Oil/Water Separation

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Many industries discharge liquid wastes contaminated with hydrocarbon or oil-like pollutants. Sources of such waste include refining and processing petroleum and petrochemicals, metal fabricating waste, utility operations, sanitary sewage, bilge and ballast wastes, and contaminated surface runoff. The total quantity of such oil waste generated in the United States alone has been estimated in excess of one billion gallons per year.

Oil discharges into the environment typically have deleterious effects. Oily waste discharges may have objectionable odors and undesirable appearances. They may burn on the surface of receiving waters, creating potential safety hazards and consuming dissolved oxygen necessary to aquatic life. Oils in drinking water sources cause objectionable taste and odors, turbidity, and film, making filtration treatment difficult. Bioassay data indicate that oil is toxic to fish; in sub-acute levels, oil taints fish and shellfish taste. It also limits oxygen transfer, hindering biological activity. Floating puddles of oily waste entrap waterfowl, damage watercraft, and wash up on recreational beaches.

Federal, state, and some local regulations have established standards for the discharge of wastewaters containing oily residues. Standards vary from specific mg/l limits to qualitative standards requiring, for example, that the wastewater have no visible sheen.

Oil in Water

Oil can exist in water in several forms.

- **Free oil** rises quickly to the water surface when given a short quiescent settling period.
- **Mechanical dispersions** are distributions of fine oil droplets ranging in size from microns to fractions of a millimeter and having stability due to electrical charges and other forces, but not due to the presence of surface active materials.
- **Chemically stabilized emulsions** are distributions of oil droplets similar to mechanical dispersions, but which have additional stability due to chemical interactions typically caused by surface active agents present at the oil/water interface.
- **Dissolved oil** is either dissolved in a chemical sense, or dispersed in such fine droplets (typically less than 5 microns) that removal by normal physical means is impossible.
- **Oil that adheres to the surface of particulate materials,** is referred to as oil-wet solids.

The degree of an oil/water separation problem depends on the oil particulate size distribution. Separation problems also involve chemicals other than oil, which have an effect on treatment required. Oil spills, leaks, and points of contamination should be contained. If possible, oil-laden wastes should be treated in their most concentrated state —at their source. To limit the dispersion of entrained oil, centrifugal pumps and other equipment that have strong shearing forces should not be used. To limit chemical emulsification, wastes containing surface active agents should not be mixed with other oil-laden wastes.

Oily wastewater is similar in many respects to the treatment of domestic sewage. In domestic sewage treatment, a primary level of treatment is employed to separate the easily settleable solids from the wastewater. In the treatment of oily wastewaters, a primary treatment is used to separate the floatable free oils from the dispersed, emulsified, and soluble fractions. Primary treatment is also used to remove oil-wet solids. Common primary separation devices use sedimentation, flotation, and centrifugation related techniques. Secondary treatment is then used to break oil/water emulsions and to remove dispersed oil. Technology typically consists of chemical treatment and filter coalescence. Tertiary treatment includes ultrafiltration, biological treatment, and carbon adsorption.

Gravity Separation

Gravity separation, the primary and most common treatment, is based on the specific gravity difference between water and immiscible oil globules, and is used to move free oil to the surface of a water body for subsequent skimming and removal. The American Petroleum Institute (API) has specified design criteria for simple gravity separators based on the removal of free oil globules larger than 0.015 cm (150 microns) in diameter.

The effectiveness of a gravity separator depends on the proper hydraulic design and the period of wastewater detention for a given rise velocity. Longer retention times generally increase separation efficiency. Effective removal of oil droplets with a given rise velocity is a function of the system geometry. The liquid detention must be sufficient to permit oil droplets rising at a given velocity to come to the fluid boundary where they can be removed by skimming.

