hydrogen. This endothermic process is conducted in a fixed-bed catalytic reactor. External cooling is usually employed between multiple catalysts beds to maintain a temperature range which is optimum for the equilibrium conversion. Excess carbon dioxide formed in the shift conversion process can be separated and vented to the atmosphere.

The shift conversion process is used to remove carbon monoxide formed during steam reforming or partial oxidation methods for hydrogen production, and also to remove carbon monoxide from acid-gas streams.

There are no secondary pollutants from the shift conversion process. However, if the chromium-iron oxide catalyst used in the shift conversion is regenerated rather than sent to disposal or metal recovery, impurities which blind or poison the catalysts may be released to the atmosphere. The most likely types of contaminants, in addition to hydrocarbons, will be trace elements such as nickel, vanadium, iron, arsenic, and selenium which may be present in the feedstock gases.

4.7 STORAGE EMISSION CONTROLS

The types of (fugitive) emissions associated with oil and gas processing and storage can be separated into three categories--vapors, aerosols or mists, and odors. Of these pollutants, the largest in quantity and concentration are hydrocarbon vapors.

Emissions of hydrocarbon vapors result from the volatility of the materials being stored. They are effected by physical actions on the material stored or on the storage itself. Changes in heat or pressure change the rate of evaporation. Heat is a prime factor and can cause unlimited vaporization of a volatile liquid. Heat is received from direct solar radiation or contact with the warm ambient air, or is introduced during processing. The rate of evaporation is correlated with atmospheric temperature, vapor space temperature, and liquid body and surface temperatures.

The vapor space of a tank can contain any degree of saturation of air with vapor of the liquid up to the degree corresponding to the total vapor pressure exerted by the liquid at storage temperatures. Since the pressure in this vapor space increases with temperature increase, some of the air-vapor mixture may have to be discharged or "breathed out" to prevent the safe operating pressure of the tank from being exceeded. These emissions are continually promoted by the diurnal change in atmospheric temperatures, referred to as the tank's breathing cycle.

When the air temperature cools, as at night, the vapor space within the tank cools and the vapors contract. Fresh air is drawn in through tank vacuum vents to compensate for the decrease in vapor volume. As this fresh air upsets any existing equilibrium of saturation by diluting the vapor concentration, more volatile hydrocarbons evaporate from the liquid to restore the equilibrium. When the atmospheric temperature increases, as occurs with daylight, the vapor space warms, and the volume of rich vapors and the pressure in the tank increase. In freely vented tanks, or when the pressure settings of the relief vents have been exceeded, the vapors are forced out of the tank. This cycle is repeated each day and night. Variation in vapor space temperature also results from cloudiness, wind, or rain.

Filling operations also result in expulsion or part of all of the vapors from the tank. The rate and quantity of vapor emissions from filling are directly proportional to the amount and the rate at which liquid is charged to the vessel. Moreover, as the liquid contents are withdrawn from the tank, air replaces the empty space. This fresh air allows more evaporation to take place.

Control of air pollution originating from storage vessels serves a three-fold purpose:

- Elimination or reduction of air contaminants,
- elimination or reduction of fire hazards, and
- economic savings through recovery of valuable products.

Methods of control include use of floating roofs, plastic blankets, spheres, variable vapor space systems, various recovery systems, and altered pumping and storage operations.

4.7.1 SEALS FOR FLOATING-ROOF TANKS

The principle by which a floating roof controls emissions from a volatile liquid is that of eliminating the vapor space so that the liquid cannot evaporate and later be vented. To be successful the floating roof must completely seal off the liquid surface from the atmosphere. The seal for the floating roof is therefore very important. A sectional view of the sealing mechanism is shown in Figure 4-2. The floating section is customarily constructed about 8 inches

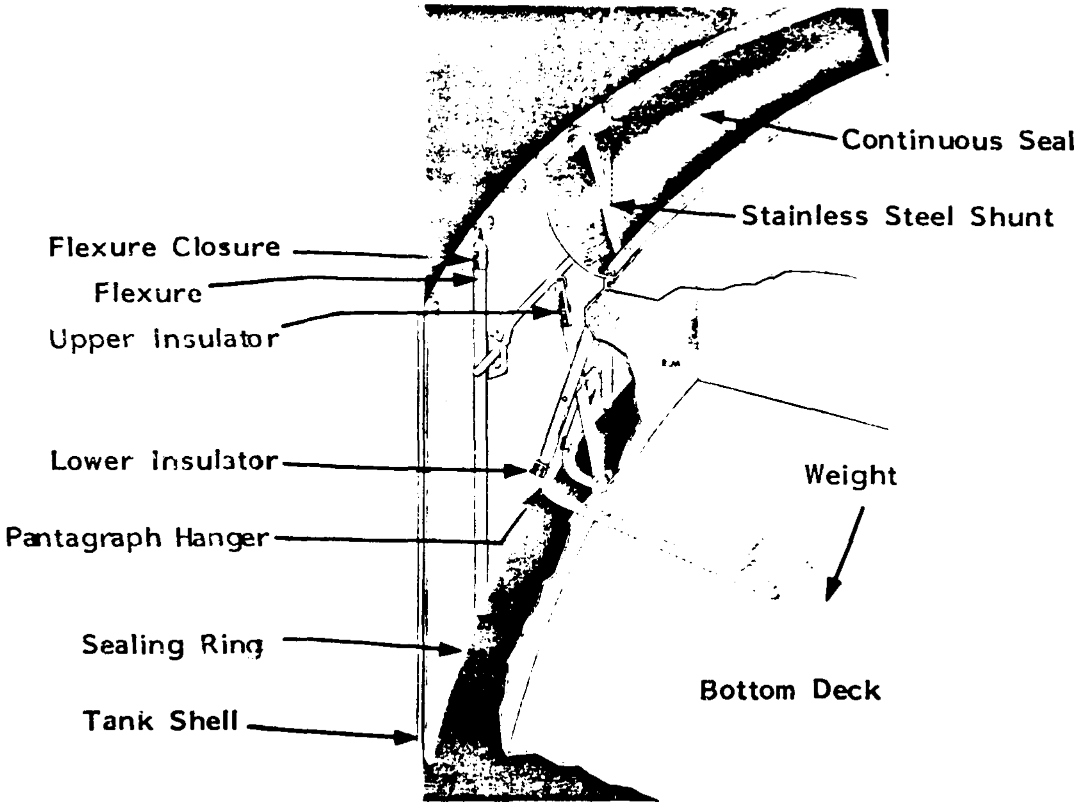

Figure 4-2 Sectional View of Double-Deck Floating Roof's Sealing Mechanism

less in diameter than the tank shell. A sealing mechanism must be provided for the remaining open annular gap. The seal also helps keep the roof centered.

Conventional seals generally consist of vertical metal plates or shoes connected by braces or pantograph devices to the floating roof. The shoes are suspended in such a way that they are forced outward against the inner tank wall. An impervious fabric bridges the annular area between the tops of the shoes contacting the tank wall and the circumference of the floating roof. To reduce emissions, a secondary seal or wiper blade has been added to the floating-roof design by extending the fabric seal or by adding a second section of fabric. This seal remains in contact with the tank wall. Its flexibility allows it to make contact even in rivet head areas of the inner shell or in places where the shell might be slightly out of round. This improvement lowers hydrocarbon emissions further by reducing the effect of wetting and wicking associated with floating-roof tanks.

Recently, other types of sealing devices to close the annular gap have been marketed. These devices consist of a fabric tube that rests on the surface of liquid exposed in the annular space. The fabric tube is filled with air, liquid or plastic material. The pneumatic, inflated seal is provided with uniform air pressure by means of a small expansion chamber and control valves. The sides of the tube remain in contact with the roof and inner shell. The liquid-filled tube holds a ribbed scuff band against the tank wall. The ribbed band acts as a series of wiper blades as well as a closure. All tubes are protected by some type of weather covering.

A weather covering can also be added to protect the sealing fabric of the conventional seals. The covering includes flat metal sections held in place by a metal band. The metal protects the fabric seal from the elements. When floating-roof sections are added to older tanks constructed of riveted sections, better contact of the shoes with the shell can be ensured by guniting or plastic coating the inner shell. The wetting condition of gunited walls may, however, offset the gain of better contact.

4.7.2 FLOATING PLASTIC BLANKETS

A floating plastic blanket operates on the same principle of control as a floating roof. It is also available as a surface cover. The blanket is usually made of polyvinyl chloride but can be made of other plastics such as polyvinyl alcohol, superpolyamides, polyesters, fluoride hydrocarbons, and so forth. The blanket's underside is constructed of a large number of floats of the same plastic material. The blanket is custom manufactured so that only a 1-inch gap remains around the periphery. A vertical raised skirt is provided at the edge of the blanket to serve as a vapor seal over the annular area. Once this area is saturated, further evaporation diminishes. The only remaining loss is gaseous diffusion. The seal is made as effective as possible by using an elastic, Z-shaped skirt.

Provisions are made in the blanket for openings fitted with vertical sleeves for measuring and sampling operations. These openings have a crosscut, flexible inner diaphragm to minimize exposure of the liquid surface. Small holes with downspouts to effect a liquid seal are used to provide drainage of any condensate from the top of the blanket. Another feature includes a stainless steel cable grid to prevent a buildup of static charges. The grid is closely attached just under the blanket in parallel lines and connected to the tank shell by a flexible conductor cable. Installation of a plastic blanket is convenient for both new and existing tanks. The blanket is made in sections and can be introduced into a tank through a manhole.

A rigid foam-plastic cover constructed of polyisocyanate foam is also available to equip small fixed-roof tanks with a floating cover. The cover is manufactured in radial sections, each equipped with a flexible neoprene seal attached on the outer edge. The sections are easily installed through roof manholes and assembled with slip-fit joints.

4.7.3 PLASTIC MICROSPHERES

An outgrowth of application of plastic material provides another type of control mechanism. This type of control is also similar to the floating roof. A phenolic or urea resin in the shape of tiny, hollow, spherical particles has been developed by Standard Oil Company of Ohio. This material has the physical properties necessary to form a foam covering over the denser petroleum products. The fluidity of the layer enables it to flow around any internal tank parts while keeping the liquid surface sealed throughout any level changes. These plastic spheres are known under their trademark names of microballoons or Microspheres. These coverings have proved to be effective controls for fixed-roof crude oil tanks. Excessive amounts of condensation or high turbulence should be avoided. The plastic foam has not proved as satisfactory for one-component liquid or gasoline products.

A ½-inch layer of foam has been found sufficient for crude oil where pumping rates do not exceed 4,000 barrels per hour. A layer 1 inch thick is recommended for pumping rates up to 10,000 barrels per hour. In order to overcome wall holdup in smaller tanks, it is suggested that a 1-inch layer be used regardless of pumping rates. For tanks storing gasoline, the recommended foam thickness is 2 inches for tanks up to 40 feet in diameter, and 1 inch for all larger diameter vessels.

Various methods can be used to put the foam covering on the crude oil. One method is to inject the plastic spheres with the crude oil as it is charged to the tank. Spheres are added by means of an aspirator and hopper similar to equipment used in fire-fighting foam systems. The spheres can also be added by placing the desired quantity on the clean, dry floor of the tank just before the crude oil is charged. A wetting agent must be used when the foam covering is to be used on gasoline products. This is accomplished by slurrying the plastic spheres, wetting agent, and gasoline in a separate container. The slurry is then injected into the tank. Changes in tank operation are not necessary except for gaging or sampling. A floating-type well attached to a common-type gaging tape allows accurate measurement of the tank's contents. A sample thief with a piercing-type bottom is needed for sampling.

Protection against excessive loss of the plastic spheres is necessary because of the relative value of the foam covering. Precaution must be taken against overfilling and pumping the tank too low. Standard precautions against air entrainment in pipelines normally safeguard against the latter. Overfilling can be prevented by automatic shutoff valves or preset shutoff operations. Low-level shutoff should prevent vortices created during tank emptying. Other than loss of the foam, no trouble should be encountered if the spheres escape into process lines. The plastic material is not as abrasive as the sand particles normally found entrained in crude oil. Excessive pressures crush the spheres and the plastic settles in the water or sediment. At high temperatures, the thermo-setting resins soften, liquefy, and mix with the fuel oil, asphalt, or coke.

4.7.4 VAPOR BALANCE SYSTEMS

Variable vapor space or vapor balance systems are designed to contain the vapors produced in storage. They do not achieve as great a reduction in emissions as an appropriately designed vapor recovery system does. A well-planned unit includes storage of similar or related products, and uses the advantage of in-balance pumping situations. Only the vapor space of the tanks is manifolded together in these systems. Other systems include a vapor reservoir tank that is either a lifter-roof type or a vessel with an internal diaphragm. The latter vessel can be an integrated vapor-liquid tank or a separate vaporsphere. The manifold system includes various sizes of lightweight lines installed to effect a balanced pressure drop in all the branches while not exceeding allowable pressure drops. Providing isolating valves for each tank so that each tank can be removed from the vapor balance system during gaging or sampling operations is also good practice. Excessive vapors that exceed the capacity of the balance system should be incinerated in a smokeless flare or used as fuel.

4.7.5 VAPOR RECOVERY SYSTEMS

The vapor recovery system is in many ways similar to and yet superior to a vapor balance system in terms of emissions prevented. The service of this type of vapor recovery system is more flexible as to the number of tanks and products being stored. The recovery unit is designed to handle vapors originating from filling operations as well as from breathing. The recovered vapors are compressed and charged to an absorption unit for recovery of condensable hydrocarbons. Noncondensable vapors are piped to the fuel gas system or to a smokeless flare. When absorption of the condensable vapors is not practical from an economic standpoint, these vapors, too, are sent directly to the fuel system or incinerated in a smokeless flare.

The recovery system, like the vapor balance system, includes vapor lines interconnecting the vapor space of the tanks that the system serves. Each tank should be capable of being isolated from the system. This enables the tanks to be sampled or gaged without a resulting loss of vapors from the entire system. The branches are usually isolated by providing a butterfly-type valve, a regulator, or a check valve. Since the valves offer more line resistance, their use is sometimes restricted. Small vessels or knockout pots should be installed at low points on the vapor manifold lines to remove any condensate.

In some vapor recovery systems, certain tanks must be blanketed with an inert atmosphere in order to prevent explosive mixtures and product contamination. In other, larger systems, the entire manifolded section is maintained under a vacuum. Each tank is isolated by a regulator-control valve. The valves operate from pressure changes occurring in the tank vapor space.

Because the vapor-gathering system is based upon positive net vapor flow to the terminum (suction of compressors), the proper size of the vapor lines is important. Sizing of the line, as well as that of the compressors, absorption unit, or flare, is based upon the anticipated amount of vapors. These vapors are the result of filling operations and breathing. The distance through which the vapors must be moved is also important.

4.7.6 MISCELLANEOUS CONTROL MEASURES

Recent tests have shown that breathing emissions from fixed-roof tanks can be reduced by increasing the storage pressure. An increase of 1 ounce per square inch was found to result in an 8% decrease in emissions due to breathing. Tanks operated at 2½ psig or higher were found to have little or no breathing emissions. The pressure setting, however, should not exceed the weight of the roof.

A major supplier of tank accessories offers another method of reducing breathing losses. The method is based upon the degree of saturation in the vapor space. A baffle located in a horizontal position immediately below the vent directs entering atmospheric air into a stratified layer next to the top of the tank. Since this air is lighter, it tends to remain in the top area; thus, there is less mixing of the free air and any of the rich vapor immediately above the liquid surface. The top stratified layer is first expelled during the outbreathing cycle. Tests data indicate a reduced surface evaporation of 25 to 50%.

Hydrocarbon emissions can be minimized further by the proper selection of paint for the tank shell and roof. The protective coating applied to the outside of shell and roof influences the vapor space and liquid temperatures. Reflectivity and glossiness of a paint determine the quantity of heat a vessel can receive via radiation. A cooler roof and shell also allow any heat retained in the stored material to dissipate. Weathering of the paint also influences its effectiveness. Vapor space temperature reductions of 60°F have been reported. Similarly, liquid-surface temperature reductions of 3 to 11 degrees have been achieved. Data gathered by the American Petroleum Institute on hydrocarbon emissions indicate breathing emission reductions of 25% for aluminum over black paint and 25% for white over aluminum paint. All paints revert to "black body" heat absorption media in a corrosive or dirt-laden atmosphere.

Insulation applied to the outside of the tank is one method of reducing the heat energy normally conducted through the wall and roof of the vessel. Another method of controlling tank temperatures is the use of water. The water can be sprayed or retained on the roof surface. The evaporation of the water results in cooling of the tank vapors. Increased maintenance and corrosion problems may, however, be encountered.

Storage temperatures may be reduced by external refrigeration or autorefrigeration. External refrigeration units require the circulation of the refrigerant or of the tank contents. Autorefrigeration is practical in one-component liquid hydrocarbon storage where high vapor pressure material is involved. The pressure in the tank is reduced by removing a portion of the vapor. Additional vapor is immediately formed. This flash vaporization results in lowering the temperature of the main liquid body.

Routine operations can be conducted in such a manner as to minimize other emissions associated with storage tanks. Use of remote-level reading gages and sampling devices reduces emissions by eliminating the need to open tank gage hatches. Emissions can be further reduced by proper production scheduling to (1) maintain a minimum of vapor space, (2) pump liquid to the storage tank during cool hours and withdraw during hotter periods, and (3) maintain short periods between pumping operations.

Using wet scrubbers as control equipment for certain stored materials that are sufficiently soluble in the scrubbing media employed is both possible and practical. The scrubbers can be located over the vent when the scrubbing medium, for example, a water scrubber for aqua ammonia storage, can be tolerated in the product. In other cases, the vent of one or more tanks can be manifolded so that any displaced gas is passed through a scrubbing unit before being discharged to the atmosphere. A typical example is a scrubber packed with plastic spirals that serves ketone storage vessels. The scrubbing liquid is water, which is drained to a closed waste effluent disposal system.

Properly designed condensers can be used to reduce the vapor load from tank vents in order that smaller control devices can be employed.

5. WATER SPRAYS

The oldest and simplest control technique is the water spray. Water sprays can be used where evaporation is possible, and if adjusted properly, the operation can have no runoff. Water sprays have potential application to: (1) spent shale disposal; (2) grinding and screening operations; (3) mining and blasting activities; (4) fugitive dusts from surface vehicles.

The efficiency of water sprays without wetting chemicals is about 80% for particles whose diameter is 5 or greater. The removal efficiency drops off as the particle size decreases and has been reported at 25% for particles in the 1μ range (1).

The addition of a wetting agent will help to reduce the surface tension and improve the wetting, spreading and penetrating characteristics of the water. Reduced surface tension allows the particles to agglutinate and increases the removal efficiency.

Spray systems have the advantage of suppressing the particulate, and the solids are carried along with the oil shale reducing one of the waste disposal problems by incorporation of the dust into the shale. It might be noted, however, that minimizing a problem in one area of particulate control could intensify the control problems of another, namely, retorting. Additional advantages of water sprays are that they are economical and easy to operate. The disadvantages of spray systems are that they can clog or clog other machinery, and if the weather turns cold, the systems can freeze.

6. NO_x REMOVAL

Significant levels of ammonia are present in the off-gases from Paraho direct mode and the MIS retorting processes--on the order of 6000 ppm. Due to the combustionless low temperature pyrolysis carried out in the TOSCO II retort, little ammonia is expected in the off-gas from this process. Inasmuch as the retort gases are eventually combusted to supply process heat or for steam and/or power generation, removal of ammonia prior to combustion is considered by the developers as the most appropriate processing procedure in order to avoid the formation of appreciable levels of NO_x in the flue gases. Combustion of ammonia can produce on the order of several thousand ppm NO_x or as much as 16 lb $NO_x/10^6$ BTU, assuming complete conversion of the ammonia to NO_x and no oxidation of atmospheric nitrogen.

6.1 WATER SCRUBBING

Due to the high solubility of ammonia in water, water scrubbing has been selected by oil shale processors as one means for removal of ammonia from retort off-gases. This process is carried out prior to treating the gas for hydrogen sulfide removal. By using this sequence the ammonia scrubbing step, in addition to ammonia removal, cools and removes particulates from the treated gas, thereby improving the efficiency of any sulfur removal process.

Ammonia scrubbing is a proven process with no operational difficulties anticipated in application to retort off-gas treatment. It is expected that residual ammonia levels in the stripped gas would be in the order of 10-20 ppm. Credit for recovered anhydrous ammonia would defray part of the cost of the foul water stripping systems to be used.

6.2 CONTINUOUS CATALYTIC ABSORPTION

Processes such as Continuous Catalytic Absorption have been developed for emission control of NO_x in gas streams (Figure 6-1). It uses a stripped nitric acid solution as the absorption medium. The conversion oxidation reaction is:

$$2NO_x + H_2O + (2.5x)O_2 = 2HNO_3$$

Fugitive HNO_3 vapor losses can be recovered by addition of water trays before the gas leaves the unit.

6.3 MODIFIED ALKALIZED ALUMINA PROCESS

The Pittsburgh Energy Research Center (1975) is modifying the Alkalized Alumina process to remove both sulfur and nitrogen oxides from flue gas (Figure 6-2). Tests showed that, by lowering the absorption temperature (from 330 to 130°C or lower), sorbent attrition is reduced, and nitrogen oxides as well as sulfur dioxide are removed with 88 and 98% removal efficiency respectively. The recovered NO_x, about two-thirds of which is decomposed to nitrogen and oxygen, can be used to manufacture nitric acid, or it can be returned to the boiler for flame destruction. Regeneration of

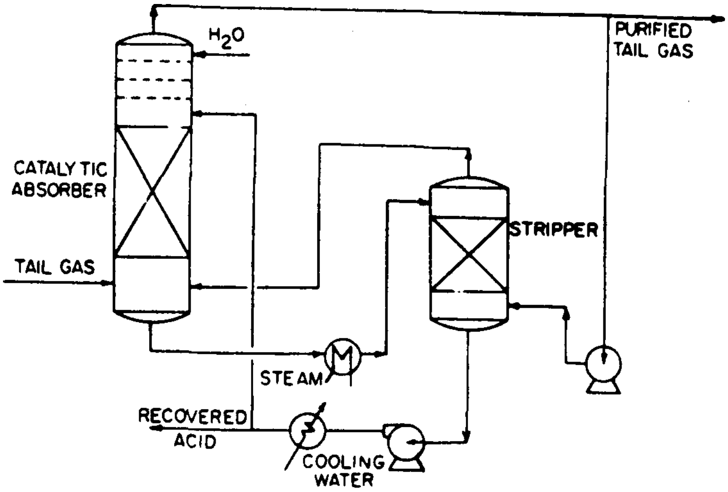

Figure 6-1 Continuous Catalytic Absorption of Nitrogen Oxides

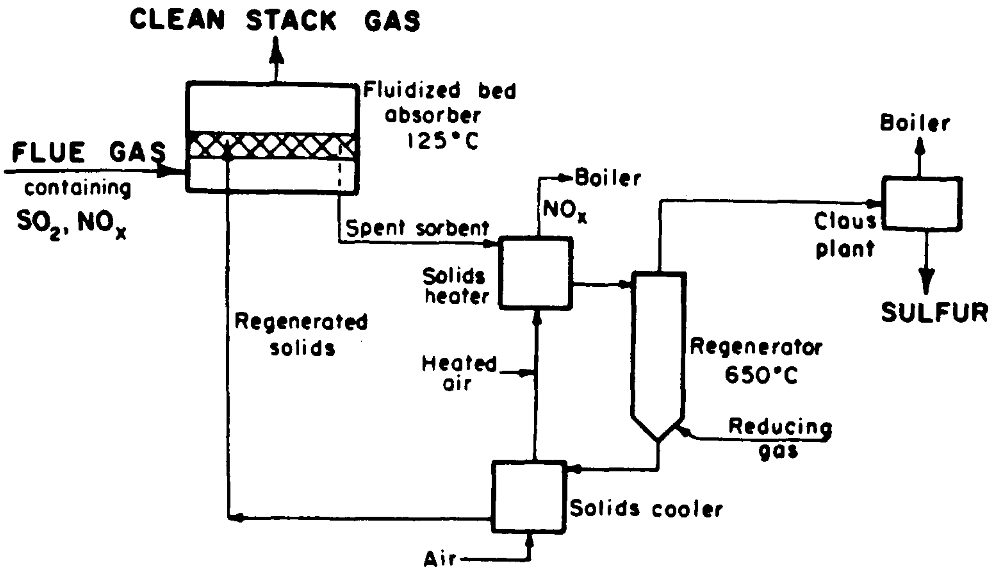

Figure 6-2 Pittsburgh Energy Research Center Stack Gas Cleaning Process for Simultaneous Removal of SO_2 and NO_x

the sorbent produces a hydrogen-sulfide-rich off-gas suitable for Claus plant conversion to elemental sulfur. Regenerated sorbent is cooled and recycled.

6.4 PHOSAM PROCESS

In a Phosam unit (Figure 6-3) ammonia is scrubbed from gas streams by using a phosphoric acid solution. The ammonia-containing phosphoric acid is detarred and fed to a stripper column and a fractionator column, producing anhydrous ammonia. Residual ammonia is about 7 ppm in the gas. The ammonia-free gas is further purified of other contaminants.

6.5 FLUE GAS NO_x CONTROLS

Three flue gas control processes have been suggested to provide reductions of NO_x.

6.5.1 LIMESTONE SCRUBBING

The limestone slurry employed for SO_2 control will also remove NO_2 or an equimolar mixture of NO/NO_2 from flue gases. The process is the same as outlined for alkaline scrubbing of sulfur dioxide except that an additional end product, calcium nitrate, is quite soluble in solution and will build up. Work done at Wisconsin Electric's Oak Creek power plant indicated about a 20% reduction in NO_x emissions using limestone slurry scrubbing.

6.5.2 CHIYODA THOROUGHBRED 102 PROCESS

The Chiyoda Thoroughbred 102 process utilizes ozone to oxidize NO_x to NO_2 and thereby enhances its absorptive properties. After oxidation, the flue gas is introduced into a packed tower and treated with dilute sulfuric acid containing a ferric catalyst. Pilot-plant studies have indicated NO_x removal efficiencies of 60%. Again, the build-up of calcium nitrate could be an operational problem.

6.5.3 SELECTIVE CATALYTIC REDUCTION PROCESSES

Several nitrogen oxide processes have been developed by the Japanese for the selective reduction of NO_x. The Kurabo process mixes the flue gas with ammonia and reacts the mixture over a bed of copper and alumina. Pilot-plant data indicate about a 90% conversion of NO_x to N_2. The Hitachi Shipbuilding process and the Sumitomo process both use ammonia injection and subsequent reduction over a metal catalyst. Based on experience with these systems, a number of very large denitrification plants are being built.

6.6 COMBUSTION MODIFICATION

The use of off-gas or any other on-site fuel combustion for steam, heat, or power generation provides the opportunity to make reductions in oxides of nitrogen produced in the flue gas. An intense heat flux, tight burn pattern and turbulent combustion conditions have been found to increase NO_x formation. By carefully designing the combustion chamber and combustion

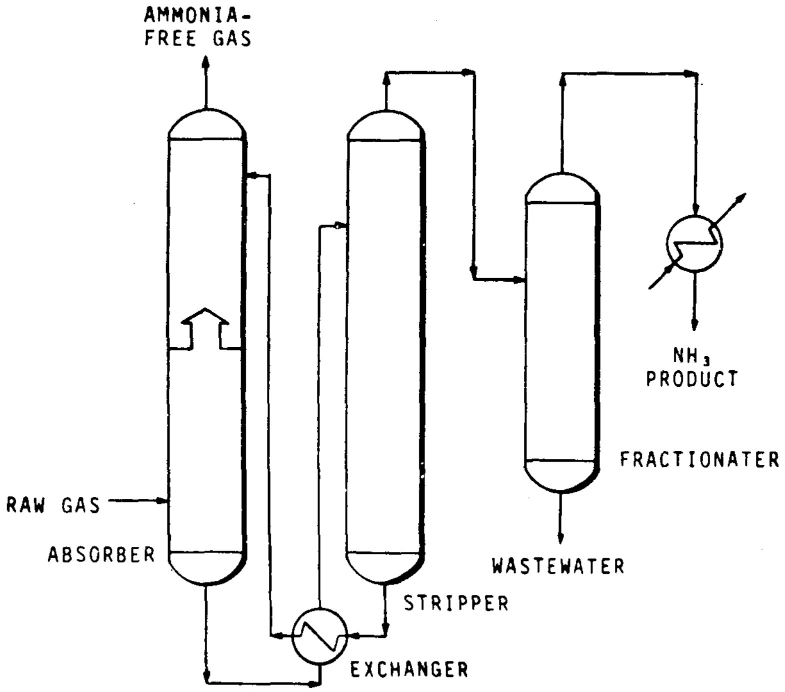

Figure 6-3 Phosam Unit for Ammonia Recovery

process these factors may be reduced. Some proposed procedures include:

6.6.1 TWO-STAGE COMBUSTION

To address the problem of combustion efficiency and NO_x emissions, a two-stage burning system was developed. In the first stage, only 85 to 95% of the stoichiometric air needed for combustion was supplied. The remaining air was injected above the burners to complete the combustion. Systems of this type have reduced NO_x emissions by about 50%.

6.6.2 TANGENTIAL FIRING

As stated earlier, the interaction between closely-spaced burners tends to elevate the NO_x emissions. Tangential firing removes some of the burner proximity, and firing is carried out on a tangent to a circle at the center of the furnace. The result is less flame interaction, more radiant heat transfer to the cooling surface, and lower concentrations of NO_x produced.

6.6.3 FLUE GAS RECIRCULATION

Flue gas recirculation has been applied to combustion sources of NO_x reduction. The gas has some sensible heat associated with it and does not quench the reaction temperature as dramatically as excess air, thereby allowing the kinetics of the formation reaction to be reversed toward molecular nitrogen and oxygen. The recirculated gases are lower in oxygen than excess air and present less of the reactant necessary for the formation of NO_x. There are, however, some problems with flame stability, and this has had some limitation on the application of this technique to NO_x reduction.

6.6.4 FUEL MODIFICATIONS

In addition to atmospheric nitrogen, fuel-bound nitrogen can be a major contribution to the NO_x problem. Any fuel burned on-site should be of such quality to assure low oxides of nitrogen emissions. Some operators have suggested the use of a portion of the shale oil as a fuel in the process itself. If this option is exercised, pretreatment of the oil should be done to reduce the high levels of nitrogen contained in the shale oil.

6.6.5 LOW NO_x BURNERS

Low NO_x burners have reduced the thermal and fuel derived NO_x emissions by various methods. One method employs a thin flame and good mixing to promote rapid combustion, thereby reducing levels of NO_x. A second method utilizes an internal recirculation of the combustion gases to reduce NO_x emissions, and a third method uses stratified combustion. The combination of one or more of these techniques is usually employed in the low NO_x burners available on the market today. The performance of these units usually results in NO_x emissions low enough to be in compliance with the air pollution regulations.

7. SULFUR CONTROL

7.1 OFF-GAS H_2S REMOVAL

7.1.1 AMINE ABSORPTION

There are numerous methods by which H_2S can be separated from hydrocarbon gas streams, and other methods are in the development stage. The iron-sponge process is not practical for large gas streams or gas streams with a high H_2S content. This process is used most commonly in desulfurizing natural gas streams, and the carbonate or amine absorption processes are used most commonly in petroleum refinery operations. Of the latter two processes, the amine is the most popular since refinery waste gases generally have H_2S concentrations well suited to this process, and a greater removal efficiency is obtained than by the carbonate process. Both DEA (diethanolomine) and MEA (monoethanolamine) are used, with DEA being preferred since chemical degradation and make-up rates are lower. Amine solutions will absorb both H_2S and CO_2 according to the following reactions:

$$RNH_2 + H_2S \rightleftharpoons RNH_3HS$$

$$RNH_2 + CO_2 + H_2O \rightleftharpoons RNH_3HCO_3$$

Absorption of H_2S occurs at 100 °F or below, and rejection of sulfide is active at 240 °F. The amine desulfurization process, therefore, involves contacting the sour (sulfur bearing) gas stream with a cool amine solution to absorb the H_2S and then regenerating the amine and stripping the H_2S from the amine solution by heating. A typical amine H_2S removal system is shown in Figure 7-1.

The treated gas leaving the amine desulfurization process will be used as fuel or be burned in a flare. It is necessary, therefore, to ensure proper capacity and functioning of the amine system. The efficiency of an operating amine system can readily be determined by laboratory analysis of the sour inlet gas, treated outlet gas, and acid outlet gas streams. It may also be necessary to verify the adquacy of a proposed new amine system, and the following parameters may be used for this purpose:

- Actual H_2S/DEA ratio versus H_2S/DEA equilibrium ratio
- Corrosion limitation
- Absorber column sizing.

The acid gas stream from typical refinery amine (or potassium carbonate) units will contain well over 95 percent acid gas (H_2S and carbon dioxide). If desired, there are processes for selective removal of the CO_2 from the acid gas, but this is not essential for processing the gas. The remainder of the stream will be largely hydrocarbons, with small amounts of carried-over amine. Without air pollution control equipment, this highly toxic and undesirable gas stream would have to be burned to convert the H_2S to SO_2, which is less toxic

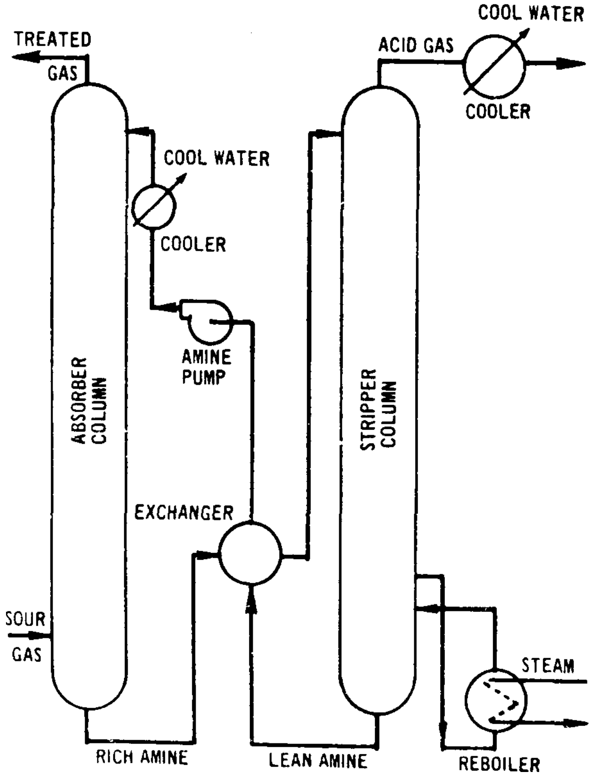

Figure 7-1 Amine Desulfurization Process

but also highly undesirable. Air pollution control equipment is required, therefore, for reduction of H_2S emission to the atmosphere without a corresponding substitution of SO_2 emission. This may be done by conversion of H_2S to elemental sulfur.

7.1.2 CLAUS SULFUR REMOVAL PROCESS

There are numerous processes by which H_2S can be removed from hydrocarbon gas streams by conversion to free sulfur, but these are primarily natural gas purification processes. The sulfur scavenger plant, however, serves solely to produce free sulfur from H_2S streams which have been removed from hydrocarbon streams by other amine, etc.) methods. The standard sulfur scavenger plant is based on the Claus process which involves oxidation of one-third of the H_2S to SO_2 and then catalytically reacting the remaining H_2S with the SO_2 to form water and free sulfur:

$$H_2S + \frac{3}{2} O_2 \longrightarrow SO_2 + H_2O$$

and

$$2\ H_2S + SO_2 \longrightarrow 3\ S + 2\ H_2O$$

The second (catalyzed) reaction usually is accomplished in two stages, but more recently, three stages are being used for more complete conversion. Final off-gas is incinerated to prevent unreacted H_2S from being emitted into the atmosphere. This results in some SO_2 emission, although only a fraction of that which would have been emitted upon combustion of all the H_2S.

A variation of the basic Claus (split-stream) process is the partial-combustion process wherein the acid gas stream is partially oxidized by controlling the supply of air. The reaction gas is cooled to condense sulfur vapors and comingled with air and a slip-stream of acid gas, which are burned "in-line" so as to reheat the mixture before it is passed to the first converter. This reaction gas is again cooled to condense sulfur vapors before being reheated by "in-line" combustion of additional slip-stream acid gas and being passed to the second catalytic converter. Again, the reaction gas is cooled for condensation of sulfur and then passed to a coalescer for removal of the remaining sulfur mist before being incinerated. All condensed sulfur drains to molten sulfur storage, from which it may be pumped out and shipped in the molten state or may be solidified, by cooling in vats or blocks, for handling in the solid state. The basic split-stream process is illustrated in Figure 7-2 more commonly used partial-oxidation process is illustrated in Figure 7-3.

In addition to supplying the correct amount of oxygen (air) to permit conversion reactions to take place, optimum operating conditions also must be maintained. The waste heat boiler, coolers, reheaters, and converters must be sized and operated to achieve conditions approximating those shown below:

- Waste heat boiler: boiler feed water to cool reaction gases to 450 °F

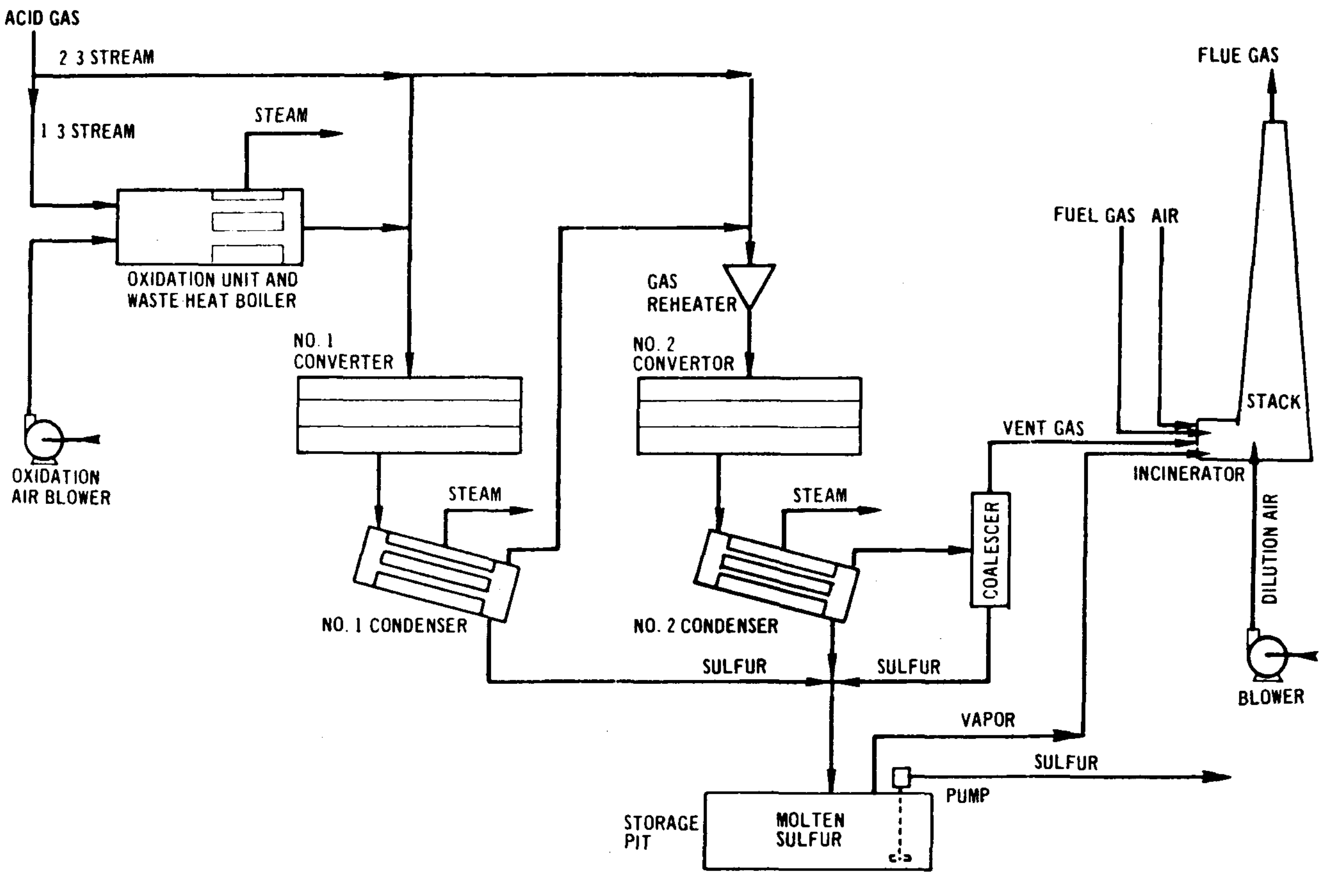

Figure 7-2 Sulfur Scavenger Plant Using the Split-Stream Process

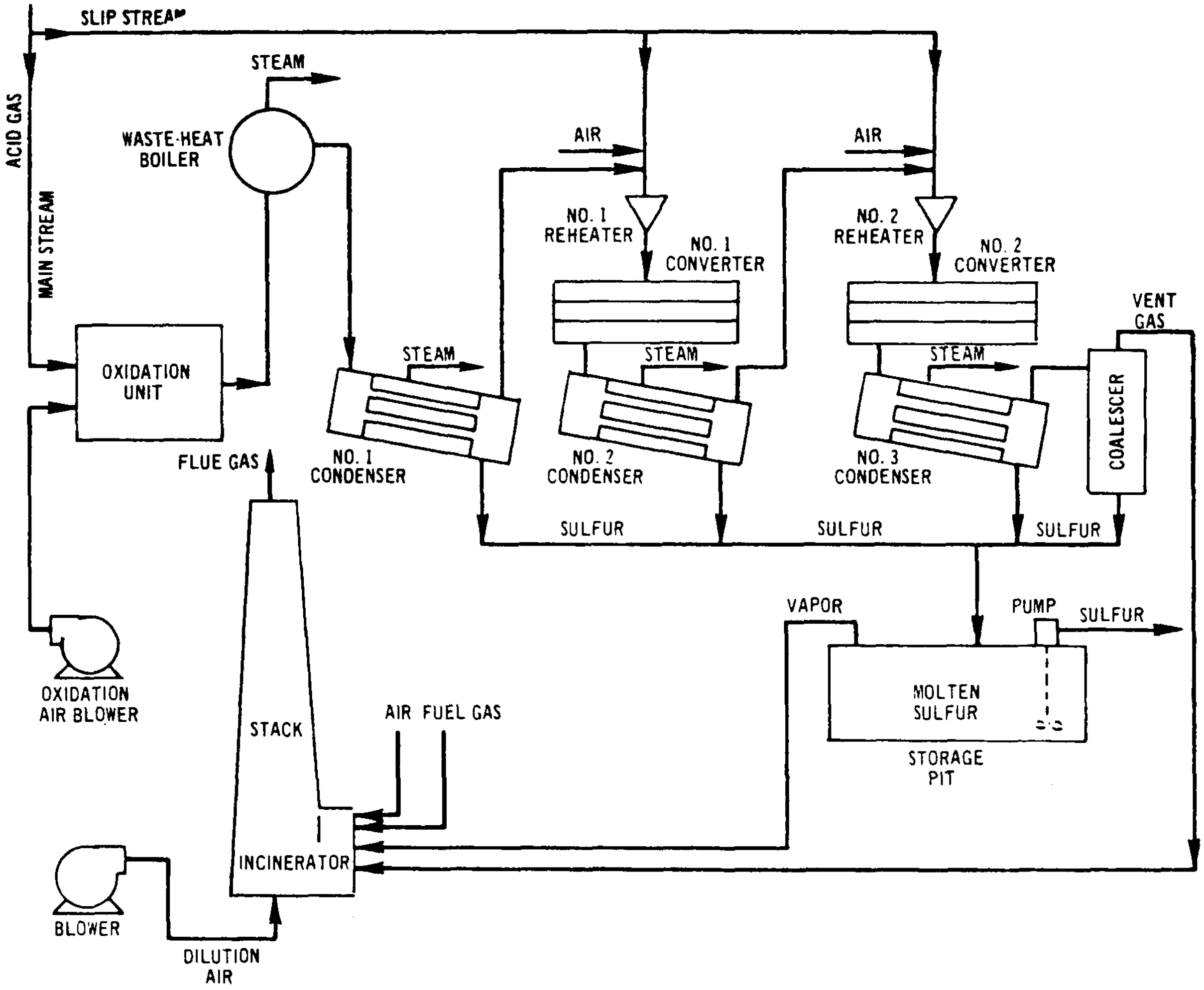

Figure 7-3 Flow Diagram of Partial Oxidation Process

- Coolers 1, 2, and 3: each to have capacity to cool gases to 300°F
- Reheater 1: In-line combustion (or other means) to reheat gases to 475°F
- Reheater 2: in-line combustion (or other means) to reheat gases to 450°F
- Converters 1 and 2: each to have sufficient bauxite catalyst that the ratio of H_2S flow (cfs) to catalyst volume (ft^3) does not exceed 2:1.

The above conditions can be achieved by various combinations of vessel sizing and/or flow rates.

However high the efficiency of a scavenger plant, the plant will be a source of SO_2 air pollution since remaining sulfur compounds in the final vent gas will be incinerated to SO_2 and then discharged through a stack to the atmosphere. Operation of the scavenger plant, however, reduces the amount of SO_2 emission in proportion to the amount of sulfur which is recovered, and this reduces overall emission of pollutants. In practice, a well designed and properly operated scavenger plant can be expected to recover more than 90% of the sulfur contained in the acid gas feed. The criterion for evaluating scavenger plants has, therefore, been the achievement of a recovery efficiency of 90% or greater. Even at satisfactory plant efficiency, however, the SO_2 concentration in incinerated flue gas may exceed allowable limits and it may, therefore, be necessary to add dilution air to the incinerated gas (see Figures 7-2 and 7-3) before discharge to the atmosphere.

7.1.2.1 PLANT OPERATION

Even in properly designed plants, operational problems which result in decreased sulfur recovery efficiency and consequent increase in H_2S vented to the incinerator are often encountered. Most of these problems stem from either variation in the feed gas stream or from inadequate reaction air and/or cooling water controls. Problems in these areas, in turn, affect the catalyst and may drastically reduce conversion efficiency.

Based upon a fixed feed stream composition, the correct amount of oxidation air can readily be controlled by flow controllers. However, feed gas composition monitoring equipment is expensive and difficult to maintain and is therefore not generally used. The H_2S content can be readily checked, and this is generally done on a periodic basis, with air supply adjustment as necessary.

A more difficult problem is an increase in the hydrocarbon content, which may not be detected until the imbalance in feed is reflected in abnormal temperature differentials in the waste heat boiler, coolers, and/or reactors. It is necessary, therefore, that operating temperatures be constantly monitored to detect hydrocarbon fluctuations. If not, the excess hydrocarbons will disrupt the oxygen supply and not permit full H_2S conversion to SO_2 in the first-stage reaction. Secondly, if not controlled, temperatures may rise to the point of equipment damage and possible breakdown. Thirdly, the excess hydrocarbons may not be fully oxidized in the controlled air supply and, particularly when the hydrocarbons are heavier than C_3 fractions, carbon may be deposited on the catalyst and thus reduce conversion efficiency.

A two-stage conversion plant should attain a sulfur recovery efficiency of at least 90%. Many modern plants will yield 94 to 96%, and the efficiencies may be raised to as high as 98% where a third stage is used. Although the addition of a third stage to an existing two-stage plant may not be economical solely on a sulfur recovery basis, the provision of a third stage in new plants is relatively inexpensive. In either case, this third stage is highly desirable from an air pollution standpoint, since large amounts of pollutant are represented by each percentage point of recovery efficiency. Also, the third stage can act as a stand-by for the other stages during upset conditions. As activity of catalyst in the first stage is reduced (by surface deposits of sulfur or carbon), abnormal quantities of H_2S will pass through. However, this can then be reacted in the subsequent stages and high efficiencies can still be maintained until the first stage catalyst is reactivated. With the additional flexibility of three stages, any one of the stages can be bypassed for replacement of inactive catalyst.

Generally, however, catalyst is reactivated rather than replaced, and this is done during periodic plant maintenance shutdown. Sour gas feed is shut off and fuel gas is burned with theoretical air in the combustion chamber until all sour gas is purged from the reaction system. Thereafter, air supply is raised to 25% excess for a period and then to 50% excess. In doing so, the hot excess air burns sufrace carbon and sulfur from the reactor catalyst, and this is reflected by a temperature rise across the reactor. When the temperature becomes equal at inlet and outlet, surface material has been fully oxidized and the catalyst is reactivated.

In all areas where either oil refining or sour natural gas processing operations take place, the sulfur scavenger plant may be one of the most, if not the most, important single air pollution control method. The provision of such plants, properly designed and efficiently operated, will prevent the emission to the atmosphere of intolerably high amounts of material which is toxic to both man and his environment.

Inasmuch as the gas treating plants, as well as the sulfur recovery facilities, are processing a highly odorous and toxic gas, it is of utmost importance that the area be designed for easy cleaning of spills, and that an efficient plant housekeeping program be followed.

7.1.2.2 TAIL GAS TREATMENT

Claus technology units, themselves, must have tail gas treatment units to reduce sulfur emissions. Unrecovered sulfur in Claus plant tail gas includes primarily hydrogen sulfide, elemental sulfur, sulfur dioxide, and lesser amounts of other sulfur compounds. Stretford units (Section 7.1.3) are not capable of recovering sulfur from carbonyl sulfide or carbon disulfide, which as a result, are presently vented to the atmosphere with fugitive hydrogen sulfide.

Options for Claus tail gas disposal include venting, incineration, which converts the sulfur compounds to sulfur dioxide, or cleanup.

A. INCINERATION REQUIREMENTS

Even in an efficient scavenger plant, a portion of the H_2S in the acid gas is unreacted and passes through the plant. The final vent gas is composed of the products of reaction (other than recovered sulfur) and the inert nitrogen contained in the air used for supply of reaction oxygen, plus the components of the feed stream which do not take part in the conversion reactions and the unreacted H_2S. Because of the remaining H_2S, this vent gas must be incinerated to convert the H_2S to SO_2 before the vent gas is discharged to the atmosphere. Although the oxidation of H_2S is exothermic, it may be necessary to supply additional heat at the incinerator in order to maintain incineration temperature for the total vent gas stream.

Oxidation of H_2S to SO_2 is rapid and essentially complete at temperatures over 1050°F, provided there is adequate air supply and mixing. For given operating conditions, additional fuel gas and air requirements may be verified.

When burning off gas to obtain the required additional heat necessary to achieve the proposed incineration temperature, additional air for combustion of this gas must be supplied. It is necessary that the incinerator mixing velocity be such that the retention time exceeds 0.3 second to ensure adequate time for conversion of H_2S to SO_2.

B. STACK DILUTION AIR

As described in the preceding section, unconverted H_2S and carried-over sulfur are burned in the incinerator to SO_2. However, even when the scavenger plant is operating efficiently, the volume concentration of SO_2 may be high. To meet acceptable concentration levels at the stack, dilution air may be added at the base of the stack.

In some localities, there may be no established criterion for maximum allowable SO_2 concentration in the flue gas. Nevertheless, SO_2 is itself toxic and it is necessary to ensure that safe ground level concentrations are not exceeded. Additionally, some of the SO_2 may be oxidized to SO_3 which, in turn, could combine with atmospheric moisture to form acid mist and lead to extensive ground level damage. The addition of dilution air, in addition to reducing SO_2 concentration, has the added advantage of "quenching" the incinerated gases and greatly reducing SO_3 formation.