API Separator Criteria

API separator design criteria control the velocities within the unit by specifying that:

- The horizontal velocity through the separator may be up to 15 times the rise velocity of the critical (i.e., slowest rising) oil globule, up to a maximum of 3.0 feet per minute. Above this limit, the effect of turbulence tends to redistribute oil droplets.
- The depth of flow in the separator should be within 3.0 to 8.0 feet. This limits the height that must be traversed by a rising oil globule.
- The width of the separator should be between 6.0 and 20.0 feet.
- The depth-to-width ratio should be between 0.3 and 0.5.
- An oil retention baffle should be located no less than 12 inches downstream from a skimming device

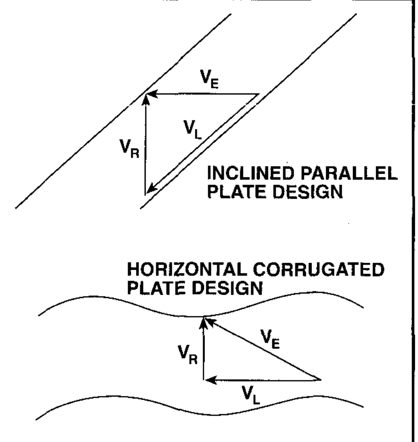


Figure 1: Gravity Separation Schemes

We use an ultrafiltration membrane to separate our oil/water emulsions. Every few days the membranes clog up and won't work well. Is there a simple cleaning method?

On a daily basis follow a simple two-step routine to maintain your membranes. Step 1—use liquid laundry detergent, mix 1 cup to 25 gallons of water and circulate through the system for 30 minutes. Step 2—dissolve 1 pound of citric acid in 25 gallons of water and circulate for 30 minutes (citric acid can be obtained from your local chemical supply house). The membranes are now clean and ready for continued use to separate oil/water emulsions. The detergent step cleans any residue oil from the membrane surface and pores. The citric acid gently dissolves any mineral scale that may have formed on the membrane.

How can I obtain water hardness and total dissolved solids numbers using my conductivity meter?

Calibrate Conductivity Meter:

A. Prepare a conductivity calibration solution by weighing out 74.264 grams reagent grade potassium chloride and dissolving in 1 liter of deionized water.
B. Make a 1:100 dilution of solution A with deionized water.
C. Immerse the conductivity electrode in solution B.
D. Adjust the CELL ADJ control to read 1.41.

Procedure:

1. Read and record conductivity of the city water.
2. Multiply conductivity reading by 500 to get total dissolved solids value.
3. Titrate same water and calculate total hardness in ppms.
4. Plot total hardness vs. conductivity.

Example:

Conductivity mS/cm x 500 = Total Dissolved Solids ppm

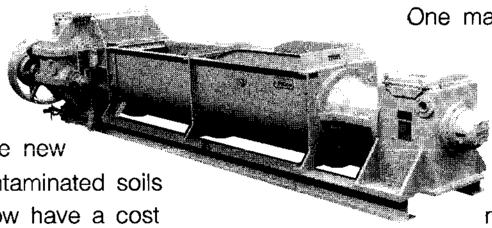
Conductivity in mS/cm	Total Dissolved Solids (ppm)	Total Hardness (ppm)
0.188	94	75
0.250	125	100
0.376	188	150
0.500	250	200
0.688	344	275
0.750	375	300
0.876	438	350

Once plotted, conductivity reading can give you total hardness.

We must often dump our chrome plating bath due to excess sulfates. Is there a way to remove the sulfates without hurting the bath?

To lower the concentration of sulfate by 0.05 g/L of sulfuric acid, add 0.01 g/L of barium-carbonate. This will precipitate the sulfate as barium sulfate which may be removed by filtration. ❑

For more information on this department, circle 179 on card.



Gravity separation often includes a provision for heating to lower the viscosity and extended plate surfaces (to decrease the effective rise height that must be traversed by a rising oil globule). This latter effect is illustrated in Figure 1. Common separator designs using a gravity differential as the primary force include those based on the above described API design criteria, CPI (corrugated plate interceptor) and PPI (parallel plate interceptor) units. Careful handling of flows in a gravity separator by these methods often permits separation of oil droplets finer than those of free oil.

Flotation Devices

Flotation devices use the gravity separation concept and are more effective than sedimentation devices in removing dispersed oil because the buoyancy differential is increased by attaching small air bubbles to the slow rising oil globules. One use of air flotation equipment is in the treatment of oil-wet solid laden wastes. Coagulant aids, such as polyelectrolytes, are commonly used to promote agglomeration of the oil-bearing matter into large flocs that are more easily removed. Air flotation devices are usually preceded by one of the gravity separation techniques described above to remove gross quantities of free oil and settleable solids. This reduces the required volume of dissolved air and flocculating chemicals to economical levels.