C. CLEANUP

Claus plant tail gas cleanup processes are of two types--low-temperature Claus processes and conversion-concentration processes. In the first, sulfur formation is promoted by operating a catalytic system at a temperature favoring thermodynamic equilibrium. In the second, sulfur compounds are converted to hydrogen sulfide or sulfur dioxide, which is then converted to elemental sulfur, sulfuric acid, or gypsum. The SCOT, Chiyoda Thoroughbred, IFP, Beavon, and Wellman-Lord processes are of the second type.

a. SHELL CLAUS OFF-GAS TREATING

The SCOT process (Figure 7-4) removes residual sulfur from Claus tail gas streams in two stages--reduction and absorption. In the reduction stage, sulfur compounds and elemental sulfur in the off-gas are reduced to hydrogen sulfide. In the absorption stage, water is removed by condensation, and hydrogen sulfide, removed by alkanolamine absorption-regeneration, is recycled to the Claus unit. The catalyst is cobalt-molybdenum-on-alumina.

b. CHIYODA THOROUGHBRED

The Chiyoda Thoroughbred process is a wet desulfurization process capable of high sulfur (SO_x) removal from flue gases, producing gypsum for resale or disposal (Figure 7-5). The process reaction sequence is as follows:

$$\text{Absorption: } SO_2 + H_2O = H_2SO_3 \; ;$$

$$\text{Oxidation: } H_2SO_4 + 1/2\ O_2 = H_2SO_4 \; ;$$

$$\text{Crystallization: } H_2SO_4 + CaCO_3 + H_2O = CaSO_4 \cdot 2H_2O\ (s) + CO_2\ (g) \; .$$

In the absorber, sulfur dioxide and sulfur trioxide in the flue gas (precooled and dust-free) are absorbed and removed by dilute sulfuric acid at 50 to 70°C. Sulfurous acid in the dilute sulfuric acid is oxidized into sulfuric acid by using a catalyst. The sulfuric acid (from the flue gas SO_2 and SO_3) is sent to the crystallizer, whereas the remainder is recirculated to the absorber. In the crystallizer, the sulfuric acid is neutralized with calcium compounds (natural limestone, quicklime, or calcium oxide, slaked lime, calcium hydroxide, and carbide residue), ultimately producing gypsum.

c. IFP (Institute Francais du Petrok)

The basic reaction used in the IFP process is the same as that used for the Claus process except that it occurs in a liquid phase rather than the gaseous phase. The liquid phase is composed of a polyalkylene glycol and a 5% by weight catalyst orthopthalic acid monopolyethylene glycol ester. Hydrogen sulfide H_2S and sulfur dioxide (SO_2) are very soluble in this system and, if the operating parameters are held at optimum conditions, efficient conversion to sulfur results. The reaction for the IFP process is:

$$2H_2S + SO_2 = 3S + 2H_2O$$

in a catalyst-containing solvent (Figure 7-6). The catalyst combines with the sulfur dioxide, hydrogen sulfide, and sulfur to yield an active complex, which in turn reacts with additional feed hydrogen sulfide and sulfur dioxide to produce

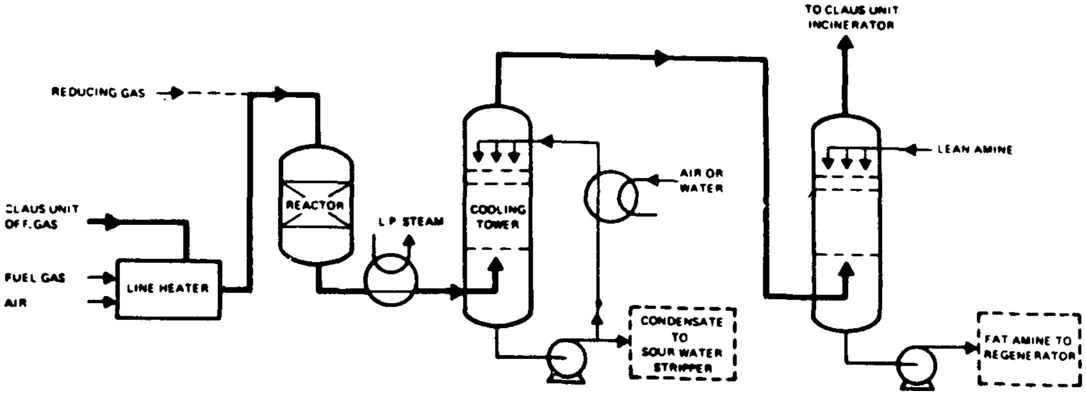

Figure 7-4 Shell Claus Offgas Treating (SCOT) Process Flow Diagram

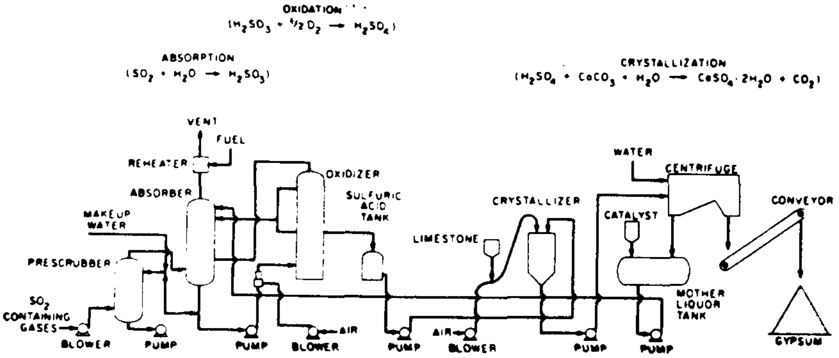

Figure 7-5 Flow Diagram of the Chiyoda Thoroughbred Process

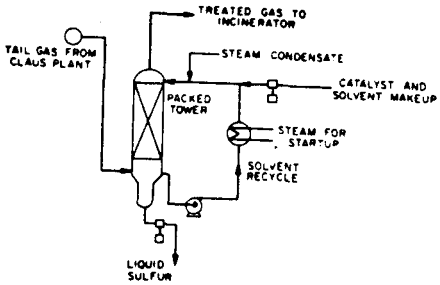

Figure 7-6 IFP Process Flow Chart

elemental sulfur. For maximum conversion, the ratio of hydrogen sulfide to sulfur dioxide should be between 2.0 and 2.4. The IFP process does not recover carbonyl sulfide and carbon disulfide, but requires their minimized production from the Claus plant. The system reduces Claus unit tail gas to 1500 to 2500 ppm after incineration or to 1000 ppm, as reported by Barry (1972). The IFP (liquid phase) process merely uses a different catalyst to extend the Claus reaction.

As noted earlier, the ratio of H_2S to SO_2 is very important. If this ratio dips below 2:1, the system can fail completely, requiring a complete replacement of the scrubbing liquor.

d. BEAVON

The tail gas from the Claus plant is heated by mixing it with hot combustion products of fuel gas and air.

In the first step of the Beavon process (Figure 7-7), Claus tail gas sulfur compounds (SO_2, S_x, COS, and CS_2) are converted to hydrogen sulfide by hydrogenation and hydrolysis in the presence of a catalyst. The stream is cooled by contact with a slightly alkaline buffer solution. A Stretford process absorber using an oxidizing alkaline solution produces elemental sulfur. Sulfur dioxide removal to 250 ppm or less is achieved.

Both the SCOT and the Beavon processes are adversely affected by high concentrations of CO_2. Since oil shale gaseous emissions are projected to be rich in CO_2, additional operating constraints such as larger recycle gas streams, more fuel consumption, and perhaps steam injection may be necessary.

e. WELLMAN-LORD

The Wellman-Lord process (Figure 7-8) is a wet regenerative sulfur dioxide, sulfur trioxide, acid mist, and fly ash removal system producing sulfur dioxide in pure gaseous or liquid forms suitable for the manufacture of sulfuric acid or elemental sulfur. It uses sodium sulfite-bisulfite solution based absorption, recovering sulfur dioxide for reuse in sulfur recovery plants. The sulfur dioxide is removed by converting the absorbent to the bisulfite form.

The basic chemical reaction of the process involves the conversion of sulfite (SO_3) to bisulfite (HSO_3) and can be summarized by the following equation:

$$SO_2 + Na_2SO_3 + H_2O \longrightarrow 2NaHSO_3$$

The bisulfite solution is pumped to an evaporator and heated by steam. The heating reverses the reaction and liberates a concentrated stream of sulfur dioxide which can be used for making either sulfur or sulfuric acid. The sodium sulfite produced by heating is dissolved and recirculated to the absorption column.

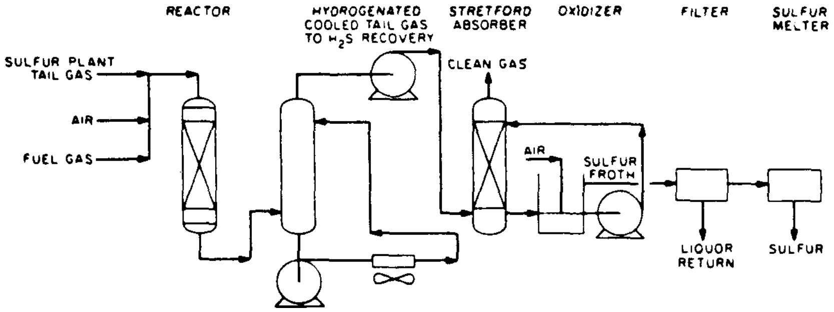

Figure 7-7 Beavon Process Flow Chart

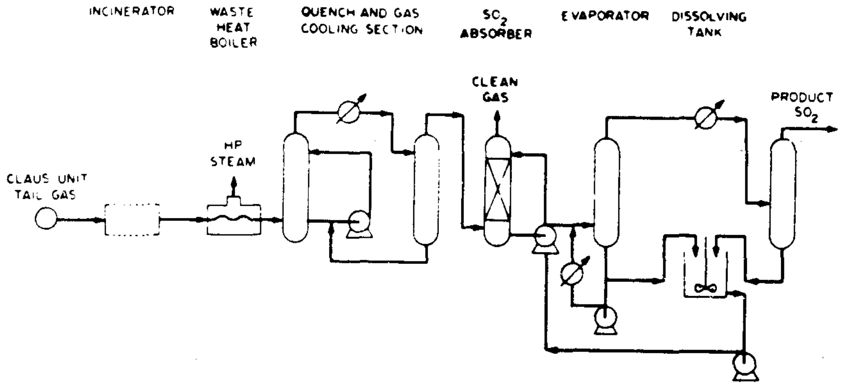

Figure 7-8 Wellman-Lord SO_2 Recovery Flow Chart

The sulfite is regenerated in the evaporator-crystallizer section by indirect heating, producing sulfur dioxide, water, and sodium sulfite crystals. Exit gas containing levels less than 100 vol ppm of sulfur dioxide (90% SO_2 removal efficiency) is incinerated to convert trace hydrogen sulfide before exhaustion. Absorbent makeup rate is about 0.45 moles of sodium hydroxide per mole of sulfur dioxide removed (10% of the sodium content); however, process improvements should reduce the makeup to 0.10 moles of sodium hydroxide per mole of sulfur dioxide removed. Sodium sulfate (formed by SO_3 absorption, disproportionation, and sulfite oxidation) and other sodium salts must be purged from the system.

7.1.3 STRETFORD PROCESS

The Stretford process removes acid gas by washing with an aqueous solution of sodium carbonate, sodium vanadate, and anthraquinone disulfonic acid (Figure 7-9). Hydrogen sulfide is dissolved in a mixture of sodium carbonate (Na_2CO_3), and sodium bicarbonate ($NaHCO_3$), and the pH of the solution is adjusted to a range of 8.5 to 9.5.

This reaction is described by:

$$H_2S + Na_2CO_3 = NaHS + NaHCO_3$$

The dissolved hydrogen sulfide is weakly ionized ($Ka_1 = 1.0 \times 10^{-7}$) and forms a small amount of hydrosulfide (HS^-). The oxidation of hydrosulfide was originally carried out with air, but the slow reaction kinetics seriously influenced the applicability of the process. Therefore vanadium (V) and sodium salts of anthraquinone disulfonic acid (ADA) were added to promote the oxidation. The hydrosulfide (HS^-) reacts rapidly with the vanadium, allowing the equilibrium,

$$H_2S = H^+ + HS^-$$

to be pushed to the right. This shift allows more hydrogen sulfide to dissolve in the scrubbing solution, and improves the removal efficiency. Hydrogen sulfide concentrations in the exhaust gas of 100 ppmv are achievable with the Streford Process. The overall oxidation-reduction reaction for the process is:

$$2H_2S + O_2 \longrightarrow 2H_2O + 2S$$

Scrubbing liquor is regenerated by air blowing, and the vanadium is restored by oxygen transfer of the ADA:

$$V^{4+} + ADA = V^{5+} + \text{reduced ADA}$$

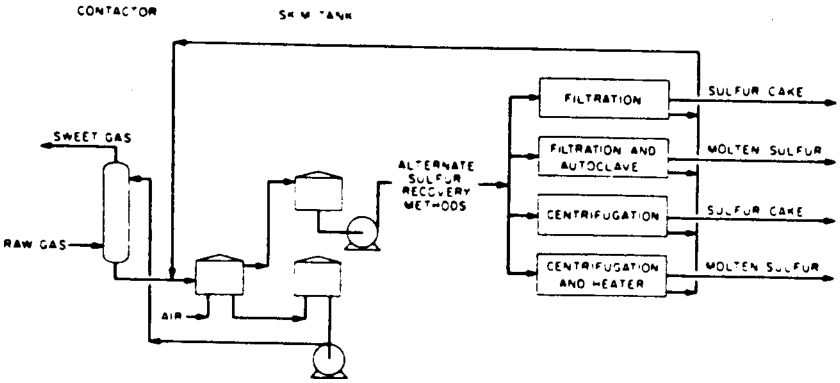

Figure 7-9 Stretford Process Flow Chart

Stretford developers have developed processes that convert organic sulfur compounds in hydrocarbon streams to hydrogen sulfide by treatment with steam over a U_3O_8-containing catalyst, enabling the resulting hydrogen sulfide to be removed in the Stretford system.

There are a number of problems associated with the chemistry of the Stretford scrubbing solutions:

- Carbon dioxide (CO_2) is usually absorbed in alkaline systems and converted to bicarbonates and carbonates. The Stretford process is no exception and carbon dioxide scrubbing can diminish the efficiency of hydrogen sulfide removal. However, if the reaction conditions are optimized, the dissolution of carbon dioxide can be minimized. A heating step in the recycling of the scrubbing liquid is required to drive off any unreacted carbon dioxide.
- Thiosulfate $(S_2O_3)^=$ can be formed in the regeneration cycle. Oxygen reacts with the hydrosulfide (HS) forming thiosulfate. The higher the pH and temperature, the higher the yield of thiosulfate.
- Vanadium, oxygen, and sulfur complexes are formed if the concentration of hydrosulfide is higher than the vanadate ion can oxidize. Potassium or Sodium Tartarte has been used to repress this reaction.
- The scrubbing solution can also be contaminated by gases containing sizeable amounts of tars or hydrocarbons which reduce the efficiency or even plug the reaction chamber.
- Hydrogen cyanide (HCN) is also collected by the Stretford system and that reaction results in thiocyanates which cannot be regenerated.
- Stretford units are not capable of recovering sulfur from carbonyl sulfide or carbon disulfide (COS and CS_2), which as a result, are presently vented to the atmosphere with fugitive hydrogen sulfide.

7.2 SO_2 REMOVAL

The sulfur dioxide stack gas pollution treatment technologies developed for industries such as sulfuric acid plants, smelters, and power plants may be immediately transferrable to Claus emissions. Sulfur dioxide removal technologies can be grouped according to whether the trapped sulfur is contained in a "throw-away" product or recovered as elemental sulfur or sulfuric acid:

Throwaway	Recovery
Dry process (lime)	Alkali absorbents
Wet processes	Alkaline earth absorbents
Direct lime-limestone scrubbing	Metal oxides
Indirect limestone scrubbing	Adsorption
	Catalytic oxidation and reduction

7.2.1 THROWAWAY PROCESSES

Throwaway operations, using lime and/or limestone, are of two types--wet or dry. Dry systems use boiler-injected limestone (as is or calcined) to recover sulfur oxides from the gas stream (Figure 7-10). However, the disadvantages of the system (low SO_2 absorption, excess limestone requirements, fouling, lowering of electrostatic precipitator efficiency) make the process inadequate for sulfur dioxide emission control.

Wet systems are of two types--direct and indirect lime-limestone scrubbers. Direct processes use limestone ($CaCO_3$) or hydrated lime [$Ca(OH)_2$] added to the scrubber circuit or limestone injected into the boiler, causing calcination to lime, followed by lime slurry scrubbing (Figure 7-11). The discharge stream from these processes, containing the throwaway reaction products, fly ash, and unreacted alkali, is dewatered and sent to a disposal pond or landfill site. The scrubbing reactions involved in these systems are:

$$\text{Limestone:}\quad CaCO_3 + SO_2 + 1/2\ H_2O = CaSO_3\cdot 1/2\ H_2O + CO_2\ ;$$

$$\text{Lime:}\quad Ca(OH)_2 + SO_2 = CaSO_3\cdot 1/2\ H_2O + 1/2\ H_2O\ .$$

The Commonwealth Edison Will County Station achieves a 75 to 85% sulfur dioxide removal efficiency; major problems are demister pluggage, mechanical problems, and waste gypsum sludge disposal. Coal-fired power plants using carbide sludge [$Ca(OH)_2$] remove up to 80 to 95% of the sulfur dioxide in the flue gases.

Indirect lime-limestone scrubbing uses a soluble medium to absorb the sulfur dioxide, followed by the scrubber effluent solution of lime or limestone for medium regeneration or neutralization. Absorbents used in this system include sodium salts, ammonium salts, water, ammonium sulfate, or carbon; the system is thus termed Double Alkali. Double Alkali flue gas desulfurization systems scrub flue gases with sodium or ammonium salts in solution. The resulting liquor is then treated with lime or limestone, producing a throwaway sludge. Reactions for this system are:

$$\text{Scrubber:}\quad Na_2SO_3 + SO_2 + H_2O = 2NaHSO_3\ ;$$

$$\text{Regenerator:}\quad 2NaHSO_3 + Ca(OH)_2 = Na_2SO_3 + 3/2\ H_2O + CaSO_3\cdot 1/2\ H_2O\ .$$

The gypsum solids require disposal. A sulfur dioxide removal efficiency of 90 to 99% is expected on the basis of pilot-scale results. Disposal options for gypsum (hydrated calcium sulfate) include adding it to the ash for landfill or minefill; thus, the term "throwaway" is used. Recent literature has detailed possible new uses for gypsum, such as wallboard manufacture. One SO_x removal process waste composed of CaO and $CaSO_4$ is being tested for wastewater treatment potential; it appears to be effective in removing turbidity and orthophosphate from wastewater. Disposal options for the ash and sludge combination wastes from wet

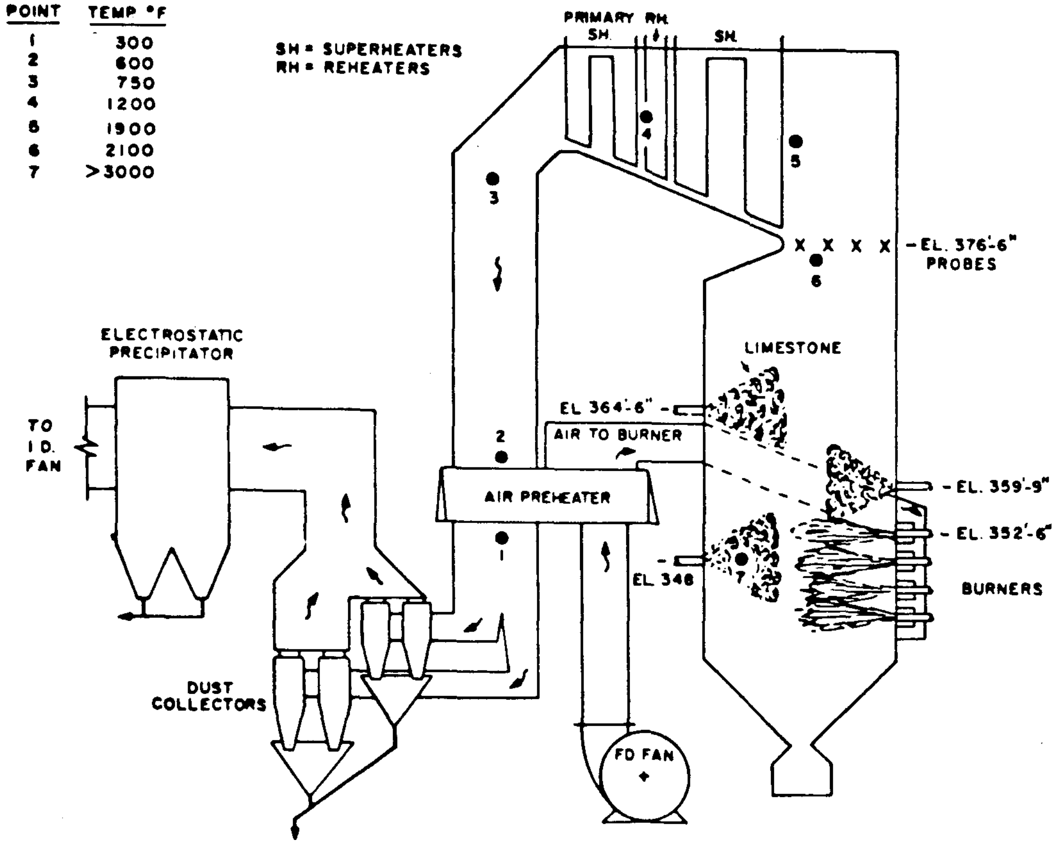

Figure 7-10 Dry System for Removing SO_2 from Stack Gas by Sorption in Limestone

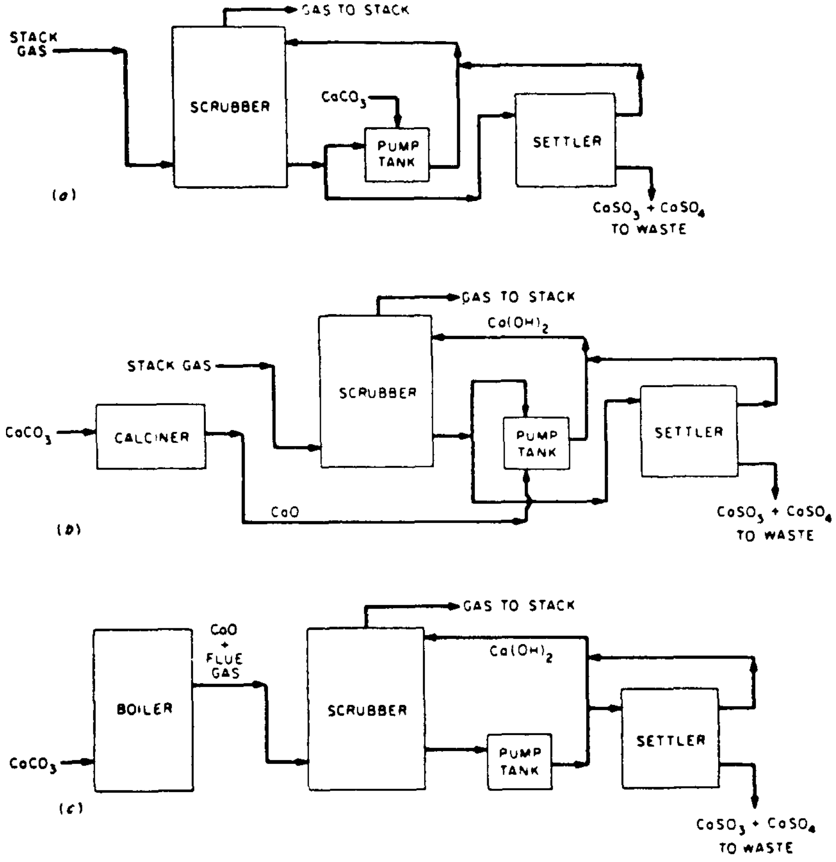

Figure 7-11 Major Process Variations for Use of Lime or Limestone for Removal of SO_2 from Stack Gases: (a) Scrubber Addition of Limestone; (b) Scrubber Addition of Lime; (c) Boiler Injection of Limestone

lime-limestone scrubbing are currently under study; however, use as a mineral aggretage or pozzolanic base appears to be the most promising option.

7.2.2 RECOVERABLE PROCESSES

7.2.2.1 CITRATE PROCESS

The Citrate process (Figure 7-12) of stack gas scrubbing has been used to treat lean smelter and coal-fired generating plant gases. The gases are cleaned of particulate matter and sulfur trioxide. In a packed absorption tower, the gas is scrubbed with a partially neutralized solution of citric acid and sodium carbonate. A sulfur dioxide removal efficiency of 90 to 95% is possible. The sulfur-dioxide-laden stream reacts with hydrogen sulfide to yield elemental sulfur, which is filtered from the recyvlable sorbent.

7.2.2.2 MAGNESIUM OXIDE PROCESS

The magnesium oxide process is similar to other alkaline flue gas desulferization processes in that the reaction products are bisulfite and sulfate. The process is different in that the magnesium oxide used for the scrubbing solution has a higher affinity for SO_2 than lime and the process is regenerable.

Removed magnesium sulfite is dried and calcined to remove the sulfur dioxide and regenerate magnesium oxide through thermal decomposition:

$$MgSO_3 = MgO + SO_2$$

The sulfur dioxide can be converted to sulfuric acid or to elemental sulfur. The MgO Scrubbing process is capable of removing 90% of the sulfur dioxide for a wide range of flue gas concentrations.

7.3 RECOVERED SULFUR DISPOSAL

The largest amounts of sulfur (ranging from 50 to 98% of the total input) are expected to be recovered by the recovery facilities and will require resale or environmentally safe disposal as land- or minefill. Options for elemental sulfur disposal now include resale, use as landfill, or return to mines; sulfuric acid allows only resale. Routes for elemental sulfur resale include production of sulfur-containing fertilizers to slow the release of urea, sulfur-based paving material as a bulk aggregate limestone substitute, sulfur foams for pavement subsurfaces, and thermal and acoustical insulation. New uses for sulfur include plastics, surface bonding structural materials, mortar and brick panels, asphalt paving mixes and binders, soil stabilizers, and electrodes for lithium batteries. Potential agricultural uses of sulfuric acid include reclamation of sodic soils to increase plant nutrient availability; treatment of alkaline or ammoniated irrigation water; control of certain weeds and pathogens; and improvement of range grass establishment.

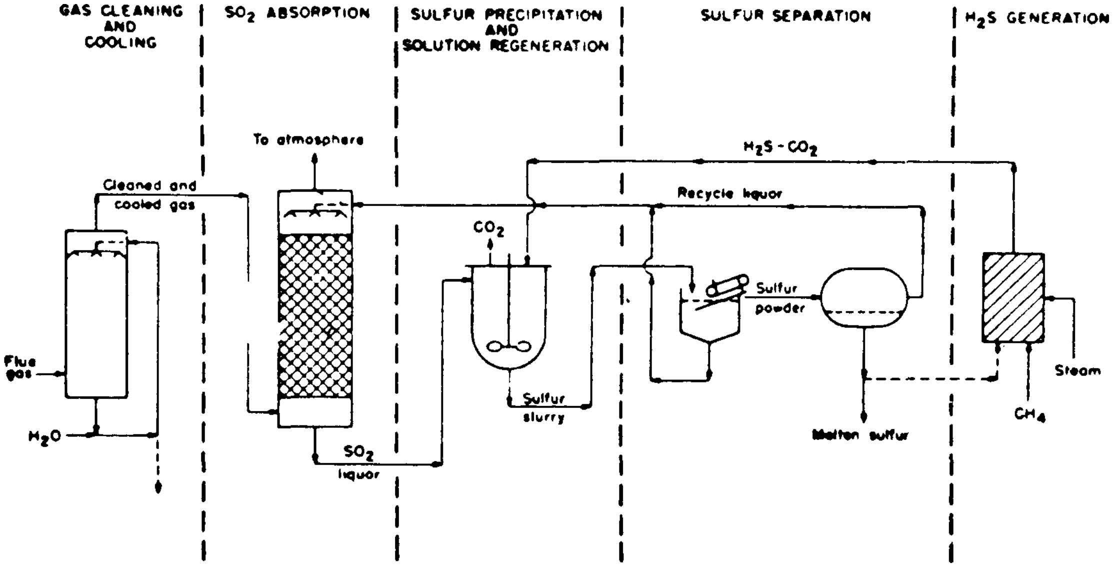

Figure 7-12 Citrate Process Flow Diagram

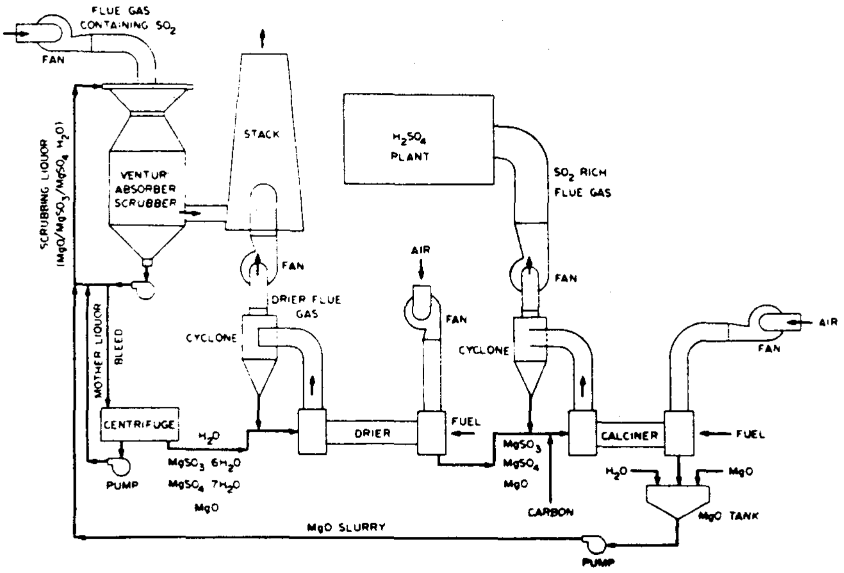

Figure 7-13 MgO Scrubbing Process Flow Chart

Finding new routes of disposal for sulfur from the oil shale industry may be important, since the amounts of sulfur anticipated only from coal desulfurization may overload the present sulfur resale market, requiring development of either new sulfur uses or acceptable methods of environmental sulfur disposal.

8. ELECTROSTATIC PRECIPITATION

Electrical precipitation is frequently called the Cottrell process for Frederick Gardner Cottrell (1877 to 1948), who designed and built the first successful commercial precipitator. It is defined as the use of an electrostatic field for precipitating or removing solid or liquid particles from a gas in which the particles are carried in suspension. The equipment used for this process is called a precipitator or treater in the United States. In Europe it is called an electrofilter.

The first recorded reference to the phenomenon of electrostatic attraction, which forms the basis for the precipitating action in an electrical precipitator, is attributed (Priestley, 1958) to Thales of Miletus about 600 B.C. He noted that a piece of amber that has been rubbed attracts small, light fibers. The word electricity came from elektron, the Greek word for amber. Pliny wrote of the attraction of chaff and other light objects to the amber spindles of wheels in Syria.

It was not until William Gilbert published his historical *De Magnete* in the year 1600 that serious progress toward understanding electrical and electrostatic phenomena commenced. Gilbert compiled a list of "electrics," materials possessing the property of attraction when rubbed, and "nonelectrics," materials not having this property. In 1732 Stephen Gray succeeded in demonstrating that the so-called nonelectrics could be given an electrical charge if they were properly insulated. Since some materials could be charged positively and others negatively, two different types of electricity were postulated. In 1754 John Canton demonstrated that materials could be charged either positively or negatively, leading to the development of the single-fluid theory of electricity proposed by Benjamin Franklin.

In 1832 Faraday proposed an atomic theory of electricity. Faraday's theory resembled both the one-fluid and two-fluid theories. He assumed two kinds of charged particles, which we now call protons and electrons. He assumed that only the negative particles (electrons) could be transferred from one body to another.

Although the fact that charged particles attract or repel each other, depending upon whether the charges are unlike or like, had been known for some time, it was not until Coulomb devised a torsion balance of sufficient sensitivity that the relationship between the charge, separation, and force was determined. Coulomb demonstrated that the force of attraction or repulsion between two static charges is proportional to the product of the charges and inversely proportional to the square of the distance between them, as expressed in the equation:

$$F = \frac{q_1 \, q_2}{D \, s^2}$$

where

F = force of attraction or repulsion between two particles, dynes

q_1, q_2 = charge on particles, statcoulombs

D = dielectric constant of medium between the particles, dimensionless

S = distance between the particles, cm.

In a vacuum, for which the dielectric constant D = 1, if the force is 1 dyne and the distance between the (equal) charges is 1 centimeter, the fundamental electrostatic unit of charge is defined. Called a statcoulomb, it is the charge associated with approximately 2.08×10^9 electrons.

The forces exerted by electrical charges are dependent upon the medium through which they are exerted. Thus, the force as defined by Coulomb's law depends upon D, the dielectric constant of the medium. Values of the dielectric constant for a number of common materials are given in Table 8-1. The dielectric constant may be taken, with negligible error, as unity for air at normal temperature and pressure.

In order to explain the phenomenon of attraction and repulsion between charges, a hypothetical electric field is postulated. The strength of an electric field at any point may be expressed as the quotient of the force exerted on a test charge placed at that point divided by the magnitude of the charge. It must be assumed, of course, that introducing a charge into an electric field does not alter the field, which is a reasonable assumption only if the charge is very small compared with the strength of the field. Field strength may also be expressed as the potential difference divided by the distance. The equation below defines the strength of a uniform electric field:

$$E = \frac{F}{q} = \frac{V_o}{S}$$

where

E = field strength or electrostatic potential gradient, statvolt/cm

V_o = electrostatic potential difference, statvolt.

The first successful commercial use of electrical precipitation was developed by Cottrell in 1907 Cottrell, while an instructor at the University of California at Berkeley, was approached by the management of the recently constructed Du Pont Explosives and Acids Manufacturing Plant near Pinole, California, about 12 miles north of Berkeley on San Pablo Bay. This plant was using the then new Mannheim process of "contact" method in place of the chamber process to manufacture sulfuric acid. In the contact process, sulfur dioxide and oxygen are passed through an iron oxide catalyst to form sulfur trioxide from which the sulfuric acid is made. Difficulty was experienced owing to arsenic, which was poisoning the catalyst. Cottrell first attempted a solution to the problem by means of collecting the acid mist with a laboratory model centrifuge. Although the centrifuge principle was moderately successful in the laboratory, the first pilot plant model tried at Pinole was a

MATERIAL	DIELECTRIC CONSTANT
Air	1.0006
Alumina	4.50 to 8.40
Ammonium Chloride	7
Calcium Carbonate	6.14
Dolomite	6.80 to 8
Quartz (fused)	3.75 to 4.10
Sulfur	4
Water	80

Table 8-1 DIELECTRIC CONSTANTS FOR SOME COMMON MATERIALS (Note: These values vary with temperature, humidity, pressure, and electrical frequency at which measured.)

failure. Before Cottrell was able to proceed further with this work, all his notes and models were destroyed in the fire that accompanied the San Francisco earthquake of 1906. Discouraged but undaunted, Cottrell rejected an appointment to head the Chemistry Department at the Texas Agricultural and Mechanical College in order to follow up an idea of collecting the acid mist by electrical precipitation.

After demonstrating that electrical precipitation would collect smoke, Cottrell made a small contact acid plant and passed the sulfuric acid mist into a round glass jar. Inside the jar was a cylinder of wire screening around which was wrapped several turns of asbestos-wrapped sewing twine. The walls of the jar became the collecting electrode. Three factors contributed to the ultimate success of his first electrostatic precipitator. The first was the use of a pubescent electrode. He also discovered that the use of negative polarity resulted in a more stable and efficient operation. The third factor was his use of rectified alternating current. For this purpose, he developed a mechanical rectifier. With financial backing from friends, Cottrell organized two corporations and constructed a pilot collector that handled 100 to 200 cubic feet of gas per minute. This pilot unit was installed at Pinole where it operated satisfactorily, handling a gas current representing about 3 tons of sulfuric acid per day and consuming less than 1/3 kilowatt.

8.1 ELECTROSTATIC PRECIPITATION MECHANISMS

The process of electrostatic precipitation consists of a number of elements or mechanisms, which are now listed.

- Gas ions are formed by means of high-voltage corona discharge.
- The solid or liquid particles are charged by bombardment by the gaseous ions or electrons.
- The electrostatic field causes the charged particles to migrate to a collecting electrode of opposite polarity.
- The charge on a particle must be neutralized by the collecting electrode.
- Reentrainment of the collected particles must be prevented.
- The collected particles must be transferred from the collecting electrode to storage for subsequent disposal.

The accomplishment of these functions by an electrical precipitator has required the development of many specialized techniques for specific materials, though the broad principles remain as enumerated.

8.2 ELEMENTS OF SINGLE-STAGE ELECTRICAL PRECIPITATORS

Essential features of precipitator design, exemplified in Figure 8-1, include the following elements: Rappers, shell, cable from rectifier, support frame, corona wires, collecting plates, gas inlet, hoppers, wire-tensioning weights, and hopper baffles.

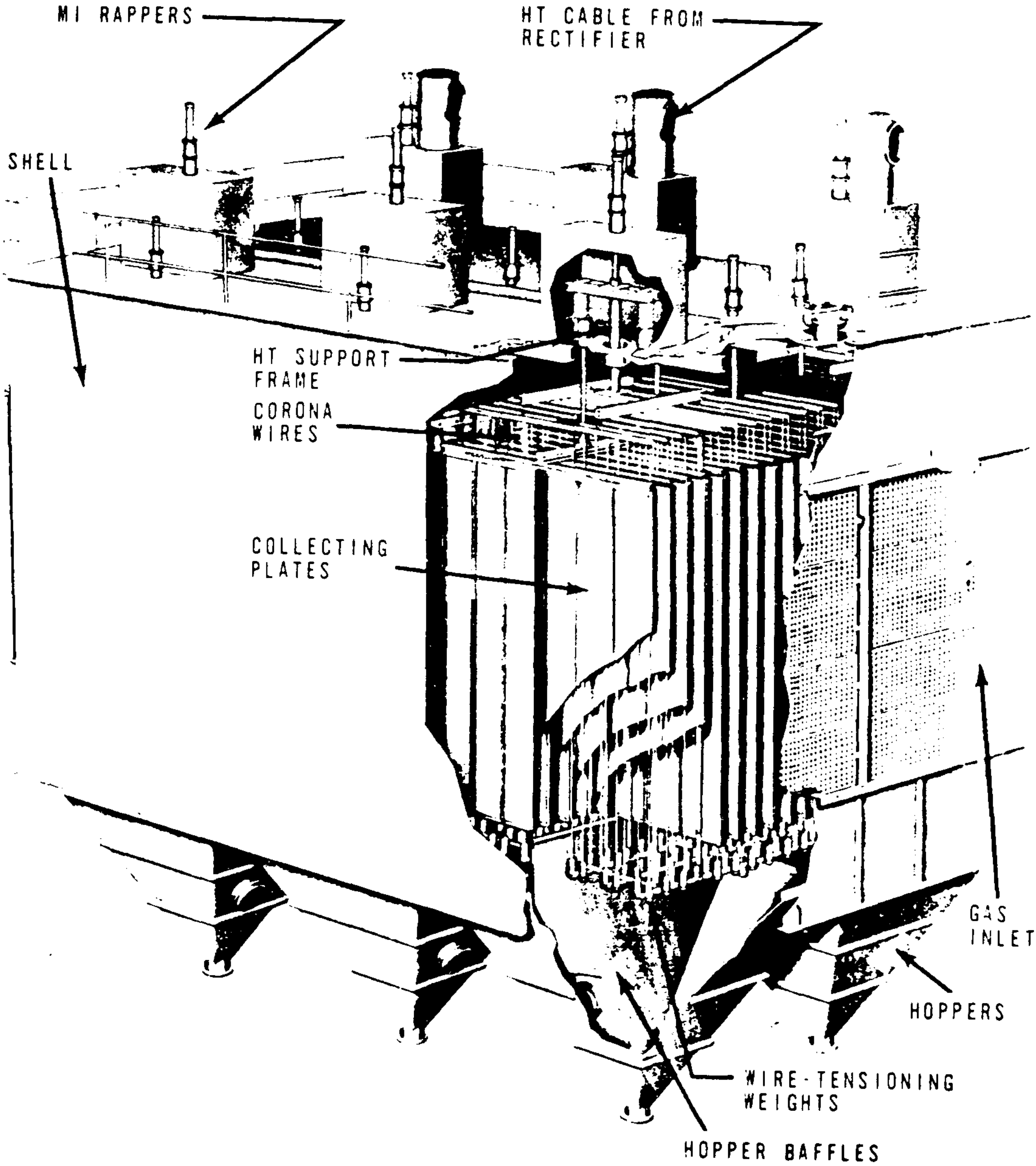

Figure 8-1 Basic Structure of a Typical Precipitator

8.2.1 DISCHARGE ELECTRODES

The discharge electrodes provide the corona, without which the precipitator cannot function. These may be round wire, square twisted rods, ribbons, barbed wire, and so forth. Steel alloys are commonly used, but other materials that have been used include stainless steel, fine silver, nichrome, aluminum, copper, hastelloy, lead-covered steel wire, and titanium alloy. While the choice of material is usually dictated by the requirements of corrosion resistance, the physical configuration must be determined to meet the electrical characteristics requirements. When round wires are used, the diameter is usually about 3/32 inch, though it may vary from about 1/16 to 1/8 inch. Conventionally, 3/16-inch-square twisted wire has been used for precipitators serving catalytic cracking units. The use of barbs and various special shapes is strongly advocated by some authorities, but others equally competent dispute these claims, pointing out that no decided advantage has ever been established for the use of special discharge electrodes.

8.2.2 COLLECTING ELECTRODES

The variety of collecting electrodes available is even more diverse. Materials of construction and special shapes appear to be limited only by the imagination of the designer. While many of these special shapes have important advantages, the use of smooth plates, with fins to strengthen them and produce quiescent zones, has become most common in recent years. The preference between one special shape and another frequently becomes one of conjecture. Some of the special collecting electrode configurations marketed include perforated or expanded plates, rod curtains, and various hollow electrodes with pocket arrangements on the outside surfaces for conducting the precipitated dust to the hopper in quiescent gas zones. Concrete plates were used at one time but were abandoned about 1930 because of excessive cost and weight. Smooth transite plates are used occasionally because of their excellent corrosion resistance. These are, however, for unusual cases, because of the severe reentrainment problem. For fly ash, perforated or expanded metal plates provide a multiplicity of closely spaced holes that hold the ash while end baffles on the plates shield the perforated surfaces from the direct scouring action of the gas. Several variations of the V electrode have also been used and have similar characteristics. The hollow or pocket-type electrodes are attractive in principle, but in practice, a large proportion of the dust actually falls on the outside of the plates. Furthermore, much of the dust collected in the upper openings actually escapes to the outside through the lower openings because of the piston action of the falling dust.

8.2.3 TUBULAR COLLECTING ELECTRODES

Plate-type precipitators are usually preferred because they can handle a larger volume of gas in a smaller space for less investment than the tube type. The tube type, often called "pipe type," lends itself more readily, however, to wet collection and is, therefore, preferred for acid mists and tars.

8.2.4 REMOVAL OF DUST FROM COLLECTING ELECTRODES

Once the dust or fume has been precipitated on the collecting electrode or plate, it must be removed to a hopper or storage depository. In order to do this, rappers are commonly employed. The plates are struck sharp, hammer-like blows to dislodge the collected dust, which then falls by gravity into the collecting hopper. Reentrainment of a portion of the dust at this point must be held to a minimum. Frequently, satisfactory collection efficiency is completely negated by improperly operated or adjusted rappers.

For fly ash precipitation, the dust buildup on the collecting plates should be allowed to reach about 1/4 to 1/2 inch before it is rapped off. Discharge electrode rappers are necessary when treating ashes predominantly composed of fine particles less than 10 microns in diameter.

A satisfactory rapping system is characterized by a high degree of reliability, by ability to maintain uniform and closely controlled raps over long periods of time without attention, and by flexible and easily controlled rapping intensity. The usual practice is to rap sufficiently to dislodge all the dust layer at one time. Stack puffs are prevented by rapping only a small fraction of the electrodes at a time and using proper sequence.

Rapping mechanisms include mechanical (electric motor operated) and pneumatic or air operated. Most new installations, however, now use magnetic solenoid-operated rappers, which can be adjusted more accurately to control both frequency and intensity of the raps.

Rapping is usually done in zones, the number and location of rappers being dictated by the size and configuration of the precipitator. Rappers are always adjusted in the field under operating conditions. Factors that influence the intensity, frequency, and number of blows required per cycle include:

- Agglomerating characteristics of the dust,
- the rate at which the dust is accumulated on the collecting electrode,
- the tendency of the dust to become reentrained,
- the effect of the accumulated dust on the electrical operation of the precipitator, and
- the cycle of operation of the equipment being served.

In some cases where reentrainment is a severe problem, precipitators may be designed so that a number of sections may be closed in turn during rapping by means of dampers. While this may reduce the reentrainment loss during rapping, the usual practice is to rap during normal operation. When the equipment being served operates in cycles, it may be possible to bypass the precipitator for rapping during periods when little or no air contaminants are being vented. In some unusual cases it may be necessary to deenergize the precipitator in order to obtain effective removal of the collected dust during rapping. In other cases deenergizing may suffice to permit the collected dust to fall to the hopper by its own weight without the need to rap. With tube-type precipitators, when operated wet, it is not necessary to use rapping. Some plate-type precipitators are also operated without rappers for various reasons. For example, when transite plates are used, rapping is undesirable because these plates do not have adequate mechanical strength to withstand repeated blows. Hence, periodic water sprays are usually used in this case to wash the collected dust off the plates. Cycling the water sprays properly makes possible keeping the plates wet between flushings, which is a great aid in improving collection efficiency by minimizing reentrainment. The water sprays, when used, temporarily disrupt the electrical operation, so that this method is employed only in unusual cases.

8.2.5 PRECIPITATOR SHELLS AND HOPPERS

Precipitator shells may be made of a variety of materials. These include ordinary mild steel, lead-coated steel, acid-resisting brick and cement, poured concrete, carbon, tile, aluminum, wood, wrought iron, alloys of steel, rubber-coated steel, and vinyl, or other plastic coatings on steel or other supporting structures.

The collected dust is ordinarily stored in hoppers below the collecting electrodes for periodic or continuous disposal. Adequate storage must be provided to accommodate the collected dust between hopper cleanouts. If the dust builds up too high a level in the hopper, there is danger of reentrainment or shorting the discharge electrodes, or both. The sides of the hoppers must have adequate slope to prevent bridging and hangup. Vibrators may be required if the dust or fume does not move freely. Discharge from the hoppers may be by means of slide gates, motor-operated rotary valves, or screw conveyors. The latter two are suitable for continuous operation.

8.2.6 ELECTRICAL REQUIREMENT

In order to achieve maximum collection efficiency, electrical precipitators are operated as close to the sparking voltage as practicable without excessive sparking. The following gives the order of magnitude of current and field strength usually encountered in practice.

$$i_o = 3 \times 10^3 \text{ to } 3 \times 10^4 \text{ statampere/cm (0.03 to 0.3 milliampere/ft)}$$

$$E = 5 \text{ to } 20 \text{ statvolt/cm (3.8 to 15.3 kilovolts/in.)}$$

The values of the potential difference used in single-stage electrical precipitation are usually from 20,000 to 100,000 volts. Since unidirectional current is required for electrical precipitation, it is necessary to transform the available power to a high voltage and then rectify the high voltage. Early precipitators used mechanical rectification exclusively, and many of them are still in use.

8.2.6.1 TUBE-TYPE RECTIFIERS

Electronic tube rectifiers were first used in electrical precipitation around 1920. The early tubes were unsatisfactory because of their short, uncertain life. These tubes have now been developed to the point where the average life in electrical precipitation service is in excess of 20,000 hours. In some cases over 30,000 hours of service have been obtained.

Filament voltage adjustment on tube rectifiers is a critical factor in tube life. As a rough guide, increasing filament voltage by 5% reduces filament life by a factor of 2 while reducing voltage by 5% increases filament life by a factor of 2. Thus, it is general practice to operate tube filaments in precipitator service at 5 to 10% below rated values, that is, at 18 to 19 volts rather than 20 volts, which is the rated value for most precipitation rectifier tubes.

8.2.6.2 SOLID-STATE RECTIFIERS

The development of solid-state rectifiers has made mechanical rectification obsolete. Selenium rectifiers provide reliable service with long life; however, they are subject to damage from excessively high temperatures. Silicon rectifiers, which are even newer in precipitation service, do not have the shortcoming of being subject to temperature damage. Although the solid-state rectifiers are somewhat more expensive than the electronic-tube type, their use is justified on the basis of a long, useful life and troublefree operation. Life expectancy of selenium rectifiers is estimated to be about 100,000 hours. Silicon rectifiers, which are hermetically sealed, appear to have unlimited life.

8.2.6.3 OPERATING REQUIREMENTS

The operating voltage of a precipitator cannot be predicted precisely. Dust conditions have an important bearing on the operating voltage. For practical purposes, each manufacturer standardizes on a limited number of basic transformer voltages. For example, one manufacturer designs all equipment around transformer ratings of 30,000; 60,000; 75,000; and 90,000 volts secondary.

The average electric power supplied to the corona commonly ranges between 40 and 120 watts per 1,000 cubic feet per minute of gas treated. In general, higher voltage and power provides higher precipitator efficiency and performance .

The use of automatic voltage control results in increased collection efficiency from the same size precipitator or permits the use of a smaller precipitator for the same collection efficiency. The precipitator voltage is maintained at the optimum value by a spark counter or current-sensing feedback circuit. Once the control has been set for the desired spark rate, the precipitator is held constantly at maximum efficiency regardless of fluctuating conditions and without attention from an operator.

8.2.7 UNIFORM GAS DISTRIBUTION

The average velocity of the gas in the duct upstream from a precipitator is usually 40 to 70 feet per second. In the treater, however, the gas velocity is 2 to 8 feet per second. Because maintaining uniform gas velocity and dust distribution in the treater is important, much attention has been paid to the transition from a high velocity in the duct to a low velocity in the precipitator. Splitters are almost universally used in all bends or elbows in the approach to the precipitator. This also helps reduce the draft loss. Distribution grids of many types have been developed. The choice of type to use in a particular installation can usually be made reliably only by means of scale-model studies. Much of the work in this field is trial and error until a reasonably uniform gas velocity distribution is obtained in the model. The percentage of open area has an important bearing on the performance of distribution grids. Experience may reduce the problem to one of degree rather than of kind so that all that need be determined is the optimum position of the grid. In some cases, installing a perforated plate at the outlet of the precipitator has been found as important as installing one at the inlet. A very common type of design consists of one or two flat perforated plates at the inlet of the treater.

The importance of uniform gas velocity through the treater cannot be overemphasized. In all precipitator efficiency equations an increase in the gas velocity or flow rate reduces the efficiency exponentially. Conversely, a decrease in gas velocity or flow rate increases the efficiency exponentially. For a constant volume of gas through the precipitator, maximum efficiency is attained when the velocity is uniform. As the velocity increases through one section of the precipitator, collection efficiency decreases. At the same time the velocity must decrease through other parts of the precipitator since the total flow rate remains the same. The efficiency for the sections having the lower velocity will increase. The increase in efficiency through the low-velocity sections of the precipitator can never compensate for the loss in efficiency through the high-velocity portions of the precipitator.

8.2.8 EFFECTS OF RESISTIVITY

A dust such as carbon with very low electrical resistivity readily relinquishes its negative charge to the collecting electrode and assumes a positive charge. Since positive charges repel each other, the carbon particle is repelled from the collecting electrode into the gas stream where it is bombarded by negative ions and becomes negatively charged again. The particles are thus alternately attracted and repelled and so skip through the precipitator, knocking other particles, which have already been collected, off the collecting electrode.

If the dust, for example powdered sulfur, has a high electrical resistivity, it is unable to give up its negative charge to the collecting electrode. As the layer of dust builds up on the electrode, it acts as an insulator. The potential drop across this dust layer may build up to high values, which may have an adverse effect on the corona discharge and may set up a secondary brush discharge at and within the dust layer. This condition is called "back discharge" or "back corona," and may seriously impair the performance of the precipitator.

When the dust, for example cement dust, has medium resistivity, it can relinquish part of its charge to the collecting electrode. The rate at which the charge leaks off increases as the dust layer builds up and the potential drop across the dust layer increases until a condition of equilibrium is achieved. Sufficient negative charge is retained by the particles to maintain a force of attraction between the particles and the collecting electrode. When the weight of the collected dust becomes sufficiently great, particles fall off, of their own weight, or are jarred loose when the electrodes are rapped.

The electrical resistivity varies with temperature and moisture for some representative dusts. Collection efficiency is adversely affected when the electrical resistivity is as low as 10^4 ohm-centimeter or as high as 10^{10} ohm-centimeter. Apparently then, for many materials, collection efficiency is adversely affected when the temperature is 250 to 400°F, the range in which it is normally desired to operate the precipitator. The adverse effects of high resistivity may be avoided by operating at a higher temperature, but this is usually not desirable because of the additional heat losses. Operation at lower temperatures to the left of the peak of the resistivity curve is frequently objectionable because of excessive corrosion. An alternative is to increase the moisture content or add other conditioning agents.

The addition of water vapor, acid, or other conducting material increases the surface conductivity of high-resistivity dusts by adsorption on the particle surfaces, which reduces the apparent electrical resistivity. Some materials used as conditioning agents include water vapor, ammonia, salt, acid, oil, sulfur dioxide, and triethylamine.

In addition to the beneficial effects on the electrical resistivity of the dust by the addition of moisture, water vapor has a pronounced effect on the sparking voltage in an electrical precipitator. In most cases the effect of the moisture on the electrical resistivity of the dust predominates when the temperature is below 500°F, and the effect of the moisture in increasing the sparking potential predominates at temperatures above 500°F.

8.3 ELEMENTS OF TWO-STAGE ELECTRICAL PRECIPITATORS

The Cottrell-type precipitator is usually designed and custom built specifically for installations required to process large volumes of contaminated air. Since 1937 a somewhat different type has been marketed. This unit, developed by Penney (1937), is now called the low-voltage, Penney, or more commonly, the two-stage precipitator. It is also occasionally referred to as the air-conditioning precipitator or "electronic air filter."

The two-stage unit differs from the Cottrell type in that the contaminated air is first passed through a variable-strength ionizing field before being subjected to a separate uniform field where the charged particles are collected. Figure 8-2 shows the fundamental arrangement of the active electrical components. Basic operating principles are the same as those discussed for the Cottrell precipitator. A high-voltage corona discharge ionizes gas molecules that cause charging of particles passing through the field. The charged particles then tend to migrate toward electrically grounded or oppositely charged surfaces where they are removed from the airstream.

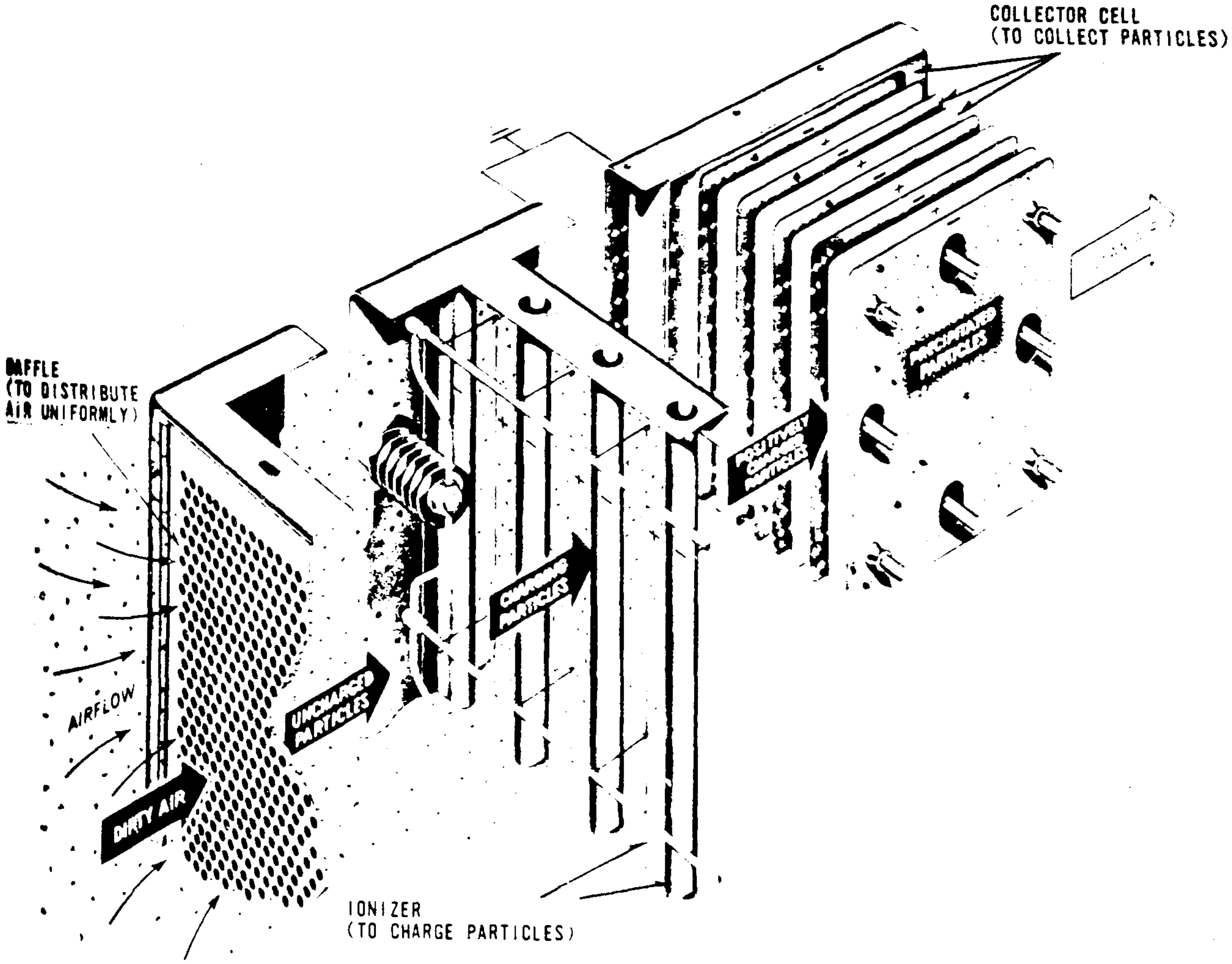

Figure 8-2 Components of Standard Two-Stage Precipitator

8.3.1 TWO-STAGE DUST SEPARATION

The physics of dust separation in a two-stage precipitator may best be understood by examining the stages separately. The function of the ionizing stage is to induce an electrical charge upon the particles in the airstream. When an electrical potential is applied between a wire and a grounded strut, an electric field is created that varies from a high strength near the wire to a low at the strut. When the potential is increased to the "critical corona voltage," local ionization of the airstream near the wire occurs and a blue corona is formed. Arcing or "sparkover" results if the voltage is further increased to a point where total ionization of the air between the electrodes occurs. This effects a short circuit, and the precipitator's efficiency drops correspondingly.

Below the corona's starting voltage or critical corona gradient, no ionization occurs and consequently no charging of particles takes place. The critical corona gradient, for round wires, is basically a function of wire size and condition.

8.3.2 ELECTRICAL REQUIREMENTS

Power consumption is a function chiefly of particle size, dust loading, voltage, and wire size. The actual power required for removal of a dust particle by precipitation is small compared with that for mechanical collectors because the energy is applied primarily to the particle only and not to the total gas stream. In practice, power requirements for standard two-stage precipitators are 15 to 40 watts per thousand cfm. The operating cost is, therefore, low.

High voltage is obtained by vacuum tube rectifying power packs that operate from a 110- to 120-volt a-c primary circuit. On small units one power pack may supply both ionizing and collecting sections. For larger volumes two or more power packs may be used in parallel for various groupings of ionizing cells with separate power packs for the collecting sections.

Normally, positive polarity in the ionizing section is used in two-stage precipitators since it is thought that less ozone and oxides of nitrogen are thus produced. With positive polarity, sparkover voltage is much closer to the critical corona voltage than is found with negative polarity. The practical operating voltage limit for standard units is about 18 kilovolts, with most operating at 10 to 13 kilovolts. Current flow under these conditions is small, 4 to 10 milliamperes. The collecting plates are usually activated at 5.5 to 6.5 kilovolts with precipitation's occurring on the grounded spacing plates. The actual current flow is very small since no corona exists between the plates.

8.3.3 AIR CAPACITY IN TWO-STAGE PRECIPITATORS

Manufacturers normally rate these units at 85 to 90% efficiency by tests based on discoloration comparisons and at velocities between 300 to 600 fpm. For air-conditioning purposes these values are usually adequate, but for cleaning process air, a more thorough evaluation is necessary. Efficiency of cleaning for this latter purpose is usually based upon weight recovery and will likely be lower than by discoloration comparison.

If dust particles move smoothly between the plates, collection efficiency is a function only of drift velocity and residence time. Penney assumes streamline flow through the precipitator, while recognizing that some turbulence occurs, in arriving at the required collector plate area for air-cleaning precipitators. Although 600 fpm is the limiting velocity for streamline flow in most two-stage units, mechanical irregularities reduce the permissible velocity.

It has been found that collection area is not always controlling. At a velocity of 300 fpm a dust particle is in the ionizing field only about 0.05 second, a very brief time when compared with 1.0 to 10 seconds for single-stage units. For some contaminants the increased efficiency at low velocity is the effect of increased ionization time rather than of streamline flow through the collector plates.

The degree of ionization may be increased by increasing the number of ionizing electrodes, either by decreasing spacing or by installing a second set of ionizing wires in series. Since decreasing spacing reduces the allowable voltage without sparkover, use of the series arrangement appears advantageous. Decreased spacing has the advantage of lower first cost and lower space requirements.

8.3.4 AIR DISTRIBUTION IN TWO-STAGE PRECIPITATORS

The distribution of the airstream entering the precipitator is as critical for high-efficiency two-stage operation as many other factors normally receiving more attention. A superficial velocity, the ratio of total airflow to precipitator cross-sectional area, is useful for equipment selection but may be misleading for close design. For conditions of low overall velocity of approximately 100 fpm, pressure drop through a precipitator is insignificant, and redistribution of high- or low-velocity areas of the airstream will not occur. Variations in airflow from 3 times average velocity to actual reverse flow have been observed in the vertical-velocity profile of these units for hot gas streams. Figure 8-3 shows that high velocity produces low efficiency while extremely low velocity does not result in compensating improvement. Overall efficiency is thus lowered. Two-stage precipitators are normally installed with horizontal airflow and frequently in positions requiring abrupt changes in direction of ductwork preceding the unit. Design such as this results in turbulent, uneven airflow. If air enters the precipitator plenum from an elbow or unsymmetrical duct, the air tends to "pile up" on the side of the precipitator opposite the entry.

Numerous methods are available for balancing the flow. A straight section of duct upstream eight duct diameters from the entry prevents transverse unevenness if a gradually diverging section precedes the precipitator. If this is not possible, mechanical means must be used. Turning vanes installed in an elbow or curve maintain a uniform distribution and also reduce pressure drop across the elbow, but do not balance flow satisfactorily. Baffles of various types or egg crate straightening vanes may be used in the transition duct. The most effective air-balancing device found consists of one or more perforated sheet metal plates that fully cover the cross-section of the plenum preceding the ionizers.

The sheet metal plates introduce an additional pressure drop that must be considered in the initial exhaust system design. A study of distribution in

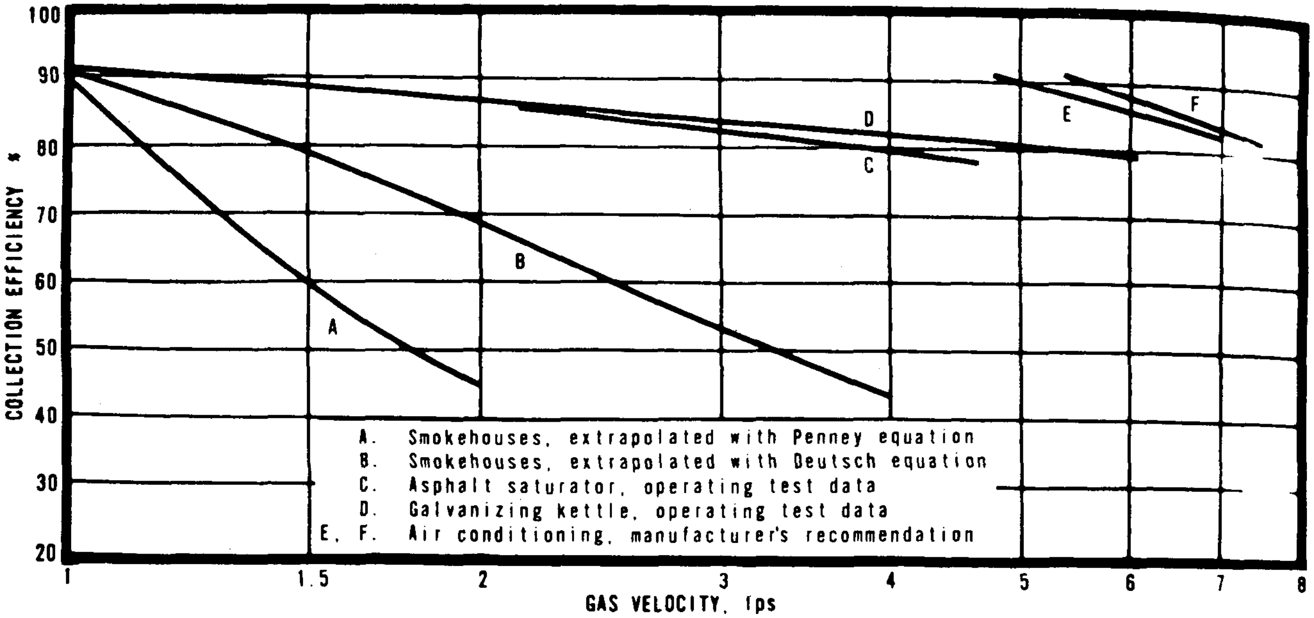

Figure 8-3 Efficiency of Two-Stage Precipitator as a Function of Velocity for Several Industrial Operations

single-stage precipitators found that each subsequent plate installed in series added materially to flow uniformity. It has also been indicated that, at low velocity, a perforated sheet immediately following the collector plates may in some cases be more effective than one preceding the ionizers. A sheet in this location also has the advantage of acting as an additional collecting surface for charged particles, though this effect is usually minor.

An open area of 40% for the perforated sheet has been found optimal, a range of 35 to 60% being generally adequate. Installations handling heated airstreams, above 100°F, at low velocities, require baffling to prevent high velocities at the top of the chamber due to thermal effects. In these cases a perforated sheet covering only the upper half of the plenum preceding the ionizers may suitably equalize the flow. Vertical-flow precipitators are not affected by thermal conditions in this manner.

8.3.5 TWO-STAGE PRECIPITATORS OF SPECIAL DESIGN

The foregoing discussion has been primarily concerned with precipitators available from manufacturers as standard units. The theory is applicable, however, to less common units. Under some conditions, dust of high resistivity, above 10^{11} ohm-centimeters, causes ionization at the collecting surface of single-stage precipitators. A decrease in the sparkover voltage results, and the impressed high voltage may have to be decreased to prevent excessive sparking. The reduction may have to approach the critical corona voltage, and if so, the corona discharge and its resultant ionization diminish with a corresponding drop in collection efficiency.

Sproull describes a two-stage unit designed to circumvent this and other effects. For avoiding back ionization at the grounded electrodes in the ionization section, wider spacing between ionizing electrodes was used. Here negative ionization was used and at a correspondingly higher voltage owing to the wide spacing. For preventing reentrainment at the collector plates and minimizing ionization and sparkover, electrodes such as parallel sheets of expanded metal were found to perform more efficiently than the usual flat plate electrodes. Optimum results with this unit were obtained by using a 33-kilovolt reversing polarity potential on the collector section.

For standard units the limiting air velocity is less than 600 fpm. White and Cole (1960) described a two-stage precipitator designed for high-efficiency collection of oil aerosols at velocities between 2,000 and 6,000 fpm. The reentrainment of precipitated oil is prevented by use of a slotted tube drain fitted over the trailing edge of the collecting surface. Units such as these are designed and manufactured to very close tolerances to permit maximum electric field strength and the least airflow disturbance. In the unit described, collection voltage is held at 20 kilovolts while ionizing voltage is about 35 kilovolts. Negative ionizing polarity is used to provide a higher sparkover level. Collection efficiencies as high as 99.8% by light diffusion standards are reported on oil mists.

For continuous removal of collected contaminants, wetted film plates have been used in the collector section. Installations have been made in which the collection section has been replaced by a water scrubber, which presumably acts as a more efficient grounded electrode for some types of contaminants. Located after the collecting plates, a perforated plate on which a flowing film of water is maintained has been found to improve efficiency slightly. The wetted baffle plate alone is not equivalent to the effect of the normal collecting electrodes.

Sulfuric acid mist is efficiently collected by two-stage precipitators constructed of corrosion-resistant alloys. The Atomic Energy Commission reports 94% efficiency, by radioactivity-testing techniques, on acidic-cell ventilation gases but adds a qualifying statement that two-stage units are not recommended as the final cleaner on exhaust gases containing radioactive agents without thorough trial in a pilot stage.

Self-cleaning precipitators are available in which the collector plates are mounted on a chain belt. The plates are slowly passed through an oil bath that removes collected solids and reapplies an oil coating to prevent reentrainment. Another somewhat similar unit uses an automatically winding dry-filter medium to trap the collected materials. Cleaning requires only the occasional replacement of the filter medium roll.

8.4 COARSE AND FINE DUST ELECTROSTATIC PRECIPITATOR DESIGN

A precipitator developed by J. Wiemer; U.S. Patent 3, 483,671; December 16, 1969; assigned to Metallgesellschaft AG, Germany, is one in which the spark or discharging or precipitating electrode hung in the tubular or pipe-type collecting or precipitating electrode in a vertical electrostatic dust precipitator is made, in the direction of gas flow through the precipitator, strongly discharging in the first third of its length, moderately discharging in the second third, and non-discharging in the last third. This causes both coarse and fine dust particles to be precipitated from the gas at a greater efficiency at a lower cost.

In all electrostatic dust collectors working with plate-type or pipe-type collecting electrodes and with vertical gas passages, it is the practice to apply uniform discharge electrodes over the entire length of the electric field and to feed the discharge electrodes from one single high tension power line. Such discharge electrodes with a uniform discharge characteristic over the entire length of the electric field are appropriate for the treatment of gases which contain coarser solid or liquid particles. In gases with a larger amount of fine solid or liquid particles with a grain size below one micron, space charges frequently occur at the inlet to the electric field. These space charges suppress a certain current flow which is necessary for an effective dust collection, while at the end of the electric field these space charges have vanished and a current flows corresponding to the normal gas property. Despite the differing electric characteristics of the gases to be cleaned or the varying electric conditions, respectively, it is desirable that a uniform discharge characteristic and thus a uniform collecting efficiency be attained over the entire length of the electrodes.

To avoid the above described disadvantages, this device is a vertical electrostatic dust collector with pipe-type collecting electrodes, and discharge electrodes having discharge points and discharge lugs, and with discharge wires of different discharge characterists with star-shaped cross-section and round cross-section, in which in each individual pipe-type collecting electrode, in the gas flow direction, approximately the lower third of the discharge electrode is strongly discharging, approximately the middle third is moderately discharging and the upper third is nondischarging.

In a modified form, the discharge electrodes are formed of round rods which have discharge points in approximately the first third of their length, and in the second third have discharge lugs or shorter spikes. In another modified form, the discharge electrodes are made of rods or wires of star-shaped cross-section having discharge points in the lower third and with the edges of the electrode being screened in the last third by a pipe sleeve.

Comparative tests revealed that with the same current the w- value of the discharge electrode of this design is about 20 to 25% higher than that of the discharge electrodes according to this state of technology which are usually used in electrostatic dust collectors having pipe-type collecting electrodes. Thus, by using the electrodes with different discharge characteristics according to this design, a considerable reduction is possible in the collector size and the high tension power line and thereby results in a decrease of the investment costs. Figure 8-4 is a sectional elevation of a precipitator according to the design.

The gases to be cleaned enter the raw gas chamber (2) of the electrostatic dust collector having pipe-type collecting electrodes through gas inlet connection (1). Below the raw gas chamber (2) is the dust hopper (3) with the dust outlet opening (4). The gases to be cleaned then pass upwardly through the pipe-type collecting electrodes (5) into the clean gas chamber (6) and leave the apparatus through the gas outlet duct (7). A hood (8) covers an insulator (9) from which is suspended a rod (10) holding a frame (11). The discharge electrodes (12) are hung from frame (11). The discharge electrodes are kept taut by means of weights (13) fastened to the lower end of the electrodes. The discharge electrodes (12 consist of a round or preferably a star-shaped rod having in the lower part discharge points (14), and in the middle part discharge lugs or shorter spikes.

8.5 ADVANTAGES AND DISADVANTAGES OF ELECTRICAL PRECIPITATION

The use of electrical precipitators for the collection of air contaminants has grown because of many inherent advantages, some of which are now listed.

- High efficiency can be attained. Efficiency may exceed 99% in some cases.

- Very small particles can be collected. There is no theoretical lower limit to the size of a particle that can be collected.

- Dusts may be collected dry for recovery of valuable material.

- Pressure and temperature drops are small. The pressure drop through an electrical precipitator seldom exceeds 0.5 inch vertical water column.

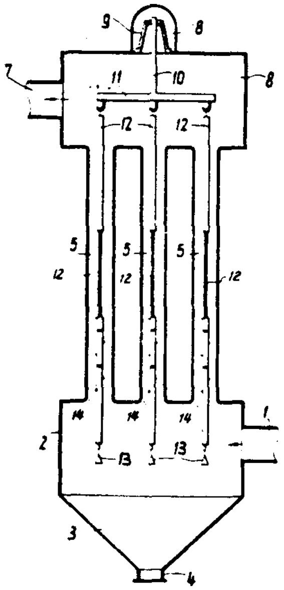

Figure 8-4 Electrostatic Dust Precipitator Specially Adapted to Handle Both Coarse and Fine Particles (Source: J. Weimer; U.S. Patent #3,483,671; December 1969)

- Precipitators are normally designed to operate continuously with little maintenance over long periods of time.
- There are very few, if any, moving parts, which tends to reduce the maintenance required.
- Precipitators can be used at high temperatures. Temperatures up to about 700°F are normal. Special designs have been used for temperatures as high as 1,300°F, but ordinarily the temperature does not exceed 1,000°F.
- Precipitators can be used to collect acid and tar mists, which are difficult, if not impossible, to collect by other methods.
- Extremely corrosive materials can be collected with special construction.
- Collection efficiency may be adjusted to suit the application by increasing the unit size.
- Very large gas flow rates can be handled.
- The power requirements for flow handled are low.

Electrical precipitators are by no means a panacea for air pollution problems. In many cases, disadvantages far outweight the advantages. Some of the drawbacks are now listed.

- Initial cost is high. In most cases the investment is greater than that required for any other form of air pollution control.
- Precipitators are not easily adaptable to variable conditions. Automatic voltage control helps to a great extent, but precipitators are most efficient when operating conditions remain constant.
- Some materials are extremely difficult to collect in an electrical precipitator because of extremely high or low resistivity or other causes. In some cases, this factor alone makes the use of electrical precipitation uneconomical, if not physically impossible.
- Space requirements may sometimes be greater than those for a baghouse. In general, this is true only when high collection efficiency is required for materials difficult to collect by precipitation.
- Electrical precipitation is not applicable to the removal of materials in the gaseous phase.
- The use of a precleaner, generally of the cyclonic type, may be required to reduce the dust load on a precipitator.
- Special precautions are required to safeguard personnel from the high voltage.

The decision whether to use an electrical precipitator, a baghouse, or some other type of collector must be made after considering all the following factors:

- Initial investment;
- maintenance, including the cost of power to operate the device;
- space requirements;
- collection efficiency, which must be evaluated in terms of the value of the collected materials or restrictions placed on the discharge of air contaminants by local regulations, or both (sometimes good public relations require an even higher collection efficiency than can be justified solely on the basis of economics).

The cost of providing high efficiency is illustrated by the fact that the cost nearly doubles when electrical precipitator collection efficiency is increased from 80 to 96% and almost triples from 80 to 99%.

B. LIQUID EFFLUENTS CONTROL TECHNOLOGY & SEWAGE ENGINEERING

9. ION EXCHANGE

Ion exchange involves the removal of ionic species, principally inorganic, from an aqueous or partially aqueous phase. The earliest applications of ion exchange (IE) were "water softening" - the substitution of sodium for calcium and magnesium in water, and the reverse substitution in sugar solutions to promote better crystallization. These applications were initiated in the late 1800's and early 1900's, using natural and synthetic zeolites (aluminosilicate minerals). Synthetic ion exchange resins were discovered in the late 1930's and were developed rapidly, particularly after World War II. Applications broadened rapidly into diverse areas such as hydrometallurgy (separations of uranium elements and the rare earth series, for example), and waste treatment (recovery and removal of chromium species). Deionization applications, especially for high quality process water (nuclear power and conventional steam generators) is probably still the most widespread application.

In simplest terms, ion exchange may be thought of as the reversible interchange of ions between an insoluble, solid salt (the "ion exchanger") and a solution of electrolyte in contact with that solid. As an example, a cation exchange material (designated R^-) having a cation (N^+) associated with it can react with a solution of an elecelectrolyte (M^+X^-) as shown below:

$$M^+ + X^- + R^-N^+ \rightleftharpoons R^-M^+ + N^+ + X^-$$

The direction (forward or reverse) and extent of the reaction are governed by the relative insolubilities of the insoluble salt(s) that can be formed [i.e., MX, NX, RM, RN] and by the equilibrium constant for the reaction,

$$K_{eq} = \frac{[RM][N^+]}{[RN][M^+]}$$

where [RM] and [RN], and $[N^+]$ and $[M^+]$ represent the concentrations of the cations in the ion exchange material, and in the solution, respectively. K_{eq} is constant for any given set of R^-, M^+, and N^+ for solution concentrations up to approximately 0.1 mol/liter, but may vary somewhat above that point. As with similar equilibrium reactions, changes in either may vary somewhat above that point. As with similar equilibrium reactions, changes in either $[M^+]$ or $[N^+]$ will result in a change in the equilibrium position, or extent, of reaction.

9.1 OPERATION

Fixed-bed ion exchange operations are straightforward systems, requiring a cylindrical ion exchange bed, tanks for solution storage, and pumps. The choice of materials is governed by the chemical environment.

Continuous ion exchange systems much more complex, requiring solids handling equipment and more intricate control systems.

9.1.1 INPUT STREAMS

Ion exchange is applicable to aqueous streams and to single-phase streams which are partially aqueous, such as ethylene glycol-water mixtures. It is also applicable to the water phase from aqueous slurries (scrubbers slurries, for example), provided that all suspended solids, which would plug the exchange bed, are removed prior to exchange.

As examples of general applicability, ion exchange can be used to remove and/or concentrate the following classes of chemicals.

- o Inorganic:
  - All metallic elements when present as soluble species, either cationic or anionic;
  - Anions such as halide, sulfate, nitrate, cyanide, etc.;
  - Neutralization of acidity or alkalinity, particularly useful for controlled neutralization by means of weak base and weak acid resins.
- o Organic (water soluble and in general ionic):
  - Acides such as carboxylics, sulfonics and some phenols, at a pH sufficiently alkaline to give the ions;
  - Amines, when the solution acidity is sufficiently acidic to form the corresponding acid salt;
  - Anionic and cationic species such as quaternary amines and alkylsulfates, frequently used as detergents.

Generally, if a species known to be exchangeable in aqueous solution can be scrubbed, dissolved or otherwise extracted from another form or phase (gaseous, liquid or solid), then ion exchange can be used to concentrate that species.

The upper concentration limit for the exchangeable ions for efficient operation is generally 2,500 mg/1, expressed as calcium carbonate (or 0.05 equivalents/1). This upper limit is due primarily to the time requirements of the operation cycle. A high concention of exchangeable ion results in rapid exhaustion during the service cycle, with the result that regeneration requirements, for both equipment and of the percentage of resin inventory undergoing regeneration at any time, become inordinately high.

The DESAL process (Rohm and Haas Company), a fixed-bed process for deionization is claimed to operate efficiently with electrolyte concentrations up to 4,000 mg/1. Continuous countercurrent operation offers advantages at high concentrations in that the resin flow (which is countercurrent to solution flow) can be relatively rapid, within certain limits, to keep up with rapid exhaustion.

There is also an upper concentration limit (around 10,000-20,000 mg/1), which is governed by the properties of the ion exchangers themselves, in that the selectivity (preference for one ion over another) begins to decrease as the total concentration of dissolved salts (ionic strength) increases.

Synthetic resins can be damaged by oxidizing agents and heat. In addition, the stream to be treated should contain no suspended matter or other materials which will foul the resin and which cannot be removed by the backwash operation. Some organic compounds, particularly aromatics, will be irreversibly absorbed by the resins, and this will result in a decreased capacity, as for example in the case of electroplating bath additives.

9.1.2 PROCESS CHEMISTRY

In the customary mode of usage, the ion exchanger is contacted with the solution containing the ion to be removed until the active sites in the exchanger are partially or completely used up ("exhausted") by that ion. The exchanger is then contacted with a sufficiently concentrated solution of the ion originally associated with it to convert ("regenerate") it back to its original form. For the general exchange

$$M^+ + X^- + R^-N^+ \rightleftarrows R^-M^+ + N^+ + X^-,$$

these steps are:

$$R^-N^+ + M^+ \longrightarrow R^-M^+ + N^+,$$

which is termed the "exhaustion", "service" or "loading" step, and

$$R^-M^+ + N^+ \text{ (high concentration) } \longrightarrow R^-N^+ + M^+,$$

which is termed the "regeneration" step. Since $[N^+]$ is higher in the regeneration step than in the service step, the solution volume for regeneration can be smaller, and consequently $[M^+]$ will be higher in the regeneration solution.

An alternative route for regenerating the ion exchanger involves a third ion (frequently a hydrogen ion in cation exchange) to give the corresponding form of the exchanger which can then be converted to the desired salt as shown below:

$$R^-M^+ + H^+ \longrightarrow R^-H^+ + M^+$$
$$R^-H^+ + N^+OH^- \longrightarrow R^-N^+ + H_2O$$

Such a sequence might be desirable in a case where H^+ was a much more effective regenerant than N^+, but where the release of H^+ into the solution being purified would be undesirable.

Thus, ion exchange provides a mechanism for removing an undesirable ion from a stream, and for transferring that ion, at a higher concentration than before, to another aqueous stream.

It is important to remember that this process is an exchange rather than a direct removal of ions, and thus does not alter the total molar equivalent concentration (i.e., total chemical equivalents of ions) of salts in the solution. In order to lower the total salt concentration in the solution (in equivalents per liter) it is necessary to perform a sequential exchange of cations and anions for hydrogen ion and hydroxyl ion respectively, thereby exchanging the salt for water. This "deionization" sequence for the salt M^+X^- is thus:

$$M^+X^- + R^-H^+ \qquad R^-M^+ + H^+X^-$$

$$H^+X^- + R^+OH^- \qquad R^+X^- + H_2O$$

The ion exchange process works well with cations (including of course, the hydrogen ion) and anions, both inorganic and organic. However, the organic species frequently interact with the exchangers (particularly the organic resins) via both absorption and ion exchange reactions, often necessitating the use of extremely high regenerant concentrations and/or the use of organic solvents to remove the organics. Consequently, most of the applications of ion exchange of interest to this study have involved inorganic species.

The relative insolubilities (or, better, the stability constants) of the possible salts that can be formed by the ions and the exchangers also enter into the K_{eq} and thus affect the extent of the exchange reaction. There are a variety of different cation and anion exchangers which form salts of more or less different stabilities with a particular ion. Thus, knowledgeable choice of a particular ion exchange material will often allow selective separation of one ion in solution from another, and afford selective removal of an undesirable ion from a number of innocuous ones.

As a general rule, ions with a higher charge will form more stable salts with the exchanger than those with a lower charge, and hence polyvalent species can frequently be selectively removed from a soltuion of monovalent ones.

In carrying out ion exchange reactions in a column or bed operation (as opposed to a stirred batch operation, which is occasionally used in chemical processing), there are four operations carried out in a complete cycle:

- o service (exhaustion
- o backwash
- o regeneration
- o rinse

The service and regeneration steps have been described above. The backwash step is one in which the bed is washed (generally with water) in reverse direction to the service cycle in order to expand and resettle the resin bed. This step eliminates channeling which might have occurred during service and removes fines or other material that may be clogging the bed. The rinse step removes the excess regeneration solution prior to the next service step.

There are three principal operating modes in use today: cocurrent fixed-bed, counter-current fixed-bed and continuous counter-current. Flow diagrams for these processes are shown in Figure 9-1.

Most ion exchange installations in use today are of the fixed-bed type, with counter-current operation coming more into favor, especially for removal (polishing) of traces of hazardous species from the stream prior to reuse or discharge.

In order to minimize regeneration chemical requirements (i.e., to make most efficient use of regenerant), many fixed-bed installations use a technique termed "staged", of "proportional", regeneration. The first part of the regeneration solution to exit from the ion exchange bed is the most enriched in the component being removed; the concentration of that component decreases in succeeding portions of the exiting regeneration solution. In staged regeneration, the solution is divided (generally in separate tanks) into two or more portions. The first portion through the bed is "discarded" (i.e., sent for subsequent treatment), while the second and succeeding portions (less rich in the species being removed) are retained. On the next regeneration cycle, the second portion from the preceding cycle is passed through the bed first (and then "discarded"), followed by the succeeding portions, the last of which is a portion of fresh regenerant. In this way, regenerant utilization can be maximized.

Continuous counter-current ion exchange systems in a variety of configurations have been offered on the commercial market over the past few years. Included in these are the Higgins-type systems, the Asahi-type, the Gravel C.I. Process, the Permutit process, and a fluidized moving-bed system. Of these, only the Higgins-type is currently being marketed by Chemical Separations Corp. with the other types being discontinued and even replaced by fixed bed units in some cases. Problems have included inefficiency stemming from the need for close flow control for upflow operation, high resin attrition, and the multitude of mechanical problems that might be expected from such complex solids-handling systems.

One other mode of ion exchange uses the so-called "powder resins." The ion exchange resins are prepared as fine powders (generally less than 400 mesh) and are applied in relatively thin layers (because of the high impedance to flow) to a filter support (plate, tubular filter, etc.) The fine particles are extremely efficient for ion exchange (large surface area and little intra-particle diffusion), but are generally not regenerated because

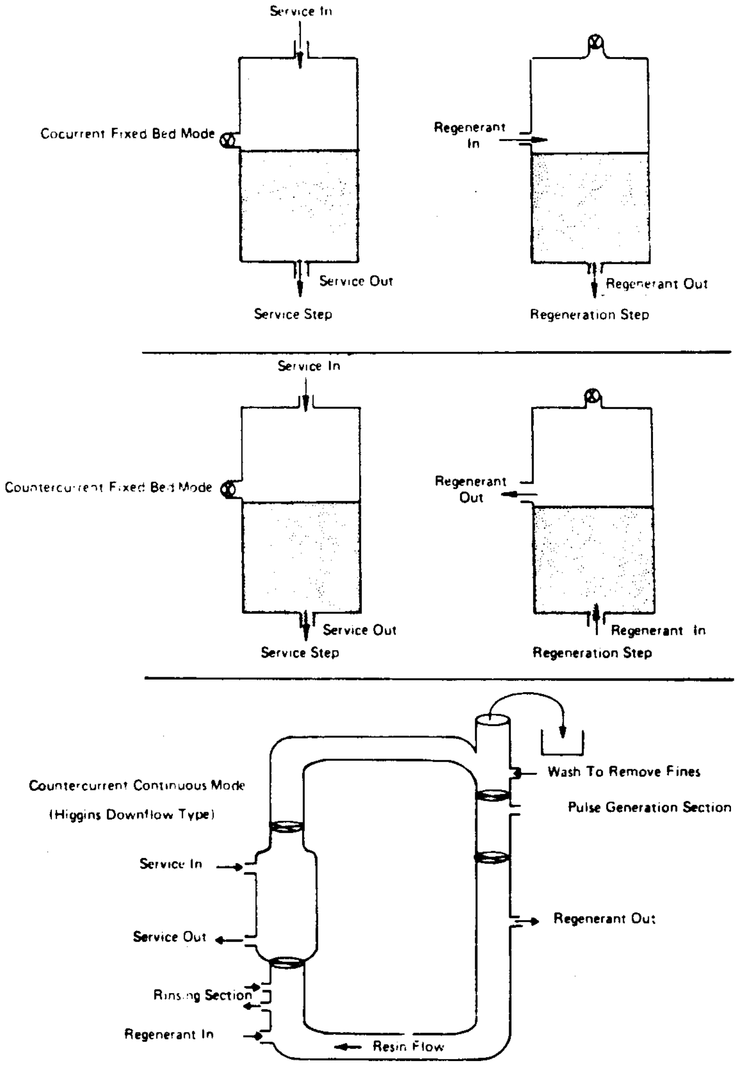

Figure 9-1 - Operational Modes for Ion Exchange of the handling, flow and pressure problems. This mode has found extensive use as disposable polishing units in the nuclear power industry and it might have analogous application in polishing effluents resulting from the treatment of extremely hazardous wastes.

9.1.3 OUTPUT STREAMS

In the usual modes of operation, the ion exchange process yields two liquid streams:

- a large-volume purified product stream depleted in the species being removed, and
- a small volume solution of used ("spent") regenerant containing a high concentration of the species removed.

The feed/regenerant ratio can be as much as 50/1 or higher for treating very dilute feed streams.

The ion exchange system is virtually always designed so that the purified product stream can be recycled, used in another process, or discharged without further treatment.

The spent regenerant must be treated to remove of detoxify the species it contains, and since that species is at a much higher concentration than in the original stream, such treatment is frequently easier and/or more economical than it would have been prior to the ion exchange treatment.

In some cases the spent regenerant containing the species it has removed and concentrated can be recycled back to a process without further treatment. This is done with chromium and nickel in some electroplating operations and with chromium in some recently developed processes for treating cooling tower blowdown.

For conventional ion exchange in waste treatment, the use of solid ion exchange materials affords three advantages over such competitive separation processes as liquid ion exchange and reverse osmosis.

- In processing small quantities (batches) of waste streams, the partially exhausted resin need not be regenerated after each batch but can be held in the "partially loaded" state for use with subsequent batches of waste.
- For the ultimate disposal of extremely hazardous wastes that are strongly bound to the ion exchanger (i.e., would not desorb under any expected conditions), the loaded resin can be encapsulated, or otherwise contained, and disposed of directly. This approach has been used in handling radioactive wastes.

- For the transport of extremely hazardous species (for example, residues from heavy metals such as thallium) between processing operations, particularly if those operations are widely separated physically or at different sites, the use of loaded solid ion exchangers may be more acceptable from an environmental standpoint than transport in solution because of the diminished hazards in the event of a spill.

9.1.4 ION EXCHANGE MATERIAL

The classes of materials that are in use or that have been proposed for use as ion exchange materials include inorganic crystals (both natural and synthetic) and synthetic organic resins. This last category is by far the most important for general ion exchange usage.

Three important parameters for ion exchange materials by which the exchangers can be selected and compared, and from which approximately exchanger and chemical requirements can be determined, are functionality, exchange capacity, and selectivity. Functionality refers to the kinds of ions (cations, anions, selected groups) that are exchanged; exchange capacity is a measure (generally in milliequivalents per gram, or per milliliter of resin) of the total uptake of a specified ion; selectivity refers to the preference for one kind of exchangeable ion over another, expressed as a ratio similar to K_{eq} at unit concentrations of $[M^+]$ and $[N^+]$.

Synthetic Ion Exchange Resins

A variety of cation and anion exchangers have been prepared by adding appropriate functional groups (exchange sites) onto solid particles (usually beads of polymeric materials. In some resins, the functional groups are introduced prior to or during the polymerization step. Most of the resins now offered commercially are either styrene-divinylbenzene copolymers or acrylate-methacrylate copolymers.

Earlier ion exchange resins were prepared from phenol-formaldehyde ("Bakelite") and related polymers; however, these materials were inferior to the present ones in stability, variety, and capacity, and only a few specialized ones are now available.

In the past, styrene-divinylbenzene materials suffered from rather large volume changes ("swelling") when cycled between different ionic forms. Newer methods of preparation and materials have now resulted in a variety of "macroreticular" resins, which combine a rigid polymer framework with a high exchange capacity and suffer only minor swelling.

Some of the more common reactive groups offered are listed below:

Relative Group	Exchangeable Ions
strong acid (sulfonic)	cations in general
weak acid (carboxylic)	cations in general
weak acid (phenolic)	cesium and polyvalent cations
strong base (quaternary amine)	all anions, esp. used for anions of weak acides (cyanide, carbonate, silicate, etc.)
weak base (tertiary and secondary amine)	anions of strong acids (sulfate, chloride, etc.)
chelating (varied, may be iminodiacetate or oxime groups)	cations, especially transition and heavy elements

Differences in the particular starting materials and preparation route frequently give rise to differences in handling properties, stability and reaction kinetics between resins that have the same polymer backbone, functional groups, and exchange capacity. Hence it is important to test a variety of resins for a particular application. A reasonably comprehensive listing of older types of resins is given in Perry's Handbook.

The synthetic resins are generally stable to strong acids and bases, but suffer irreversible damage from oxidizing agents, high temperature, and radiation.

A number of new ion exchange resins have been tested on the laboratory and pilot scale for general use. Many of these resins are of the macroreticular type, and are thus less subject to fouling the loss of capacity than older materials, a property which is of extreme importance in the treatment of wastes where foulant materials such as oils and soaps commonly may be present.

Inorganic Ion Exchangers

Both naturally-occurring and synthetic zeolites (aluminum silicate minerals) have been used as cation exchangers. The majority of these materials are stable only over a narrow pH range (neutral) and are somewhat fragile. A major use of these materials is water softening. Newer synthetic materials such as ziroconium phosphates have improved physical and chemical (acid range) properties.

These materials are never used in continuous operation because their geometry (non-spherical), density and fragility preclude effective solids handling operations.

The inorganic exchangers are less affected by oxidants, heat and radiation than are the synthetic resins, and consequently have found use in the processing and disposal of radioactive wastes.

Ion Exchange Liquids

The so-called liquid exchange process (often termed "solvent extraction") in which the ion exchanger is a water-insoluble liquid, resembles a liquid/liquid extraction process in operation rather than conventional ion exchange; this technique is the subject of a separate report.

Recently, there have been reports of impregnating beds of synthetic resin with liquid ion exchangers to produce an exchange material that could be handled via conventional ion exchange operations and could have some important advantages in selectivity.

9.2 APPLICATIONS

9.2.1 DEIONIZATION

Industrial deionization, which in its broadest meaning includes processes yielding products ranging from potable water to boiler water for steam production, is by far the most frequent application of ion exchange, apart from domestic softening. (This latter area involves only exchange of sodium for calcium and magnesium under ambient conditions and affords little information for waste treatment application). Deionization applications generally operate on a relatively clean feed, at worst brackish water, which has been pretreated where necessary to remove most foulants. The product must often meet stringent quality standards, particularly for newer boiler-water applications. Information on reliability of equipment operation can be had from the manufacturers of ion exchange equipment. Since this application is generally a steady-state operation, such information can be used to set upper limits on the reliability of equipment, particularly for newer modes of operation such as continuous counter-current.

9.2.2 ELECTROPLATING WASTEWATERS AND RESINS

Ion exchange is used extensively in the electroplating industry, especially in large installations, to remove ionic impurities from rinse water enabling re-use of the water and for further treatment of the impurities prior to disposal or recycle. Some new installations are being designed to meet the "zero discharge" requirements anticipated in the near future. In certain cases, the electroplating bath itself may require a cleanup treatment, but this is not usually done directly via ion exchange.

Ion exchange is used most frequently in combination with other techniques such as reverse osmosis or precipitation to yield an optimal solution for the particular application; in general, ion exchange is employed as the final or "polish" step, particularly if the stream to be treated contains higher concentrations of the species to be removed than can be easily handled by this process. Small-scale portable (skid-mounted) units incorporating carbon adsorption filters with series and parallel beds of appropriate ion exchange resins (cation, anion and chelating) have been marketed for cleaning up individual rinse tanks on-site. These units are regenerated separately off-site.

9.2.3 MIXED WASTE STREAMS

In the general metals finishing business it is quite common to have a single solution waste handling system that can only be described as "mixed waste". Obvoiusly a variety of waste treatment schemes would be needed in order to be able to treat mixtures with constituents including suspended metal particulates, oil and grease, chromium (III and VI), iron phosphate, cyanide, zinc, etc. A common thread among most treatment schemes is the frequent use of some sort of ion exchange step for final treatment before re-use or discharge. The major amounts of materials in mixed wastes are removed or destroyed by precipitation, filtration, or a membrane separation and ion exchange is used as the "polishing" step.

9.2.4 INORGANIC AND ORGANIC STREAMS

Iion exchange is used for the removal and recovery of ammonium nitrate from fertilizer manufacturing waste streams by means of continuous counter-current systems.

Ion exchange processes have been employed at one time or another to remove and/or separate organic materials and inorganic salts from mixtures of industrial origin.

The DESAL process (weak base resin in bicarbonate form, followed by weak acid resin in acid form) was used to treat "sour water" condensate from a petroleum refinery and achieved the results shown below.

	Before (mg/1)	After (mg/1)
Total dissolved solids	1310	210
H_2S	1150	3
NH_3	390	5
Phenol	365	20

10. PRECIPITATION AND COAGULATION (FLOCCULATION)

Precipitation removes a substance in solution and transforms it into a second phase, often in the form of solid particles that may be small or even colloidal. Flocculation transforms small suspended particles into larger suspended particles so that they can be more easily removed. Figure 10-1 diagrams the conventional precipitation, flocculation, and sedimentation (see Section 13) relationship.

10.1 PRECIPITATION

Precipitation is a physicochemical process whereby some or all of a substance in solution is transformed into a solid phase and thereby removed from solution. Precipitation involves an alteration of the chemical equilibrium relationships affecting the solubility of the component(s). This alteration can be achieved by a variety of means. Most precipitation reactions for industrial or waste treatment purposes are induced by one or a combination of the following steps:

- o Adding a substance that will react directly with the substance in solution to form a sparingly soluble compound.
- o Adding a substance that will cause a shift in the solubility equilibrium to a point which no longer favors the continued solubility of the substance originally in solution.
- o Changing the temperature of a saturated or nearly saturated solution in the direction of decreased solubility; since solubility is a function of temperature, this change can cause ionic species to come out of solution and form a solid phase.

The most common precipitation reactions involve the removal of inorganic ionic species from various aqueous media.

Zinc chloride is highly soluble in water, as is sodium sulfide. Zinc sulfide, however, has an extremely low solubility in water. Thus, if an aqueous solution of zinc chloride is mixed with an aqueous solution of sodium sulfide, zinc ions and sulfide ions will rapidly combine to form solid zinc sulfide particles,

$$Zn^{2+} + 2Cl^- + 2Na^+ + S^{2-} \longrightarrow \underset{\substack{\downarrow \\ \text{(solid)}}}{ZnS} + 2Na^+ + 2Cl^-$$

Approaching equilibrium from the reverse direction, if a strong caustic such as sodium hydroxide is added to an aqueous (and necessarily slightly acidic) solution of ferrous ions, the solubility product of $Fe(OH)_2$ will be exceeded, thus causing the creation of a solid ferrous hydroxide phase as the solution returns to equilibrium.

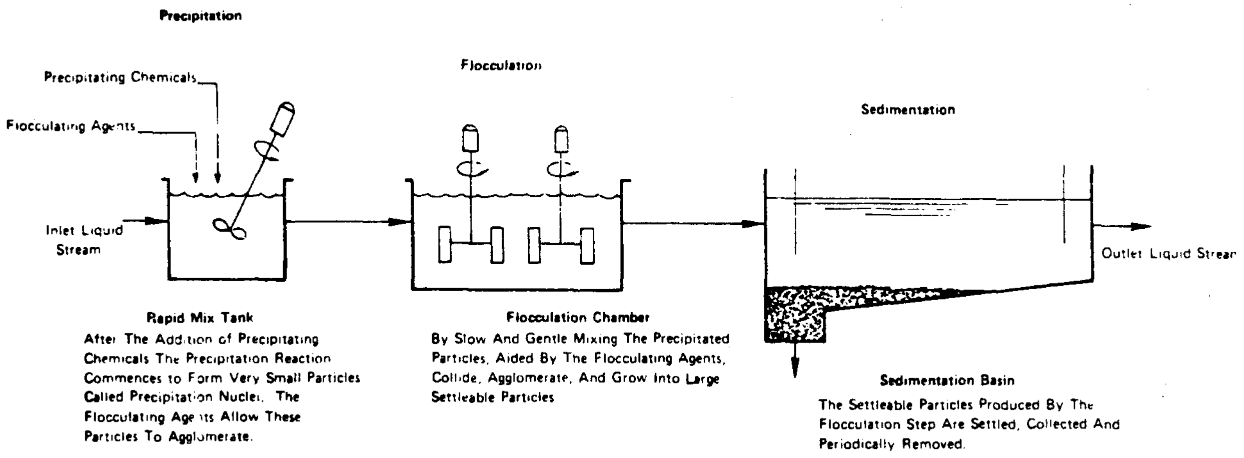

Figure 10-1 - Representative Configuration Employing Precipitation, Flocculation, and Sedimentation

In certain industrial applications, precipitation of a desired product material is induced by chilling a saturated solution. Since most salts are less soluble at lower temperatures (calcium carbonate and calcium sulfate being two notable exceptions), chilling a saturated solution of such salts causes the equilibrium to be disturbed. The equilibrium is readjusted by the removal of ions from solution and the creation of a solid phase. This technique has very limited applications for waste treatment purposes, mainly due to the fact that solubility of most slightly soluble compounds used in precipitation schemes is a weak function of temperature, and therefore, very large differences in concentration cannot usually be achieved.

Physically, most precipitation reactions are carried out by adding the appropriate chemicals to the solution and mixing thoroughly. Although most precipitation reactions take place extremely rapidly, a moderate amount of time is usually required to allow the chemicals to be dispersed throughout the solution. Characteristically, the solid particles, when first formed, are very small. Depending on the nature of the chemical system involved and the types of further treatment applied, the solid particles can remain as submicroscopic precipitation nuclei, or very small colloidal particles; or they can grow into larger particles. The particles may either be crystalline or amorphous.

It is important to recognize that the term precipitation, as strictly defined, refers only to the conversion of dissolved substances into insoluble ones in order to facilitate their subsequent removal from the liquid phase. Precipitation, per se, does not refer to any of the liquid-solid separation processes that are required to remove the precipitated solid particles from the original volume of liquid. In order to effect the removal of precipitated particles from a volume of liquid, it is very often necessary to apply additional process steps, and these often involve flocculation, sedimentation, and/or some control which will determine the final particle size -- and produce an easily separable solid (or crystal).

10.2 COAGULATION

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. Distinctions between the two terms frequently appear in the water and waste treatment literature; however, the definitions used are often conflicting, and the result is that there are really no precise and universally accepted technical definitions of these terms. For the purpose of this study, the term "flocculation" shall be defined so as to encompass all of the mechanisms by which the above-mentioned suspended particles agglomerate into larger particles. As a general term used in this study, no distinction will be made between coagulation and flocculation.

Many liquid-solid separation processes, such as sedimentation, are based on the use of gravitational and/or inertial forces to remove solid particles from a liquid. It is generally true that the larger the particle size, the easier will be the removal of the particle from the liquid.

There are a variety of forces acting on particles suspended in a liquid. There are gravitational and inertial forces which are related to the mass of the particles; and there are also electrostatic and interionic forces which are surface-related. Thus, in the regime of very small particles the surface-related electrostatic and interionic forces which are surface-related electrostatic and interionic forces tend to predominate; while in the regime of larger particles, the gravitational and inertial forces predominate. The surface-related electrostatic and interionic forces typically tend to repel particles away from each other. These forces are often the reason why very fine particles suspended in a liquid can sometimes remain suspended indefinitely. In the size regime of the small particles, the forces repelling the particles from each other are often greater than the gravitational forces tending to amke the particles settle. The purpose of what we describe as flocculation is to overcome the above repulsive forces and to cause small particles to agglomerate into larger particles, so that gravitational and inertial forces will predominate and effect the settling of the particles.

In flocculation, as defined, there are a variety of mechanisms involved in the process 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.

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

2. Chemical bridging and physical enmeshment between the now non-repelling particles, thus allowing for the formation of large particles.

Typically, chemicals used to cause flocculation include alum, lime, various iron salts (ferric chloride, ferrous sulfate). Relatively recently, 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 itself.

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 hydrolize and form fluffy, gelatinous precipitates of aluminum hydroxide. These precipitates, partially due to their large surface area, act to enmesh small particles and thereby create larger particles. Lime and iron salts, as well as alum, are used as flocculants primarily because of this tendency to form large fluffy precipitates of "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. Table 10-1 lists some chemical compounds used in flocculation processes.

In actual practice, the flocculation process entails the following steps:

1. Addition of the flocculating agent to the liquid.
2. Rapid mixing to disperse the flocculating agent throughout the liquid.
3. Slow and gentle mixing to allow for contact between small particles and agglomeration into larger particles.

In the flocculation process it is essential that the slow mixing step is very gentle and is 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. An illustrative flocculation process is shown and described in Figure 10-2.

10.3 PRECIPITATION/COAGULATION APPLICATION

Theoretically, when applying precipitation to the removal of toxic or hazardous materials (such as heavy metals) from aqueous waste streams, it should be possible to achieve an effluent concentration of the particular ion of concern equal to the solubility of the ion relation to its precipitated solid phase. In theory, the solubilities of the hydroxides of iron, zonc, chromium, mercury, lead, copper, and many other heavy metals are less than 1.0 ppm, under slightly alkaline conditions. Actual attempts at precipitating these metals from real aqueous waste streams generally do not achieve effluent concentrations equal to the theoretical solubility limits for a variety of reasons, some of which are listed below:

- Many metals exhibit a strong tendency to form organo-metallic complexes with a variety of natural and synthetic organic compounds. Often, these complexes are far more soluble than the ion by itself, and the presence of complexes can often impede many precipitation reactions. Cyanide ion can form complexes with a number of metallic ions, resulting in a situation in which it is difficult both to destroy the cyanide by oxidation and to precipitate the metal as a hydroxide of sulfide. Many amine compounds also form metal complexes.

Table 10-1 Chemical Compounds Used in Coagulation Process

Compounds	Formula	Commercial strength	Grades available	Weight, lb/cu ft	Remarks
		COAGULANTS			
Aluminum sulfate	$Al_2(SO_4)_3 \cdot 18H_2O$	17 percent Al_2O_3	Lump, powder, granules	Powder: 38–45 Other: 57–67	Coagulation and sedimentation systems; prior to pressure, filters for removal of suspended matter and oil
Sodium aluminate	$Na_2Al_2O_4$	55 percent Al_2O_3	Crystals	50–60	Usually added with soda ash to softeners
Ammonium alum	$Al_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	11 percent Al_2O_3	Lump, powder	60–68	Coagulation systems—not widely used
Potash alum	$Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$	11 percent Al_2O_3	Lump, powder	64–68	Coagulation systems—not widely used
Copperas	$FeSO_4 \cdot 7H_2O$	55 percent $FeSO_4$	Crystals, granules	63–66	Suitable coagulant only in pH range of 8.5–11.0
Chlorinated copperas	$FeSO_4 \cdot 7H_2O + \frac{1}{2}Cl_2$	48 percent $FeSO_4$			Ferrous sulfate and chlorine are fed separately
Ferric sulfate	$Fe_2(SO_4)_3$	90 percent $Fe_2(SO)_3$	Powder granules	60–70	Coagulation—effective over wide range of pH, 4.0–11.0
Ferric chloride hydrate	$FeCl_3 \cdot 6H_2O$	60 percent $FeCl_3$	Crystals		Coagulation—effective over wide range of pH, 4.0–11.0
Magnesium oxide	MgO	95 percent MgO	Powder	25–35	Essentially insoluble—fed in slurry form
		COAGULANT AIDS			
Bentonite			Powder	60	Essentially insoluble—fed in slurry form
Sodium silicate	$Na_2O(SiO_2)_{1-25}$	40 Bé solution	Solution	86	
		pH ADJUSTERS			
Lime, hydrated	$Ca(OH)_2$	93 percent $Ca(OH)_2$	Powder	25–50	pH adjustment and softening
Soda ash	Na_2CO_3	99 percent Na_2CO_3	Powder	34–52	pH adjustment and softening
Caustic soda	$NaOH$	98 percent $NaOH$	Flake, solid, ground, solution		pH adjustment, softening, oil removal systems
Sulfuric acid	H_2SO_4	100 percent H_2SO_4	Liquid		pH adjustment

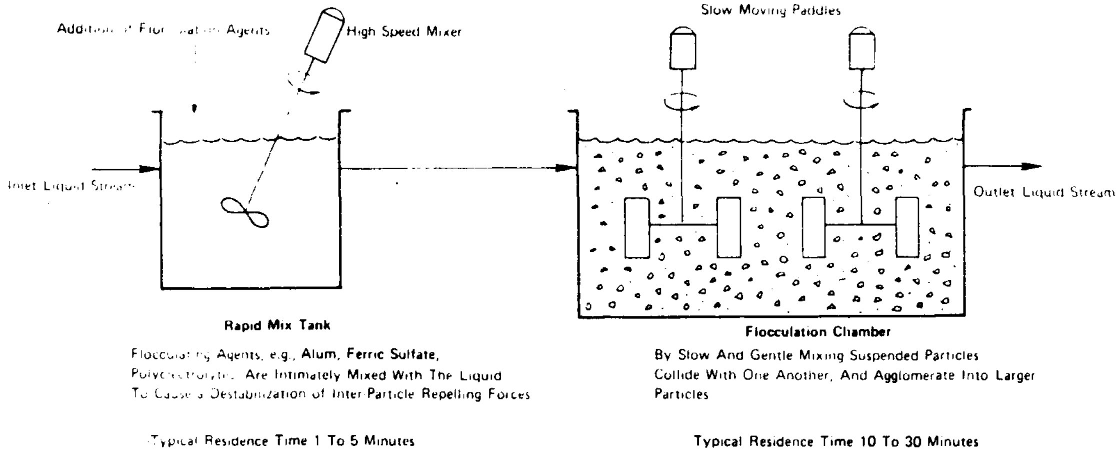

Figure 10-2 - Illustrative Flocculation Process

- Even though adequate flocculation and sedimentation may be applied, it is never possible to cause all of the precipitated particles to form readily settleable floc particles. Thus while the desired ions may be removed from solutions and transformed into suspended solid particles, a certain fraction of those particles is generally too small in size to be removed by conventional means.

- Metal ions can sometimes adsorb onto the surfaces of colloidal organic or inorganic solid particles. In such cases it is often difficult to completely isolate the desired metal ion from other components of the waste stream.

In spite of such impeding influences, it is often possible to achieve metal ion concentrations in the treated effluent which are within an order of magnitude of the theoretical solubility limit. Frequently when a slightly acidic waste is treated with lime (which always contains some $CaCO_3$), CO_2 is liberated in the waste and most effectively reduces the solubilities of the various metal species by producing basic carbonates, i.e., metal hydroxide and metal carbonate.

Where several metal ions are present in a given waste stream and where there is a very high concentration of colloidal yet potentially settleable (through flocculation) inert solids, it is seldom possible to effect a sharp separation of the various metal species by means of precipitation. Due to coprecipitation effects, in which two or more ions precipitate together as a single compound, and due to the tendency for many inert colloidal particles to flocculate and settle with the desired precipitated metal, it is often not possible to isolate a particular hazardous metallic species as a pure hydroxide of sulfide sludge. Often, the metal is lost within the total sludge matrix consisting of other metal precipitates and/or settled particles.

While it is generally possible, through the selection and use of the proper flocculating agents, to achieve at least some degree of flocculation in most waste streams containing suspended solids, flocculation is seldom complete, and there is always a certain fraction of particles which do not properly flocculate. In many cases, excessively high dosages of flocculating agents must be used, thus contributing to the total sludge volume as a result of their mass.

The use of reactor-clarifies for the coagulation-precipitation removal of suspended and colloidal pollutants in refinery-petrochemical wastewaters is effective for selected streams. The applicability of this process in the removal of these pollutants can be determined through the use of a bench-scale jar test noting the change in organics or the critical pollutant in the upper layers of the liquid following chemical addition, rapid mix, flocculation, and sedimentation. An assessment of the effect of pH, flocculation time, and chemical selection on pollutant removal can be used to optimize the process.

The most common use of reactor-clarifiers in the treatment of refinery and petrochemical wastewaters is the removal of suspended and colloidal material from solution which is pollutional in nature. This process also is effective in reducing nutrients (for example, through the precipitation of phosphates) and in reducing heavy metals since most drop out as insoluble metallic hydroxides in the higher pH range. Water-soluble, alkyl-aryl sulfonates can be removed by coagulation with lime which forms an insoluble precipitate.

It should be recognized that sludge handling and disposal may be the most important component of the reactor-clarifier treatment unit. Landfills are the most common form of inorganic sludge disposal, while organic sludges generally are dewatered and buried or incinerated.

11. DISTILLATION

Distillation is the boiling of a liquid solution and condensation of the vapor for the purpose of separating the components.

It is a unit operational process which is most often employed in industry to segregate, separate, or purify liquid organic product streams, some of which contain aqueous fractions. Sometimes the operation is used to recover one product; sometimes it is used to produce many desirable fractions from a process stream. Distillation is usually non-destructive and can produce products of any desired composition. Practical limitations are primarily economic ones, i.e., both operational and equipment costs.

Until now, organic solvent recovery has been justified only when the economics warranted it. However, with the recent enforcement of stringent air pollution regulations, most organic solvents are prohibited from entering the atmosphere. This is being accomplished in a number of ways, such as direct condensation, demisting, absorption, etc. Often, regeneration of absorption media produces aqueous and/or organic streams. Distillation is often employed to recover the organics.

In the recovery of other waste solvents such as painting or plating wastes or plastic coating wastes, distillation cannot directly compete with other recovery or with disposal processes. However, this can be offset when favorable byproduct credits exist. With more and more stringent regulations on air, liquid effluents, and land site disposal, the rising cost of organic chemicals (i.e., increased byproduct credit), and the newer concept of waste management (resource recovery), distillation should become more competitive with other methods for liquid organic recovery or disposal.

The basic principle of distillation is as simple as it is old: when a liquid solution is boiled, the vapor usually differs in composition from the liquid that remains. Man has long made use of this knowledge to concentrate solutions by boiling them and condensing the vapors that are driven off. The distillation of what are essentially binary (two-component) mixtures of ethanol and water has been practices by brewers and distillers for centuries. It has only been since the 19th Century, however, that distillation has been developed on a large-scale basis as a steady-state operation. The major contributions in this field have come from engineers in the petroleum industry, where large numbers of multistage distillation towers operate on a continuous basis.

In the distillation process there are two phases, the liquid phase and the vapor phase. The components which are to be separated by distillation are present in both phases but in different concentrations. If there are only two components in the liquid, one concentrates in the condensed vapor (condensate) and the other in the residual liquid. If there are more than two components, the less volatile components concentrate in the residual liquid and the more volatile in the vapor or vapor condensate.

The ease with which a component is vaporized is called its volatility, and the relative volatilities (ratio of equilibrium ratios) of the components determine their vapor-liquid equilibrium relationships.

Equilibrium Ratio - An equilibrium ratio expresses a relationship between a vapor and a boiling liquid in physical equilibrium with one another. For each component, $y = K_x$, in which "y" is the mole fraction* of a particular component in the vapor state, "x" is the mole fraction of that component in the liquid state, while "K" is termed the equilibrium ratio. For any system, there are as many such relationships as there are components.

Relative Volatilities - Because distillation separates by virtue of inequalities in volatilities, equilibrium ratios are less important than are their relationships to each other. These secondary relationships are termed "relative volatility." The relative volatility (α_{AB}) of component A to component B is defined by $\alpha_{AB}=K_A/K_B$.

11.1 TYPES OF PROCESSES

11.1.1 BATCH DISTILLATION

The simplest form of distillation is a single equilibrium stage operation and is carried out in a "still" in which the reboiler equivalent consists of a steam jacket or a heating coil. The liquid is "boiled"; the vapor is driven off, condensed, and collected in an accumulator (a condensed vapor collector) until the desired concentration of the "product" has been reached. As the remaining liquid becomes leaner in the volatile component and richer in the less volatile component, its volume diminishes. If the residual liquid is the product, then "bottoms" concentration will be the controlling parameter.

The batch still, as previously described, consists of a vessel which provides one equilibrium stage. By adding a condenser and recycling some of the condensed vapor, a second vapor/liquid equilibrium stage is added and the separation is improved (Figure 11-1).

11.1.2 AZEOTROPIC DISTILLATION

An Azeotrope is a liquid mixture that maintains a constant boiling point and produces a vapor of the same composition of the mixture when boiled.

Because the composition of the vapor produced from an azetrope is the same as that of the liquid, an azeotrope may be boiled away at a constant pressure without change in concentration in either liquid or vapor. Since the temperature cannot vary under these conditions, azeotropes are also called constant boiling mixtures.

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*Mole fraction is the ratio of the number of molecules of a particular component to the total number of molecules of all the components in a phase.

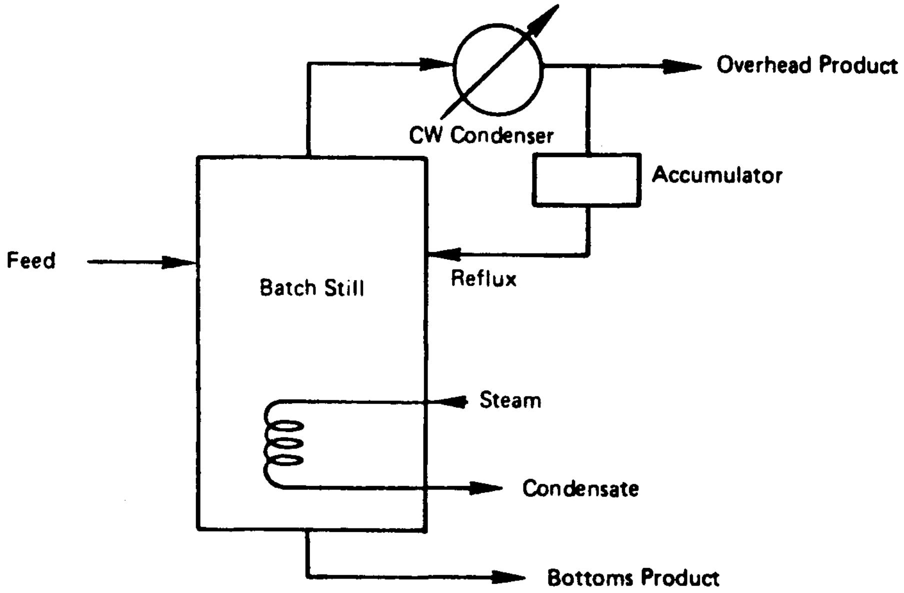


Figure 11-1 Batch Fractionation With Reflux and Internal Heating Coil

An azeotrope cannot be separated by constant pressure distillation into its components. Furthermore, a mixture on one side of the azeotrope composition cannot be transformed by distillation to a mixture on the other side of the azeotrope. If the total pressure is changed, the azeotropic composition is usually shifted. Sometimes this principle can be applied to obtain separations under pressure or vacuum that cannot be obtained under atmospheric pressure conditions. Most often, however, a third component -- an additive, sometimes called an entrainer -- is added to the binary (2-component) mixture to form a new boiling-point azeotrope with one of the original constituents. And the volatility of the new azeotrope is such that it may be easily separated from the other original constituents.

11.1.3 EXTRACTIVE DISTILLATION

This is a multi component rectification method of distillation. A solvent is added to a binary mixture which is difficult or impossible to separate by ordinary means. This solvent alters the relative volatility of the original constituents, thus permitting separation. The added solvent is of low volatility and is not appreciably vaporized in the fractionator.

11.1.4 CONTINUOUS FRACTIONAL DISTILLATION COLUMN

A steady stream feed enters the column. The column contains plates or packing (packing is normally used only in small-scale equipment) which provide additional vapor/liquid contact (equilibrium) stages. Overhead vapors and bottoms are continuously withdrawn. Vapor from the top plate is condensed and collected in a vessel known as an accumulator. Some of the liquid in the accumulator is continuously returned to the top plate of the column as reflux while the remainder of the liquid is continuously withdrawn as the overhead product stream. Shown in Figure 11-2.

At the bottom of the column the liquid collects in the reboiler, where it is heated by steam coils or a steam jacket. The function of the reboiler is to receive the liquid overflow from the lowest plate and return a portion of this as a vapor stream, while the remainder is withdrawn continuously as a liquid bottom product.

11.2 OPERATION

Although the term distillation is sometimes employed for those processes in which a single constituent is vaporized from a solution, e.g., in "distilling" water, this term is properly applied only to those operations in which vaporization of a liquid mixture yields a vapor phase containing more than one component, and it is desired to (1) recover one or more of the components in a nearly pure state or (2) obtain a mixture different from that of the original mixture. Thus, the separation of a mixture of alcohol and water into its constituents is accomplished by distillation, whereas the separation of brine into salt and water is evaporation, even in those cases where the salt is not desired and the condensed water is the valuable product.

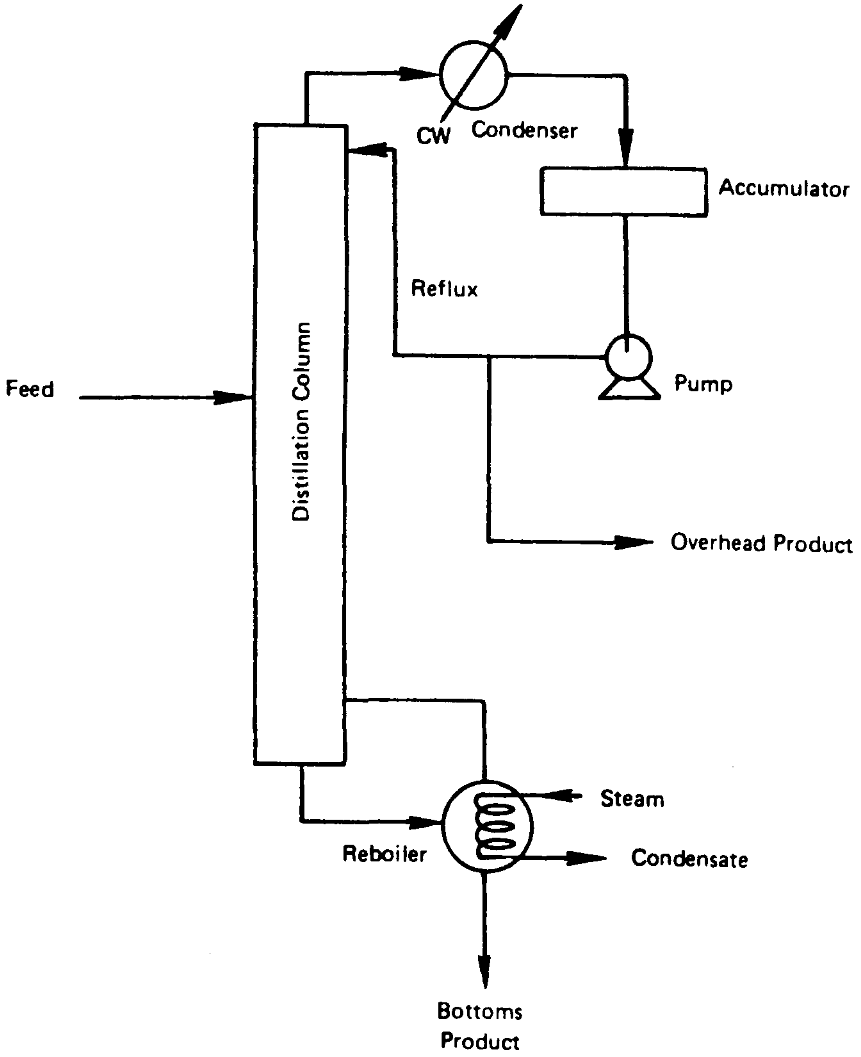


Figure 11-2 Continuous Fractional Distillation Column

11.2.1 FEED (INPUT) STREAMS

It is preferred that the materials being distilled do not contain appreciable quantities of solids or non-volatile materials. It is also best to avoid feeds that tend to polymerize.

The presence of formation of these contaminants in the feed can cause considerable operating difficulties. Operation of a conventional distillation system on a feed which is "dirty" could cause plugging of equipment or costly maintenance problems. This could precipitate in inefficient separation of feed components or produce excessive "flooding" conditions. This is a situation in which the vapor rate is reduced nearly to zero because of increased pressure drop in the vapor caused by having to travel through deep layers of liquid. Another effect might be long downtime periods required for equipment cleaning.

If it is known in advance that feeds of this nature must be handled, steps can be taken to design equipment which would minimize the associated problems (e.g., sieve-type trays might best be able to handle liquids which contain tars). Sometimes, steps can be taken to avoid the problem completely -- such as pre-treatment by filtration, for removal of suspended solids or the use of a thin film evaporator to separate the volatile (liquid) fraction from the solid or non-volatile component(s). When the problems associated with "dirty" feed cannot be easily handled or are unavoidable, duplicate equipment may be the only answer. This measure prevents disruption in production. When one set of equipment is down for cleaning or maintenance, the other system can take over operation.

In terms of physical separation of liquid components, there are no limitations in feed composition or in reaching the desired composition in any of the product streams. Theoretically, distillation can generate products of 100% absolute purity. There are, however, some physical parameter restrictions, such as entrainment effects, which limit the degree of attainable purity to the (10^{-9} to 10^{-14}) range of impurities. The attainment of these limits of purity is usually not necessary, nor are the limits normally attempted, because of requirements of highly specialized equipment, extreme equipment size, excessive capital investment, or energy considerations.

The term "fractionation" (see Figure 11-3) means separation of a material into its component parts where more than one part is a desired product, while the term "distill" is sometimes used, in the colloquial sense, to mean the driving off of a volatile component and the collection of the condensed volatile liquid as the one product (e.g., the distilling of alcohol from a water-alcohol mixture). In distillation, the term "fractionate" means to separate a liquid feed into a series of fractions containing different ratios of the components present in the original feed.

The liquid (or vapor) being introduced into the distillation column is called "feed." The section of the column above the feed location is called the enriching or rectifying section. In this section, the more volatile component is concentrated. The portion of the column below the feed location is the stripping section. Here the liquid becomes richer in the less volatile component as the more volatile component is removed (stripped).

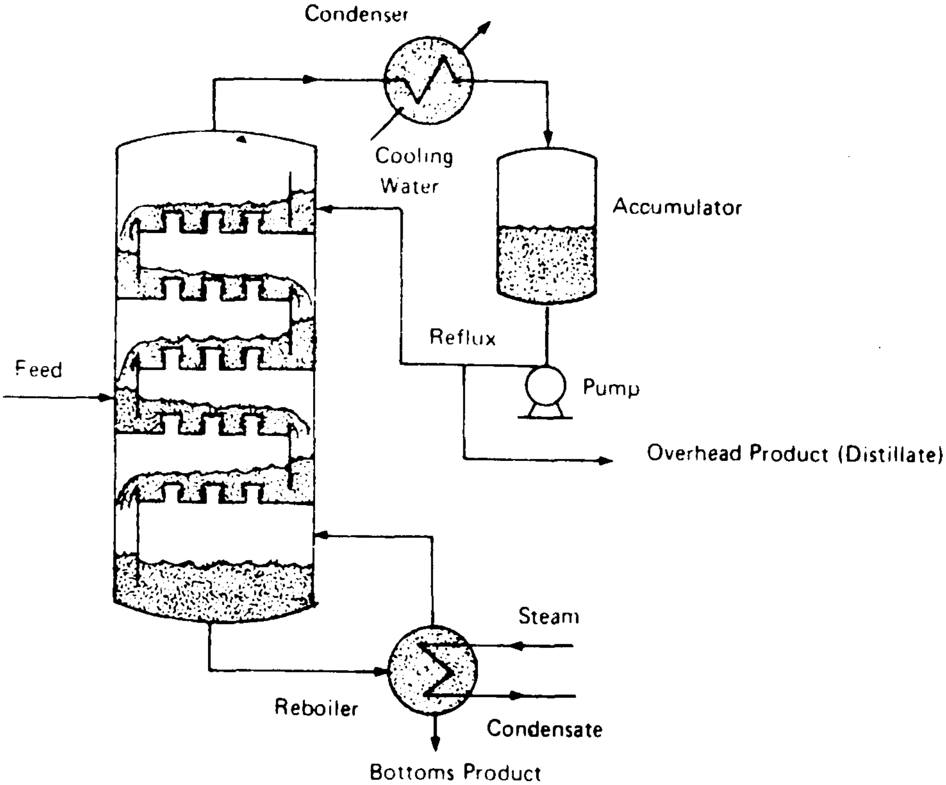


Figure 11-3 Schematic Diagram of Operation of a Fractionating Column Containing Bubble-Cap Plates

- Binary Liquid Feed -- In the case of distillation, a binary system consists of two liquid components in solution with one another.
- Multi-component Liquid Feed -- In multi-component distillation, the liquid being processed is composed of more than two components.

An "equilibrium stage" occurs when the liquid and the vapor phases are in equilibrium with one another. This equilibrium may occur on a single tray or plate (or within a given height of packing in a packed column) where the rising vapor and falling liquid (condensed vapors) contact each other.

In an ideal, or equilibrium stage the phases are mixed long enough so that the streams leaving the stage are in equilibrium, and the individual phases are homogeneous (i.e., there are no concentration gradients). By contrast, in a real stage there may not be sufficient contact between the phases to bring the streams into equilibrium. Such a stage accomplishes less interphase transfer than an ideal stage; it is less efficient than an ideal stage. The degree to which a stage approaches ideality is termed "stage efficiency."

11.2.2 OUTPUT STREAMS

The liquid recovered from the bottom of the column is called "bottoms." It is generally richer in the less volatile components. The term "still bottoms" refers to the undesirable non-volatile residue materials, such as tars and sludges, which are periodically removed from the reboiler or from the bottoms product tank These materials, which usually enter with the feed or are sometimes formed to a slight degree by polymerization reactions, must generally be disposed of.

The vapor which is evolved at the top of the column is called the "overhead." All or part of the overhead may be withdrawn as product. This is called "overhead product." The overhead product may be withdrawn as a vapor or condensed and collected as a liquid.

When all or part of the overhead is recycled back to the column (usually to the top stage or plate), that recycled portion is termed "reflux."

This term can either refer to the ratio of the reflux to feed, or to the overhead product.

11.2.3 DISTILLATION AND FRACTIONATION COLUMNS

The types of distillation columns are so varied they defy concise description. The distillation process could be carried out in wide cylindrical columns up to 40 feet or more in diameter, or in tall columns 200 feet high (or more) in the air, or even in small laboratory equipment.

11.2.3.1 RECTIFYING COLUMNS

These are fractionating columns in which the feed enters the bottom of the column as a vapor. An overhead product is produced which is usually quite rich in the more volatile component while the bottoms product contains a high proportion of the less volatile component.

11.2.3.2 STRIPPING COLUMNS

These are fractionating columns in which the liquid feed is supplied to the top of the column. The feed is usually a saturated liquid, and the overhead product is the vapor rising from the top plate. This vapor is somewhat richer in terms of the more volatile component than is the feed. However, it is usually not a stream of very great purity. The only stream leaving the stripping column that has a very high concentration of a component (the less-volatile) is the saturated-liquid bottoms product.

11.2.3.3 COMPLETE FRACTIONATING COLUMNS

Figure 11-4 shows a column with sections both above and below the feed injection point, where a possibility exists of producing both rich overhead and bottom products. Thus, the complete fractionating column combines the properties of both enriching and stripping columns. The complete column has both a reflux condenser and a reboiler.

To facilitate mass transfer, columns always contain internals that provide for increased vapor to liquid interfacial area. The designs of these internals are many and varied. By convention, the various internals are grouped into two broad classifications: trays and packings.

A distillation tray is a horizontal plate that holds a pool of the downflowing liquid through which the upflowing vapor passes. To permit passage of the vapor, the plate must have openings of some kind. Depending on the design, liquid may flow down through the same openings that the vapor is flowing up through, or it may flow across the plate to a vertical "downcomer" (a channel or pathway that directs the liquid to the next lower tray). (See Figures 11-5 and 11-6)

Like trays, packings are installed in distillation columns to improve the contacting of the downflowing liquid with upflowing vapors. Originally, "packing" meant small, irregular solids that, when installed in a random fashion, left irregular passages for countercurrent travel of vapor and liquid. Currently, packings are so diverse that the only inclusive definition is: vapor-liquid contacting devices not classified as trays. Figure 11-7 shows various packings and Figure 11-8 shows a packed tower in cross-section.

All packings function by providing surface area over which the downflowing liquid distributes itself, thus increasing the area of the liquid-vapor surface. Some packings function as do trays, in that they promote the formation of pools of liquid through which the vapor bubbles.

11.2.4 REBOILERS

Energy is required to vaporize the liquid phase. Heat is applied to the liquid phase to provide the energy of vaporization. This energy may be applied externally to the column by circulating liquid from the column through a heat exchanger called a reboiler. Sometimes a vapor is employed as the heat exchange medium (as in steam distillation), and sometimes the column is jacketed and the heat transfer medium is circulated in the vessel jacket.

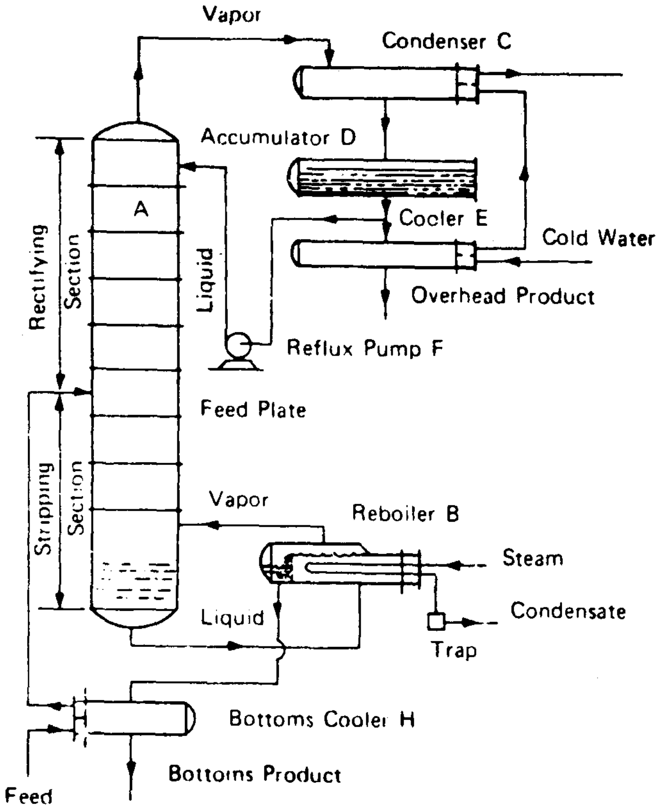


Figure 11-4 A Typical Complete Fractionating Column Equipped With a Necessary Auxiliaries and Containing Rectifying and Stripping Sections

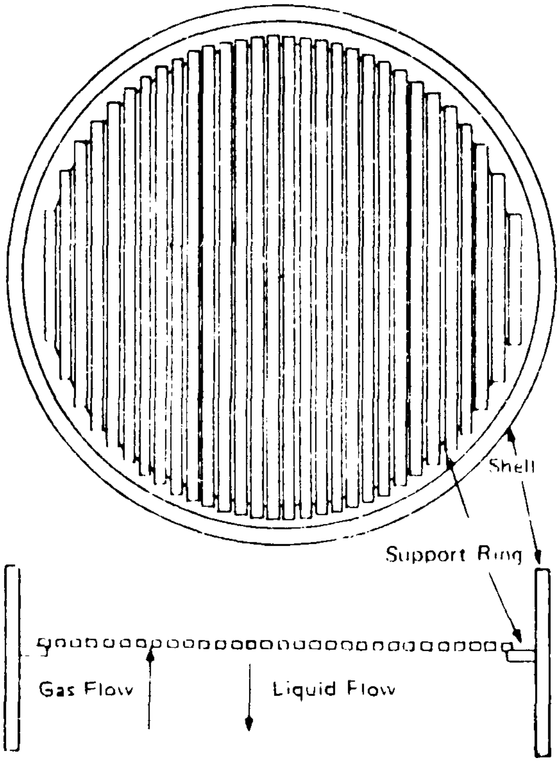


Figure 11-5 An Example of a Simple Tray Type Containing Device

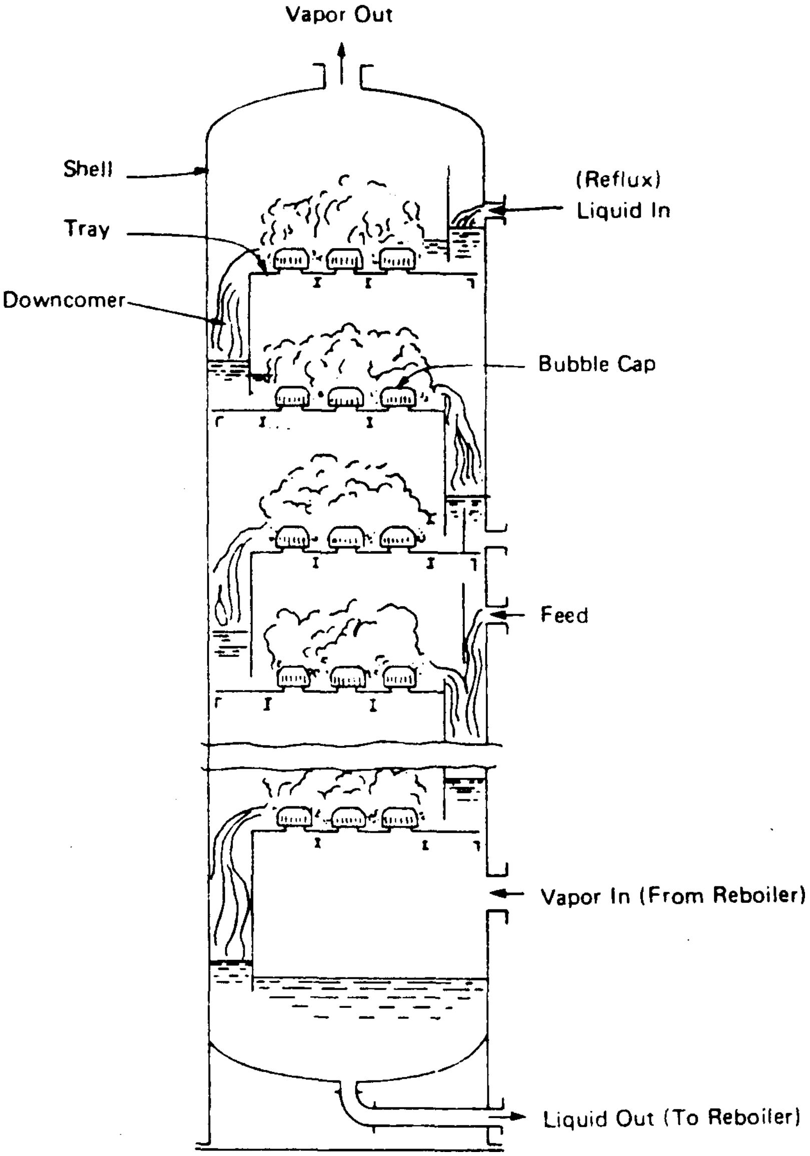
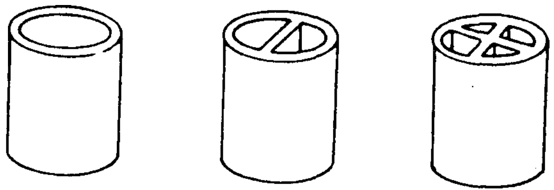
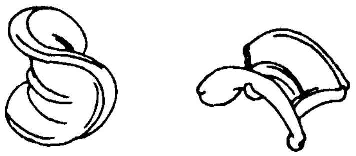


Figure 11-6 Schematic Diagram of Bubble-Cap Tray Tower



(a) Raschig Ring (b) Lessing Ring (c) Partition Ring



(d) Berl Saddle
(Courtesy, Maurice
A. Knight)

(e) Intalox Saddle
(Courtesy, United States
Stoneware Co.)

Figure 11-7 Random Tower Packings

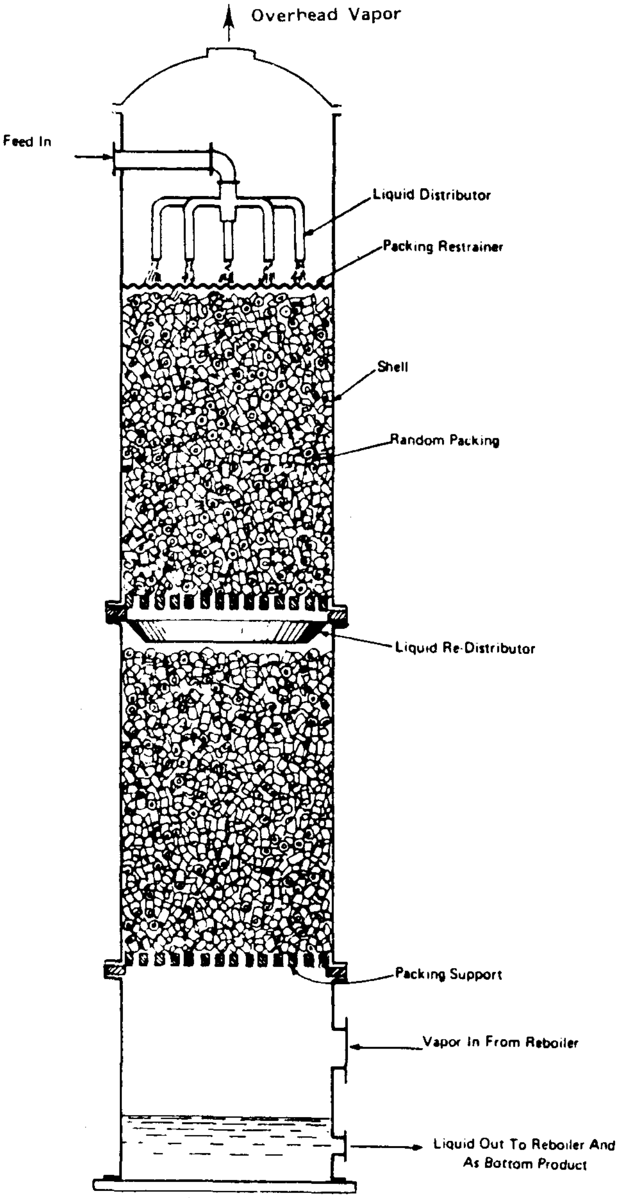


Figure 11-8 A Packed Tower Which is Used for Continuous Countercurrent Contact of Liquid and Vapors has been Filled With Packing or Devices of Large Surface Contact Area

11.2.5 CONDENSERS

Energy must be removed to condense the vapor phase. This is usually provided via a heat exchanger (condenser) through which a cooling medium is passed or circulated. Sometimes, part of the energy used to heat up or partially vaporize the liquid phase that is to be distilled is "recovered" from the condensing vapor phase.

11.2.6 ACCUMULATORS

The accumulator is a tank located on the downstream side of the overhead vapor condenser. Its purpose is to collect the condensed vapor, as a small intermediate storage vessel. This helps to promote stability of operation.

11.2.7 PUMPS

Most of the pumps employed in modern distillation units are either the centrifugal or the rotary type. Rotary pumps are often employed when the liquid contains suspended solids, but special centrifugal pumps have given good service in the pumping of slurries.

11.2.8 VACUUM EQUIPMENT

Vacuum equipment could be either steam jet eductors or mechanical vacuum pumps. Eductors have high reliability and low capital cost compared to mechanical vacuum pumps; this is offset, however, by relatively low efficiencies and high operating costs.

12. STEAM STRIPPING

Steam stripping is a proven process which is generally used for removing volatile (organic chemical) compounds from aqueous process water or wastewater. Sufficient data exists for the design of steam strippers for many industrial production processes and wastewater treatment applications.

Steam stripping has been used for many years for the recovery of ammonia from coke oven gas. Indeed, this was at one time the only industrial source of ammonia. The flue gas from the coke oven gas is scrubbed with water and then the ammonia is recovered by adding lime to the scrubber water and steam stripping out the ammonia.

Sulfur is recovered from refinery "sour water" as H_2S by steam stripping the sour water. Along with the H_2S, ammonia and a small amount of phenol are also removed from the sour water in the steam stripping operation.

Recently, as water effluent regulations have become more stringent, other aqueous waste streams are being treated by this unit operation for removal of volatile organic components (i.e., methanol from pulp mill condensate).

12.1 OPERATION

Steam stripping is essentially a fractional distillation of volatile compounds from a wastewater stream. The volatile component may be a gas or volatile organic compound with solubility in the wastewater stream. In most instances, the volatile component, such as methanol or ammonia, is quite water soluble. More recently, this unit operation has been applied to the removal of water immiscible compounds (chlorinated hydrocarbons) in wastewater that must be reduced to trace levels because of their toxicity.

Steam stripper efficiency is not only a function of the number of vapor/liquid contact stages and steam input, but also temperature and pH. Temperature affects the solubility of gases in water. The vapor pressure of gases that dissolve in water to form acids or bases in solution are influenced by the pH of the wastewater. By lowering the pH, more dissolved ammonia (as ammonium ion) is "tied up" as the ammonium salt of the added acid, thus liberating the H_2S. Removal efficiency of H_2S is therefore increased by adding acid. Likewise, ammonia removal efficiency is increased by adding caustic to the wastewater.

At one time, the only objective in stripping sour water was to remove hydrogen sulfide (H_2S), but more stringent effluent water quality regulations now require efficient removal of ammonia. Shell and Chevron steam strip sour water in two stages (at different pH's) in order to maximize both hydrogen sulfide and ammonia removal.

Other factors that effect steam stripper removal efficiency include feed concentration and condensate tank temperature and pressure.

The input to the steam stripping process is a wastewater stream containing dissolved gases or volatile organic compounds and the outputs are a concentrated vapor or liquid solution containing most of the gases or volatile organics and a very dilute treated wastewater stream containing only very small amounts of dissolved gases or volatile organics.

The equipment required for steam stripping (as shown in Figure 12-1) is nearly the same as that required for conventional fractional distillation (i.e. packed column or tray tower, reboiler, reflux condenser and feed tanks and pumps). In steam stripping, however, there are several differences. A heat exchanger is used for heating the feed entering the column and cooling the stripped wastewater leaving the column. Also, the reboiler is often an integral part of the tower body rather than a separate vessel.

The choice of materials of construction for steam stripping systems depends on the operating pH and the presence (or absence) of corrosive ions present (i.e., sulfides, chlorides). In a single-column sour-water steam stripper, the high pH, from the presence of ammonia, allows mild steel to be used. If the sour water is stripped into two columns (H_2S removed in one and HN_3 removed in the other) the material of construction of the unit in which the H_2S is removed should be alloy steel or alloy clad steel.

Steam stripping is usually conducted as a continuous operation in a packed tower or conventional fractionating distillation column (bubble cap or sieve tray) with more than one stage of vapor/liquid contact. The preheated wastewater from the heat exchanger enters near the top of the distillation column and then flows by gravity countercurrent to the steam and organic vapors (or gas) rising up from the bottom of the column. As the wastewater passes down through the column, it contacts the vapors rising from the bottom of the column that contain progressively less volatile organic compound or gas until it reaches the bottom of the column where the wastewater is finally heated by the incoming steam to reduce the concentration of volatile component(s) to their final concentration. Much of the heat in the wastewater discharged from the bottom of the column is recovered in preheating the feed to the column.

Reflux (condensing a portion of the vapors from the top of the column and returning it to the column) may or may not be practiced depending on the composition of the vapor stream that is desired. By using a reflux in sour water stripping, the concentration of the hydrogen sulfide and ammonia in the vapor stream leaving the column can be increased, reducing the water load to the sulfur recovery unit or incinerator. This increased concentration of stripped gases can, however, lead to ammonium sulfide deposits in the vapor duct and corrosion unless the vapor lines are adequately insulated and heated.

In the case of pulp mill condensate stripping, the "foul oil" and water vapor are condensed from the vapors leaving the stripping column, the oil and water are separated by gravity, and the saturated water returned to the stripper. The "foul oil" (which contains turpentine) is sent to turpentine recovery.

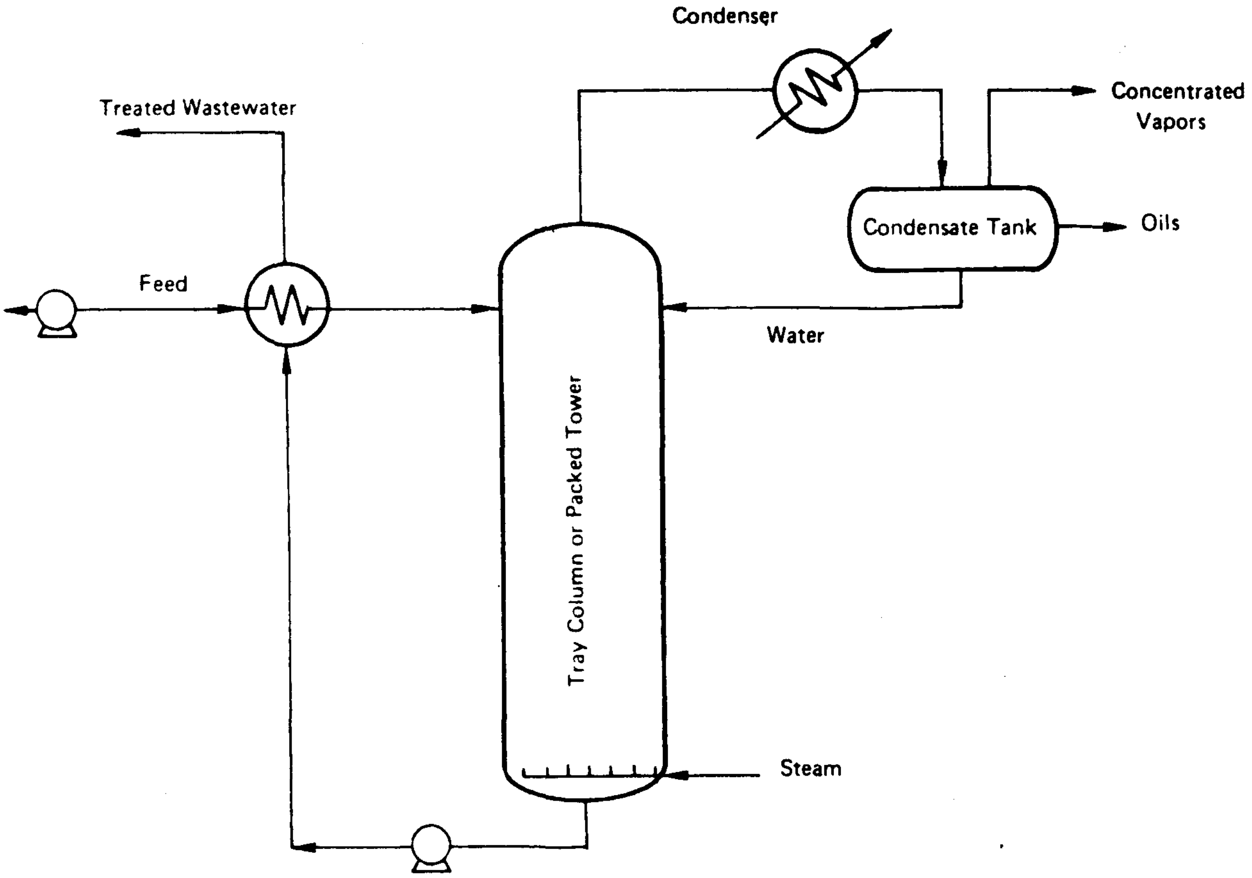


Figure 12-1 - Typical Steam Stripping System

Uncondensed vapor (containing sulfides, mercaptans, methanol, and water) is sent to the incinerator or lime kiln to be burned.

Although many of the steam strippers in industrial use introduce the wastewater at the top of the stripper, there are advantages to introducing the feed to a tray below the top tray when reflux is used.

Introducing the feed at a lower tray (while still using the same number of trays in the stripper) will have the effect of either reducing steam requirements (due to the need for less reflux) or yield a vapor stream richer in volatile component. The combination of using reflux and introducing the feed at a lower tray will increase the concentration of the volatile organic component beyond that obtainable by reflux alone. Increasing the organic vapor concentration decreases the water load on the sulfur recovery unit or incinerator.

Until recently, little attention was given to optimizing the design of sour water strippers for ammonia removal since the prime concern was removal of H_2S. The H_2S removed in the stripper was sent to a sulfur plant for recovery or was incinerated. Operation of a (steam) sour water stripper in a pH range of 6-7 at 110°C will result in over 99% removal of H_2S, but very little (less than 30% removal) of NH_3. With more stringent effluent requirements, more efficient removal of NH_3 is required. By increasing the pH to between 8 and 9, NH_2 removal is increased to between 85 and 95% but H_2S removal efficiency drops to about 98%. With a further increase in pH and the H_2S removal efficiency will drop off sharply. Since the concentration of both H_2S and NH_3 in the sour water feed to the stripper are typically between 2,000 and 10,000 ppm, it is important to remove both of these components. Two solutions for more efficient NH_3 and H_2S removal have been proposed. One solution proposes introducing caustic soda near the bottom of the stripper to increase the pH in this zone of the stripper and release NH_3 after the H_2S has been removed in the upper section of the stripper.

The second solution, which has been proven industrially, allows separate removal of the H_2S and NH_3 in two stripping towers at different pH's. The following stream compositions are reported for one such system.

	ppm By Weight		
Stream	Ammonia	Hydrogen Sulfide	Water
Stripped Water	50	5	Balance
Ammonia	Balance	5	-
Hydrogen Sulfide	50	Balance	5000

Since the input stream to the stripper in this plant contains about 15-30,000 ppm ammonia and 35-70,000 ppm hydrogen sulfide, this represents over 99.7% removal of ammonia and about 99.99% removal of hydrogen sulfide.

In this particular system, the steam is supplied by boiling the wastewater in the bottom of the column using an external heat exchanger rather than injecting live steam into the wastewater in the bottom of the column.

The advantage of this system over a conventional single-stage stripper is the complete separation of the H_2S and NH_3, while the disadvantage is the higher capital cost. The columns used for sour water steam stripping range in size from 2 to 10 feet in diameter and 20 to 40 feet in height. Feed rates to the column range from about 40 to 250 gpm.

The steam stripped volatiles are usually processed further for recovery or incinerated. If the stripped volatiles contain sulfur and are incinerated, the impact of SO_2 emissions must be considered. The impact of the stripped wastewater would depend on the quantity and type of residual volatile organics remaining in the stripped wastewater. Land requirements for this treatment system are small and there are generally no discharges except for the treated wastewater.

13. SEDIMENTATION

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. Basically, particles are made to settle out of a liquid by creating conditions in which the gravitational and inertial forces acting on the particle in the desired direction of setting are greater in magnitude than the various forces (drag forces, inertial forces) acting in the opposite direction. This force differential causes the particles to travel in the desired direction.

The fundamental elements of most sedimentation processes are:

- 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.
- A means of directing the liquid to be treated into the above basin in a manner which is conducive to settling.
- A means of physically removing the settled particles from the liquid (or the liquid from the settled particles, whichever the case may be).

13.1. OPERATION

Sedimentation can be carried out as either a batch or a continuous process. Continuous processes are by far the most common, particularly when large volumes of liquid are to be treated.

In a continuous process there is an inherent velocity as the liquid flows through the basin or container. Due to this velocity, there is a drag force exerted by the liquid on the particle in the direction of the liquid flow, resulting in a tendency for the particle to travel in the direction of the flowing liquid. There is also a gravitational force acting on the particle in a downward direction. For this gravitational force to result in a downward movement of the particle, the particle's density must be greater than that of the liquid it is suspended in. (If its density is less, the particle will tend to float rather than settle.) The rate of settling will depend on the particle size, particle density, liquid density and liquid viscosity. For settling to take place in a continuous system, the resultant force vector acting on the particle must be such that the trajectory of the particle is in a direction that will cause the particle to be retained within the container as the liquid flows through the container. (In certain types of sedimentation equipment, inertial forces supplement gravitational forces by means of causing the liquid stream to abruptly change direction.)

Depending on the specific process configuration, the settled particles are either removed from the bulk of the liquid, or the liquid is separated from the settled particles by decantation. Either way, the end result and single purpose of sedimentation is liquid/solid separation. The fraction of liquid containing the settled particles is commonly referred to as "sludge."

Sedimentation can be carried out in rudimentary settling ponds, conventional settling basins, or in more advanced clarifiers which are often equipped with built-in flocculation zones and tube-like devices that enhance settling.

13.1.1. SETTLING PONDS

In settling ponds (Figure 13-1), the liquid is merely decanted as the particles accumulate on the bottom of the pond and eventually fill it. Often the pond is periodically emptied of particles by mechanical shovels, draglines, or siphons. Sedimentation basins and clarifiers are more sophisticated and usually employ a built-in solids collection and removal devide such as a sludge scraper and draw-off mechanism. Sedimentation basins tend to be rectangular in configuration, usually employ a belt-like collection mechanism, and tend to be used more for the removal of truly settleable particles from a liquid.

13.1.2. PRIMARY CLARIFIERS

Settling basins that receive raw waste water prior to biological treatment are called primary tanks. Figure 13-2 is a sectional view of a rectangular tank. Raw waste water enters through a series of ports near the surface along one end of the tank. A short baffle dissipates the influent velocity directing the flow downward. Water moves through at a very slow rate and discharges from the opposite end by flowing over multiple effluent weirs. Settled solids are scraped to a sludge hopper at the inlet end by redwood flights that are attached to endless chains riding on sprocket wheels. Sludge is withdrawn periodically from the sludge hopper for disposal. The upper run of flights protrude through the water surface pushing floating matter to a manual skimmer placed in front of the effluent weir. The scum trough is a cylindrical tube with a slit opening along the top. When manually rotated, scum collected on the surface flows through the slot into the tube that slopes toward a scum pit. Length to width ratio of rectangular tanks varies from about 3:1 to 5:1 with liquid depths of 7 or 8 ft. The bottom has a gentle slope toward the sludge hopper.

Views of a circular primary clarifier are shown in Figure 13-3. Raw waste water enters through ports in the top of a central vertical pipe, and flows radially to a peripheral effluent weir. The influent well directs flow downward to reduce short-circuiting across the top. A very slowly rotating collector arm plows settled solids to the sludge drawoff at the center of the tank. Floating solids migrating toward the edge of the tank are prevented from discharge by a baffle set in front of the weir. A skimmer attached to the arm collects scum from the surface and drops it into a scum box that drains outside the tank wall. Circular tanks are from 30 to 250 ft in diameter, although some are as large as 200 ft. Side water depths range from 7 to 12 ft, and bottom slopes are about 8%.

Circular basins are generally preferred to rectangular tanks in new construction because of lower installation and maintenance costs. Bridge or pier supported, center-driven collector arms have fewer moving parts than the chain-and sprocket scraper mechanisms in rectangular tanks. Although inlet turbulence is greater behind the small influent well of a circular clarifier, as the flow radiates toward the effluent weir the waste-water movement slows, thus reducing the exit velocity. Greater weir lengths can be more easily achieved around the periphery

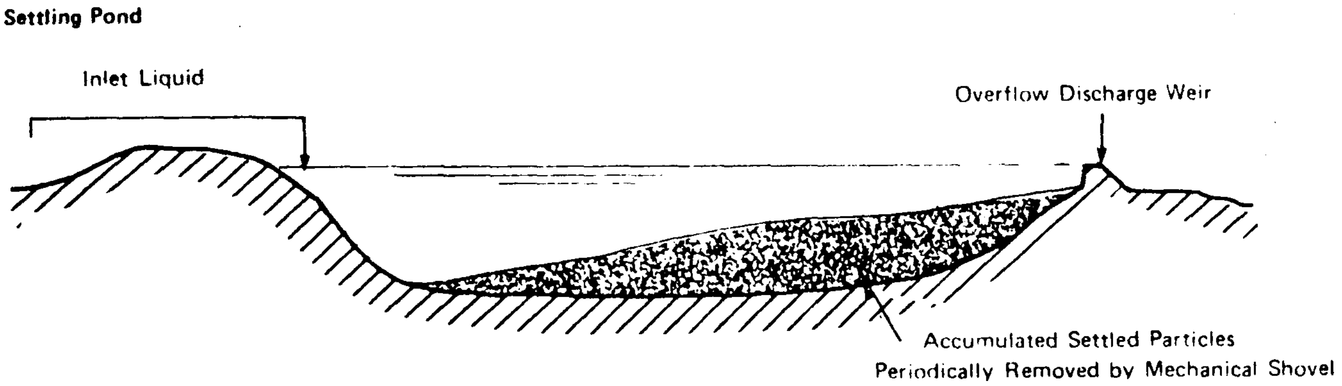


Figure 13-1 - Settling Pond (Cross-Section)

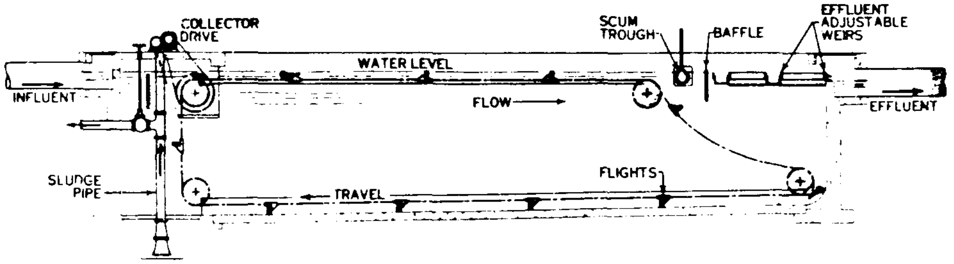


Figure 13-2 - Longitudinal Section of a Rectangular Primary Settling Tank. Sludge Collector Scrapes Settled Solids to Hopper at Inlet End. The Upper Run of Flights Pushes Floating Matter to a Scum Trough.

of a circular tank than across the end of a rectangular one. A typical installation of two primary settling basins located on opposite sides of a sludge pumping station is pictured in Figure 13-3. Pumps housed inside draw sludge from the bottom of the clarifiers at preset time intervals and discharge it to holding tanks for further processing. (Where holding tanks are not employed, sludge is allowed to accumulate in the clarifiers and is pumped directly to digesters or dewatering equipment.) Scum boxes drain to pits adjacent to the pump building so that the scum can be disposed of with the waste sludge. On the right side of the picture are two aerated grit chambers with grit washers housed in an attached building.

To prevent short-circuiting and hydraulic disturbances in the basin, flow enters behind a baffle to dissipate inlet velocity. Overflow weirs, placed near the effluent channel, are arranged to provide a uniform effluent flow. Floating materials are prevented from discharge with the liquid overflow by placing a baffle in front of the weir. A mechanical skimmer collects and deposits the scum in a pit outside of the basin. Settled sludge is slowly moved toward a hopper in the tank bottom by a collector arm. Clarifiers following activated sludge may be equipped with hydraulic pickup pipes for rapid sludge return.

Criteria for sizing settling basins are: overflow rate (surface settling rate), tank depth at the side wall, and detention time. Surface settling rate is defined as the average daily overflow divided by the surface area of the tank, expressed in terms of gallons per day per square foot. Area is calculated by using inside tank dimensions, disregarding the central stilling well or inboard weir troughs. The quantity of overflow from a primary clarifier is equal to the waste-water influent, since the volume of sludge withdrawn from the tank bottom is negligible. However, secondary settling tanks may have recirculation lines drawing liquid from the tank bottom, for example, recirculation of activated sludge, in which case the influent flow is equal to the effluent plus returned flow. For these, the flow used for design is the effluent, or overflow, and not the influent which includes recirculation.

$$V_0 = \frac{Q}{A}$$

where V_0 = overflow rate (surface settling rate), gallons per day per square foot

Q = average daily flow, gallons per day

A = total surface area of basin, square feet

Detention time is computed by dividing tank volume by influent flow expressed in hours. Numerically, it is the time that would be required to fill the tank at a uniform rate equivalent to the design average daily flow. Depth of a tank is taken as the water depth at the side wall measuring from the tank bottom to the top of the overflow weir; this excludes the additional depth resulting from the slightly sloping bottom that is provided in both circular and rectangular clarifiers. Effluent weir loading is equal to the average daily quantity of overflow divided by the total weir length, expressed in gallons per day per linear foot.

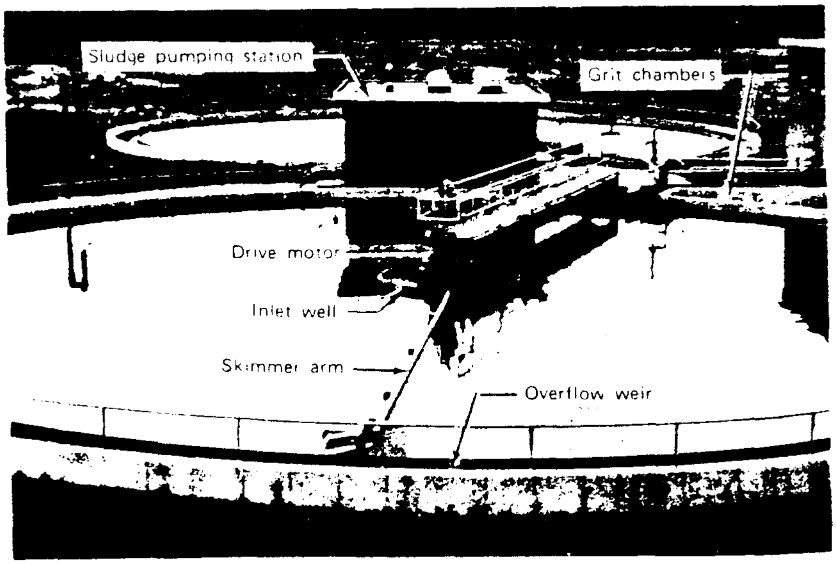


Figure 13-3 - Two 90 ft. Diameter, Primary Settling Basins Located on Opposite Sides of a Sludge Pumping Station. Waste Sludge Drawn from the Clarifiers is Pumped to Sludge Holding Tanks at Present Time Intervals. Floating Solids are Collected by Skimmers and are Deposited in Scum Boxes that Drain to a Pit for Disposal with the Waste Sludge.

$$t = 24 \frac{V}{Q}$$

where

t = detention time, hours
V = basin volume, million gallons
Q = average daily flow, million gallons per day
24 = number of hours per day

13.1.3. INTERMEDIATE CLARIFIERS

Sedimentation tanks between trickling filters, or between a filter and subsequent biological aeration, in two-stage secondary treatment are called intermediate clarifiers. Accepted standards recommend the following criteria for sizing intermediate settling tanks: overflow rate should not surpass 1000 gpd/sq ft, minimum side water depth of 7 ft, and weir loadings less than 10,000gpd/lin ft for plants of 1 mgd or smaller and should not be over 15,000 for larger plants.

13.1.4. FINAL CLARIFIERS

Settling tanks following biological filters are similar to the one illustrated in Figure 13-4 . Sometimes the effluent channel is an inboard weir trough that allows overflow to enter the channel from both sides to reduce weir loading. Common criteria for final clarifiers of trickling filter plants are: overflow rate not exceeding 800pgd/sq ft, minimum side water depth of 7 ft, and maximum weir loadings the same as for intermediate tanks, although lower values are preferred.

The purpose of gravity settling following filtration is to collect biological growth, or humus, flushed from filter media. These sloughed solids are generally well-oxidized particles that settle readily. Therefore, a collector arm that slowly scrapes the accumulated solids toward a hopper for continuous or periodic discharge gives satisfactory performance. Gravity separation of biological growths suspended in the mixed liquor of aeration systems is far more difficult. Greater viability of activated sludge results in lighter, more buoyant flocs with reduced settling velocities. In part, this is the result of microbial production of gas bubbles that buoy up the tiny biological clusters. Depth of accumulated sludge in a trickling filter final is normally a few inches if recirculation flow is drawn from the tank bottom. Even if sludge is drained only twice a day, the blanket of settled solids rarely exceeds 1 ft. In contrast, the accumulated microbial floc in a final basin for separating activated sludge may be 2 to 2 ft thick in a well-operating plant. During peak loading periods, the sludge blanket may expand further to incorporate one third to one half of the tank volume; this is particularly true in high-rate aeration systems.

The clarifier in Figure 13-5 is specially designed for an activated sludge secondary. The liquid flow pattern is the same as that of other circular clarifiers but the sludge collection system is unique. Uptake tubes are attached to and

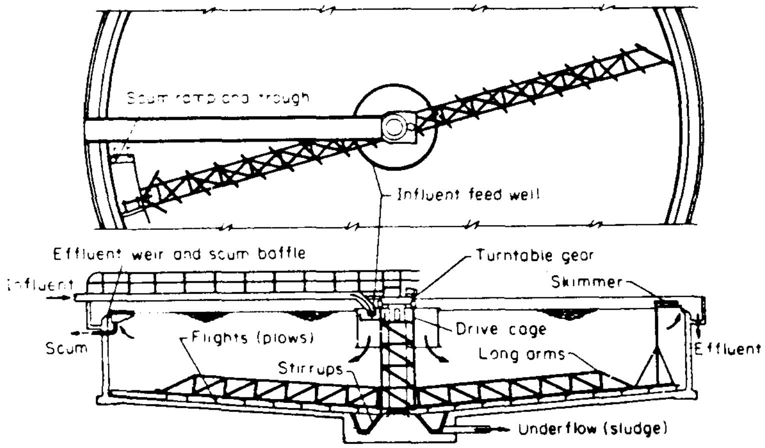


Figure 13-4 - Primary Circular Clarifier

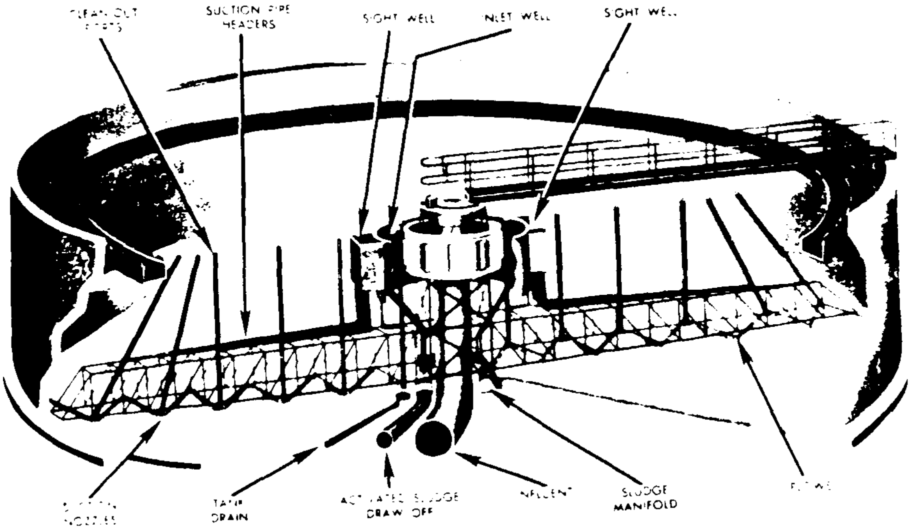


Figure 13-5 - Fine Clarifier Designed for Use with Biological Aeration. Activated Sludge is Drawn through Uptake Pipes that are Located Along the Collector Arm for Rapid Return to the Aeration Basin. Sludge Flowing from Each Pipe can be Observed in the Sight Well.

spaced along a V-plow-scraper mechanism rotated by a turn-table above the liquid surface. Discharge elevation of suction pipe headers in the sight well is lower than the water surface in the tank so that sludge is forced up and out of the uptake pipes by hydraulic action. Sludge flows by gravity from the sight wells to a manifold encircling the bottom of the center-drive cage and out under the basin. Rate of discharge is controlled by an adjustable weir outside the tank. Cleanout ports are provided to permit easy rodding in the event of nozzle plugging. While the unit illustrated is referred to as a sight well clarifier, other manufacturers produce similar units using descriptive titles such as rapid sludge removal clarifier, suction collector, or manifold draw collector. Each has advantageous features that may be of distinctive importance in the design of a specific biological aeration system. For example, one proprietary unit separates sludge collected by the uptake pipes from the heavier solids that are plowed to a sludge hopper. The former is returned as activated sludge while the solids scraped from the bottom are wasted.

Rapid uniform withdrawal of sludge across the entire bottom of an activated sludge final clarifier has two distinct advantages. The retention time of solids that settle near the tank's periphery is not greater than those that land near the center; thus, aging of the biological floc and subsequent floating solids due to gas production is eliminated. With a scraper-type collector, the residence time of a settled solids depends on the radial distance from the sludge hopper. The second advantage is that the direction of activated sludge return flow is essentially perpendicular to the tank bottom, rather than horizontally toward a centrally located sludge hopper. Downward flow through a sludge blanket enhance gravity settling of the floc and increases sludge density. This is an important factor when one considers that the return flow may be as great as one half of the influent flow.

14. FILTRATION

Filtration is one of several well-developed liquid/solid separation processes currently being applied to the full-scale treatment of many industrial wastewaters and waste sludges. For the treatment of hazardous wastes, filtration can be used to perform two distinctly different functions:

- Removal of suspended solids from a liquid (usually aqueous) waste stream with the objective of producing a purified liquid;
- Secondly, increasing the solids concentration, and thereby reducing the volume, of a high concentration liquid/solid mixture (sludge) by removing liquid from the mixture (this application is commonly referred to as "sludge dewatering").

The process of filtration is old, and rudimentary filtration devices date back to antiquity. The basic types of filtration devices have been in general use throughout the industry since the early 20th century. Whenever it is necessary to separate solid particles from a fluid, filtration is potentially applicable.

In considering applications, it is useful to divide filtration into two major categories, according to desired objectives:

- Those applications in which the objective is the production of a purified liquid stream, in which the filter serves to remove solids from the liquid;
- Those applications in which the objective is the concentration or dewatering of a slurry or sludge, in which the filter serves to remove liquid from the solids.

While there are a large number of commercially available filtration devices, there are but three representative types of filters generally used in large-scale waste treatment applications: granular media filters are most commonly used to remove suspended solids from a liquid waste stream; vacuum filters and Chamber Pressure Filters (the "filter press")--both of which are usually employed to provide sludge dewatering.

As a wastewater treatment process, filtration is usually most applicable when following some form of flocculation and/or sedimentation. As a sludge dewatering process filtration is usually technically and economically competitive with other dewatering processes.

14.1. OPERATION

Filtration is a physical process whereby particles suspended in a fluid are separated from it by forcing the fluid through a porous medium. As the fluid passes through the porous medium, the suspended particles are trapped on the surface of the medium and/or within the body of the medium itself. The fluid may be gaseous or liquid, but in this discussion primary attention will be focused on liquids.

The mechanisms by which the particles are removed as the fluid passes through the medium are complex. The dominant mechanisms depend on the physical and chemical characteristics of the filter medium and the rate at which the fluid is forced through the medium. The type of mechanisms that predominate are thus dependent on the nature of the specific application and the type of filter employed. For example, in those filtration applications where the particles are removed on the surface of the filter medium and the particles are large, the predominant mechanism is usually simple mechanical straining. However, in those applications where the particles are small and are removed within the body of the filter medium, the mechanisms can include straining through the interstices of the filter medium, coupled with gravitational settling, diffusion, interception, and inertial impaction, all within the voids of the porous filter medium. In such cases the mechanisms are greatly influenced by the dynamics of the particle/fluid flow patterns. Also important are various attachment mechanisms that affect the manner in which the particles are retained within the filter medium. These can include electrostatic interactions, chemical bridging, or specific adsorption phenomena. Often, the particles retained on or in a filter medium will in themselves form a porous filter medium, thus altering the filtration characteristics as the filtration proceeds. While a number of mathematical filtration models based on the above theoretical mechanisms have been developed, the design of commercially available filters for specific applications is typically based largely on empirical data.

The many types of applications and process requirements have resulted in a wide variety of commercially available filtration equipment. Generally, the following features are common to all filtration systems.

- A porous filter medium.
- An induced pressure differential across the filter medium that causes the fluid to flow through the filter medium.
- A mechanical device which contains or supports the filter medium and directs and controls the flow of fluid to and from the filter medium.
- A means of removing the entrapped particles from the filter medium (alternatives can include removal and disposal of the filter medium itself).

Filter media can be divided into three general classes:

a. A thick barrier composed of a layer of granular media such as sand, coke, coal, or porous ceramics.

b. The thin barrier exemplified by a filter cloth, or filter screen.

c. A thick barrier composed of a disposable material such as powdered diatomaceous earth or waste ash.

The pressure differential required to move the fluid through the medium can be induced by gravity, by positive pressure, or by vacuum.

Most filtration applications involve the separation of solid particles from a liquid (usually aqueous) stream. Other applications can involve the separation of two immiscible liquids (such as oil and water), or the removal of particulate matter or liquid droplets from a gas stream. The intended filter application has a great influence on both the basic type of filter used and the nature of its specific physical features.

In the realm of liquid/solid separation (the most common waste treatment application), an important factor determining the type of filter used is the intended product of the filtration process. In some applications the intended product is a purified liquid stream from which suspended particles are to be removed. In other applications, the objective is just the opposite, in that solids concentration of the mixture is already high enough so that the liquid portion is of relatively little value, and the primary objective is to concentrage the solids to facilitate handling and ultimate disposal. In aqueous systems, this process is called "dewatering of sludges." The distinction between whether the waste treatment objective is to remove solids from a liquid or liquid from solids is an important one, for it determines which class of filters can be applied.

While there are a large number of commercially available and proprietary filtration devices, in terms of basic process parameters, there are but a few representative types of filters, which are described below.

14.1.1. GRANULAR MEDIA FILTERS

Granular media filtration, one of the oldest and most widely applied types of filtration for the removal of suspended solids from aqueous liquid streams, utilizes a bed of granular particles (typically sand or sand with anthracite coal) as the filter medium. The bed is commonly contained within a basin or tank and is supported by an underdrain system which allows the filtered liquid to be drawn off while retaining the filter medium in place. The underdrain system typically consists of metal or plastic strainers located at intervals on the bottom of the filter. As suspended particle-laden water passes through the bed of the filter medium, particles are trapped on top of and within the bed, thus reducing its porous nature and either reducing the filtration rate at constant pressure or increasing the amount of pressure needed to force the water through the filter. If left to continue in this manner, the filter would eventually plug up with solids. The solids, therefore, must be removed. To do this, a wash water stream is forced through the bed of granular particles in the reverse direction of the original fluid flow. The wash water is sent through the bed at a velocity sufficiently high so that the filter bed becomes fluidized and turbulent. In this turbulent condition, the solids are dislodged from the granular particles and are discharged in the spent wash water. This whole process is referred to as "backwashing." When the backwashing cycle is completed, the filter is returned to service. The spent backwash water contains the suspended solids removed from the liquid, and therefore presents a liquid disposal problem in itself. The volume of the backwash water stream, however, is normally only a small fraction (1-4%) of the volume of the liquid being filtered. Consequently, the suspended solids concentration of the backwash water is far greater than that of the liquid filtered. Granular media filtration essentially removes suspended solids from one liquid stream and concentrates them into another, but much smaller, liquid stream.

depending on the specific process configuration, backwash water itself can be treated to remove suspended solids by flocculation and/or sedimentation or by returning it to the portion of the process from whence the liquid stream subjected to filtration originated; e.g., a settling pond. A typical granular media filter is shown in Figure 14-1.

Most filter designs employ a static bed with vertical flow either downward or upward through the bed. The downflow designs are traditionally used in potable water treatment. The European biflow design employs both flow directions with the effluent withdrawn from the interior of the bed. Upflow washing is used regardless of the operating flow direction. Two special filter designs employ horizontal radial flow through an annular bed. Media is cycled downward through the bed, withdrawn at the bottom, externally washed, and returned to the top. An upflow filter is shown in Figure 14-2.

Granular media filters are primarily used to produce a purified liquid stream of low suspended solids concentration. The suspended solids concentration of the filtered liquid depends a great deal on particle size distribution, but typically, granular media filters are capable of producing a filtered liquid with a suspended solids concentration as low as 1-10 mg/liter.

While granular media filters can produce a high quality effluent with respect to suspended solids concentration, they cannot effectively filter liquids having high suspended solids concentrations. Typically, for most granular media filters to operate properly, the inlet suspended solids concentration must be well below 200 mg/liter; otherwise, problems with excessively frequent backwashing are usually experienced. Very often, granular media filters are installed downstream of sedimentation processes in order to effect additional removal of suspended solids and reduce the suspended solids load on the filter by having most of the suspended solids removed in the sedimentation step.

14.1.2. FIXED MEDIA, CONTINUOUSLY RENEWED SURFACE FILTRATION

A very large number of filtration devices can be categorized under this term, including rotary drum vacuum filters, microstrainers, and disk filters. Probably the most common and most representative type of filter within this general group is the rotary vacuum filter.

Rotary vacuum filtration is the most common mechanical method to dewater sludge. The cylindrical drum covered with a filter medium rotates partially submerged in a vat of chemically treated waste. The filter medium may be a belt of synthetic cloth, woven metal, or two layers of stainless steel coil springs arranged in corduroy fashion around the drum. As the drum slowly rotates, vacuum is applied immediately under the filter medium to attract sludge solids as the drum dips into the vat. Suction continues to draw water from the accumulated solids as the filter slowly rotates. Radial vacuum pipes convey filtrate from collecting channels in the drum surface behind the media. In the discharge sector, suction is broken and the belt or coil springs are drawn over a small diameter roller for removal of the dried cake. Fork tines help release the solids layer. The filter medium is washed by water sprays, located between wash and return rollers, before it is reapplied to the drum surface for another cycle.

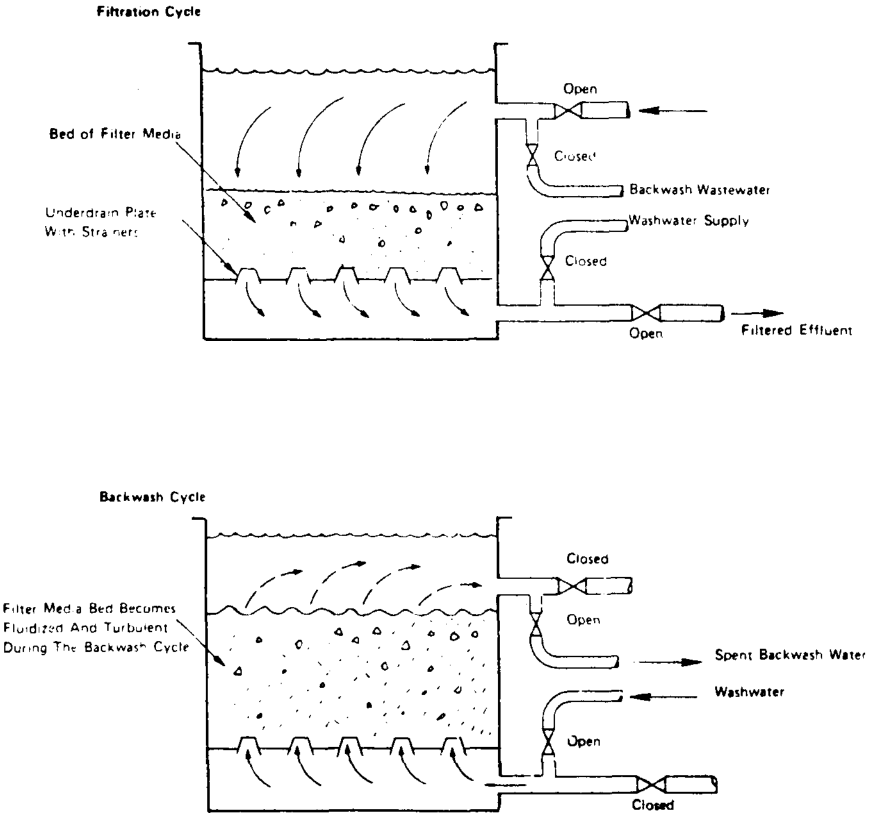


Figure 14-1 - Granular Media Filter (Cross-Sectional View)

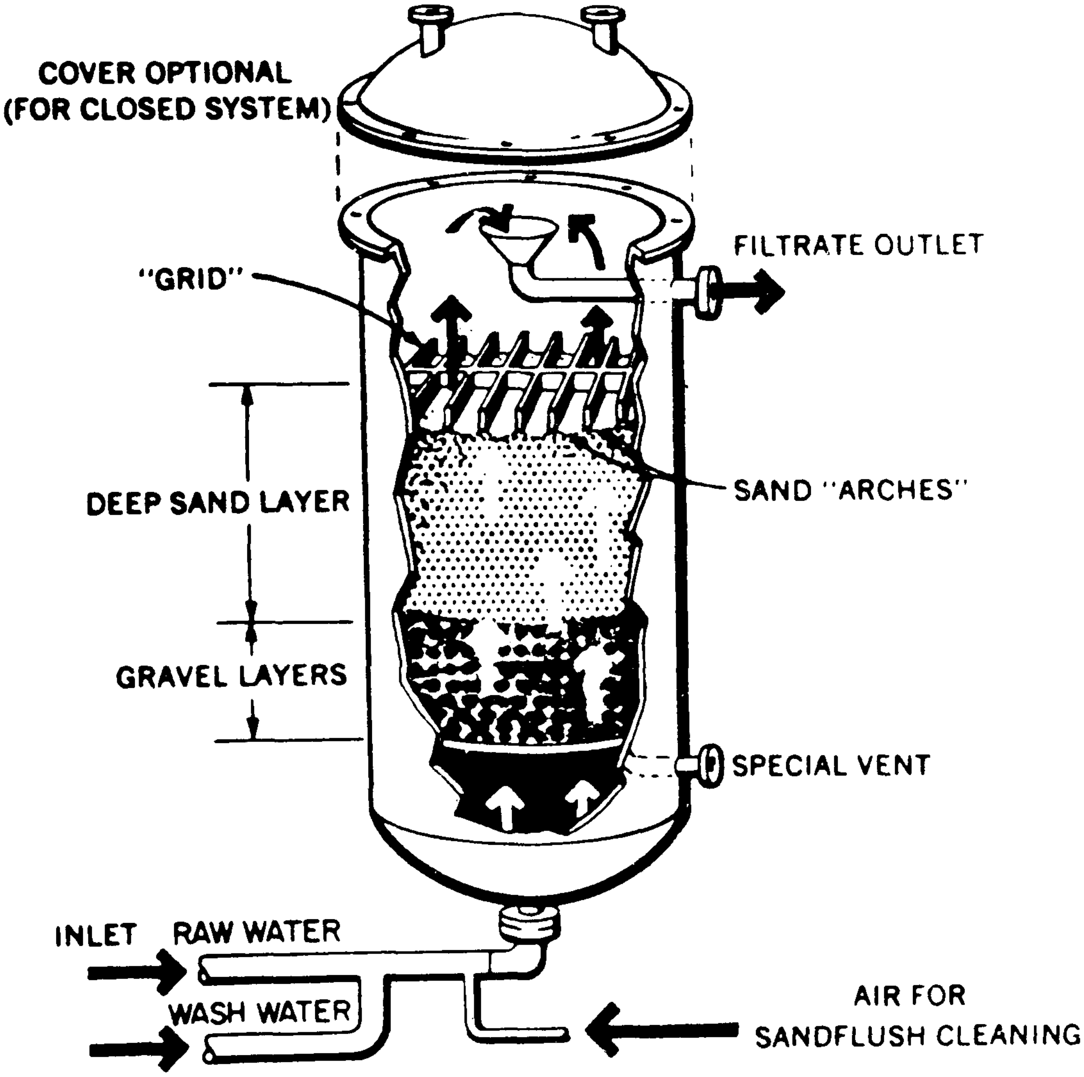


Figure 14-2 - Cross Section of Upflow Filter

Many small plants draw settled sludge directly from the primary tanks without thickening. Although this is often satisfactory for trickling filter installations, vacuum filtration of unthickened sludges from aeration plants often leads to unsatisfactory performance. The generally accepted minimum solids concentration for economical filtration is 4%.

Mixtures of raw primary and secondary wastes are gravity thickened, while waste activated may be increased in solid content by flotation. Digested sludge seldom is thickened separately because of its high density when drawn from digesters. However, elutriation may be practiced to remove alkalinity and fine solids to improve filter yields and reduce chemical dosage. This process consists of countercurrent washing of the digested sludge with plant effluent.

Components of a vacuum filter installation are illustrated in Figure 14-3. Positive displacement pumps meter sludge to a conditioning tank. Here chemicals are mixed with the liquid to flocculate the solids. Chemical treatment is necessary to capture fines that would otherwise be drawn through the medium, and to prevent cracking of the filter cake during dewatering, which would result in excess air entering the vacuum system. The mixture of filtrate and air drawn by the vacuum pump is separated in a receiving vessel. Air is exhausted through a silencer to reduce noise, and the water is pumped back to the inlet of the treatment plant. Cake peeled from the filter drops onto a belt conveyor for transporting to a truck for hauling to landfill, or directly to an incinerator. Filtrate return accounts for the majority of the process discharge. For example, dewatering 1000 gal of sludge with 5% solids to a 30% cake results in 830 gal of extracted water and about 140 lb of wet cake; this amounts to a wet sludge weight reduction of 83%.

A variation of this application is the precoat vacuum filter. Typically a layer of powdered material, such as diatomaceous earth, is deposited on the surface of the previously described vacuum filter as a slurry. Solids are then trapped on the surface of this layer as it rotates, dipping in and out of the trough. To prevent clogging, a thin layer of the precoat material (along with the entrapped solids) is continuously cut away by a slowly advancing blade. When the entire layer has been removed, the filter is taken out of service, given a fresh precoat, and is then ready to resume filtration. The fine pore structure of the precoat material enables much smaller particles to be removed, as compared to the unprecoated vacuum filter.

In many vacuum filtration applications, filter aids are used to improve dewaterability of certain sludges. Lime and ferric chloride are commonly used as dewatering aids. Their use improves filterability by precipitating a coating (ferric hydroxide) onto the fine sludge particles, making them larger so that they have less tendency to clog the filter media. The use of lime and ferric chloride also reduces the suspended solids concentration of the filtrate.

Vacuum filters and similar devices are primarily designed for the dewatering of waste sludges or useful products, such as TiO_2, ZrO_2, pigments, polymers, etc. They are less commonly used to produce a purified liquid stream. (For the purpose of this study, a sludge is defined as a liquid stream having a suspended solids concentration greater than 2% by weight.)

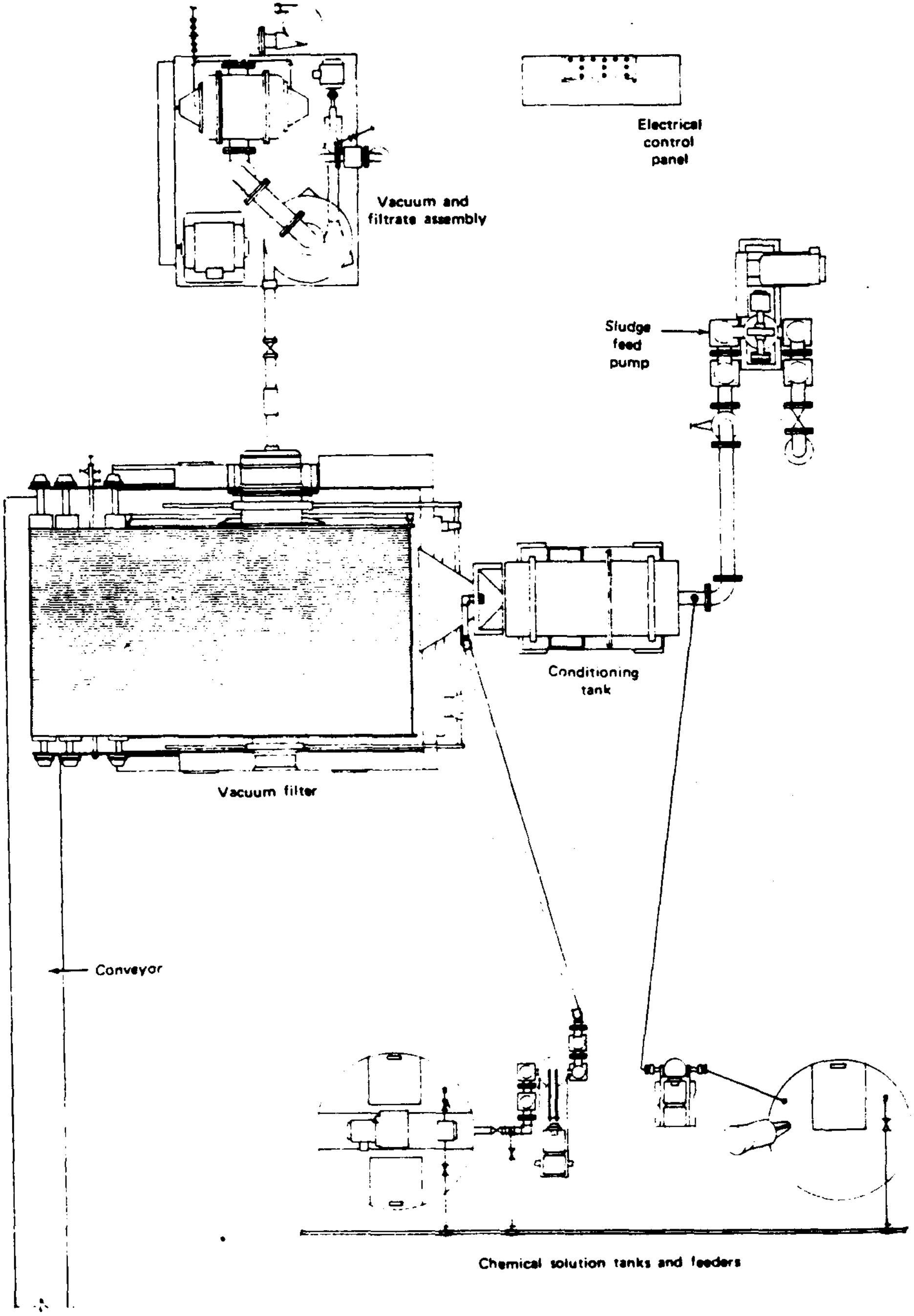


Figure 14-3 - Schematic Layout Showing the Major Components of a Vacuum Filtration System

The final suspended solids concentration of a sludge dewatered by vacuum filtration depends greatly on the specific sludge, but typically, the solids concentration will vary from as low as 10% to over 40%. Unless the material being dewatered is composed of relatively large discrete particles, it is seldom possible to dewater a sludge by vacuum filtration to a solids concentration of much greater than 40%.

Due to the nature of the filter medium used, the filtrate from a vacuum filter typically has a suspended solids concentration of several hundred to several thousand mg/liter, and therefore it is not usually suitable for discharge to a receiving stream without further treatment. In most cases, the filtrate is returned to the clarifier or sediment basin from which the sludge was drawn, where it is incorporated with the incoming waste stream to eventually become part of the sludge once more.

14.1.3. CHAMBER PRESSURE FILTERS

In one large category of filters, rigid individual filtration chambers are operated in parallel under relatively high pressures (up to 250 psi). This category includes pressure leaf filters, horizontal plate filters, tube element filters, and the plate-and-frame or so-called "filter press." The filter press is the most common and representative of this group.

The filter press consists of a series of plates and frames, alternately arranged in a stack and "pressed" together by a large screw jack or hydraulic cylinder, hence the term "filter press."

Referring to Figure 14-4, the liquid to be filtered enters the cavity formed by frame "B." Pressed against this hollow frame are plates "A" and "B" which consist of perforated metal plates covered with a fabric filter medium. As the liquid flows through the filter medium, solids are entrapped and build up within the cavity. When the solids build up to a certain level, the plates and frames are separated, the solids scraped away into a receiving hopper, the media washed, and then the whole assembly is returned to service by pressing the plates together and resuming the flow of liquid.

In certain applications, the medium is covered or "precoated" with a powdered filter aid such as diatomaceous earth. The precoat material enables the removal of smaller particles. Lime and ferric chloride filter aids are also frequently used in filter press applications to effect more complete removal of solids. The filter media is precoated by feeding a water suspension of diatomaceous earth. Precoat prevents binding of the filter cloth with sludge particles and facilitates discharge of cake at the end of the filter cycle. Conditioned sludge enters the center feed port immediately after the precoat slurry and is distributed throughout the chambers located between the individual plates. Water is forced through the filter cloth and out through drains between the frames. When the chambers have filled with accumulated solids, a high-pressure cycle consolidates the cakes. Compressed air at about 200 psi is applied to the sludge inlet and maintained until the desired density is obtained. After the filter cycle, a core flow valve opens and compressed air blows the feed sludge remainint in the center feed port back to a holding tank. The filter plates are

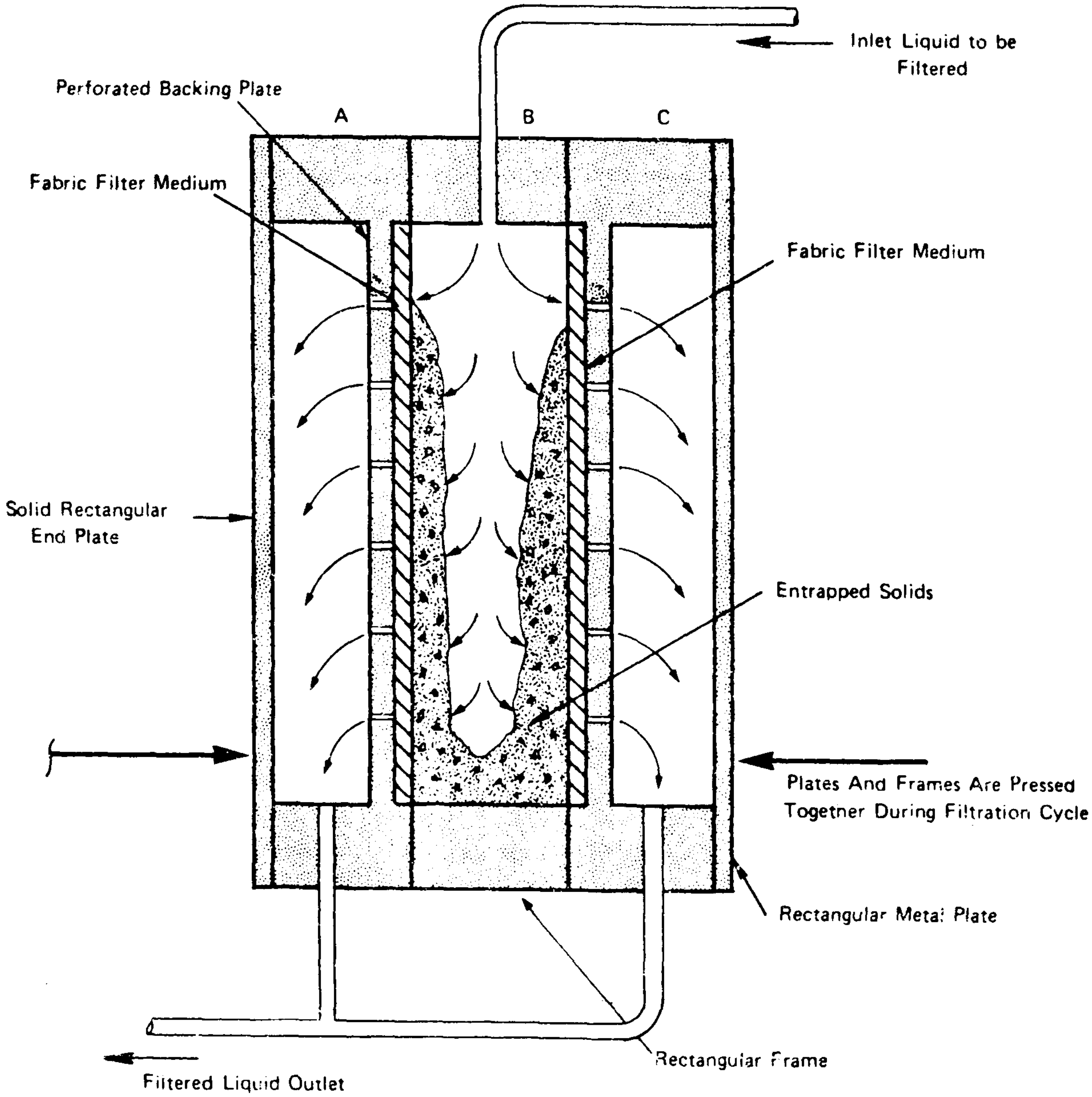


Figure 14-4 - Filter Press (Illustrative Cross-Sectional View of One Rectangular Chamber) then separated and the dewatered sludge cakes drop into a hopper equipped with a conveyor mechanism. The filter cycle, taking from 1 to 2 hr, is completely automated including precoat, filtration, and discharge. Some of the advantages attributed to pressure filtration are high solids concentration in the filter cake, clear filtrate with low suspended solids, and minimum operator supervision.

Pressure filtration appears to be particularly advantageous for thickening alum sludges where a high solids content is most desirable. With lime or polymer conditioning, aluminum hydroxide sludges can be pressed to a solids content of 30 to 40%, which is adequate for hauling by truck.

Filter presses are generally more effective in dewatering difficult-to-filter sludges of a sticky or gelatinous nature. Also, for a given type of sludge, the filter press is usually capable of producing a dewatered sludge of a higher solids concentration. These advantages over the vacuum filter are usually balanced off by slightly higher capital and operating costs.

14.2. FILTRATION APPLICATIONS

- Arsenic has been removed as the sulfide from industrially contaminated municipal wastewater by means of precipitation, flocculation, and sedimentation followed by sand and coal granular media filtration.

- Cadmium has been removed as the sulfide from wastewater on a pilot plant scale by means of flocculation, sedimentation and multi-media granular filtration.

- Chromium is typically removed from metal finishing wastewater by chemical reduction to the trivalent state followed by lime precipitation as the hydroxide, flocculation and sedimentation. Often granular media filtration is used to improve the removal of chromium hydroxide precipitates.

- Lead is removed from wastewater from a tetraethyl lead plant by hydroxide precipitation with lime. The precipitates, after settling, are dewatered by means of rotary vacuum filtration.

- Mercury is effectively removed from wastewater by the reduction of mercury ions to metallic mercury by means of reaction with sodium borohydride. The metallic mercury particles are removed by filtration (either rotary vacuum or filter presses).

- Nickel is removed from plating wastewater by means of hydroxide precipitation with lime. Granular media filtration can often be used to improve the removal of precipitated particles.

- Zinc is often removed from wastewater by means of hydroxide precipitation with lime at controlled pH followed by sedimentation. The settled precipitates are often dewatered by means of rotary vacuum filters.

o Waterborne oily wastes are removed by various types of filtration devices in series with the more traditional types of oil separators to improve the overall oil removal efficiency.

o Waste lube oil from automobiles, trucks and industrial applications contains a variety of hydrocarbon compounds, many of which are considered hazardous. In addition, many of these oils also contain colloidal metal particles. The reprocessing of waste oil can be considered a hazardous waste treatment technique, since a volume of oil that is reclaimed is a volume of oil that is not disposed of. In the waste oil reclamation process, one of the treatment steps involves a dewaxing operation in which wax crystals must be removed from the reclaimed oil. Filtration is used for the removal of the wax crystals.

o Sulfur dioxide air pollution control systems. Most air pollution control systems intended for the removal of sulfur dioxide from stationary combustion sources use alkaline scrubbing solutions and remove the sulfur dioxide as a calcium sulfite/sulfate sludge. Vacuum filtration has been used to dewater this sludge prior to final disposal.

o Dewatering of waste sludges from biological treatment systems. Biological treatment is extensively used for the treatment of wastewater from the pulp and paper industry, petroleum refining industry, and organic chemicals industry. Waste sludges from the biological treatment systems are frequently dewatered by vacuum filtration prior to land disposal or incineration.

In the cleaning or "backwashing" of granular media filters, a small solids-contaminated wastewater stream is generated. If the solids are considered hazardous, this stream must be treated prior to disposal. Typically, when filters follow sedimentation basins, the backwash water is returned to the sedimentation basin where (after particles are removed) it will eventually be sent through the filter again. If this option is not available, the backwash water would have to be subjected to further treatment.

In rotary vacuum filters and filter presses used for sludge dewatering, the solids produced are the intended product. These applications also face a disposal problem associated with the liquid (filtrate) that has been removed from the sludge.

The only energy requirement associated with filtration is the energy required to pump the fluid through the filter medium. Compared with many other processes applicable to the treatment of hazardous wastes, the energy requirements of filtration are low. For example, a vacuum filtration system capable of dewatering a 36,000 gpd sludge stream containing 6 tons of solids will typically have a total installed power requirement of only 25 horsepower.

Vacuum filters and filter presses generally consume more energy than granular media filters. In general, energy consumption is not a major factor in the selection of a liquid/solid separation process for waste treatment applications.

Whenever suspended particles are present in a fluid stream, filtration is potentially applicable to effect a separation between the particles and the fluid. The fundamental requirement is that the suspended particles either be of sufficient size or be capable of being increased in size by flocculation such that they can be trapped in or on the filter medium. For this reason, the basic types of filtration devices described in this report are sometimes marginally effective in removing very small truly colloidal particles, unless those particles can be made larger by flocculation. In cases where it is not possible to flocculate such particles (as in the case of many oil/water emulsions), more advanced techniques such as ultrafiltration are more applicable.

Filtration is a purely physical separation process. Depending on the application, filtration can either serve as the sole liquid/solid separation process, or it can be used in conjunction with other liquid/solid separation processes (such as flocculation and/or sedimentation or centrifugation).

14.3 ULTRAFILTRATION

Ultrafiltration is a membrane separation system capable of segregating dissolved or suspended species from a liquid stream on the basis of size. These species may range from large organic molecules (mol. wt 1000) to larger agglomerations.

Ultrafiltration presently has commercial applicability in several industrial situations and is increasing its markets. There are several suppliers of equipment offering a wide range of designs and membrane materials.

Operating costs are higher than those of reverse osmosis to which ultrafiltration is related, due to small unit sizes, shorter equipment life, and higher pumping costs. Reclamation of valuable components may be necessary to justify these higher costs.

Ultrafiltration is uniquely capable of making certain separations especially from concentrated streams. However, each installation must be carefully piloted, as the system design and determination of operating parameters is critical.

Ultrafiltration is a membrane filtration process which separates high molecular weight solutes or colloids from a solution or suspension. The process has been successfully applied to both homogeneous solutions and colloidal suspensions, which are difficult to separate practically by other techniques. To date, commercial applications have been entirely focused on aqueous media.

The basic principle of operation of ultrafiltration is illustrated in Figure 14-5. Flowing by a porous membrane is a solution containing two solutes: one of a molecular size too small to be retained by the membrane, and the other of a larger size allowing 100% retention. A hydrostatic pressure, typically between 10-100 psig, is applied to the upstream side of the supported membrane, and the large-molecule solute or colloid is retained (rejected) by the membrane. A fluid concentrated in the retained solute is collected as a product from the upstream side, and a solution of small-molecule solute and solvent is collected from the downstream side of the membrane. Of course, where only a single solute is

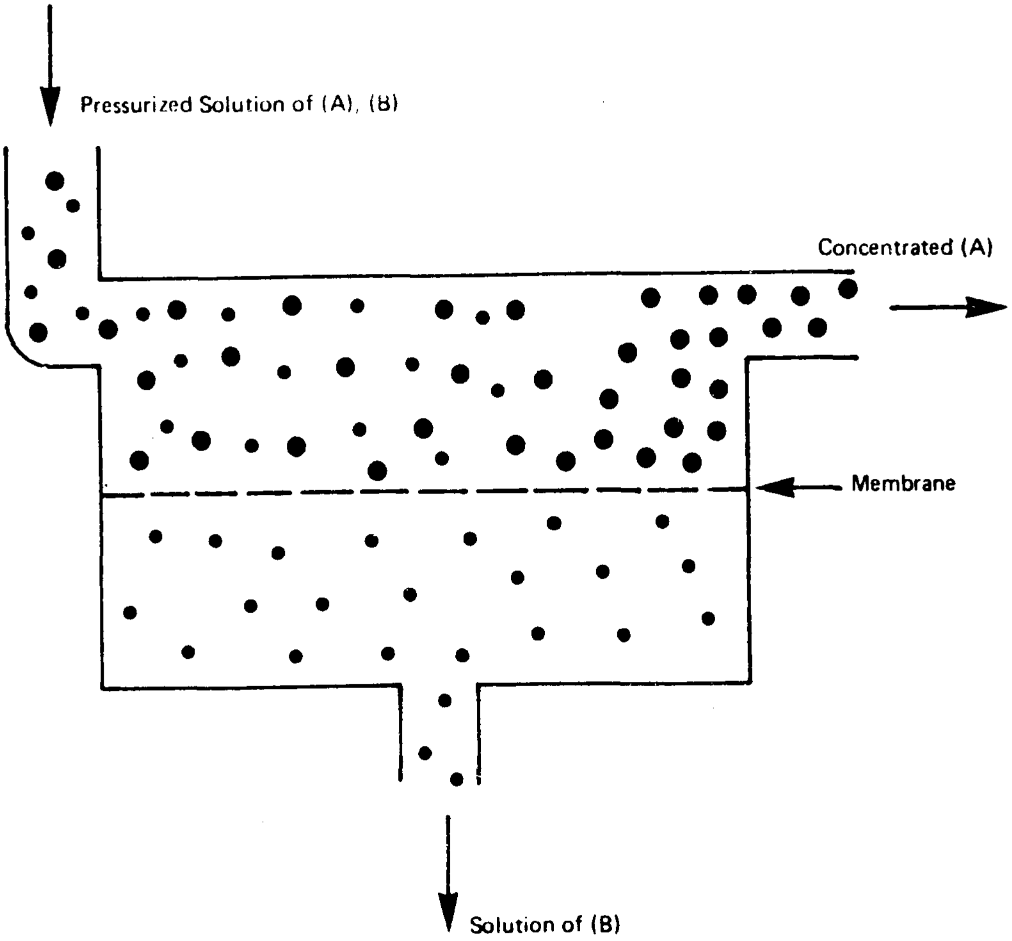


Figure 14-5 - Schematic Diagram of Membrane Ultrafiltration Process present and is rejected by the membrane, the liquid collected downstream is (ideally) pure solvent.

Retained solute (or particle) size is one characteristic distinguishing ultrafiltration from other filtration processes. Viewed on a spectrum of membrane separation processes, ultrafiltration is only one of a series of membrane methods which can be used. For example, reverse osmosis, a membrane process capable of separating dissolved ionic species from water, falls further down the same scale of separated particle size. At the small-molecule/low-flux end of the spectrum lies the commercial cellulose acetate reverse osmosis membrane, with the capability of retaining hydrated sodium and chloride ions. Next come ultrafiltration membranes with pores of about 0.5 to 10 gallons/sq ft/day/psi of pressure driving force. Microporous filters capable of virus and bacteria retention cover the pore size range of about 0.01 to 1.0 microns, with fluxes of 10-1000 gallons/sq ft/day/psiΔp.

In a sense, any reverse osmosis membrane also ultrafilters, although perhaps at very low flux states. In turn, some ultrafiltration membranes may exhibit a slight degree of retention of ionic species.

Ultrafiltration membranes are asymmetric structures, possessing an extremely thin selective layer (0.1-1.0 microns thick) supported on a thicker spongy substructure. Controlled variation of fabrication methods can produce membranes with desirable retentive characteristics for a number of separation applications. Indeed, it has become possible to tailor membranes with a wide range of selective properties. For example, tight membranes can retain organic solutes of 500-1000 mol wt while allowing passage of most inorganic salts. Conversely, loose membranes can discriminate between solutes of 1,000,000 vs. 250,000 mol wt.

Ultrafiltration membranes are different from so-called "solution-diffusion" membranes, which have been the subject of study for a wide variety of gas and liquid-phase separations. The latter group possesses a permselective structure which is non-porous, and separation is effected on the basis of differences in solubility and molecular diffusivity within the actual polymer matrix. Reverse osmosis membranes generally fall into this category.

Membranes can be made from various synthetic or natural polymeric materials. These range from hydrophilic polymers such as cellulose, to very hydrophobic materials such as fluorinated polymers. Polyarylsulfones and inorganic materials have been introduced to deal with high temperatures and pH values.

Membranes of this type are in many respects similar to reverse osmosis membranes except for the openness of their pores. Other forms and materials are available, as well, including porous zirconia, deposited on a porous carbon substrate and on a porous ceramic tube. The latter two systems, while more expensive than the former, are capable of use to very high pH values and temperatures.

The properties of ultrafiltration membranes lead to a range of applications quite distinct from those of conventional filtration. Where solutes are being separated from solution, ultrafiltration can serve as 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 separation task, because it produces a concentrated rather than a solvent-free product, and the concentrate requires further processing if a pure solute is to be recovered.

Applications of ultrafiltration may fall into one of three categories:

- Concentration, where the desired component is rejected by the membrane and taken off as a fluid concentrate;

- Fractionation, for systems where more than one solute are to be recovered, and products are taken from both the rejected concentrate and permeate;

- Purification, where the desired product is purified solvent.

Electrical energy is the only energy input required for ultrafiltration. It supplies the pumping power required to maintain good flow rates at the operating pressures, usually 60-200 psi. In certain instances, energy costs may run as high as 30% of total direct operating costs but are generally less.

Since ultrafiltration involves no chemical conversion, residues from the process are typically a concentrate of the undesirable or hazardous components. The process generally serves to provide a greatly reduced volume of the hazardous waste, but does not inherently provide any elimination of the waste. The noteworthy exceptions, of course, are those cases where a pollutant can be recovered as a valuable by-product. Otherwise, organic concentrates require further processing for ultimate disposal, such as additional concentration and incineration. In the case of some fractionation applications of ultrafiltration, the concentrate and ultrafiltrate require further processing before end disposal occurs.

15. ADSORPTION

15.1 CARBON ADSORPTION

Adsorption of activated carbon, while considered advanced waste treatment in certain areas, has a long history. Some medicinal properties of charcoal were known over 3,500 years ago, and the decolorization and gas adsorption properties of various chars were first investigated in the late 19th Century. Commercial activated carbons first appeared in the early part of the 20th Century and their development was given a large push by applications in the sugar industry (decolorization) and by the need to develop gas adsorbents to protect against the poison gases used in World War I.

Carbon adsorption systems have been demonstrated to be practical and economical: (1) for the reduction of COD, BOD and related parameters in secondary municipal and industrial wastewaters ("tertiary treatment"); (2) for the reduction of COD, BOD and related parameters in primary municipal and industrial wastewaters ("physical-chemical treatment"); (3) for the removal of toxic or refractory organics from isolated industrial wastewaters; (4) for the removal and recover of certain organics from wastewaters, and (5) for the removal, at times with recover, of select inorganic chemicals from aqueous wastes.

The term activated carbon applies to any amorphous form of carbon that has been specially treated to give high adsorption capacities. Typical raw materials include coal, wood, coconut shells, pulp mill residues, petroleum base residues, and char from sewage sludge pyrolysis. A carefully controlled process of dehydration, carbonization, and oxidation yields a product which, while not pure carbon, is called activated carbon. This material has a high capacity for adsorption due primarily to the large surface area available for adsorption, 500-1500 square meters/gram, resulting from a large number of internal pores. Pore sizes generally range from 10-100 Angstroms in radius. Most of the available surface area is non-polar in nature, but the interaction with oxygen (in production) does produce specific active sites which give the surface a slightly polar nature.

Adsorption on activated carbon occurs when a molecule is brought up to its surface and held there by physical and/or chemical forces. This process is reversible, thus allowing activated carbons to be regenerated (and reused) by the proper application of heat and steam, or solvent.

Carbon adsorption should thus be given serious consideration when it is desirable to remove mixed organics from wastewaters, to remove select inorganics from wastewaters, or to recover select organic or inorganic species from aqueous solution. The concentration of adsorbates in the influent should be less than 1% when recovery is not involved; concentrations up to 5% are acceptable when recovery is involved.

After initially contacting an activated carbon with a solution, an equilibrium will eventually be reached such that the rates of solute adsorption and desorption are equal. The amount of solute absorbed per unit weight of carbon will increase as the concentration of the solute in the solution is increased. In general, adsorption equilibria are governed by two types of interactions: solute-adsorbent and solute-solvent. Thus, the forces favoring dissolution and the forces favoring adsorption are in competition; any change in a system which tends to decrease the dissolution forces or increases the adsorption forces will shift the equilibrium towards higher adsorption per unit weight of carbon.

Some important, but general, rules resulting from considerations relating to the above factors are given below:

- Higher surface areas will give a greater adsorption capacity.
- Larger pore sizes will give a greater adsorption capacity for large molecules.
- Adsorptivity will increase as the solubility of the solute (in the solvent) decreases. Thus, for hydrocarbons, adsorption increases with molecular weight.
- For solutes with ionizable groups, maximum adsorption will be achieved at a pH corresponding to the minimum ionization.
- Adsorption capacity will decrease with increasing temperature (since adsorption is an exothermic process). In practice, this effect is generally small.

The above factors all related to adsorption capacity; the rate of adsorption is also an important consideration. For example, while capacity is increased with the adsorption of higher molecular weight hydrocarbons, the rate of adsorption is decreased. Similarly, while temperature increases will decrease the capacity it may -- depending on the rate limiting step in the overall process -- increase the rate of removal of solute from solution.

One additional point ot remember is that biological activity will usually take place in a carbon bed; if the concentration of adsorbed species is high enough, and the material is biodegradable and non-toxic to the bacteria, then biological degradation may significantly increase the effective removal capacity. Biological activity usually becomes important after many hours of operation. During this time the bacteria have become acclimated and the colony has grown to a significant concentration. In some cases the absorptive life of the activated carbon is doubled.

15.1.1 OPERATION

The process of carbon adsorption involves two basic steps as shown in Figure 15-1. First, the waste stream is contacted with the carbon which selectively absorbs the hazardous material and allows the purified stream to pass through. Second, when the carbon reaches its maximum capacity for adsorption (or when the effluent is unacceptable for discharge, i.e., when a breakthrough of hazardous material occurs), it must be removed for disposal, destruction, or regeneration. If a breakthrough of impurities occurs long before the full absorptive capacity is reached, then either the rate of feed is reduced or the carbon is replaced. In some cases, carbon can be regenerated in such a way that absorbed material is recovered.

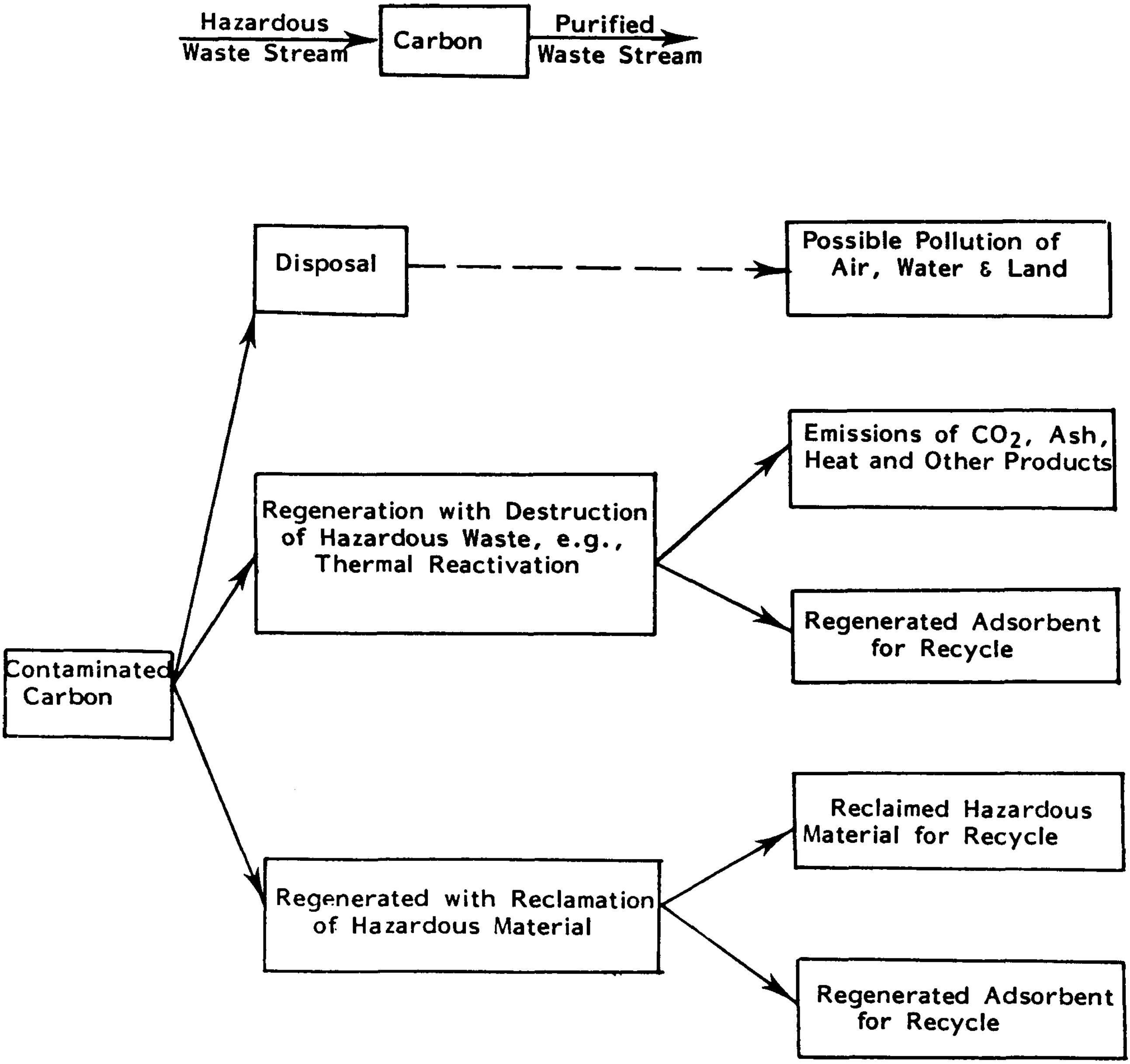


Figure 15-1 - Carbon Adsorption Process

Activated carbon is available in both powdered and granular form. Powdered carbon is less expensive and may have a slightly higher adsorption capacity, but it suffers from four drawbacks: it is difficult to regenerate (without high losses); it is more difficult to handle (the settling characteristics may be poor); in the presence of suspended solids coagulation may occur (since powdered carbon is a good coagulant); and larger amounts (on a lb/1000 gal basis) may be required than for granular systems in order to obtain good contact.

In some systems, contacting must be periodically stopped and the carbon column backwashed with water to remove suspended solids that have been filtered out of wastewater by the carbon bed. In the case of downflow contactors, which may be designed to act in part as a suspended solids filter, frequent backwashing with bed expansions of up to 50% may be required. The backwash water is usually recycled to the primary sedimentation for treatment.

The equipment needed for carbon adsorption systems can be quite complex and costly. Figure 15-2 shows a complete system incorporating thermal reactivation.

Tanks must be constructed of stainless steel or coated (rubber or epoxy) steel to prevent corrosion. If gravity contacting is possible, then cement may be used for adsorber construction.

There are a wide variety of carbons currently available. It is usually necessary to carry out laboratory tests with several different carbons before a final choice is made (e.g., adsorption capacity, resistance to abrasion, pressure drop in a column, ease of regeneration, etc.).

15.1.1.1 CONTACTING SYSTEMS

There are several ways that waste streams can be contacted with carbon, based on the choice of influent characteristics, effluent criteria, flow rate and economics. Four of which are listed here:

o Adsorbers in Parallel	For high volume applications Can handle higher than average suspended solids (~65-70 ppm) if downflow Relatively low capital costs Effluents from several columns blended, therefore less suitable where effluent limitations are low

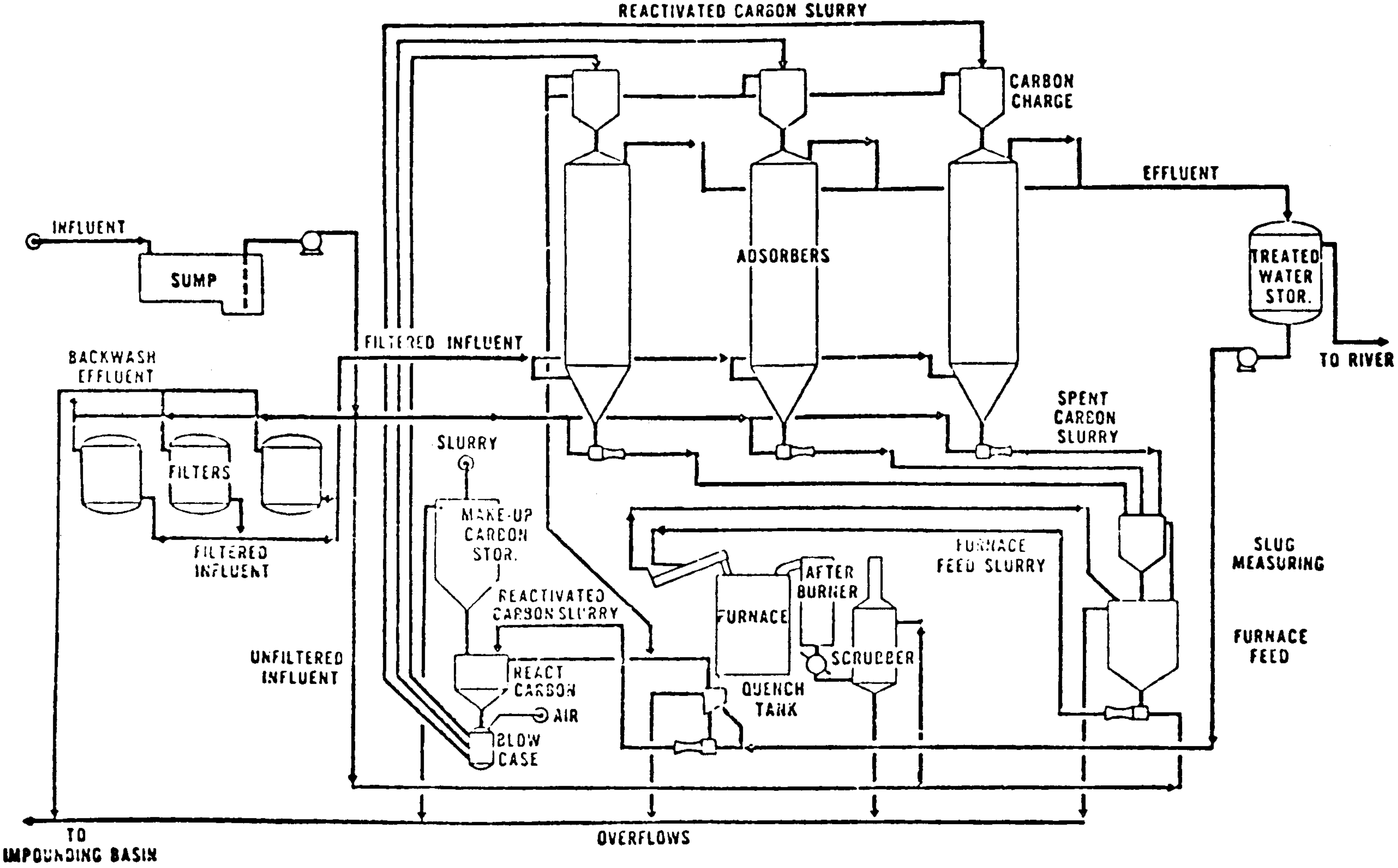


Figure 15-2 - Schematic Diagram of a Carbon Adsorption System Incorporating Thermal Regeneration of the Carbon

o Adsorbers in Series	Large volume systems Countercurrent carbon use Effluent concentrations relatively low Can handle higher than average suspended solids (65-70 ppm) if downflow Capital costs higher than for parallel systems
o Moving Bed	Countercurrent carbon use (most efficient use of carbon) Suspended solids must be low (10 ppm) Best for smaller volume systems Capital and operating costs relatively high Can use such beds in parallel or series
o Upflow-expanded	Countercurrent carbon use (if in series) Can handle high suspended solids (they are allowed to pass through) High flows in bed (15 gpm/ft^2)

In the above systems, flow rates will generally be in the range of 2-10 gpm/ft^2 for downflow operation, 2-7 gpm/ft^2 for upflow operation (without expansion) and around 15 gpm/ft^2 for upflow -- expanded with about 10% bed expansion. Downflow operation may be either by gravity or pressure; the former is clearly less expensive but only applicable if suspended solids in the influent are low.

Finally, there is an additional method of contacting which is significantly different from the types described above. Powdered or granular carbon can be added to a conventional biological wastewater treatment system (e.g., to the aeration basin) and yield significant improvements in pollutant removal). This method is currently being used in at least three industrial waste treatment plants and one waste management facility. Contacting by this method may be followed by biological regeneration of the carbon.

15.1.1.2 REGENERATION

If a large quantity of carbon is used (per unit time) then regeneration is carried out to recover and reactivate the carbon. The most common method is thermal reactivation (which destroys the adsorbed organic solutes), but non-destructive chemical regeneration may be possible in some cases.

- Thermal Reactivation -- Reactivation is carried out in a multiple hearth furnace or a rotary kiln at temperatures from 870°C to 980°C as shown in Figure 15-3. Required carbon residence times in a furnace are of the order of 30 minutes. Steam is usually introduced to assist, the reactivation at the rate of 1 lb steam/lb of carbon. Fuel requirements are about 4000-5000 Btu/lb of carbon. With

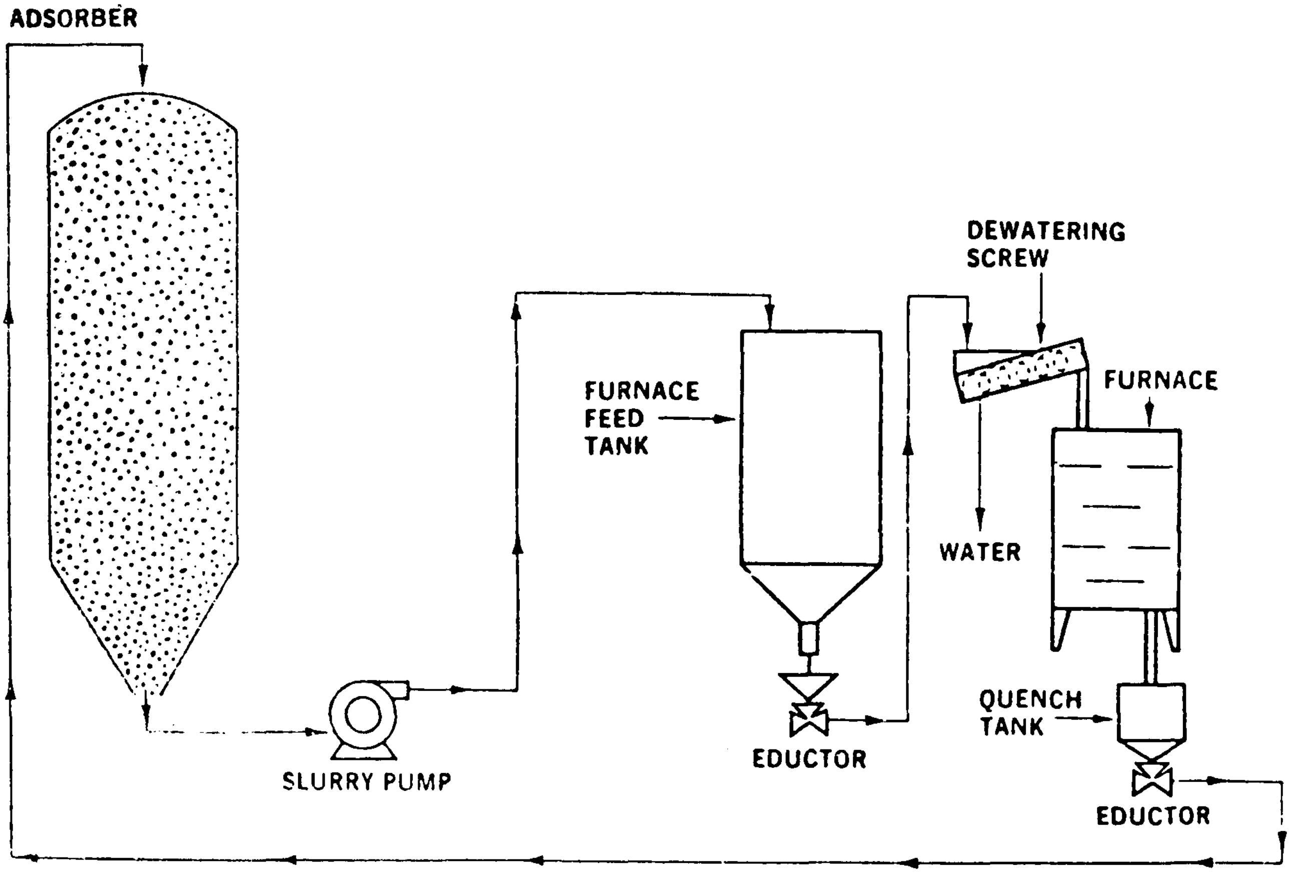


Figure 15-3 - Granular Carbon Thermal Reactivation Cycle proper control, the carbon may be returned to its original activity; carbon losses will be in the range of 4%-9% and must be made up with fresh carbon. Afterburners (operating on the effluent vapors) to ensure complete destruction of organic compounds, followed by a scrubber to remove any particulates. An additional 2000-4000 Btu/lb of carbon may be required for operation of the afterburner.

Sometimes thermal reactivation of granular carbons may not be possible; e.g., (1) when inorganic salts have deposited (or may deposit) on the carbon, though a preliminary acid wash may help avoid this problem; (2) when the carbon contains adsorbates that would cause air pollution problems upon regeneration (NO_x, radioactive materials, etc.); (3) when the adsorbates were explosive (e.g., TNT); or (4) when the loaded carbon was excessively corrosive.

- Alkaline Regeneration for Acid Adsorbates -- In some industrial wastewater, the major organic component is acidic, and adsorption, carried out under acidic conditions, may be followed by removal of the solute (i.e., regeneration) under basic conditions.

- Acid Regeneration for Basic Adsorbates -- Certain basic adsorbates, adsorbed under basic conditions, may be recovered by washing with acid.

- Solvent Regeneration -- If the adsorbate easily dissolves in an organic solvent, it may be washed off the carbon and recovered after separation from solvent, e.g., via distillation.

- Steam Regeneration -- If the adsorbate is volatile enough, recovery may be carried out by passing steam through the carbon bed.

- Biological Regeneration -- Attempts have been made to utilize biological regeneration. The effectiveness of this method will clearly depend on the biodegradability of the adsorbed organics. Complete regeneration is not achieved, and thermal regeneration may be required periodically. The preferred mode of operation is to incorporate the carbon in a biological treatment system (for adsorption and assistance in biodegradation), recover the carbon with some activated sludge in the clarifier, and regenerate the carbon by aeration of the carbon/sludge mixture.

There are no serious environmental impacts from carbon systems using thermal reactivation since the only output streams are (1) a purified liquid (e.g., water), and (2) furnace gases, which have been through an afterburner and a scrubber, and in some cases, a dust filter.

Where the carbon is chemically regenerated, the major output streams consist of the purified liquid, a recovered material, and used carbon, becuase carbon will lose some activity in successive chemical regenerations and will have to be replaced periodically.This waste carbon, which may be burned or buried, would constitute a minor environmental impact upon disposal.

15.1.1.3 INPUT STREAMS

In actual applications, both aqueous and non-aqueous liquids are treated with carbon. The non-aqueous streams include petroleum fractions, syrups, animal and vegetable oils, and pharmaceutical preparations; color removal is the most common application in such cases. Current waste treatment applications are limited to aqueous solutions.

Suspended solids in the influent (which lead to premature pressure drops in a carbon bed) should generally be less than 50 ppm to minimize backwash requirements; a downflow carbon bed can handle much higher levels (up to 2000 ppm), but frequent backwashings would be required. Backwashing more than two or three times a day is not desirable; at 50 ppm suspended solids, one backwash per day will often suffice. In any upflow packed bed excessive suspended solids can lead to clogging. Oil and grease should be less than about 10 ppm. A high level of dissolved inorganic material in the influent may cause problems with thermal carbon reactivation (i.e., scaling and serious loss of activity) unless appropriate preventive steps are taken; such steps might include pH control, softening, or the use of an acid wash on the carbon prior to reactivation.

Technically, there are no limits on the concentration of the solute(s) in the feed stream, but in practice about the highest concentration influent that has been treated on a continulus basis contained about 10,000 ppm TOC. One important factor concerning concentration must be kept in mind; since the slopes of adsorption isotherms are almost always positive, the weight percent pickup (solute on carbon) will be higher for the more concentrated influent leading to more efficient solute removal. Additionally, if the carbon is to be regenerated after use, then higher concentration influents may also involve less frequent regeneration, especially if the slope of the adsorption isotherm is greater than 1. When using carbon adsorption to clean up an industrial waste stream the controlling parameter is the quality of the effluent. Concentration of toxic materials in the feed must be balanced against feed rate, and the activity of the carbon to attain effluent quality.

There are no technical limits on the flow rate of the feed stream. The main consideration is cost. Carbon adsorption will benefit significantly from the economics of scale, especially the thermal reactivation portion. If carbon usage is less than roughly 1,000 lbs/day, it may be cheaper to dispose of the carbon than to reactivate it thermally on site. The real economies of carbon adsorption with on-site thermal reactivation will not be realized until carbon usage is above about 8,000 lbs/day. Using the lower figure 1,000 lbs/day and, as an example, an industrial effluent (e.g., effluent from a biological treatment system) that required the use of 5 lbs of carbon/1,000 gallons of wastewater, the indicated flow is 200,000 gallons/day. This example should not be considered a cut-off point; in practice, industrial waste streams with flows in the range of 10,000 to 40,000 gallons/day have been successfully treated with carbon adsorption systems incorporating thermal reactivation. For lower flows, there are three options: disposal (i.e., incineration or land fill) of the carbon after use, or storage of the used carbon until an adequate amount is available to send to a central carbon reactivation service center, or non-thermal regeneration (e.g., with acid, base or solvent).

A wide variety of organic and inorganic solutes may be efficiently adsorbed on activated carbon. Applications involving organic solutes are more prevalent and will be most attractive when the solutes have a high molecular weight, low water solubility, low polarity, and low degree of ionization. Highly water soluble organics which often contain two or more hydrophylic groups are difficult to remove. For example, the adsorption of glycols from an industrial waste stream was found to be unfeasible in one recent study due to the low capacity of the carbon for the glycols. In another case, the treatment of wastewaters from a polyvinyl chloride production plant was found to be impractical; poor adsorption characteristics were attributed to the presence of long-chain organic soaps contained in the wastes. For some examples low adsorption efficiency, e.g., acetic acid adsorption, the higher process costs may be off-set by solute recovery. Macromolecules, including certain dyes, may be too large to reach a significant fraction of the carbon's internal pores and therefore difficult to remove. Most industrial waste streams contain multiple impurities, some of which are easily adsorbed on carbon, while others are not. In considering the use of an activated carbon system a series of laboratory tests is mandatory. Such tests should include both equilibrium adsorption isotherms and carbon column studies.

Carbon adsorption of inorganic compounds, e.g., the removal of cyanide and chromium from electroplating wastes has been found to be practical. Other sources indicate that a wide variety of other inorganics will adsorb on activated carbon. However, adsorption may be quite variable from chemical to chemical, is like to be highly pH dependent, and thermal or chemical regeneration may not be feasible. In general, strong electrolytes will not be adsorbed on carbon. A summary of some of the inorganic species that may be removed by carbon is given in Table 15-1. Removal of inorganic solutes by carbon will generally involve influent concentration of less than 1,000 ppm preferably less than 500 ppm. Processes other than physical or chemical adsorption may be involved. Plating may occur in some cases (e.g., with ferric salts) and chemical reactions in others (e.g., reduction of ammonia to chloramines followed by adsorption of the chloramines).

15.1.1.4 OUTPUT STREAMS

Air and water emissions from carbon regeneration are relatively innocuous. The treated water is generally suitable for discharge to surface waters but may in some cases, require reaeratin (to raise the level of dissolved oxygen), or other treatments to remove solutes not adsorbed by carbon. Other water streams associated with carbon systems (e.g., backwash, carbon wash and transport waters) are recycled or sent to a settling basin. Emissions will result from thermal reactivation, but when afterburners and scrubbers are used, the emissions are non-polluting. In some installations, particulates must be removed from this air stream (e.g., via a cyclone and baghouse) and this will result in a solid waste. Table 15-2 shows one example of air emissions from a carbon regeneration system.

Table 15-1 Some Inorganic Chemicals Which May be Removed by Carbon Adsorption

HYDROGEN SULFIDE
AMMONIA
CHLORIDE
CYANIDE
ARSENATES
COBALT
MERCURIC CHLORIDE
ZINC
LEAD
SELENIUM

Table 15-2 Emissions From Carbon Regeneration

Pollutant		Baghouse Outlet	Afterburner Outlet
Particulates	Grains/SCF	0.298	0.0455
Nitrogen Oxide	PPM NO_2	-	166
Sulfur Dioxide	PPM SO_2	-	217
Hydrocarbons	PPM C	3900	660
Carbon Monoxide	% vol. dry	0.56	0.20
Odor	Units/SCF	20,000	10

When carbon is not regenerated after use, then the loaded carbon must be discarded. This will arise when carbon usage is small, i.e., regeneration is not economical, the carbon was used to adsorb materials that are difficult to regenerate (e.g., carbon loaded with TNT cannot be thermally reactivated), or the carbon contained adsorbates that would cause serious pollution problems upon regneration (e.g., NO_x, radioactive materials).

15.1.2 APPLICATIONS OF CARBON ADSORPTION

The principal liquid-phase applications of activated carbon include sugar decolorization, municipal water purification (i.e., for water supply systems), purification of fats, oils, foods, beverages and pharmaceuticals, industrial/municipal wastewater treatment, and other miscellaneous liquid-phase applications.

Three specific systems that utilize carbon adsorption are described below:

- Tertiary Treatment Plants

  Carbon adsorption, when applied to well-treated secondary effluent, is capable of reducing COD to less than 10 mg/1 and the BOD to under 2 mg/1. Removal efficiencies may be in the range of 30% to 90% and vary with flow variations and different bed loadings. Carbon loadings in tertiary treatment plants fall within the range of 0.25 to 0.87 lbs of COD removed/lb of carbon, and if the columns are operated downflow, over 90% suspended solids reduction may be achieved.

- Physical-Chemical Treatment (PCT)

  Physical-chemical treatment acts on the effluent of a primary treatment system to remove BOD, COD, suspended solids, and (if present) some color. Effluent concentrations of BOD and COD are somewhat higher than for tertiary treatment systems. Carbon adsorption in conjunction with lime clarification (PCT) has been shown capable of achieving over 90% BOD and suspended solids reduction which is at least equivalent to secondary treatment. Carbon loadings for PCT plants have been measured as high as 1.0 lb COD removed/lb carbon but will typically be in the range of 0.4-0.6 lbs COD/lb carbon and 0.15-0.3 lbs TOC/lb carbon. It is clear that both tertiary and PCT plants have biological activity taking place in the carbon beds which increases the apparent carbon capacity. PCT plants currently being designed or constructed will have similar characteristics to tertiary treatment plants.

- Treatment of Industrial Waste Streams

  Quite frequently, segregated industrial waste streams are treated with activated carbon. The contaminants removed include BOD, TOC, phenol, color, cresol, polyethers, polynitrophenol, TNT, toluene, xylene, wood chemicals, p-nitrophenol, p-chlorobenzene, chlorophenols, resorcinol, xylol, insecticides, refinery wastes, cyanide, acetic acid, and other chemicals, mostly organic. The flows being treated are generally small in comparison with tertiary or PCT systems. Several systems treat less than 20,000 gpd, the lowest being 3,000 gpd. Some installations reactivate their carbon chemically and the adsorbate is recovered. Recoverable adsorbates are known to include phenol, acetic acid, p-nitrophenol, p-chlorobenzene, p-cresol, and ethylene diamine. Other adsorbates are recovered, but their identity has not been made known. Longer contact times are usually employed in such systems, e.g., 50-200 minutes, and in one case 540 minutes for a system that involves no pretreatment.

Carbon loadings approach 1 lb COD removal/lb carbon in installations where the adsorbates are easily adsorbed, biodegradable, and present in relatively high concentrations, e.g., a wood chemical plant that will use carbon to treat a stream containing about 700 ppm COD, and 200 ppm TOC; reductions are expected to be about 80% for both of these parameters. In other cases where influent concentrations are lower, and where the adsorbates are not readily adsorbed, much lower loadings will result. For example, it was determined that brine wastewaters containing 150-750 ppm phenol and 1500-1800 ppm acetic acid could be reduced to about 1 ppm phenol and 100-200 ppm acetic acid with phenol loadings in the range of 0.09-0.16 lbs/lb and acetic acid loadings in the range of 0.04-0.06 lb/lb. Another example related to the reduction of COD in refinery wastewaters from an average influent of 233 ppm to an average effluent of 48 ppm; the indicated loading in this case is 0.18 lb COD/lb carbon.

Loadings for cyanide removal from electroplating wastes have been found to be on the order of 0.01 lb CN/lb carbon for influent concentrations around 100 ppm. Loadings for removal of hexavalent chromium from electroplating wastes have been shown to be as high as 0.07 lb Cr/lb carbon at 100 ppm and 0.14 lb Cr/lb carbon at 1000 ppm.

15.2 RESIN ADSORPTION

Adsorption of organic chemicals on synthetic resins was first reported around 1945, but apparently little effort was made to commercialize the process until the 1960's. Some of the early work was done with ion exchange resins and probably was related, in part, to the growing awareness of the nature and extent of fouling of ion exchange resins by organic chemicals.

By the mid-1960's, enough information was available to generate serious interest in resin adsorbents for waste treatment. Some of the earliest government-sponsored studies were carried out at the University of California starting in 1966 with funds from the Federal Water Pollution Control Administration. One study looked at the reduction of COD, color, and odor in secondary municipal wastewater and the other looked at phenol adsorption.

In the former, color and odor removal were found to be very good, but the COD removal efficiencies were not outstanding. The most promising system investigated consisted of a resin column followed by a carbon column.

At about the same time, other investigators were also claiming good removal of both refractory organics and dissolved mineral solids from secondary municipal effluents with a weak-base anion exchange resin.

A large number of the more recent studies on resin applications in wastewater treatment have focused on color removal with several of these looking at general organic removal as well. Also of some interest has been the adsorption of phenols. Other investigations have looked at detergent adsorption, munitions wastewater treatment, e.g., TNT removal, fatty acids, proteins and viruses, dehydroabietic acid, municipal effluents, and metals removal.

Attention has been focused recently on the use of synthetic resins in connection with water quality analyses. Some of the results of these studies may be helpful in estimating the degree of adsorption that could be expected for organic chemicals present in low concentrations in wastewaters since the chemicals being analyzed were generally present in ppm concentrations. There also is interest in vapor phase adsorption with resin systems.

Resin adsorption is a process which may be used to extract, and, if desired recover dissolved organic solutes from acqueous wastes. Ion exchange, a resin process for the separation of inorganic ions, is covered in another section of this report. The nature of the resin adsorption process is similar to carbon adsorption and the two processes may be competitive in several applications. The most significant difference between carbon and resin adsorption is that resins are always chemically regenerated (by use of caustic or organic solvents) while carbons, because the adsorption forces are stronger, must usually be thermally regenerated thus eliminating the possibility of material recovery. On the other hand, resins generally have a lower adsorption capacity than carbons.

Resin adsorption should be given serious consideration:

- For the treatment of highly colored wastes; BOD and COD may be high.
- When material recovery is practical.
- Where selective adsorption is desired.
- Where low leakage rates are required.
- Where carbon regeneration is not practical.
- Where the waste stream contains high levels of dissolved inorganic solids.

Resin adsorption is not likely to be competitive with carbon for the treatment of high volume waste streams containing moderate to high concentrations of mixed wastes with no recovery value. A combination of resin and carbon adsorption may be attractive, however.

Relatively little information is available on the few systems that are currently in operation and thus there are areas of uncertainty concerning practicability, start-up problems, realistic operating costs, etc.

Energy requirements for resin adsorption systems are minor except where solvent and solute recovery via distillation are involved. In systems where distillation is not required, the energy requirements consist only of electricity for pumps, stirrers and controls and may only account for about 5% of the direct operating costs.

In the worst case, where both solvent and solute recovery are via distillation, up to three distillation columns may be needed. If, additionally, the influent solute concentration is high, frequent bed regeneration may be required and large quantities of steam will be used for the distillation columns. Electricity requirements will also be higher. In such a case, energy requirements may account for over half of the direct operating costs.

The only major environmental impacts resulting from the use of resin adsorption systems are related to the disposal of the used regenerant solution or the extracted solutes when they are not recycled. For example, when highly colored wastewaters are treated, the used regenerant solution (containing 2-4% caustic plus the eluted wastes) is not recycled and must be disposed of, usually by evaporation and incineration. A second example would be the removal of pesticides from water, with regeneration being effected by an organic solvent. In this case, the solvent would be recovered, probably by distillation, resulting in a concentrated waste (still bottoms) to be disposed of, probably by incineration. In both of these examples where incineration is used for the eventual destruction of the wastes, the environmental impacts would be on air quality (from incinerator emissions), energy use (for the incinerator fuel), and land use (from the disposal of unburned residues).

Only minor environmental impacts might be associated with the rinse waters discharged. In most cases, these effluents can be adequately treated by conventional means or safely discharged to surface waters.

Resin adsorption systems are relatively compact and thus require little space. The systems do not have any known health or safety problems associated with their operation.

Adsorption on synthetic resins is being considered here as a process for the removal of organic chemicals from liquid waste streams.

While the earliest investigations of adsorption on synthetic resins date back to the mid-1940's, the technique has found its way into industrial use only in the last decade. The use of these resins is increasing at present as more becomes known about their capabilities and as a wider variety of resins are manufactured for separation purposes.

In many respects, adsorption on resins may be considered similar to adsorption on carbon; and thus more researchers are investigating both types of adsorbents when conducting treatability studies on industrial waste streams. A combination of both carbon and resin adsorption has been proposed as being particularly attractive in some situations; thus this alternative should be kept in mind.

15.2.1 OPERATION

Waste treatment by resin adsorption involves two basic steps: contacting the liquid waste stream with the resins and allowing the resins to absorb the solutes from the solution; and subsequently regenerating the resins by removing the adsorbed chemicals, often effected by simply washing with the proper solvent.

The chemical nature of the various commercially available resins can be quite different; perhaps the most important variable in this respect is the degree of their hydrophilicity. The adsorption of a non-polar molecule on to a hydrophobic resin (e.g., a styrene-divinyl benzene based resin) results primarily from the effect of Van der Waal's forces. In other cases, other types of interactions such as dipole-dipole interaction and hydrogen bonding are also important. In a few cases, an ion-exchange mechanism may be involved; this is thought to be true, for example, in the adsorption of alkylbenzene sulfonates from aqueous solution on to weakly basic resins; e.g., a phenol-formaldehyde-amine based resin.

While it is not possible to predict accurately the degree of adsorption that will take place in any case, it is a useful general concept that hydrophobic or nonpolar molecules (or portions of molecules) are attracted to hydrophylic surfaces.

An important aspect of resin adsorption is that the strength of the attractive forces between the solute molecules and the resin is usually weaker than that associated with adsorption on carbon. This allows for easier adsorbent regeneration along with improved potential for recovery of the adsorbed substances; with carbon, thermal regeneration is usually required and this does not allow solute recovery.

Resin adsorbents are used in much the same way as granular carbon. Commonly, a typical system for treating low volume waste streams will consist of two fixed beds of resin. One bed will be on-stream for adsorption while the second is being regenerated. In cases where the adsorption time is very much longer than regeneration time (as might be when solute concentrations are very low), one resin bed plus a hold-up storage tank could suffice.

The adsorption bed is usually fed downflow at flow rates in the range of 0.25 to 2 gpm per cubic foot of resin; this is equivalent to 2-16 bed volumes, hr., and thus contact times are in the range of 3-30 minutes. Linear flow rates are in the range of 1-10 gpm ft/^{2}. Adsorption is stopped when the bed is fully loaded and/or the concentration in the effluent rises above a certain level.

Regeneration of the resin bed is performed in situ with basic, acidic, and salt solutions or regenerable non-aqueous solvents being most commonly used. Basic solutions may be used for the removal of weakly acidic solutes and acidic solutions for the removal of weakly basic solutes; hot water or steam could be used for volatile solutes; methanol and acetone are often used for the removal of non-ionic organic solutes. A prerinse and/or a postrinse with water will be required in some cases. As a rule, about three bed volumes of regenerant will be required for resin regeneration; as little as one and a half bed volumes may suffice in certain applications.

Solvent regeneration will be required unless the solute-laden solvent can be used as a feed stream in some industrial process at the plant, or the cost of the solvent is low enough so that it may be disposed of after a single use. Solvent recovery, usually by distillation, is thus most common when organic solvents are used. Distillation will, of course, allow solute recovery for reuse if such is desired.

Equipment needed for resin adsorption systems is relatively simple. The adsorption system will generally consist of two or more steel tanks (stainless or rubber-lined) with associated piping, pumps, and (perhaps) influent hold-up tank. Regeneration takes place in the same tanks, and thus the extra equipment needs for regeneration will consist only of such items as solvent storage tanks, associated solvent piping and pumps, and solvent (and perhaps solute) recovery equipment, e.g., a still. Up to three stills may be required in some systems.

Materials needed include a regenerant solution (e.g., aqueous caustic solution or organic solvent), and resin. In one full-scale installation for the removal of organic dye wastes from water, two different resins are employed. In this case involving the waste stream is first contacted with a normal polymeric adsorbent and then with an anion exchange resin.

Surface areas of resin adsorbents are generally in the range of 100-700 m^2/g; this is below the typical range for activated carbons (800-1200 m^2/g) and, in general, indicates lower adsorptive capacities, although the chemical nature and pore structure of the resin may be more important factors. This has been demonstrated in one application relating to color removal.

Tests should be run on several resins when evaluating a new application. Important properties are the degree of hydrophilicity and polarity, particle shape (granular versus spherical), size, porosity, and surface area.

It is frequently possible to "tailor" a resin for specific applications because much greater control over the chemical and surface nature can be achieved in resin production than in activated carbon manufacturing. The cost of developing a totally new resin would be prohibitive for most applications, but minor modifications of currently available resins are often feasible.

15.2.1.1 INPUT STREAM

The feed stream into a resin adsorption system must be a single liquid phase; in most cases this will be an aqueous solution, but there is no basic reason that an organic solution could not be treated so long as the resin is not chemically or physically harmed by the solution. Other limitations include the following:

- Suspended Solids should be no higher than 50 ppm and may have to be kept below 10 ppm in some cases to prevent clogging of the resin bed.

- pH may vary widely; some resins have been able to operate as low as pH 1-2 and as high as pH 11-12. In many cases, adsorption will be pH dependent, and will thus require pH control.

- Temperature may also vary significantly. Resins have been used in applications where the influent temperature was as high as 80°C. Adsorption will, however, be favored by lower temperatures. Conversely, regeneration will be aided by higher temperatures.

- High levels of Total Dissolved Solids (particularly inorganic salts) do not interfere with the action of resin adsorbents on organic solutes. There are clear indications that some organic chemicals are more easily removed from solutions with high concentrations of dissolved salts than from salt-free solutions. In some cases of high salt content, the adsorbent may be to be pre-rinsed before regeneration.

- Concentration of Organic Solute(s) in the feed stream should probably be at least a factor of ten less than the maximum amount that can be adsorbed in a resin bed divided by three bed volumes*; this will allow a reasonably long cycle time.

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*A "bed-volume" is simply the volume of liquid required to fill a resin bed (i.e., container filled with resin beads).

Higher influent concentrations may be treated if more frequent resin regeneration is acceptable. In the case of phenol adsorption, the upper limit on concentration is probably about 8% phenol by weight. There is no lower limit in concentration for resin adsorption, though it should be remembered that, as with carbon adsorption, adsorption is generally more efficient** at higher concentrations.

15.2.1.2 OUTPUT STREAMS

Output streams from a resin adsorption system will vary from system to system. All systems produce a treated effluent from which a significant portion of the organic solute(s) has been removed. If effluent guidelines or material recovery economics require a high degree of removal, this can usually be achieved by the proper adjustment of pH, flow, and contact time. In phenol removal (examples given in Section IV-C), the influent phenol concentrations of 1-5% are lowered to less than 10 ppm in the treated effluent. When a complex mixture of solutes is present in the influent, removal efficiencies may not be uniformly high.

Prerinse and/or postrinse of the resin bed (with water) is often required and will result in an aqueous effluent containing organic and/or inorganic solutes depending on the system. Treatment of these effluents will generally be required either for pollutant removal (before discharge) or for solvent recovery.

Each regeneration of a bed will result in about three bed volumes of regenerant effluent containing the solutes that had been washed off the resins. This effluent may:

- Be further treated for both solvent and solute recovery in which case no significant effluents result.
- Be treated only for solvent recovery, e.g., by distillation, in which case a concentrated effluent would result from the still bottoms, or
- Be directly disposed of following any necessary treatment; in the case of caustic regeneration (typically 2-4% NaOH), evaporation followed by incineration may be used.

Resin lifetimes may vary considerably depending on the nature of the feed and regenerant streams. Regeneration with caustic is estimated to cause a loss of 0.1 to 1% of the resin per cycle; replacement of resins at such installations may be necessary every two to five years. Regeneration with

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**i.e., the amount of solute adsorbed per unit of adsorbent will be higher.

hot water, steam, or organic solvent should not affect the resins, and in this case lifetimes will be limited by slow fouling or oxidation resulting in a loss of capacity; actual experience indicates that lifetimes of more than five years are obtainable.

15.2.2 APPLICATIONS OF RESIN ADSORPTION

Resin adsorption (excluding ion exchange with inorganic species) is expected to be applicable for the removal of (1) organic solutes from aqueous wastewaters, and (2) organics or inorganic solutes from non-aqueous liquid wastes, but the latter cannot be expected in the near term because so little has been done in these areas.

When aqueous waste streams are involved, resin adsorption may be considered particularly attractive in the following situations.

Treatment of Highly Colored Wastes

Resins have proven to be very efficient for color removal (primarily color associated with organic molecules) and to be capable of removing a significant fraction of COD and BOD at the same time.

For Material Recovery

When one or more solutes of commercial value are present in high enough concentrations to merit consideration of material recovery, resins should be considered since it is relatively easy to recover certain solutes following resin adsorption.

Where Selective Adsorption (and Perhaps Recovery) is Wanted

Resins may be designed to be selective. For example, special resins may be made that will a) selectively remove aromatics from linear hydrocarbons (especially hydrophylic ones), b) selectively remove amines from other hydrocarbons, c) selectively remove weak organic acids from other hydrocarbons, and d) selectively remove macromolecules (e.g., dye bodies) from wastewaters containing other material.

Where Low Leakage Rates are Required

In two studies (the removal from water of low levels of pesticides, and chemical carcinogens) resins were chosen, in part, because of the low leakage rate. This apparently results from rapid adsorption kinetics.

Where Carbon Regeneration is Not Practical

If an adsorption process on a moderate-to-high volume waste stream is desirable, and carbon could not be regenerated in such an application, then resin adsorption may be more economical; e.g., with munition plant wastewaters which contain explosives thermal regeneration of carbon is not safe, and chemical regeneration of carbon is not practical; thus carbon must be used on a throwaway basis.

Where the Waste Stream Contains High Levels of Inorganic Dissolved Solids

High levels of inorganic dissolved solids can pose problems for carbon adsorption systems. They may deposit on the carbon during thermal regeneration, and cause severe scaling, resulting in appreciable loss of activity. This is not a problem with resins which are not thermally regenerated, though they may require a prerinse with water before solvent regeneration.

Resin adsorption systems would not normally be economically competitive with carbon systems for high volume waste streams containing moderate to high concentrations of mixed wastes with no recovery value. Such streams would include municipal and combined industrial effluents. A combination of resin and carbon adsorption may, however, be attractive.

Future developments may improve the attractiveness of resin adsorption in two ways. First, new resins may become available that will show improved performance (higher capacity and better selectivity). Second, increased use of such systems, along with increased competition for the sale of resins, may result in lower resin prices.

Most of these applications take advantage of some of the best features of resin adsorbents which include (1) the potential for chemical selectivity; (2) rapid adsorption kinetics; and (3) efficient chemical regeneration.

The principal disadvantages of the process are associated with the following:

- Generally lower adsorption capacity than activated carbon (surface areas are smaller).
- Susceptibility to certain poisons such as oxidants or organic foulants that are not efficiently removed by the regenerant;
- The necessity of keeping suspended solids in the influent low enough to prevent clogging in the bed.
- The relatively high cost of the resins versus cost for activated carbon.

The cost comparison with carbon will be unfavorable to synthetic resins when both can be chemically regenerated. In situations where carbon must be thermally regenerated, the added costs of such regeneration may offset the lower cost of the adsorbent because of high losses of carbon, typically 4-9% per regeneration.

16. REVERSE OSMOSIS

The earliest RO units were constructed in the late 1950's at UCLA, and at Aerojet General utilizing a plate and frame construction similar to conventional filter presses. Membrane supports were porous stainless steel or bronze. Such a design was suitable for early work but did not allow good enough control of the feed flow to optimize performance. It was also cumbersome and heavy and there were difficulties with maintaining good seals.

About 1961 the tubular design made its appearance, consisting of perforated stainless steel tubes with "liners" of the reverse osmosis membrane having the active or "skinned" side of the membrane facing inwards. Feed was pumped at high pressure through tubes, allowing good control of the flow dynamics. Several tubes could be arranged in a bundle, similar to a tube-and-shell condenser, with the permeate being collected from the shell side. This system performed well but was expensive to fabricate.

Subsequently, Havens Industries introduced a similar but refined system utilizing porous fiberglass tubular supports. While some sealing problems remained, leaks could develop because of the slight solubility of the glass fibers in the pure water permeate; the system was a significant advance and also permitted the use of unfiltered feed water without danger of plugging. In fact, the tubes could be mechanically cleaned if necessary. A typical tubular module is shown in Figure 16-1.

The next design development was that of the spiral-wound cell. This design uses envelopes of flat-sheet cellulose acetate or other membrane material wound in a spiral to produce a continuous thin channel through which the feed flows at high laminar shear rates. Spacers of netting maintain optimum distances within and without the envelope and the permeate produced is collected in a perforated mantel to which the envelope is fastened at one end on which it is wound. This configuration is inexpensive, produces high water fluxes, and uses the membrane area efficiently. The membrane and support are in compression and leaks are not a major problem. Although filtration of the feed is usually recommended, plugging of the channels is not a major problem.

In the last few years a reverse osmosis system using a multitude of hollow nylon or polyamide fibers have shown considerable utility on commercial waste streams and for water purification. DuPont and Dow pioneered this activity. As illustrated in Figure 16-2, a bundle of fibers, with the "active" side of the nylon membranes on the exterior of the fibers, is encased in a module. (A typical fiber may have an external diameter of 50-80u and an internal diameter of 20-40u). Feed water is passed at high velocities between the fibers, and fresh product water permeates into the interior lumens of the fibers from which it is collected. This configuration results in rather low utilization of membrane area, but, since the cost per unit of the membranes is considerably lower than the cost of the cullulose acetate membranes, the ultimate cost of water recovery is competitive for low-salinity feed streams. This configuration is more susceptible to fouling or plugging

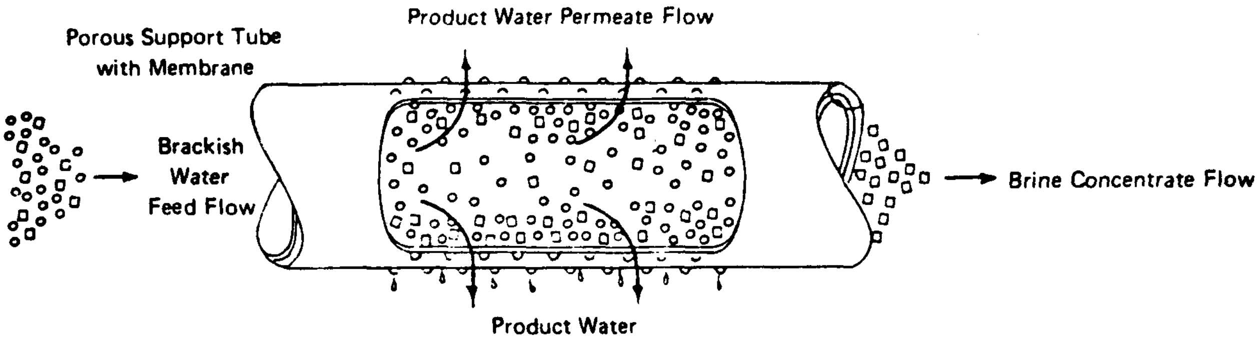


Figure 16-1 - Tubular Reverse Osmosis Module

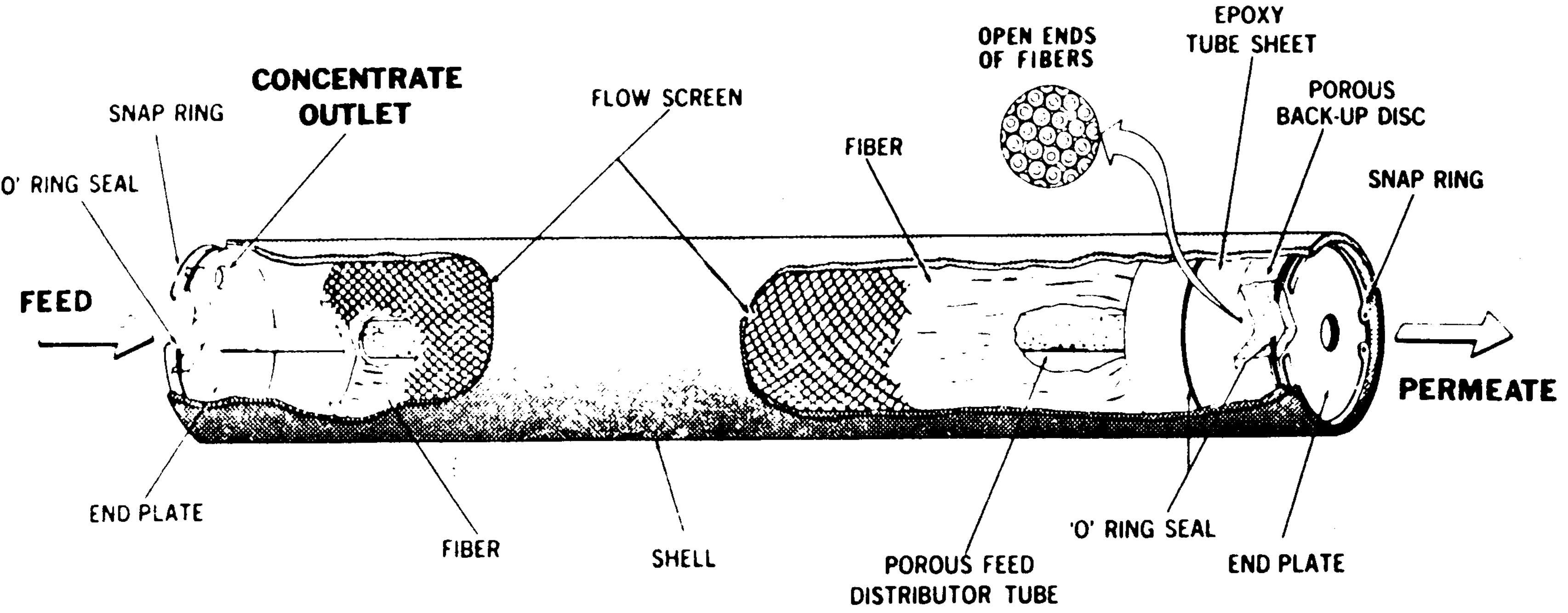


Figure 16-2 - Hollow Fiber Module (DuPont Permasep) by suspended solids than the spiral-wound configuration and requires very thorough preprocessing of the feed stream. One additional design worthy of mention is the "sand-log" tubular system marketed over the last several years by Westinghouse but just recently acquired from them by Union Carbide. This system, shown in Figure 16-3 is a special form of tubular reverse osmosis in which a resin-bonded porous sand cylinder with a hollow core is encased in a steel pressure jacket. This cylinder serves as the porous support for "active" membrane material which is deposited on the walls of the core. One advantage of the design may be the incompressability of the sand core, which could minimize the degradation of performance.

Whichever system is eventually chosen, individual modules are then assembled, as shown in Figure 16-4 to achieve the desired capacity and degree of separation.

Since 1960, reverse osmosis has developed into a technology that is used widely in chemical processing and in the production of fresh water. (In fact, much of the early research and development work was supported by the U.S. Department of the Interior Office of Saline Water). At the beginning of 1975 nearly 300 large (25,000 gpd) plants were reported in operation around the world producing a total of 45 million gallons per day of purified water for municipal or commercial use from the sea or brackish sources.

The number of plants in use to treat industrial process streams is more difficult to ascertain but, if not comparable, is at least very significant. Specific applications include the preparation of pure water and process feed water, preparation of rinsewater for use in semiconductor and electronic manufacturing (a major application), purification of water for hospital use, reclamation of electroplating chemicals and water, and recovery of sugar wastes by candy manufacturers.

Present full-scale waste treatment is operational in the electroplating and related industries to process rinse waters that not only have metal salt concentrations which are not legally "dischargeable," but which represent significant expense because of lost chemicals. Reverse osmosis may successfully avoid the dumping problem and provides clean water and concentrated chemicals solutions for reuse. (In fact in such cases, the economic benefits of reuse may become sufficiently large that the user may no longer perceive the process as a form of waste treatment). A limited number of other full-scale uses are found in the paper industry (sulfite streams), in food processing, and in other processing plants. RO is beginning to appear in designs for cooling tower systems to prevent salt build-up in the system and to concentrate that salt for eventual disposal.

In general, reverse osmosis may be considered whenever one must concentrate a waste stream that contains dissolved salts or organic materials to permit their reuse or to reduce the volume of the waste stream prior to evaporation or other disposal.

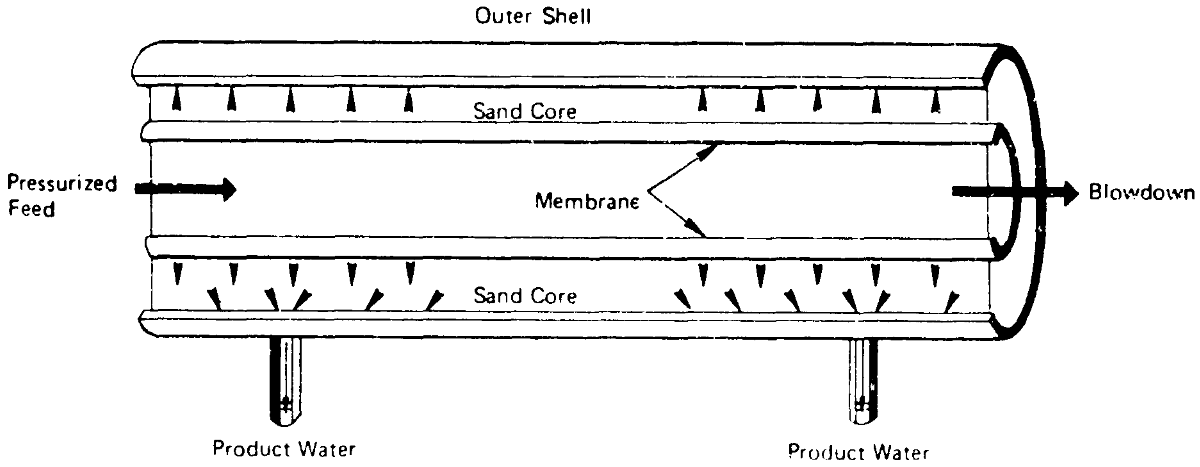


Figure 16-3 - Sand-Core Type of Reverse Osmosis Module

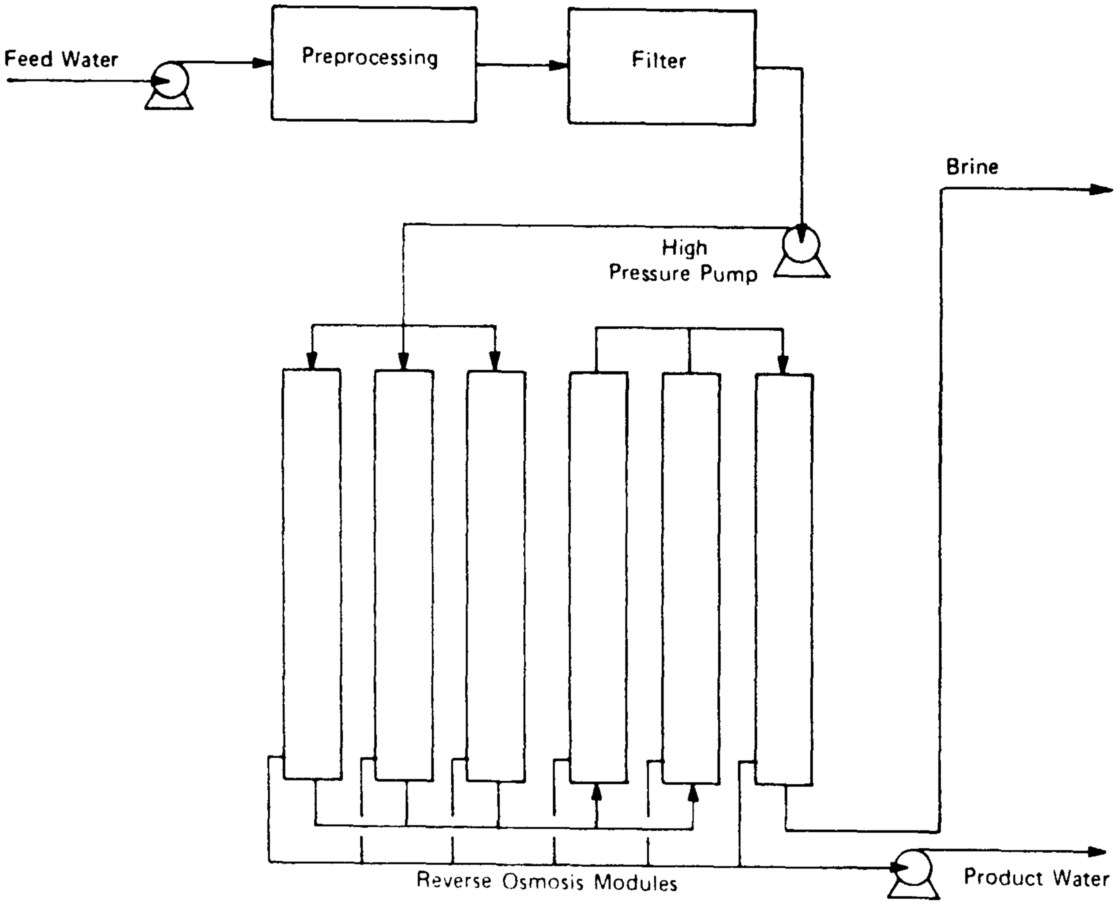


Figure 16-4 - Reverse Osmosis Plant Flowsheet

16.1 OPERATION

Reverse osmosis (RO) employs a semipermeable barrier which will pass only certain components of a solution, and a driving force to separate these components at a useful rate. The membrane is permeable to the solvent but impermeable to most dissolved species, both organic and inorganic. The driving force for its separation is an applied pressure gradient.

Conventional "forward" osmosis transfers solvent through a semipermeable separator from more dilute to more concentrated solution, driven by the difference in solvent vapor pressure on either side of the separator. The osmotic pressure Π, or magnitude of this driving force, is given by the equation:

$$\Pi = \frac{RT}{v} \ln \frac{P_1}{P_2}$$

in which R is the gas constant, T is the absolute temperature, v is the molar volume of the solvent, and P_1 and P_2 are the solvent vapor pressure in the solutions on either side of the membrane. (Note that is independent of the specific membrane material).

If a pressure equal to Π is applied across the membrane counter to normal solvent flow, no transfer will take place. If a pressure greater than Π is applied, solvent will be transferred from the more concentrated to more dilute solution, resulting in both a concentration of solute and purification of solvent. This is reverse osmosis.

The dilute solvent flux, J (frequently expressed in gallons/ft^2-day), is given by:

$$J = K(\Delta P - \Pi)$$

in which ΔP is applied pressure and K is a constant for the membrane-solvent system. As can be seen from this equation, the product-water flux rate decreases with increasing salinity (increasing osmotic pressure) of the feed solution. Thus, the difficulties (and cost) of recovering clean water also increase with increasing salinity of the feed stream. (This principle must be considered when the economics of salt removal from waste streams is calculated; at some point the stream will become sufficiently concentrated to make it more feasible to evaporate the residual brine than to continue reverse osmosis).

The design of the modules containing the reverse osmosis 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 ($\Delta P-\Pi$)decreases with increasing concentration, polarization can have a very deleterious effect on water flux.

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.

The chemical nature of the membrane material is important, because it affects the transport of solvent and rejection of solute. There have been two major hypotheses regarding the functioning of an RO membrane - the pore theory and the diffusion theory. The pore theory suggests that the membrane surface contains pores only a few angstrom units in diameter and molecules are selected for passage on the basis of size. In addition, according to the pore theory a layer of pure water is formed at the membrane surface by the repulsion of ionic species from the surface by their "reflected charge" and this layer of pure water is drawn off through the pores.

The diffusion theory proposes that the surface of the membrane is in fact a thin homogeneous film and that membrane specificity or rejection is the result of widely diffusing permeation rates of solvent and solutes across this layer. The weight of the support has swung to the side of the diffusion theory, on the basis of its ability to correctly predict the effect of changes in pressure and concentration or rejection rates.

Reverse osmosis also differs from "conventional" filtrations in that the flow of the feed is not normal to the membrane surface but tangential to it in an effort to keep it clean of debris and to reduce surface concentration effects. RO membranes do not become "plugged" but they may become fouled by film-forming organics or by insoluble salts and scaling. Much of the prefiltering of the feed water is in fact aimed at preventing the narrow flow channels of the assembled device from becoming plugged.

Cellulose acetate membranes remain the most popular. Ion exchange membranes also produce specific selectivity but are rarely used; polyamide materials, nylons, and polyarylsulfones have recently appeared. Because of the need for high solvent flux rates while withstanding high pressure differentials, most membranes in use today are of the "skinned" type in which membrane casting technique is controlled to produce a very thin homogeneous film or skin upon a more open porous substrate of the same material. (After extended use at high pressures, these may "compact" and lose a significant amount of their permeability).

Total dissolved solids (TDS) in the feedwater may be as high as that of sea water (34,000 ppm) and product water TDS as low as 5 ppm.

Cellulose acetate membranes have been the most frequently used in the past, but polysulfones and polyamides (nylon) are increasingly popular for use at high pH values. The hollow fiber type of module has gained rapid acceptance and in terms of total operating units may be the most prevalent.

Because of the susceptibility of the membranes to chemical attack and fouling, and the susceptibility of the flow system to plugging and erosion, it is common to preprocess feed water as necessary to remove oxidizing materials. These include iron and manganese salts, to filter out particulates and, to remove oils, greases, and other film forms. If there is likelihood of fouling by living organisms, chlorination or UV treatment may be employed as well to insure that maximum flux rates may be obtained.

Power requirements for reverse osmosis are generally about 10 kWh/1000 gallons of product water. Energy savings have been sought by reducing the concentrated brine to atmostpheric pressure through a hydraulic turbine but this is generally not practical. In specific instances the feed solution may be at an elevated temperature. If the RO system can be designed by choice of membrane material to operate at this elevated temperature and to return a hot permeate stream to the plant for re-use, there may be some energy savings overall.

There is no air or solids pollution from a reverse osmosis plant and the only liquid pollution hazard is the concentrated brine or solute solution, which may be recycled or else disposed of in an acceptable manner.

17. FLOTATION

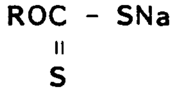
Flotation is a process of ore concentration developed and used principally by the mineral industry. Valuable ore constituents are separated as a "concentrate" from the waste products called "tailings."

The process is a physical-chemical method (carried out in a wet environment) for concentrating finely ground ores. A necessary and important step to prepare the ore for flotation is crushing and grinding, which is designed for each particular application to separate the individual mineral particles that make up the ore by reducing them to their natural grain size. Also, in some cases, the removal of "slimes" is necessary before flotation.

The flotation process itself involves chemical treatment of an ore pulp or slurry to create conditions favorable for the attachment of selected mineral particles to air bubbles formed therein. The air bubbles carry the selected minerals to the surface of the pulp and form a stabilized froth which is skimmed off while the other waste minerals remain in the pulp.

The process of contacting the ground ore pulp with reagents is called "conditioning" and is usually done with reagents being added in an agitator for mixing with pulp just before flotation. However, at times, benefits are obtained by adding reagents in the grinding stage. A sketch of a typical flotation flowsheet is shown in Figure 17-1.

The ability of an air bubble to pick up a heavy mineral sulfide particle is illustrated in Figure 17-2. The mechanism of collection and attachment is generally well understood , for example, from Figure 17-2, xanthate is used as a collector for galena. Xanthate, the collector molecule, has a hydrocarbon chain with a sulfur attached as follows:



$$\mathrm{RO}\underset{\underset{\displaystyle \mathrm{S}}{\|}}{\mathrm{C}} - \mathrm{SNa} \qquad \mathrm{R} = \text{hydrocarbon group}$$

In collection, the sodium ion goes into solution, leaving the free sulfur atom to attach to and fit into the Pb-S atomic structure of the galena surface, leaving the hydrocarbon chain sticking out. This makes the galena surface hydrophobic and pushes the galena grains into the air bubble which lifts them to the surface. The collection and flotation of other minerals with various types of reagents in general functions in the same way.

The selectivity of the process can be very good. For example, it is possible to separate KCl from NaCl, two very similar salt type minerals by using the right reagent and conditions.

The hazardous waste forms that can possibly be handled by conventional flotation are slurries, sludges, or any solid mixture in an aqueous or possibly non-aqueous solution. The best application for the process as indicated above is for separating, say, a hazardous solid from one that is not. Thus, any

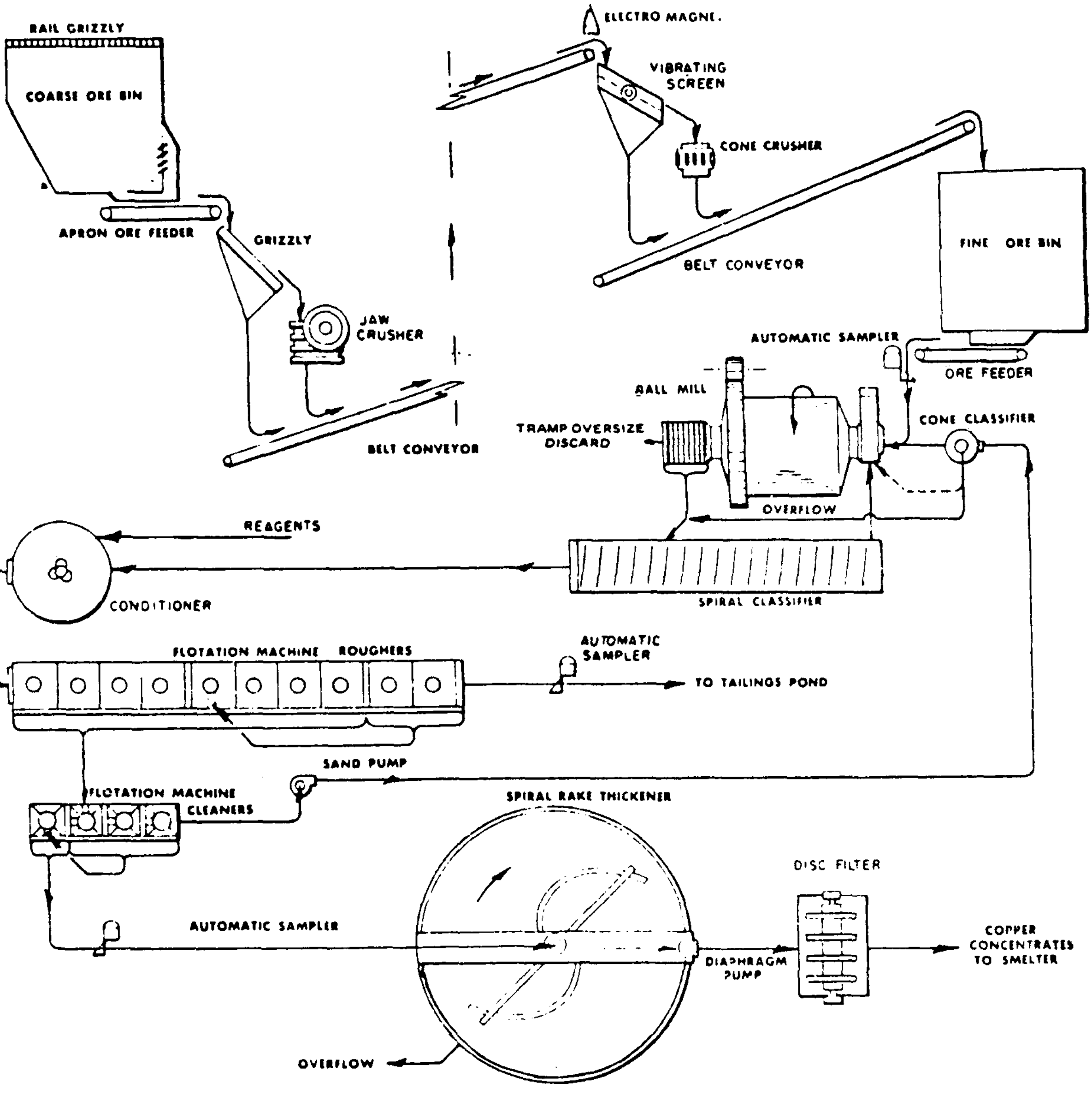
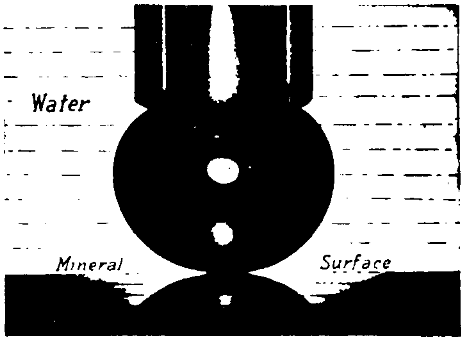
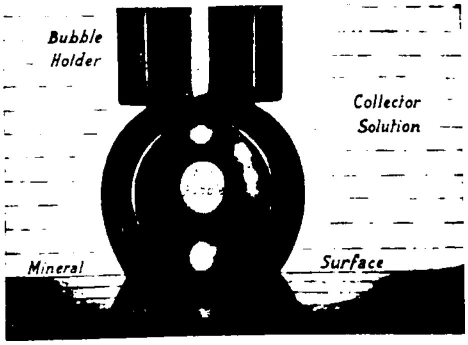


Figure 17-1 - Typical Ore Flotation Flowsheet



A - An Air Bubble does not stick to a clean, polished Galena surface



B - An Air Bubble adhers to Galena immersed in a solution of Ethyl Xanthate

Figure 17-2 The Adhesion of Mineral Particles to an Air Bubble (Galena Particles-PbS) single solid component type in a slurry could be floated. This component would be recovered as a froth concentrate which would require further processing by thickening and/or filtration for recovery as a moist solid filter cake. This could then be dried or processed in any way necessary for reuse, sale, storage or safe disposal.

The ion and precipitate flotation variations of the flotation process discussed previously could be used for the removal of some hazardous materials in solution. Specific examples of ions which might be removed by flotation are: heavy metal ions (copper, nickel, cadmium) and cyanides. We believe many other heavy metal ions might also be amenable to removal by these processes, as well as other inorganics such as carbonyls and fluorides.

There is another aspect of the flotation process that must be considered. Many different reagents can be and are used. Though the process is operated with just enough reagent to make the required separation, some reagents can still appear in the waste tailings discarded from the process.

Most of the added reagents are more or less consumed during the flotation process due to adsorption on the mineral surfaces or complexing with the appropriate ions in solution. Trace amounts of organic reagents, such as hydrocarbons, alcohols, and esters are left in the tailings water, evaporate, decompose, or biodegrade. However, some toxic reagents, if used in flotation carelessly, can constitute a hazard, and great care must be exercised in their use and control.

17.1 OPERATION

The flotation process as previously stated is particularly useful for removing selected portions from mixtures of solid materials such as ores. Ores are aggregates of minerals in which any number of distinct minerals can be present. By grinding to the appropriate size, the contained minerals can be physically separated from each other and then be selectively removed from the physical mixture by any number of processes such as sedimentation, tabling, and flotation. In flotation, ground ore or mineral mixtures are mixed with water to form a slurry or pulp for flotation treatment. In principle, however, the flotation method can be used with liquid media other than water and can be used for emulsions, sludges, slurries or any physical mixtures which can be converted into such suspensions in a liquid medium. Flotation is not restricted to any particular group of materials, but as stated is most prevalently used for ore and mineral separation with the useful products to be separated out generally present in amounts less than ten percent.

17.1.1 REAGENTS

The operation of the flotation process is based on the use of chemical reagents that selectively will attach to and alter the surface characteristics of the mineral particles to be floated. Such reagents are called "collectors." A whole spectrum of reagents has to be considered to meet the various requirements of the flotation process. Common flotation reagents are grouped as follows:

- Modifiers -- Basically used to control the pH of the separation which is crucial in many cases. They are acids, lime, soda ash, and caustic soda

- Activators -- Used to "activate" or prepare the mineral surface for the collector. They are chemicals such as sodium sulfide and copper sulfate.

- Depressants -- Used to prevent flotation of minerals that one does not want to float. They are chemicals such as dextrin, sodium cyanide, starch, and guar gum.

- Collectors -- This group of reagents can be divided into three specific groups as follows:

    - Anionic -- for floating non-sulfide minerals: xanthates, dithiophosphates, thiocarbanilide, thionocarbamates, xanthogen formates, etc.

    - Anionic -- for floating non-sulfide minerals: fatty acids of various types.

    - Cationic -- for floating non-sulfide minerals: alkyl amines and quarternary ammonium salts.

- Frothers -- Used to form a reasonably stable froth so the collected particles can be recovered. They are chemicals such as pine oil and cresylic acid, but today M.I.B.C. (methyl isobutyl carbinol) is almost the universally used frother.

- Flocculants -- Used in the thickening operation following flotation. Lime or some of the high molecular weight, water soluble, non-ionic polyacrylamides are most commonly used.

17.1.2 PROCESS OPERATION AND ADAPTATIONS

The actual flotation separation is carried out in "flotation cells" which are only a small part of the overall process as indicated in Figure 17-1.

The flotation cell is a simple tank with an agitator mechanism with means to admit air at the bottom. Cells can be from 10 to 200 cu ft in size depending on the separation being made and the tonnage being processed. Large plants can have many hundreds of cells. The agitation, with the introduced air, forms tiny air bubbles which contact the prepared particles and bring them to the surface where they overflow the top of the cell or are at times removed or assisted with paddle wheel scrapers.

Many flotations are carried out where only one valuable component is separated from a waste material. However, many others separate two, three or even four valuable products from the waste material. In this case, the process is usually referred to as "differential flotation." A good example of this is the case of mixed sulfides ores of copper, lead, and zinc. In this operation, separate copper, lead, iron, and zinc concentrates can be produced by suitable selection of flotation conditions and reagents. Another example in the nonmetallic area is the flotation of pegmatites where separate concentrates of mica, spodumene, feldspar, and quartz can be produced.

Flotation can also be done in a liquid medium other than plain water. For example, soluble salts are floated in saturated brine solutions, and some flotations are carried out using sea water where fresh water is scarce.

While the flotation process has been applied principally to mineral processing, there have been a number of applications and potential applications in related as well as different areas.

- Precipitate Flotation

It is possible to float precipitates that have been made in a solution and recover them as a froth concentrate. In this application the metal to be removed from solution is precipitated before the addition of a collector.

One example of this in the mineral processing industry is the leach-precipitation-flotation process (L.P.F.) which is used on mixed oxide-sulfide copper ores. In the L.P.F. process, the ore is treated with sulfuric acid which dissolves the oxide copper minerals. Powdered iron is then added to the slurry which precipitates the copper as metallic copper particles. The whole mixture is then floated, and the precipitated copper as well as the unaffected sulfide copper particles are collected as a froth concentrate.

Another possible application of precipitate flotation is the flotation of complexed cyanide as a means of removing cyanide from solutions or mixed suspensions. If ferrous iron is added to a cyanide-containing solution, a ferro-cyanide precipitate can be formed which can then be floated from the solution. Test results in one case indicated that about 95% of the complexed cyanide could be removed under the proper conditions.

- Agglomerate Flotation (Emulsion Flotation)

The typical flotation process takes place on ground ores where the top particle size is on the order of 40 mesh (about 400 microns). It is difficult for an air bubble to pick up a particle much bigger than that.

However, coarser particles up to about 10 mesh in size (2000 microns) can be floated after conditioning by carrying out the separation on a vibrating table or similar device. This is called agglomerate or table flotation, and is practiced in the phosphate industry where coarse apatite particles are separated from quartz grains using a fatty acid-fuel oil emulsion as a collector.

o Ion Exchanger Flotation

Work has shown that ion-exchange resins can be contacted with solutions to pick up or exchange particular ions in the solution. The resin particles can then be removed by flotation. There is no application of this process as far as we know. Resin particles can usually be more simply removed by screening.

o Ion Flotation

In ion flotation a surfactant ion of opposite charge to the inorganic ion to be removed from solution is added in stoichiometric amounts. The surfactant "collector" must be added in such a way that it exists in solution as simple ions. The collector reacts with the inorganic ion to form an insoluble "soap" which can be levitated to the surface with a gentle bubbling action to form a foam or scum which can be removed.

One ion flotation system that has been investigated was the removal of dissolved copper with a sodium lauryl sulfate collector. There are no practical operating plants using the technique as far as we know.

Other systems that have been studied have involved the ion flotation of cadmium, nickel, and iron cyanide complexes with collectors such as dodecylamine chloride.

The possibilities for these kinds of separations are almost unlimited if specific and selective "soaps" can be developed.

o Foam Fractionation

This is a process for concentrating metals in solution and is not strictly a flotation process.

When a solution containing surface active solutes is exposed to a gas, the solutes tend to migrate to the gas-liquid interface. Therefore, the surface layer is richer in the solute than the bulk of the liquid. Therefore, when gas is bubbled through such a solution, it foams and creates a large amount of surface. Collecting the froth on the surface will yield a concentrate rich in the desired solute.

Such foaming systems have only two phases, a gas and a liquid, and thus differ from the usual flotation processes with their solid phases as well as a gaseous and liquid phase.

18. AIR STRIPPING AMMONIA REMOVAL

Air stripping of ammonia from biologically treated domestic wastewater is being developed as a means of reducing nitrogen content in wastewater. Ammonia removal efficiencies of over 90% have been obtained in pilot scale tests using packed towers and a wastewater containing 60 ppm (ammonia) nitrogen. Air stripping systems other than packed towers (such as holding ponds, holding ponds with surface agitation and spray ponds) have been investigated as means of stripping ammonia from wastewater, but the packed tower appears to be the most compact and efficient.

Ammonia removal efficiencies in a full-scale, 15 mgd, air stripping tower at the Orange County, California Water District Plant have averaged only 60-65%, but they expect to increase this to up to 95% with tower modifications.

Air stripping of the wastewater, removes the ammonia nitrogen from the wastewater and discharges it to the air. The concentration of ammonia in the air leaving the South Tahoe, California, stripping tower is about 6 mg/m^3, well below the odor threshold of 35 mg/m^3.

Air stripping of ammonia from wastewater is limited to dilute ammoniacal solutions, since the atmospheric emission level of ammonia would be too high from a concentrated solution. In addition, ammonia would be more efficiently recovered from concentrated solution by steam stripping.

Ammonia is quite soluble in water, but this solubility is temperature dependent. The solubilities of ammonia in water at different temperatures are presented below:

Temp.	gmNH_3/gm water (at 1000 mmHg)
0°C	1.094
20°C	0.629
40°C	0.386

The relationship between temperature and the solubility of ammonia for dilute ammonia solutions is expressed by Henry's Law:

$$y = Mx$$

where:

y = mole fraction NH_3 in the vapor

x = mole fraction NH_3 in the liquid

M = Henry's constant

Henry's constant (M) is a function of temperature. By raising the temperature of the wastewater the vapor pressure of the ammonia is increased and ammonia removal efficiency increased.

Another factor in ammonia removal efficiency is the pH of the wastewater. A portion of the ammonia dissolved in the water reacts with the water to give the following equilibrium:

$$NH_3 + H_2O = NH_4^+ + OH^-$$

By increasing the pH (concentration of OH^-) the equilibrium is shifted to the left, reducing the concentration of NH_4^+ and increasing the concentration of free dissolved ammonia.

To obtain reasonable ammonia removal efficiencies (or rates) by air stripping, either the temperature or the pH of the wastewater must be increased. In steam stripping ammonia from "sour water" the temperature of the wastewater is increased from about 38°C to about 110°C. The pH of the "sour water" ranges from 8-9 (unless it is not acidified to aid release of the H_2S).

In air stripping of ammonia from dilute solution in wastewater, it would not be practical to heat the wastewater hot enough to remove the residual ammonia. If ambient air were used for stripping, the wastewater heat loss would be extremely high.

The other means of increasing the ammonia removal rate (and efficiency) is to increase the pH. This method is ideally suited to the removal of ammonia from tertiary treated domestic wastewater since the phosphate removal step in tertiary treatment requires a high pH. Lime slurry is added to the wastewater prior to air stripping and then is recovered using flue gas from the recalciner. The recalciner calcines the recovered lime slude to generate reactivated lime and carbon dioxide for the recarbonators.

18.1 OPERATION

Removal of ammonia from biologically treated domestic wastewater by air stripping as part of a tertiary treatment system offers a unique economic opportunity. This is because part of the tertiary treatment scheme involves lime addition for phosphate removal. This lime addition significantly increases the pH. The wastewater can then be air stripped at this high pH.

Figure 18-1 is the flow diagram for the air/ammonia stripping system as applied to the treatment of domestic wastewater. This same system could be used fro treating other aqueous ammonia or volatile organic containing wastes, but would be subject to air emission regulations and the fact that the ammonia or organic in the dilute air stream leaving the towers could not be economically incinerated or recovered.

The ammonia containing wastewater and the lime slurry are fed to a rapid mix tank. Following the rapid mix tank are flocculators and a settling basin, where calcium phosphate precipitates and recirculated calcium carbonate settle out. The clarified, lime-treated, wastewater is pumped to the top of two packed towers. In each of the towers, six fans developing 350,000 cfm each draw air up through the tower countercurrent to the failing wastewater.

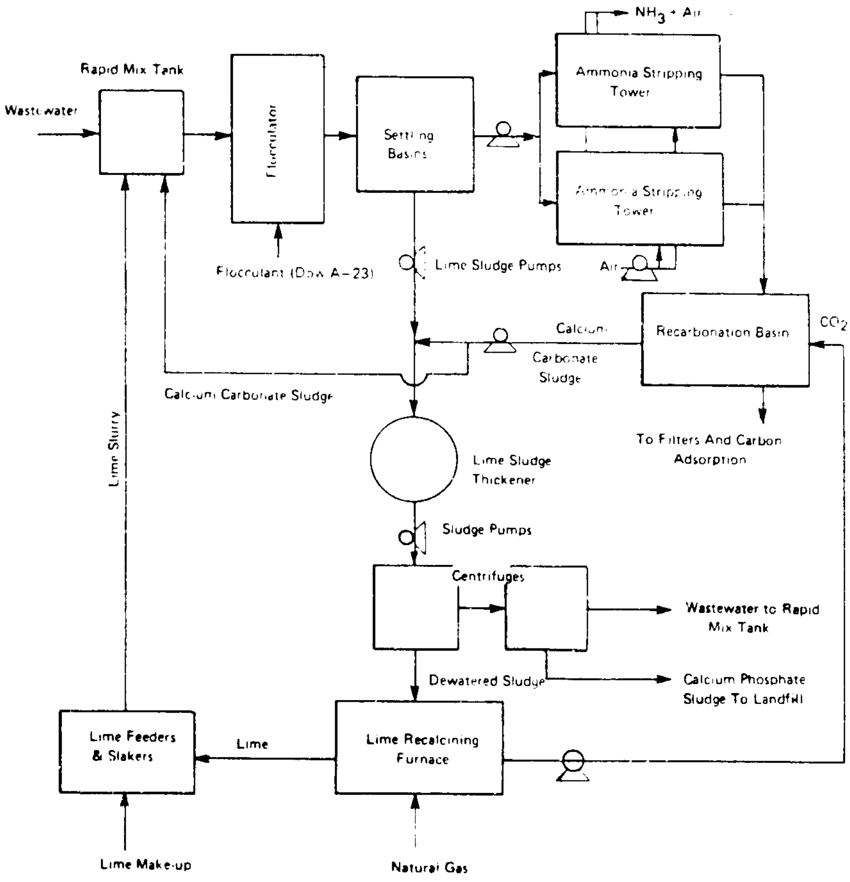


Figure 18-1 - Air Stripping of Ammonia from Biologically Treated Domestic Wastewater

The "packing" in the tower is actually a series of bundles of 1/2 inch PVC pipe with the pipe sections spaced 2-3 inches on center. The pipe sections are horizontal and the direction of each row alternates. The design criteria for this unit are as follows:

Hydraulic loading:	1 gpm/sq ft
Air Flow:	400 cu ft/gal
Depth of "Packing":	25 ft
Temperature of Operation:	16-40°C

As discussed earlier, the ammonia removal efficiency in this unit varied with temperature averaging 65% for April-June and 60% for Sept.-Dec. This efficiency is expected to be increased to up to 95% with modifications to prevent bypassing of the air flow around (rather than through) the tube bundles.

After the wastewater has been air stripped of ammonia, it flows into the recarbonation basin where compressed carbon dioxide rich gas from the lime recalcining furnace is bubbled through it to precipitate calcium carbonate. Some of the calcium carbonate sludge is returned to the rapid mix tank to enhance flocculation while the remainder of the calcium carbonate sludge and the phosphate slude from the settling basins are sent to the centrifuges. Here the sludges are fractionally centrifuged to yield two dewatered sludges, one rich in calcium carbonate that is sent to the lime kiln and one containing phosphate that is sent to landfill.

The calcium carbonate is recalcined to supply regenerated lime to the system. About 24 tons lime per day are recycled to the process when the system is operated at a 15 mgd wastewater flow rate, 6 tons per day of make-up lime is required.

When the concentration of ammonia in the wastewater is about 23 ppm and the air to water ratio is 500 ft^3/gal, the concentration of ammonia in the saturated air leaving the tower is about 6 mg/m^3. This is well below the odor threshold concentration of 35 mg/m^3. The treated wastewater should be low enough in residual ammonia (~ 5 ppm) to allow safe discharge to a receiving body of water.

About 25 tons per day of dewatered calcium phosphate, magnesium and calcium carbonate sludge must be disposed of by landfill for a 15 mgd plant. This sludge disposal will require a significant amount of land, but should not pose any environmental hazard.

Studies have been conducted using higher concentrations of ammonia (approximately 100 ppm) in untreated wastewater.

When 300 cu ft of air were applied per gallon of wastewater, the ammonia removal was found to be 85% at a pH of 10.5 and 34% at a pH of 9.4. In another study, in which the wastewater was passed through a closely packed aeration tower with 480 cu ft of air supplied per gallon, ammonia-nitrogen removal by air stripping was found to be very effective (more than 95% removal) any any pH above 9.0. When the pH fell below 9.0, the ammonia-nitrogen removal decreased sharply. The removal fell to 91% at a pH of 8.9 and to 58% at a pH of 8.8.

19. STABILIZATION PONDS

Waste stabilization ponds depend on the natural aquatic processes of bacterial and algal symbiosis, requiring sunlight as a primary energy source, and have been used successfully in the treatment of refinergy and petrochemical wastewaters. Ponds are classified as facultative, tertiary, aerated, and anaerobic according to the type of biological activity that takes place in them. Although ponds are often used to provide long-term polishing for effluents discharged from upstream biological units, they have been used in some instances as a total treatment system.

19.1 FACULTATIVE PONDS

These are the most common lagoons employed for stabilizing municipal waste water. The bacterial reactions include both aerobic and anaerobic decomposition and, hance, the term facultative pond. Waste organics in suspension are broken down by bacteria releasing nitrogen and phosphorus nutrients, and carbon dioxide. Algae use these inorganic compounds for growth, along with energy from sunlight, releasing oxygen to solution. Dissolved oxygen is in turn taken up by the bacteria, thus closing the symbiotic cycle. Oxygen is also introduced by reaeration through wind action. Settleable solids decomposed under anaerobic conditions on the bottom yield inorganic nutrients and odorous compounds, for instance, hydrogen sulfide and organic acids. The latter are generally oxidized in the aerobic surface water thus preventing their emission to the atmosphere.

Bacterial decomposition and algal growth are both severely retarded by cold temperature. During winter when pond water is only a few degrees above freezing, the entering waste organics accymulate in the frigid water. Microbial activity is further reduced by ice and snow cover that prevents sunlight penetration and wind reaeration. Under this environment, the water can become anaerobic causing odorous conditions during the spring thaw, until algae become reestablished. This may take several weeks depending on climatic conditions and the amount of waste organics accumulated during the cold weather.

Operating water depths range from 2 to 5 ft., with 3 ft. of dike freeboard above the high water level. The minimum 2 ft. depth is needed to prevent growth of rooted aquatic weeds, but exceeding a depth of 5 ft. may create excessive odors because of anaerobiosis on the bottom.

Typical construction is two or more shallow pools with flat bottoms enclosed by earth dikes. Waste water enters through an inlet division box, flows between cells by valved cross-connecting lines, and overflows through an outlet structure. Inlet lines, controlled by stop gates in the division box, discharge near the pond centers. Operating water depth is managed by a valving arrangement in the discharge structure. Connections between cells permit either parallel or series operation. Dikes are constructed with relatively flat side slopes to facilitate grass mowing and reduce slumping of the earth wall into the lagoon. Often the inside slopes along the waterline are protected by stone riprap to prevent erosion by wave action. If the soil is pervious, the pond bottoms should be sealed with bentonite clay, or lined with plastic, to prevent groundwater pollution. The area should be fenced to keep out livestock and discourage trespassing.

BOD loadings on stabilization ponds are expressed in terms of lb BOD applied per day per acre of water surface area, or sometimes as BOD equivalent population per acre. The maximum allowable loading is about 20 lb BOD per acre per day in northern states to minimize odor nuisance in the spring of the year. In those climates where ice coverage does not prevail, higher organic loadings may be used, for example, in the south and southwest a loading of 50 lb BOD per day per acre is practical. These loadings are 0.9 to 1.3 BOD per 1000 cu ft per day for a 5 ft water depth, which are substantially less than the volumetric loads applied to aeration and filtration units. Retention time of the waste water in lagoons is 3 to 6 months depending on applied load, depth of waste water, evaporation rate, and loss by seepage.

Lagoon treatment is regulated by the sequence of pond operation and water-level control. Series operation prevents short-circuiting and increases BOD reduction, but the load on the first cell is increased and may cause odor problems. Functioning in parallel distributes the raw BOD load but allows short-circuiting. Regulating lagoon discharge to a receiving stream can minimize water pollution. Pond water level may be slowly lowered in the fall and early winter when there is adequate dilution flow in the receiving stream. Discharge in the winter is then minimized or stopped, and influent waste water is stored until spring. Overflow is then permitted after the weather warms and the biological processes reduce the BOD concentration in the impounded water to an acceptable effluent level.

Facultative ponds treating only domestic waste water normally operate odor free except for a short period of time in the spring of the year. On the other hand, lagoons treating municipal waste water that include industrial wastes can produce persistent obnoxious odors. Often this is the result of organic overload from food-processing industries or a result of the odorous nature of the industrial waste itself or both. The best solution is to require pretreatment of the offending waste waters prior to discharge to the sewer system.

Meeting the effluent standard of 30 mg/l of suspended solids is a serious problem in lagoon treatment, since algae suspended in the water generally contributes 50 to 70 mg/l. In some instances, the effluent standard can be met by series operation and careful control of effluent discharge. Alternatives are land disposal or installation of an additional treatment unit to remove the suspended solids prior to disposal. Colloidal and particulate solids may be removed by a gravity filter similar to that used in water treatment when this is preceded by chemical flocculation, or it can be taken out by an upflow filter. The latter passes water up through the filter media at a controlled rate to capture a portion of the suspended solids. The most common land disposal system is spray irrigation. In addition to solids separation, pond overflow may require chlorination to meet the effluent quality for fecal coliform bacteria.

In summary, facultative ponds are best suited for small towns that do not anticipate industrial expansion, and where extensive land area is available for construction and effluent disposal. The advantages of low initial cost and ease of operation, as compared to a mechanical plant, can be offset by operational difficulties. The key problems are poor assimilative capacity for industrial wastes, odorous emission, and meeting the minimum effluent standards for disposal in surface waters.

19.2 TERTIARY PONDS

These units, also referred to as maturation or polishing ponds, serve as third-stage processing of effluent from activated sludge or trickling filter secondary treatment. Stabilization by retention and surface aeration reduces suspended solids, BOD, fecal microorganisms, and ammonia. The water depth is generally limited to 2 or 3 ft. for mixing and sunlight penetration. BOD loads are less than 15 lb BOD per acre per day, and detention times are relatively short at 10 to 15 days.

19.3 AERATED LAGOONS

Complete-mixing aerated ponds, usually followed by facultative ponds, are used for first-stage treatment of municipal waste waters and for pretreatment of industrial wastes. The basins are 10 to 12 ft deep and are aerated with pier-mounted or floating mechanical units. The aerators are designed to provide mixing for suspension of microbial floc and to supply dissolved oxygen. The biological process does not include algae, and organic stabilization depends on the mixed liquor that develops within the basin, since there is no provision for settling and returning activated sludge. BOD removal is a function of aeration period, temperature, and nature of the waste water. Design aeration periods are normally in the range of three to eight days depending on the degree of treatment desired and waste-water temperature during the cold season of the year. For example, aerating a typical municipal waste water for five days at 20°C provides about 85 percent BOD reduction while lowering the temperature to 10°C reduces the efficiency to approximately 65 percent.

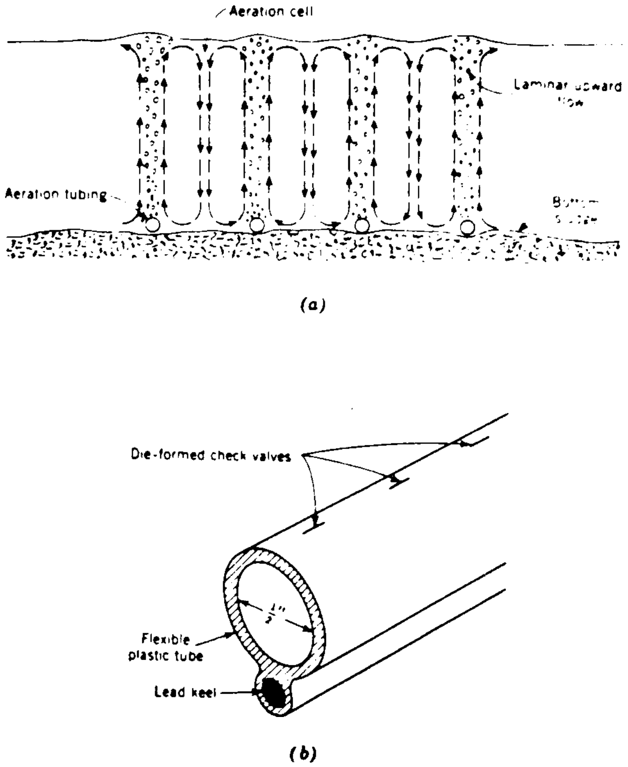
Problems of odors and low efficiency result when aerated lagoons are improperly designed or poorly operated. Thorough mixing and adequate dissolved oxygen insure odor-free operation. If the aeration equipment is inadequate, deposition of solids and reduced oxygenation can result in anaerobic decomposition that leads to foul odors. Pretreatment and control of industrial wastes are required, since large inputs of either biodegradable or toxic wastes can cause process upset. Infiltration entering the sewer collection system during wet weather can have a detrimental effect on an aerated lagoon by reducing the aeration period and flushing microbial floc out of the basin. Where infiltration is a problem, it is best to divert a portion of wet-weather flow around the aerated lagoon to the second-stage facultative ponds, thus preventing undesirable hydraulic loading on the aerated basins. In the winter, the aerators should be adjusted and windbreaks should be set up to reduce cooling of the lagoon water.

A second type of aerated stabilization pond is illustrated in Figure 19-1. Compressed air is introduced through rows of plastic tubing strung across the pond bottom. Streams of bubbles rising to the surface provide vertical mixing and distribution of dissolved oxygen. The cells normally have 10 ft. of liquid depth and operate in series with a total detention time of 25 to 35 days. Tube aeration systems have been most successful in locations where the pond surfaces are frozen for several months in the winter and an external air supply is needed to maintain aerobic conditions. In this climate, the effluent of unaerated facultative ponds is generally unsatisfactory and surface aerators are impaired by ice formation.

19.4 ANAEROBIC LAGOONS

Bacteria anaerobically decompose organic matter to gaseous end products of carbon dioxide and methane. In addition, intermediate odorous compounds, such as organic acids and hydrogen sulfide, are formed. The two primary advantages of anaerobic treatment compared with an aerobic process are the low production of waste biological sludge and no need for aeration equipment. The disadvantages are that incomplete stabilization requires a second-stage aerobic process and the relatively high temperature required for anaerobic decomposition. The important characteristics for a waste water to be amenable to anaerobic treatment are: high organic strength particularly in proteins and fats, relatively high temperature, freedom from toxic materials, and sufficient biological nutrients. The basins are constructed with steep side walls and a depth of 15 ft. to minimize the surface area relative to total volume. This construction allows several inches of grease accumulation to form a natural cover for retaining heat, suppressing odors, and maintaining anaerobic conditions. Influent waste water enters near the bottom so that it mixes with the active microbial solids in the sludge blanket. The discharge pipe is located on the opposite end and is submerged below the grease cover. Upward flow of the discharge allows settling of the bacterial floc so that the anaerobic mixed liquor is retained in the lagoon. Sludge recirculation is not necessary, since gasification and the inlet-outlet flow pattern provides adequate mixing. Series operation is not recommended because it is difficult to maintain an adequate grease cover on a second-stage lagoon.

The normal operating standards to achieve a BOD removal efficiency of, at least, 75 percent are a loading of 20 lb BOD per 1000 cubic feet per day, a minimum detention time of four days, and a minimum operating temperature of 75°F. The most common operating problems result from reduced temperature in the liquid caused by an insufficient cover of grease for thermal insulation and protection from wind mixing. Too low a BOD loading and overlay efficient pretreatment can result in inadequate grease input to build up and maintain a cover layer. Anaerobic lagoons do not create serious odor problems when operating properly, that is, when there is complete anaerobiosis and adequate grease cover. One exception is when the water supply to the industry is high in sulfate ion which is reduced in the anaerobic environment and emitted as hydrogen sulfide.



(a)

(b)

Figure 19-1 - Stabilization Pond Aerated and Mixed by Compressed Air Emitting from Plastic Tubing Laid on the Bottom of the Lagoon. (a) Schematic of Aerating and Mixing Action. (b) Detail of Aeration Tube.

Application of relationships used to design domestic wastewater ponds relies upon certain assumptions, however, and may not apply to the waste stabilization pond treatment of refinery and petrochemical wastewaters. For example, ponds are susceptible to wind action and short-circuiting which would prevent conformance to predictive efficacy and performance. Moreover, the accumulation of emulsions in waste stabilization ponds prevents sunlight penetration, resulting in excessive anaerobic action.

The tendency is to construct single ponds although series ponds may be more efficient since short-circuiting is reduced and overall organic removal may possibly be increased. The first pond is usually anaerobic because of the imposed surface loading and will be odoriferous. It does trap floating organic material, however, and provides for easier removal of these floating materials. The retention time in waste stabilization ponds ranges from 1 to 90 days. The exact retention time depends on the land available as well as the design requirement. As land is generally quite expensive in are contiguous to refinery and petrochemical operations, the use of waste stabilization ponds is limited. Additionally, new effluent guidelines are in most cases too stringent for pond capability. The proliferation of algal and bacterial material in ponds, for example, adds to the effluent suspended solids level even though the soluble organic fraction may bed reduced to acceptable levels.

20. CHEMICAL OXIDATION

Oxidation reactions are among the most common of chemical reactions. The experience with these reactions for waste treatment is primarily related to removal of trace contaminants in water effluents and for cyanide treatment from operations such as plating and metal finishing. The former are of interest only as they identify potential oxidants and type of materials that can be oxidized. The latter, while often relating to dilute cyanide rinse wastes, can be extended to more concentrated solutions which have relevance to this contract.

The processes are based on chemical oxidation as differentiated from thermal, electrolytic, and biological oxidation. While oxidation using air or oxygen in solution can be used for waste treatment on sulfites, sulfides and ferrous iron, these oxidations typically are catalyzed with small amounts of materials such as cobalt to increase the reaction rate.

Chemical oxidation of selected waste streams within a refinery or petrochemical complex may be an appropriate method of treatment, depending on the oxidation reaction time, the characteristics of the oxidation products, and overall process economics. Chemical oxidation, raising the oxidation level of a substance or reducing its BOD and COD, can be accomplished using the primary oxidizers of oxygen, ozone, permanganate, chlorine, or chlorine dioxide. Catalytic oxidation offers a practical means of oxidizing small volumes of concentrated organic waste which are not susceptible to other forms of treatment.

20.1 OPERATION

Oxidation-reduction, or "redox" reactions are those in which the oxidation state of at least one reactant is raised while that of another is lowered. In the reaction below in alkaline solution:

$$(1) \quad 2MnO_4^- + CN^- + 2OH^- \rightleftharpoons 2MnO_4^{2-} + CNO^- + H_2O$$

the oxidation state of the cyanide ion is raised from -1 to +1 (the cyanide is oxidized as it combines with an atom of oxygen to form cyanate); the oxidation state of the permanganate decreases from -1 to -2 (permanganate is reduced to manganate. This change in oxidation state implies that an electron was transferred from the cyanide ion to the permanganate. The increase in the positive valence (or decrease in the negative valence) with oxidation takes place simultaneously with reduction in chemically equivalent ratios.

Fluorine is a powerful oxidizing agent. The other halogens, including chlorine, are also good oxidizing agents. The positive ions of noble metals are good oxidizing agents. Many of the oxygenated ions, such as BrO_3^- and NO_3^- are strong oxidizing agents in acid solution.

Oxidizing agents vary in strength as illustrated by the following half-reactions arranged in order of decreasing oxidation potentials (i.e., tendency to pick up electrons):

Half-reaction	Oxidation Potential (E_0), Volts
$F_2 + 2H^+ + 2e^- \rightarrow 2HF(aq.)$	3.06
$H_2O + 2H^+ + 2e^- \rightarrow 2H_2O$	1.77
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.695
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1 359
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33
$2H^+ + 2e^- \rightarrow H_2$	0

Some oxidations proceed readily to CO_2. In other cases the oxidation is not carried as far perhaps because of the dosage of the oxidant, the pH of the reaction medium, the oxidation potential of the oxidant, or the formation of stable intermediates. The primary function performed by oxidation in the treatment of hazardous wastes is essentially detoxification. For instance, oxidants are used to convert cyanide to the less toxic cyanate or completely to carbon dioxide and nitrogen. The oxidant itself is reduced. For example, in the potassium permanganate treatment of phenolics, the permanganate is reduced to manganese dioxide. A secondary function is to assure complete precipitation, as in the oxidation of Fe^{++} to Fe^{+++} and similar reactions.

Liquids are the primary waste form treatable by chemical oxidation. The most powerful oxidants are relatively non-selective; therefore, any easily oxidizable material in the waste stream will be treated. If for instance an easily oxidizable organic solvent were used, little of the chemical effect of the oxidizing agent could be used on the hazardous constituent. This, therefore, essentially limits the use of the most commonly used oxidants to aqueous wastes.

Gases have been treated by scrubbing with oxidizing solutions for the destruction of odorous substances, such as certain amines and sulfur compounds. Potassium permanganate, for instance, has been used in certain chemical processes, in the manufacture of kraft paper and in the rendering industry. Oxidizing solutions are also used for small-scale disposal of certain reactive gases in laboratories.

Oxidation has limited application to slurries, tars, and sludges. Because other components of the sludge, as well as the material to be oxidized, may be attacked indiscriminately by oxidizing agents, careful control of the treatment via multi-staging of the reaction, careful control of pH, etc. are required.

The chlor-alkali industry is reported to use chemical oxidative techniques to remove mercury from ores as well as from the cell-wastes. Mercury removal rates of over 99% are claimed for concentrated ores, and residual mercury levels of less than 0.1 ppm for chloralkali sludge.

The first step of the chemical oxidation process is the adjustment of the pH of the solution to be treated. In the use of chlorine gas to treat cyanides, for instance, this adjustment is required because acid pH has the effect of producing hydrogen cyanide and/or cyanogen chloride, both of which are poisonous gases. The pH adjustment is done with an appropriate alkali; sodium hydroxide, for example. This is followed by the addition of the oxidizing agent. Mixing is provided to contact the oxidizing agent and the waste. Because some heat is often liberated, more concentrated solutions will require cooling. The agent can be in the form of a gas (chlorine gas) or as a solution (hydrogen peroxide) or perhaps as a solid if there is adequate mixing. Reaction times vary but are in the order of seconds and minutes for most of the commercial-scale installations. Additional time is allowed to ensure complete mixing and oxidation. At this point, additional oxidation may be desired and, as with cyanide destruction, often requires the readjustment of the pH followed by the addition of more oxidant. Once reacted, this final oxidized solution is then generally subjected to some form of treatment to settle or precipitate any insoluble oxidized material, metals, and other residues. A treatment for the removal of what remains of the oxidizing agent (both reacted and unreacted) may be required. A product of potassium permanganate oxidation is manganese dioxide (MnO_2) which is insoluble and can be settled or filtered for removal.

20.1.1 OXIDIZING AGENTS

Gaseous or dissolved oxygen is used both as a stripping agent for such gases as carbon dioxide, hydrogen sulfide, methane, and other low boiling organic compounds as well as for chemical oxidation. Although the use of pure oxygen may be applicable from a process point of view, economics may render it impractical. Pure oxygen is, however, being used for biological systems with reported savings in cost over conventional systems. Air oxidation is used for sulfide oxidation as well as for removal of divalent forms of iron and manganese. The oxidation of iron, however, is strongly pH dependent.

The chemistry and theory behind the oxidation of sulfides is well documented. Most sulfide oxidation units presently used are patented designs. The design criteria and operating conditions for several of these units are listed in Table 30. All of the units mentioned oxidize 100 percent of the influent sulfides, but if large quantities of mercaptans or mercaptides are present in the waste, a reoxidizer may be required to ensure complete oxidation. The reoxidizer should be operated at a temperature of 130 to 150°F with a pressure of 50 psi to prevent mercaptan stripping. The data in Table 30 indicate that sulfides can be oxidized to thiosulfates more easily than to sulfates. It is possible that some sulfate was produced in the towers but, to obtain maximum conversion, low sulfide loadings are required. The oxidation of sulfides in a liquid phase using a typical sulfide oxidation unit is shown in Fig. 20-1.

Only very simple equipment is required for chemical oxidation. This includes storage vessels for the oxidizing agents and perhaps for the wastes, metering equipment for both streams, and contact vessels with agitators to provide suitable contact of oxidant and waste. Some instrumentation is required to determine the concentration and pH of the water and the degree of completion of the oxidation reaction. The oxidation process may be monitored by an oxidation-reduction potential (ORP) electrode. This electrode is generally a piece of noble metal (often platinum) which is exposed to the reaction medium, and which produces an EMF output that is empirically related to the reaction condition by revealing the ratio of the oxidized to the reduced constituents. Heavy oils should be eliminated from the waste prior to oxidation since pilot-plant studies indicated that 5 percent of such oil could decrease the oxidation rate by 50 percent.

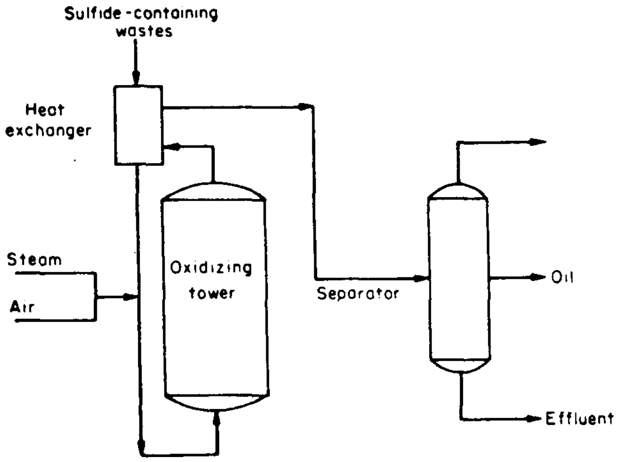


Figure 20-1 A Typical Sulfide Oxidation Process Flow Sheet

Ozone is an oxidizing agent used for phenols, cyanides, and unsaturated organics destruction since it is a considerably stronger oxidizing agent than chlorine. It is a powerful oxidant which reacts rapidly with a majority of organic compounds and microorganisms present in wastewaters. The primary disadvantage is the high capital cost associated with the ozone-generation equipment. It does, however, effectively oxidize many constituents and is used for color removal, disinfection, iron and manganese removal, phenol oxidation, and cyanide oxidation.

Permanganate oxidation has been and is being used in treating water to remove taste, odor, iron, and manganese but is not generally used for the specific removal of BOD.

Chlorine has been applied in oxidizing phenol and cyanides in petrochemical wastes. The oxidation of phenols, however, must be carried to completion to prevent the release of chlorophenols which can cause objectionable odors and tastes in drinking water, even at very low concentrations. An excess of chlorine usually is required because of the reaction with various other chemical compounds (such as ammonia, sulfides, and various organics which can interfere with the chlorination process). To prevent the formation of chlorophenols, the pH of the waste is kept at 7 or higher and the usual reaction time required is 1 to 2 hr. Chlorine can be applied either as free chlorine or as hypochlorite. Cyanides can be oxidized to carbon dioxide and nitrogen by chlorination. The wastewater must be kept at a pH value greater than 8.5 during treatment to prevent the release of toxic cyanogen. Ammonia, which is being singled out as an initial pollutant in refinery and petrochemical effluents, can be oxidized by chlorine to free nitrous oxide gas. However, the chlorine demand is high and the process economics should be evaluated. Nevertheless, chemical oxidation of ammonia may be more practical from an economic and process viewpoint than alternate ammonia removal processes.

Chlorine dioxide has gained wide acceptance in water treatment and can be considered in refinery wastewater treatment for certain applications since phenol oxidation using chlorine dioxide avoids the formation of chlorophenols. Like ozone, the instability of gaseous chlorine dioxide necessitates generation in situ, and initial capital costs for these systems are quite expensive.

20.1.2 OUTPUT STREAMS

While some stream components may be added or removed, the output stream from chemical oxidation is very similar to the input stream. Oxidizing agents such as potassium permanganate and potassium dichromate introduced to the reaction mixture ions that are not easily separable from the product streams. Oxidizing agents such as oxygen and hydrogen peroxide have the advantage that they introduce no such foreign ions to the reaction mixture. Oxidizing agents often have a reaction product, such as MnO_2, that is insoluble and can be removed by filtration.

One disadvantage of chemical oxidation for waste treatment is that it introduces new metal ions into the effluent. If the level of these new contaminants is high enough to exceed effluent regulations, additional treatment steps will be required. Often these are steps such as filtration or sedimentation. Potassium permanganate used to treat wastes will be reduced to MnO_2 in the process. This can be reduced by filtration to levels less than 0.05 mg/1 in the final effluent.

On the other hand, oxidation with hydrogen peroxide adds no harmful species to the final effluent (except perhaps excess peroxide) since its product is water.

Whether the products of incomplete oxidation are an environmental hazard depends upon the specific situation. Cyanate, the product of potassium permanganate oxidation of cyanide, is not completely oxidized. Treatment with another oxidant, or acid hydrolysis after permanganate oxidation can oxidize the cyanide completely to CO_2 and N_2. Cyanate, however, is at least a thousand times less toxic than free cyanide. The conversion of benzidine to the products of diazotization is another case in which the treated waste is less hazardous than the first, but still is considered a problem.

Often the extent to which excess chlorine must be added for waste oxidation is such that the residual chlorine in the effluent becomes a problem. Careful in-process control or recycling of the oxidizing solution may be necessary to reduce this level to meet regulation limits. Also, hydrogen peroxide has been used as a reducing agent in some applications as an "antichlor" to destroy the chlorine remaining in the stream after purification.

With the exception of escape of chlorine, which is a potential hazard wherever chlorine is used, the only other air emission problem identified was the possible production of HCN from the destruction of cyanide wastes when the reaction medium is allowed to become acidic.

From most chemical oxidations there will be a residue for disposal unless the concentration of the waste constituent is so low that the oxidant waste products (if any) and the oxidized (and de-toxified) waste can be carried away with the effluent. Most of the residue develops from the use of caustic or lime slurry with chlorine gas in alkaline chlorination. Smaller amounts of residue result from oxidations using hypochlorites.

21. BIOLOGICAL (TRICKLING) FILTRATION

Fixed-growth biological systems are those that contact waste water with microbial growths attached to the surfaces of supporting media. Where the waste water is sprayed over a bed of crushed rock, the unit is commonly referred to as a trickling filter. Unfortunately, this is a misnomer and a better term would be biological bed, because the process is one of biological extraction rather than filtration. With the development of synthetic media to replace the use of stone, the term biological tower was introduced, since these installations are often about 20 ft. in depth rather than the traditional 6 ft. rock-filled filter.

Trickling filters have been used in treatment for industrial wastes for many years although the trend is away from filters as high-rate secondary treatment facilities in the refinery-petrochemical industry. They do, however, have some application as roughing devices preceding other biological or physical-chemical units.

The trickling filter is a packed-media bed covered with biological slime through which the wastewater is passed. As the organic-laden waste flows over the slime, organics and oxygen diffuse into the biological mass where they undergo biochemical oxidation to carbon dioxide, water, and metabolic by-products. Granular media is generally used to support the biological mass although the introduction in recent years of synthetic filter media has caused a variety of changes in the design and construction of trickling filters. These media, with low bulk density, have resulted in the use of deeper filters operated at greatly increased organic and hydraulic loading rates.

Most designs to date are formulated on empirical standards which must be modified to accomodate the nature of the industrial wastewater. The number of variables which influence trickling filter performance have complicated the development of a dependable model which can be applied or modified to existing conditions.

Some of the variables of design and operation include organic loading, hydraulic loading, nature of organic constituent, temperature, media type and distribution, and filter geometry and construction. Control of ventilation and plugging is necessary because anaerobic action (which is always present to some extent in a filter) becomes excessive when plugging occurs and ventilation is inadequate.

The recorded performance of trickling filters in the treatment of refinery and petrochemical effluents ranges from 10 to 20 percent removal when used as a roughing device to 50 to 90 percent when applied as a total process for secondary treatment.

The trickling filter process is a proven technology for the decomposition of organics in aqueous waste streams (less than 1% suspended solids). The process brings the wastewater in contact with aerobic microorganisms, by trickling the wastewater over media supporting microorganisms. BOD removal efficiencies range from 50-85%.

The microbial activities of trickling filters are similar to those of activated sludge treatment. While the activated sludge system cannot tolerate shock loadings, the trickling filter is used in industry to accept shock loads and provide a relatively uniform effluent for treatment by other biological processes. The ability of trickling filters to accept variable hydraulic and organic loadings is founded in the short residence time of the wastewater in the process. Extremes in loading should, however, be avoided so that the biomass does not slough off the filter.

Trickling filters may be employed as an intermediate process in industrial waste treatment. Preceding activated sludge, trickling filters would even the load to that process in addition to removing a significant portion of the biodegradable organics.

Energy demands for the trickling filter process are low, as little as one-tenth the demand for activated sludge treatment of the same waste stream. As a result, the total costs for trickling filter treatment are slightly lower than those for activated sludge treatment.

21.1 OPERATION

In the trickling filter process, wastes are sprayed through the air to absorb oxygen and are allowed to trickle through a bed of rock or synthetic media coated with a slime of microbial growth. The microbial slime is able to decompose organic matter in the waste stream. Process modifications employ various media and depths of media to retain the microorganisms under varying hydraulic conditions.

The trickling filter process relies on media support of immobile microorganisms which receive their organic substrate as waste is trickled over their cell surface. The primarily metabolic processes are aerobic, and the trickling filter system utilizes the same types of aerobic heterotrophic bacteria as the activated sludge system. In fact, in the petroleum industry, trickling filters precede the activated sludge unit and produce a continuous population of microorganisms for activated sludge treatment. The aerobic microorganisms produce enzymes which perform oxidation and hydrolysis catalysis for the decomposition of simple and complex organics. Intermediate decomposition by-products, namely organic alcohols and acids, are utilized by the bacterial cells for both metabolic energy and substrate for cell synthesis.

The microbial slime, which coats the trickling filter media, remains aerobic primarily at its surface where air and water interface with the cells. The underlying portion, adjacent to the media, may become anaerobic. Some anaerobic decomposition results, as simple organics are hydrolyzed to organic acids, and in turn are oxidized to methane and carbon dioxide.

Periodically, the microbial slime coating sloughs off the trickling filter media. This sloughing off may occur for several reasons. As the microorganisms grow and reproduce, the slime coating may become too heavy to remain adhered to the media. Also as the substrate becomes limited to the underlying respiration, the microorganisms become more dense and their adhesive polysaccharide cell coating diminishes.

Trickling filters decompose all types of organics, as does activated sludge treatment. Because of the relatively short residence time of wastewater contact with microorganisms, the percentage removal of organics is not as complete as in activated sludge treatment. Greater removals are achieved as the depth of media and the recycle ratio are increased. Trickling filters with 30 foot depth of media and recycle ratios of 3:1 are not uncommon in industry today.

Trickling filters have been used satisfactorily to decompose oil and phenol. In refinery wastes 30 mg/l of oil have been effectively decomposed. Trickling filter pilots of 3:1 recycle have decomposed 125 ppm phenol to 0 ppm.

Trickling filters are reported to have successfully handled the following waste constituents: acetaldehyde, acetic acid, acetone, acrolein, alcohols, benzene, butadiene, chlorinated hydrocarbons, cyanides, epichlorohydrin, formaldehyde, formic acid, ketones, monoethanolamine, propylene dichloride, resins, and rocket fuels. Study on the trickling filtration of nitrilotriacetic acid, which is normally used in the building of detergents, showed levels of up to 16 mg/1 nor harmful to the process.

Trickling filters provide media for support of biomass, rather than having suspended biomass as in the activated sludge treatment process. The wastewater is trickled through the media and collected in an underground drain. Suspended solids, including microbial slime which has sloughed off the media, are typically clarified from the underflow. The clarified underflow may be either recycled to the trickling filter head or sent to following treatment units.

A cutaway view of a trickling filter is shown in Figure 21-1. The major components are a rotary distributor, underdrain system, and filter media. Influent waste water is pumped up a vertical riser to a rotary distributor for spreading uniformly over the filter surface. Rotary arms are driven by reaction of the waste water flowing out of the distributor nozzles. Bed underdrains carry away the effluent and permit circulation of air. Ventilation risers and the effluent channel are designed to permit free passage of air. In some installations, the underdrain block empty into a channel between double exterior walls to allow improved aeration and access for flushing of underdrains.

The most common media in existing filters are crushed rock, slag, or field stone that are durable, insoluble, and resistant to spalling. The size range preferred for stone media is 3 to 5 in. diameter. Although smaller stone provides greater surface area for biological growth, the voids tend to plug and limit passage of liquid and air. Bed depths range from 5 to 7 ft.;

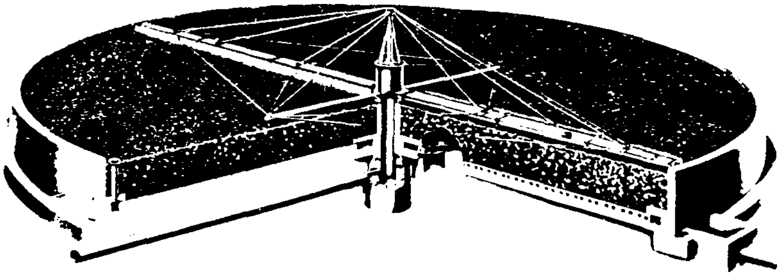


Figure 21-1 - Cutaway View of a Rock-Filled Trickling Filter greater depths do not materially improve BOD removal efficiency. Rock-filled filters in the treatment of municipal wastes are always preceded by primary settling to remove larger suspended solids.

Media used in filter packing allow various process modifications. The use of synthetic media allows deep filters because of their lessened tendency to clog and become anaerobic. Also, their comparatively light weight allows higher packings. Filter packings of up to 40 foot depth are reasonable where synthetic media are employed.

Hydraulic loading rates for trickling filters are generally less than 0.5 gpm/ft2; however, loadings up to 4 gpm/ft^2 have been employed. As the hydraulic loading rate increases, removal efficiency decreases. Generally, recirculation of the filter effluent improves the removal of biodegradable organics.

It appears that the short residence time characteristic of the trickling filter process allows greater variations in influent waste composition to occur without inhibiting microbial activity. The process is reputed to handle shock loadings of organic wastes, and also to be less inhibited by metals concentrations. In fact, the system is often called a roughing filter, used to level loads and reduce biodegradable organics concentrations prior to other biological treatment processes.

The trickling filter process provides aerobic microbial degradation of organics. Air is entrained into the wastewater influent as it is sprayed onto the filter packing's surface. Aeration continues as the wastewater flows in thin streams over the filter media with its microbial slime. Synthetic media provide better ventilation because they can be placed with maximum spacing to avoid clogging. The extent of aeration within the filter packing is affected by the hydraulic loading rate and the influent level of organic and suspended solids loadings.

The trickling filter process involves open tanks or towers to house the filter packing, and open tanks to clarify the filter effluent. Additional equipment may include recycle pumps to continuously recirculate filter effluent to the head of the process. The filter tank or tower employs a rotary spray dosing system which uniformly feeds influent wastewater to the filter surface.

As mentioned previously, the filter media may be either rock or synthetic. Rocks may be 2-4 inches long and provide a surface area of 9-25 ft^2/ft^3. Synthetic media often consist of flat or corrugated grating assembled in a criss-crossed or honeycombed manner. Synthetic media allow greater surface area; and 20-35 ft2/ft^3 of surface area may be provided by plastic packing.

No chemicals are required for the trickling filter process unless the influent wastewater stream is so nutrient poor or nutrient imbalanced that nutrients must be added.

Trickling filters have been extensively employed in the treatment of sanitary sewage. They have also been used extensively in the treatment of refinery wastewaters containing oil, phenol, and sulfide. Trickling filters are essentially applicable to the same industrial waste streams as the activated sludge treatment process, including cannery, pharmaceutical, and petrochemical wastes.

Trickling filter biological treatment of aqueous wastes for the biodegradation of organics is a proven technology with application to industrial waste treatment. It is principally applicable as a roughing filter which would establish relatively uniform loadings for subsequent biological processes. By placing trickling filters in sequence with activated sludge treatment, the filters could be used to even out loading variations while the activated sludge achieves high organic removal efficiencies. Even though trickling filters are more amenable to load variations than activated sludge systems, extremes should be avoided and we recommend the process be preceded by equalization.

Because of the short residence time of wastewater contact with microorganisms in trickling filters, decomposition of organics is not efficient enough to recommend this process as the sole means of biodegradation. Recycle increases the biodegradation of the influent organic loading, while also increasing the process design capacity needs.

Energy is needed for pumping and distributing wastewater. The energy demand of distributing wastewater over the filter surface depends upon the head loss with respect to filter depth and underdrain collection. Pumping energy requirements are based on the hydraulic head of the various process units and the recirculation ratio. For trickling filters without recycle, the power consumption is only about one-tenth that required for supplying air to the activated sludge process. Less than one-tenth of the total operating costs for trickling filters is attributed to energy demand.

Trickling filters rely on microbial biodegradation of organics for processing waters. As a result, the process effluents are a liquid wastewater from which a portion of the organics have been decomposed and a biomass sludge. The sludge is similar to the biomass residue obtained from the activated sludge process.

No exotic compounds are formed from trickling filtration, and there are no gaseous emissions aside from carbon dioxide, and perhaps methane.

22. ACTIVATED SLUDGE

The activated sludge process, a continuous system where a biological population is mixed with wastewater and then separated by gravity from the treated liquor, is effective in the treatment of refinery-petrochemical effluents.

The basis for the design of an activated sludge system is predicated on producing and maintaining an environment of microorganisms so that their growth and activity are as near optimal as possible. The activated sludge system, by virtue of its high mixed liquor suspended solids (MLSS) concentration accomplished through recycle, is classified as a high-rate biological process and therefore can tolerate higher contaminant concentration in the influent wastewater. Major design considerations for the successful activated sludge treatment of refinery-petrochemical wastewaters include:

1. The organic loading in terms of BOD applied per day per unit weight of mixed liquor biological solids
2. The BOD removal kinetics of a specific refinery-petrochemical wastewater
3. The organic and inorganic fluctuations of the feedwater to the activated sludge system
4. The free oil loading to the system
5. The temperature effects of the biological removal capacity of the system
6. The potential biotoxic or biostatic effects of the refinery-petrochemical effluents on the biological system
7. The oxygen requirements and biological sludge production rates of the given activated sludge system treating a wastewater of specified quality
8. The ability of the biological sludge in the system to separate from the treated liquor by gravity in the secondary clarifier, and to concentrate to the point of obtaining the desired MLSS level in the aeration basin through recycle
9. Operational flexibility to maximize process stability and continuity through the inclusion of parallel aeration basins, equalization facilities, off-spec holding basins, complete mixing, etc.

In general, refinery wastewaters are highly amenable to high-rate biological treatment using the activated sludge process; thus these systems are widely applied throughout the United States. The exact treatability of a refinery-petrochemical installation is, of course, a function of the effluent quality which depends on the classification of the refinery, the type of crude charge, the age of the facility and nature of its collection system, the relative effluent volume attributed to utility water blowdown, and the degree of in-plant control. For these reasons, design practices of the basic activated sludge process may vary from one installation to another. Treatability studies using bench- or pilot-scale process simulation techniques therefore are used to formulate the basic design criteria and predict treated effluent quality. It should be recognized, however, that the accuracy of information developed from these treatability studies depends on the accuracy of several assumptions.

These include

- o The characteristics of the wastewater used in the activated sludge tests are representative of those anticipated in field tests.
- o The physical nature of the bench- or pilot-scale process is similar to the proposed full-scale unit.
- o Independent and dependent operational variables are considered.
- o Environmental parameters affecting process efficiency are defined.

It is apparent from these constraints that process simulation techniques can provide predictor relationships and mathematical expressions for the activated sludge treatment process receiving the refinery effluent in question, but they do not necessarily define a specific model with general applications. However, a treatability study which is properly programmed and judiciously implemented does afford the basis for the logical development of unit process selection, design, and predictive performance.

The design organic load for most activated sludge systems ranges from 0.10 lb BOD_5/(day) (lb MLSS) (extended aeration) to as high as 0.8 to 1.0 lb BOD_5/(day) (lb MLSS). Higher loadings can be imposed, but generally at the expense of poorer efficiency and higher organic levels in the treated effluent.

Oil and grease are of paramount importance when designing activated sludge systems for wastewaters such as those discharged from petroleum refinery and petrochemical installations. Hexane extractable adversely affect a biological system as the concentration in the mixed liquor approaches 50 to 75 mg/l. A recent study conducted for the Environmental Protection Agency indicated that an activated sludge system will perform satisfactorily with a continuous loading of hexane extractables of 0.1 lb/lb MLSS. It was recommended that the influent to the biological system should contain less than 75 mg/l hexane extractables and preferably less than 50 mg/l. The most significant problem related to oils in biological systems was attributed to lowering floc density to a level where the sludge-settling properties were destroyed. The removal of free and, to some extent, emulsified oils through gravity separation, air flotation, or possibly filtration, is therefore required in most instances.

Temperature is a particularly important variable in the biological treatment of refinery petrochemical wastewaters. If the combined effluent flow contains a proportionately high volume of cooling tower blowdown, cooling might be required during summer months to satisfy effluent temperature criteria. Conversely, excessive temperature losses through a biological system during winter months in the northern climate might lower biological activity to the point of failing to meet effluent BOD quality standards. As most of the new activated sludge systems are using mechanical aerators to oxygenate and mix the contents of the aeration basin, an approach was developed recently to predict the temperature in activated sludge basins. The approach assumes the usual "water warmer than air" case, predicts the basin temperature by calculating the heat balance around the system and plots the calculated aeration basin temperature as a function of the wastewater temperature at the inlet to the aeration basin. The influence of temperature on biochemical reactions is well documented. The most traditional expression for relating the organic removal rate via biochemical oxidation with temperature is the Phelps equation

$$K_T = K_{20^\circ C}\, \Theta^{(T-20)}$$

where K_T = organic (BOD) removal rate at temperature T

$K_{20^\circ C}$ = organic (BOD) removal rate coefficient at 20°C

T = liquid temperature, °C

Θ = temperature coefficient

The coefficient 0 is a function of many variables; namely, the nature of the wastewater and type of biological process. Few investigations recognize the significance of the type of wastewater on the temperature effect. This is attributed to the fact that both wastes were easily degradable by many biological genera and some removal was undoubtedly the result of biosorption which is not as temperature-dependent as straight biochemical oxidation. However, activated sludge treatment of a complex chemical petrochemical waste, mostly soluble, was significantly affected by basin temperature. From these plots and other available data, it can generally be stated that the temperature effect is more pronounced with increasing solubility and complexity.

22.1 OPERATION

The activated sludge process is used to convert nonsettlable substances, in finely divided, colloidal, and dissolved form, into biological floc. This newly formed biological floc, termed sludge, is removed from the system through sedimentation, thereby providing a high degree of secondary treatment. The biological floc is developed in aeration tanks and settled out in final settling tanks.

The conversion of nonsettlable solids and dissolved substances into biological floc is the process that forms the basis for understanding what the activated sludge process is, what it does, and how and why it must be controlled. This understanding also gives insight into the variations that can upset normal operation of the process.

The conventional activated sludge process is a tradional basic approach to secondary biological treatment of wastewater. The modifications made in the conventional process were made in response to peculiarities of incoming wastes and are readily explainable in terms of the basic theory of the process. These modifications will be discussed in a later section.

The activated sludge process and its modifications may be defined as the contacting of preformed biological floc (activated sludge) with incoming waste in an aeration tank supplied with sufficient DO (dissolved oxygen) to maintain aerobic conditions throughout the process, followed by liquid-solids separation in a settling tank. To ensure an adequate supply of preformed floc with the desired adsorptive and settling characteristics needed to purify additional incoming wastewater in the continuous flow-through process, a certain proportion of the settled, separated sludge must be returned to the aeration tank. This returned portion is termed return activated sludge. Because the activated sludge is constantly increasing in quantity as it removes organic material from the wastewater, and as microorganisms continually grow, it is necessary to remove the excess quantity from the system. The sludge removed is termed waste activated sludge. The flow diagram (Figure 22-1) shows the different flows associated with the conventional activated sludge system.

To produce an acceptable effluent, activated sludge systems are designed to meet the following requirements:

1. An adequate number of active microorganisms is maintained in the system to completely assimilate the suspended, colloidal, and dissolved organic material in wastewater to form final end products of carbon dioxide, water, and inert materials.

2. The environment in the aeration tanks is acceptable to the active microorganisms. Of prime importance is the maintenance of sufficient DO, substrate, and nutrients in the aeration tanks. Substrate and nutrients supply the food and inorganic compounds, respectively, in the wastewater that are required for cell growth and energy.

3. The activated sludge separates readily from the treated wastewater in the final settling tanks.

It is thought that the activated sludge process takes place in two steps: the removal of organic materials from the wastewater by the sludge floc and the aerobic digestion of the materials so removed by the microorganisms in the floc.

The sludge floc is formed by mutual coagulation of bacteria with other suspended and colloidal materials. The floc gradually increases to a maximum size. The size depends on how much movement (shear) through the water the floc particle can stand without breaking apart. As the sludge floc moves through the aeration tank, it collides with the suspended and colloidal particles, which then stick to the floc. The sites for collision and sticking (a process called sorption, because it may be absorption, adsorption, or other surface phenomena) are soon occupied, and no more collisions accompanied by sticking may occur.

It is at this point that the role of the microorganisms present in and on the floc becomes truly appreciated. They not only formed the floc to begin with, but now use the materials sorbed to the floc for food and, in the process, reopen the sorptive sites, allowing more waste material to be trapped by the floc. The sorptive sites present on the sludge floc thus are regenerated continuously by the organisms living there. In fact, it is the sorptive power of activated sludge that makes the sludge activated.

This sorption, or, as it is commonly called, adsorption and/or absorption, occurs very quickly in activated sludge treatment processes, requiring only 15 to 30 min to be essentially complete. Reactivation of activated sludge by conversion of the sorbed waste to carbon dioxide, water, and more activated sludge requires a longer period of time.

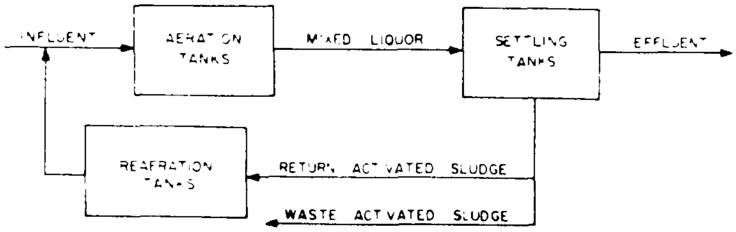


Figure 22-1 Sludge Reaeration Flow Diagram for a Conventional System

Reactivation of return activated sludge by reaeration in a separate aeration tank, without the presence of new incoming waste, is an efficient process. In the ordinary activated sludge plant, both sorption and conversion are accomplished in the same aeration tank and are taking place each in varying degree, throughout the aeration period.

As the sludge is returned from the final settling tank it is aerated in a separate tank before being added to the wastewater to be treated. Treatment occurs by sorption in the aeration tank, and reactivation occurs in the reaeration tanks.

The principal advantage of reaeration in a separate tank is that it increases sludge stability and the capacity of the activated sludge system to take shock loads and recover quickly. The ability of an activated sludge system to resist changes depends on the quantity and quality of sludge in the system. Reaeration in a separate tank frequently allows more solids to be retained in the system.

The aeration tank is the heart of the activated sludge process. Here, oxygen is introduced into the system to satisfy the requirements of the activated sludge organisms and to keep the activated sludge dispersed in the aeration liquor.

The tank is sized to provide enough detention time to accomplish the treatment required. Detention time usually varies from as low as 0.5 h to as high as 24 h depending on the treatment scheme used, the type of waste present, and the results required. The sizing of the tanks is an engineering design decision based on the best data available. The plant operation will use the process variables that can be controlled to make the best use of the system provided by the design engineer.

The oxygen supply available to the activated sludge system is limited by engineering design of the aeration equipment and its placement. Proper aeration or oxygen transfer capabilities are required to ensure good treatment. The plant operator may improve the operation of his plant by recognizing oxygen transfer limitations and bringing these limitations to the attention of those responsible for subsequent plant modifications.

Oxygen transfer to the activated sludge floc is usually accomplished by (a) oxygen absorbed from diffused bubbles of air entrained in the mixed liquor by subsurface injection and (b) mechanical or natural surface agitation in which oxygen is adsorbed from the air above the tank surface.

The rate of oxygen transfer for a given aeration system depends largely on the contact time between the bubble and the liquid, the size of the bubble, and the turbulence in the liquid. Good transfer efficiencies will result if the contact time is as long as possible, the bubble size is maintained as small as possible, and the turbulence is such that the bubble is held in the liquid as long as possible before reaching the surface.

The two most common types of aeration systems are subsurface diffusion and mechanical aeration.

In the diffused air system, compressed air is introduced at the bottom of the tank near one side. This causes the tank's contents to be circulated by the air-lift effect. Many different patterns of diffuser placement are being used. Systems that allow longer and more complete contact between the air and the liquid are preferred. Coarse bubble diffusion devices such as spargers or large-hole diffusers will produce larger bubbles than do porous plates, porous tubes, or synthetic socks. The larger bubble provide less surface area for air-liquid contact that will result in less oxygen transfer efficiency than that obtained with fine bubble diffusers. In many plants, however, the fine bubble diffusers cannot be kept from clogging, thus resulting in injection inefficiencies. Regardless of the air diffusion system, the operator's main responsibility is keeping the diffusers clean to ensure an even and adequate supply of air to the aeration tank.

There are several main types of mechanical aeration devices. The floating or fixed bridge aerators are quite common. Some use a blade to agitate the surface of the tank and disperse air bubbles into the aeration liquor. Others circulate the aeration liquor by an updraft or downdraft pump or turbine. This action produces surface and subsurface turbulence, at the same time diffusing air through the liquid mass.

Some plants use an oxidation ditch in which rotating brushes or blades are rotated partially submerged in the aeration liquor. The turbulence produced entrains the air bubbles and keeps the aeration liquor in motion.

Other systems use both compressed air and a mechanical device to entrain the bubbles. In one such system, air is ejected below a rotating turbine blade that shears and disperses the air. This is known as submerged turbine aeration.

More recently, the oxygen activated sludge process has gained in popularity. In these systems, high-purity oxygen is injected into aeration basins. Mixers disperse the oxygen. The high-efficiency of gas transfer resulting from oxygen use results in higher available concentrations of biological floc and shorter wastewater retention times.

The basic function of separating the newly formed activated sludge from the treated wastewater cannot be accomplished without proper operation of the final settling tank. The final settling tank follows the aeration tank in the treatment scheme.

It is good practice to operate final settling tanks with a sludge inventory as small as possible. Minimal sludge may be accomplished by removing solids at the same rate as they are applied. If solids output does not equal input, solids will accumulate in the final settling tank and eventually spill over the effluent weir. As a result, solids may become too heavy to be pumped or to flow by gravity, the sludge blanket may become anaerobic, and an increasing portion of the settling zone of the settling tank will become occupied by solids. The final settling tank is not intended to be a storage tank for solids. Its function is liquid-solid separation, solids concentration, and solids return. If it is desirable that solids are to be stored, such storage frequently is in the reaeration and/or aeration basins, in which the solids may best be used to maintain or improve high-quality treatment.

The most practical method of preventing solids accumulation in the final settling tank is to test frequently for the final settling tank solids level with an electrical, mechanical, or optical level sensing device. If solids are accumulating, the operator will recognize that the sludge withdrawal rate must be increased. Normal fluctuations in plant loadings will cause changes in the solids level, and only operating experience will provide the necessary background for altering the sludge withdrawal rate. Analytical methods of solids control will be discussed in a later section of this chapter.

The rate of solids settling in final settling tanks is usually expressed in gallons of aeration tank effluent applied to the settling tank per day per area of tank surface. This rate of application, often referred to as the surface overflow rate, is established during the design of the facility. The operator has little control over the total load to the unit and the resulting overflow rate. However, it is the operator's task to recognize the approach of excessive average surface overflow rates and suggest to management the need for extra capacity.

Even with surface overflow rates that are not excessive, a settling tank may operate poorly if velocity currents exist because of improper design, ineffective baffles, or poor weir adjustment. These deficiencies may be noticed by the operator and some can be corrected by him. Visual awareness by the operator will detect unequal weir overflow, improper velocity currents, and the resulting solids losses. Uneven weir height and liquid overflow may be corrected by weir adjustment or reconstruction.

Improper or poor performance of the final settling tanks makes the activated sludge system ineffective because the unsettlable solids converted to settlable biological solids in the aeration tank may be lost over the effluent weirs and discharged into the receiving stream.

The activated sludge system depends on groups of microorganisms, primarily bacteria and protozoa, feeding on the wastewater solids and soluble organic materials. The microorganisms, as every living creature, perform two basic functions: they keep themselves alive and reproduce when conditions permit. To perform these functions, and, by so doing, treat the wastewater, the environment in which the microorganisms live must be acceptable.

For effective treatment and to provide an acceptable environment for the microorganisms present in the system, the following variables must be managed effectively:

1. Adequate food;
2. Adequate oxygen;
3. Desirable wastewater temperature and,
4. Elimination of toxic wastes or wastes not readily utilized as food.

23. NITROGEN (AMMONIA) WASTEWATER CONTROLS

Ammonia in solution favors the absorption of hydrogen cyanide in the condensate. Thus, ammonia and hydrogen cyanide are likely to appear together in wastewater streams. Dissolved ammonia is either treated for removal or recovered for resale. Recovery facilities include the Phosam and Chevron processes.

In Phosam unit ammonia is stripped from the wastewater by using low pressure steam. Residual ammonia is about 150 ppm in wastewater. The Phosam unit operations are diagrammed in Figure 23-1.

The Chevron Waste Water Treatment (WWT) process (Figure 23–2) is capable of processing sour water to separate (1) high-purity hydrogen sulfide (99.9%), high-purity ammonia (99.9%), and clean water (99.9+%) or (2) pure sulfide and water, but a lower-quality ammonia for incineration; or the WWT process may be added to the existing foul-water treatment process for additional recovery. Ammonia can be recovered as anhydrous liquid or as 25% aqueous solution for fertilizer sales. The wastewater stream is fed to a degassing unit to remove dissolved hydrogen, methane, and other light compounds and to a surge tank to remove floating hydrocarbons by skimming. Hydrogen sulfide is then stripped and sent to a recovery plant. The ammonia is stripped from the water in a fractionator. Ammonia is about 98% pure when it leaves the condenser; after leaving the scrubbing system, where trace hydrogen sulfide and water is removed, the ammonia is of high purity (99.9%).

Practical technologies for removing ammonia from industrial wastewaters include biological synthesis, nitrification, ion exchange, air and steam stripping, and chlorination. Residual ammonia (amounts too low to allow recovery and fugitive emissions from the recovery unit) is usually sent to biological oxidation report 90% ammonia removal, 57% cyanide removal, and 17% thiocyanate removal, the latter being more resistant to biodegradation. Activated carbon can be used as a final water treatment following the biological oxidation to remove remaining trace contaminants.

Biological nitrification (oxidation to nitrites or nitrates) by an activated-sludge type process removed ammonia at concentrations as high as 500 mg/liter with 90% efficiency when using a single-stage system and 97% efficiency when using a two-stage system. In the two-stage system for industrial wastewaters, biochemical oxygen demand is reduced in a separate aeration basin-clarifier system, followed by nitrification in an aeration basin-clarifier system. If inhibitors of biodegradation are present or if effluent levels less than 5 mg/liter of ammonia-nitrogen are required, a two-stage system will probably be required. Limiting factors for nitrification are temperature (optimum, 28 to 32°C), shock loading, pH (7.8 to 8.3), dissolved oxygen (below 3.0 mg/liter for larger flocs), and toxicity of other compounds in the wastewater (heavy metals, cyanides, halogenated compounds, phenols, mercaptans, quinidines, and thiourea) to the organisms. The presence of even trace amounts of these toxic compounds may lower the nitrification rate. For consistent nitrification of higher-strength wastes, the activated sludge process is the most dependable.

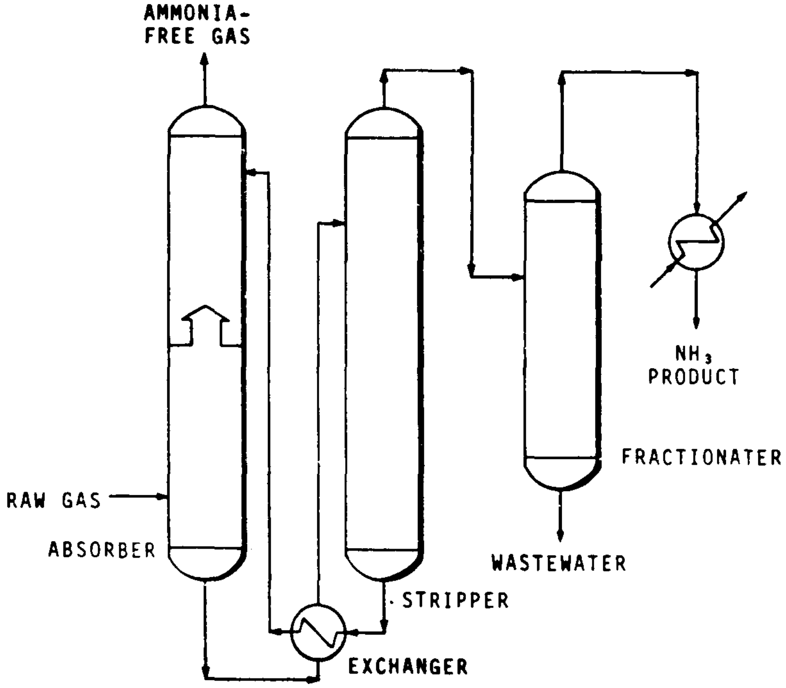


Figure 23-1 Phosam Process Unit Operations

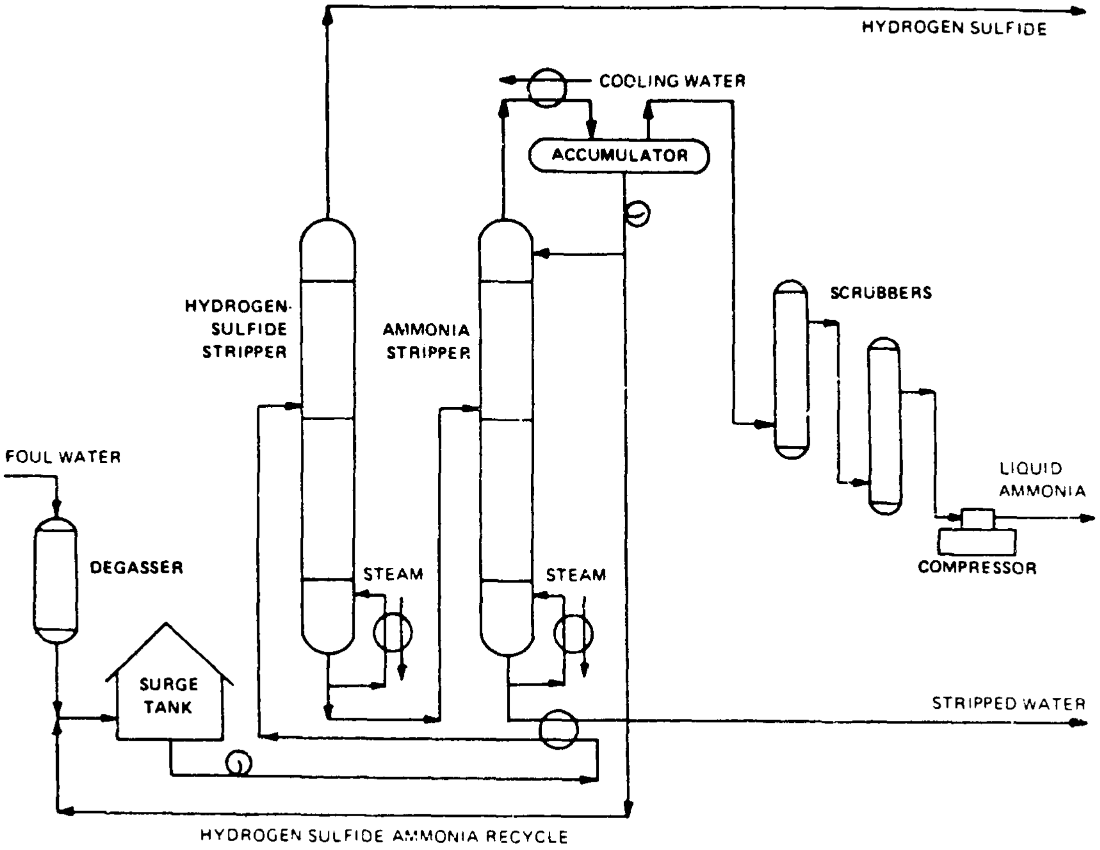


Figure 23-2 Chevron Waste Water Treatment Process - Hydrogen Sulfide and Recovery Process Flow Sheet

Laboratory and pilot plant studies of the biological treatment of concentrated ammonia wastewaters (725 mg/liter) from the manufacturer of ammonium nitrate and urea fertilizers show that the system should achieve about a 90% reduction of the ammonia-nitrogen and should produce an effluent having 75 mg/liter of ammonia-nitrogen, 75 mg/liter of nitrate-nitrogen, and 575 mg/liter nitrite-nitrogen.

Biological mechanisms are the most practical and dependable methods for removal of nitrate and nitrated compounds from industrial wastewaters where ion exchange is inapplicable. Assimilatory or dissimilatory mechanisms are involved in biological nitrate reduction. Nitrate-nitrogen is used as a nitrogen source by conversion to ammonia and is subsequently incorporated into the cell for assimilatory reduction. In nitrogen dissimilation, nitrate serves as the terminal hydrogen acceptor in place of molecular oxygen, producing nitrite, ammonia, nitrous oxide, or nitrogen gas, depending on the organisms and pH of the system. Denitrification systems include anaerobic activated sludge, anaerobic ponds, and upflow anaerobic filters. Methanol is the most economical external carbon source on the basis of cost and available carbon when required.

Biological nitrification-denitrification systems include two or three-stage sludge systems (Figures 23-3 and 23-4). Improved nitrogen removal may be accomplished by the three-stage system, but it involves increased capital investment.

Removal of the ammonia wastewater by ion exchange uses the strong, selective affinity of clinoptilolite, a natural zeolite, for the ammonium ion in solution. The clinoptilolite can be regenerated with sodium or calcium salts (sodium chloride, calcium chloride, or lime) at high pH, air-stripped to remove the ammonia, and recycled. Clinoptilolite use has been limited to low-strength municipal wastewater, and applicability to industrial wastewater is limited. However, synthetic ion exchange resins have been used for industrial wastewater treatment. At Farmers Chemical Association, Inc., Harrison, Tennessee, a cation resin was used to remove the ammonium ion, and an anion resin was used to remove the nitrate ion. Ion regenerants were nitric acid (cation) and aqua ammonia (anion), forming ammonium nitrate as the spent regenerant. Regenerant solutions were blended and concentrated by evaporation to produce a marketable by-product fertilizer. The presence of organic material may severely retard the effectiveness and useful life of the resins; thus, synthetic ion exchange is presently limited to wastewaters of primarily inorganic nature. Clinoptilolite columns containing 15 mg ammonia-nitrogen per liter of unclarified secondary effluent report 93 and 97% removal efficiencies, respectively.

Chlorination to convert ammonia in wastewaters produces monochloramine, trichloramine, and dichloramine. Disadvantages in using breakpoint chlorination include high cost, neutralization if hydrochloric acid is formed, and possible necessity for dechlorination. However, experiments have shown that chlorination followed by activated carbon treatment removed ammonia nitrogen at the 100% level, although some residual nitrate-nitrogen was formed. An advantage is the short detention time.

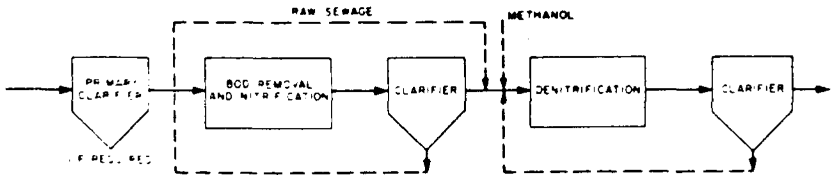


Figure 23-3 Two-stage Sludge System for Nitrogen Removal

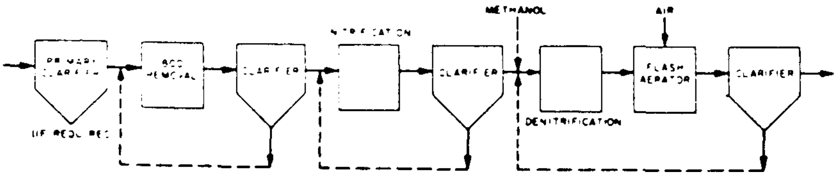


Figure 23-4 Three-stage Sludge System for Nitrogen Removal

C. SOLID WASTE DISPOSAL TECHNOLOGIES

24. HAZARDOUS SOLID WASTE DISPOSAL

Four burial schemes that provide a measure of protection against groundwater contamination from solid wastes are described below.

The first plan involves disposing of solid waste into an excavated pit. The walls and floor of the pit will be lined with compacted clay to prevent seepage into groundwater or infiltration of subsurface waters. Compacted fill (overburden material) will be placed from the bottom of the pit up to a point at least ten feet above the groundwater table. The solid waste will then be placed and the pit will be covered with the following combinatin of materials; four feet of overburden, two feet of compacted clay, four feet of overburden, and six inches of topsoil. The reclaimed area is then contoured and vegetated to blend with the natural features of the surrounding land. This plan is illustrated in Figure 24-1.

The second scheme (see Figure 24-2) is just a modification of the first in that the clay liner is placed only on the bottom of the pit and not on the side walls. This modification increases the capacity of the pit and reduces some expense. The covering and reclamation procedures are the same as the first plan.

The third plan involves discharge of solid waste into a below-grade impoundment consisting of individually constructed cells excavated to a depth of 40 to 50 feet below the existing ground surface.

The sides and bottom of each cell will be lined with a synthetic liner. Each cell will be surrounded by an above-grade dam (40' high) that will provide an evaporation pond for the any water entrained in the solid waste and prevent any surface runoff from flowing into the solid waste impoundment. During operations, waste will be deposited sufficiently below the natural grade to allow for the placing of 15 feet of overburden cover and topsoil over the cells without creating an above-ground mound. Following completion of reclamation, the cover over the cells will be contoured to the natural levels present prior to cell excavation. The use of several disposal cells provides for staged reclamation of the disposal area. This plan is diagrammed in Figure 24-3.

The fourth scheme involves use of a natural valley. The area is surrounded on three sides by the natural ridge slopes and a dam will be built on the lower fourth side. The floor of the basin will be lined with two feet of compacted clay which will be keyed into the clay core of the dam. After the solid waste is loaded, a three-foot covering of compacted clay, five feet of overburden, and one foot of topsoil will be put in place. The area will be contoured and revegetated with appropriate natural species. An important feature of this program is that final contouring will provide for sloping the area towards a concrete spillway located on the side of the area. This is designed to divert water runoff from topping the dam and thereby minimize water erosion of the downstream side of the dam over the long term. This scheme is shown in Figure 24-4.

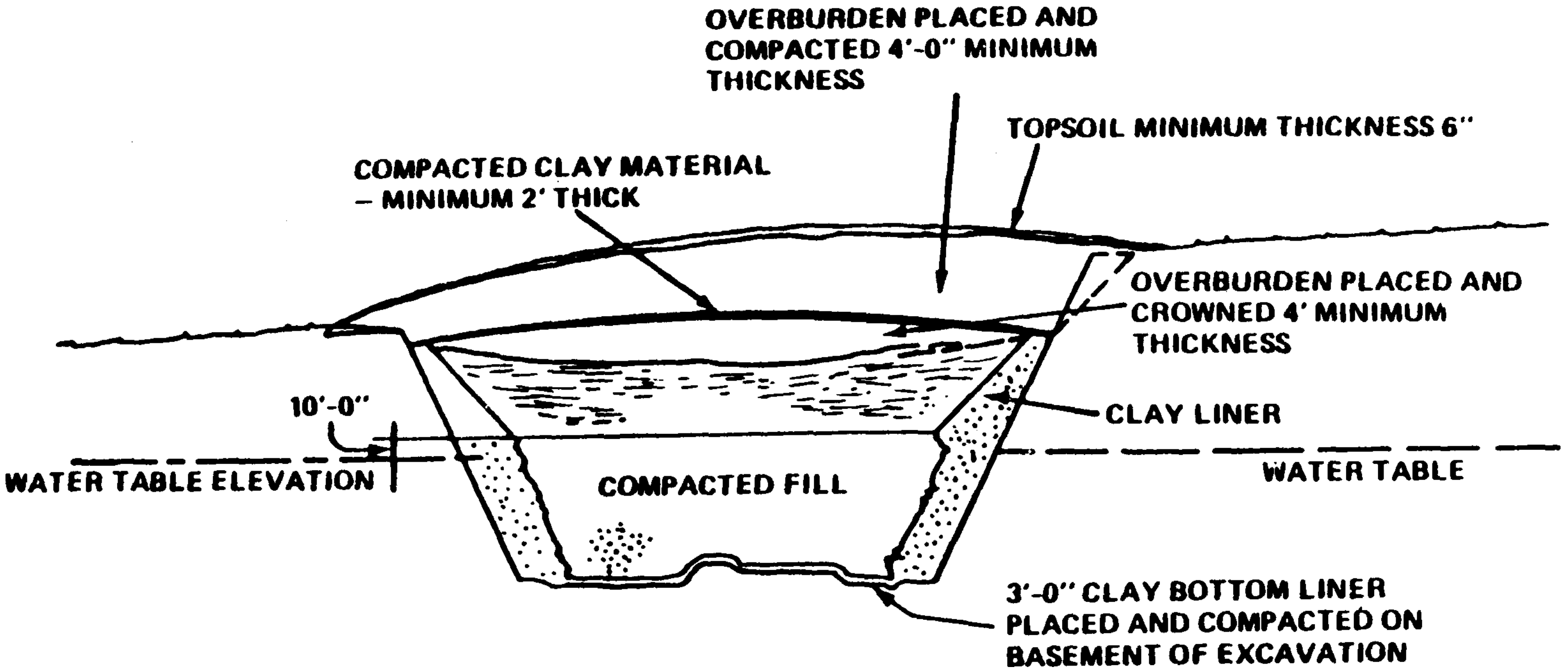


Figure 24-1 Clay-Lined Disposal Pit

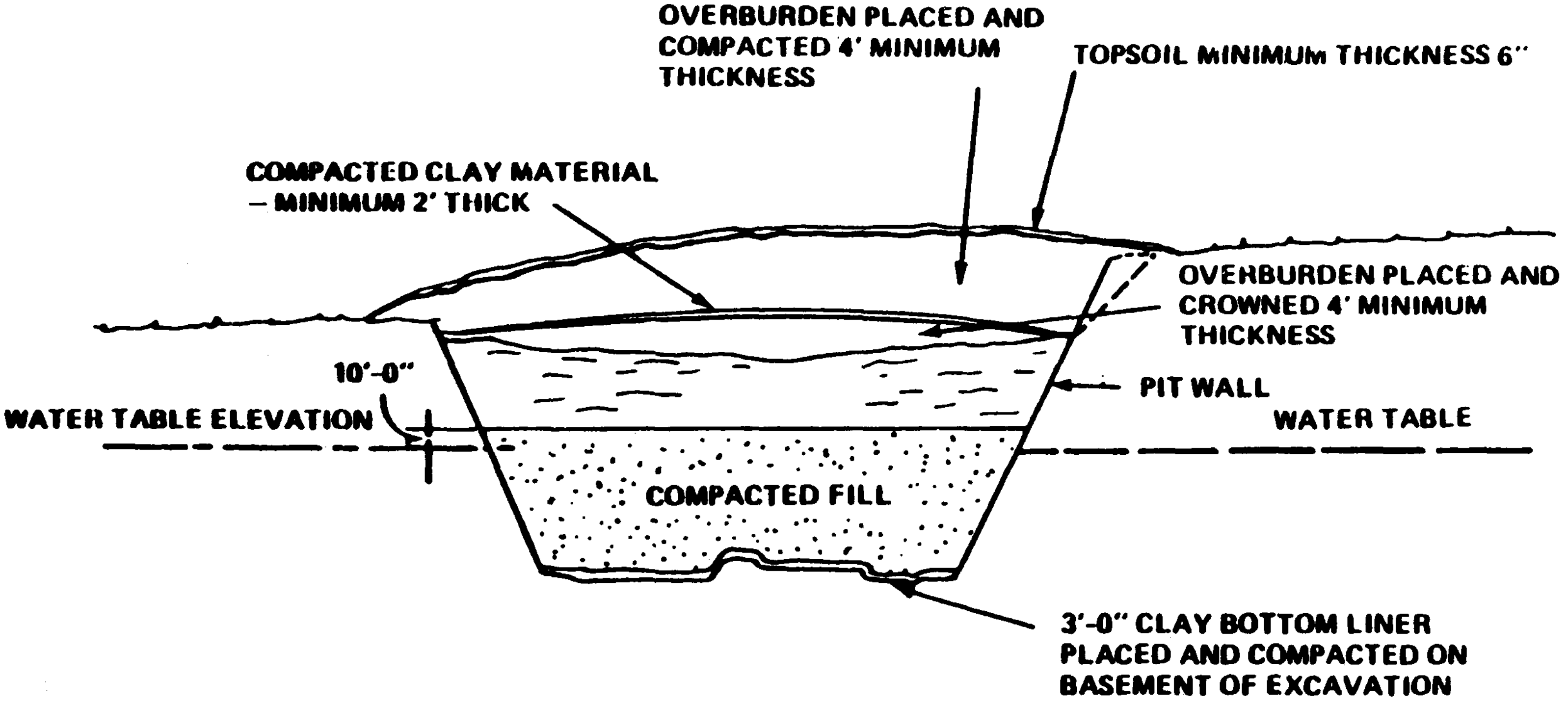
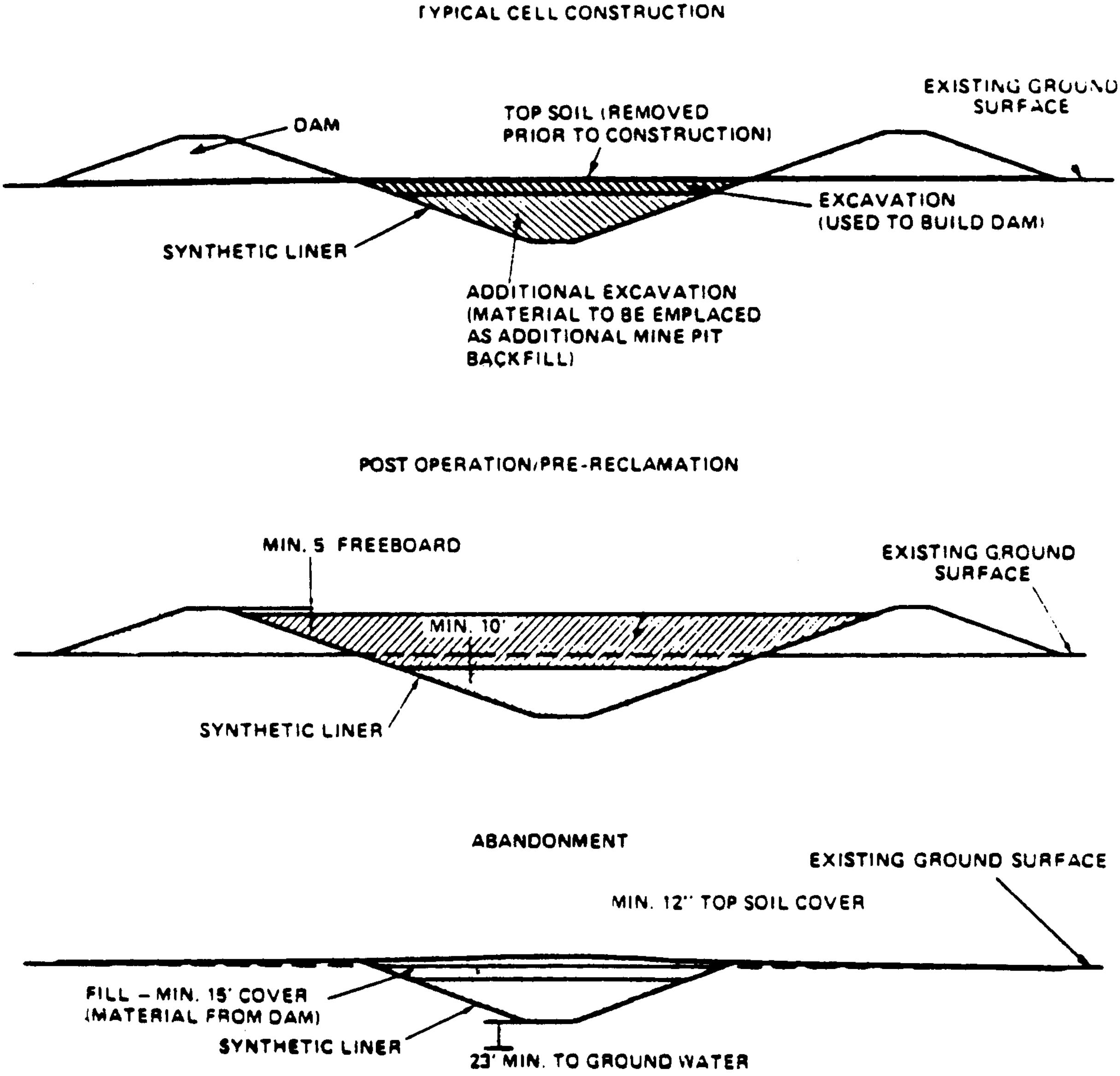


Figure 24-2 Modified Clay-Lined Disposal Pit



TYPICAL CELL CONSTRUCTION

POST OPERATION/PRE-RECLAMATION

ABANDONMENT

Figure 24-3 Below-Grade Disposal Cells

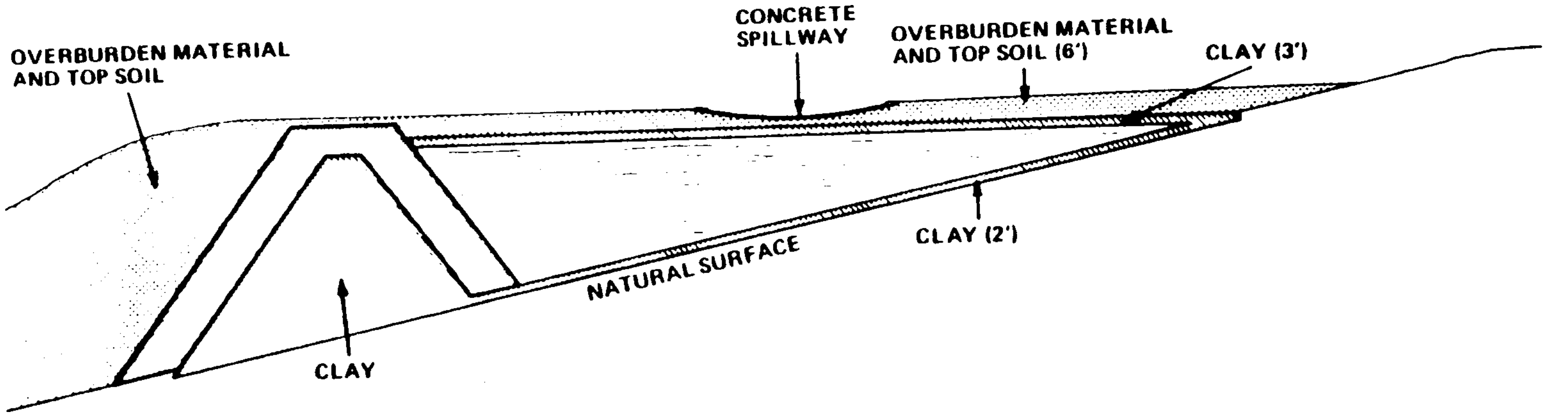


Figure 24-4 Valley Disposal Scheme

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