Two methods are commercially used to form the minute air bubbles. One involves aerating the waste to saturate it with air at atmospheric pressure, releasing the excess air, and then forming the small bubbles by applying a vacuum of approximately 9 inches of mercury. In the other method, air is dissolved into the waste under two to three atmospheres of pressure before the pressure is released, forming the minute bubbles. The latter method is more common in the treatment of oily wastes. There are three variations of this latter method, full-flow, split-flow, and recycle operation.

In full-flow operation, shown in Figure 2, the entire waste stream is saturated under pressure, followed by the subsequent release of pressure and bubble formation at the inlet to the flotation chamber. This scheme offers several advantages.

- It provides maximum gas solution at any particular pressure, thereby achieving maximum bubble formation and bubble contact.
- For equal flow rates, a small flotation chamber is required.

However, this orientation requires a pressurizing pump large enough to handle the full waste flow, and the raw waste, which may be loaded with solids, must pass through the pressurizer.

Split-flow operation, shown in Figure 3, consists of pressurizing and dissolving air in only part of the waste flow and diverting the remainder directly into the flotation chamber, where it is mixed with the pressurized fraction. Split-flow operation uses a smaller pressurizing pump than full-flow operation, reduces the amount of emulsion that might be formed by the pressurizing pump, and relies on a small flotation chamber.

Recycle operation, depicted in Figure 4, consists of pressurizing and dissolving the air recycle stream of clarified effluent. The pressure is released and the bubble-containing recycle stream is mixed with the wastewater influent flow. The recycled stream usually is 20 to 50 percent of the influent flow. This system uses the smallest pressurizing pump and operates the pressurization at a constant flow rate. It minimizes emulsion formation and plug problems by pressurizing clear effluent. In systems incorporating flocculation, it tends to disintegrate the floc by the shearing action of the pressurization pump.

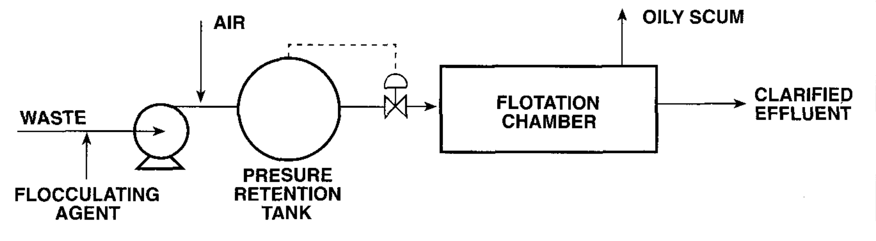


Figure 2: Full-Flow Air Flotation

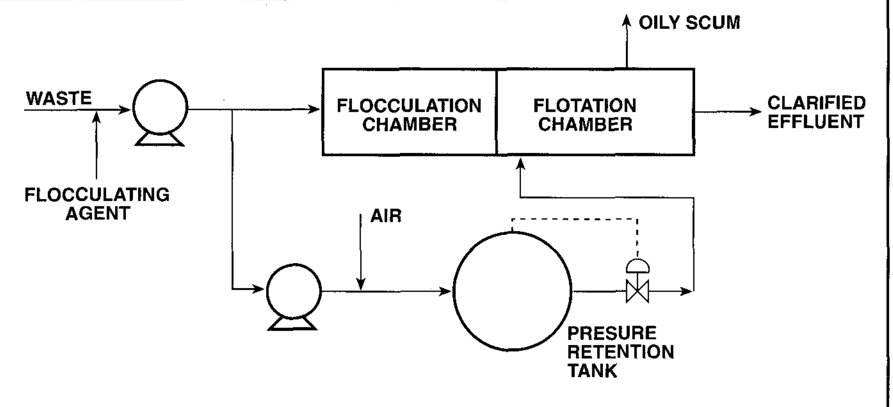


Figure 3: Split-Flow Air Flotation

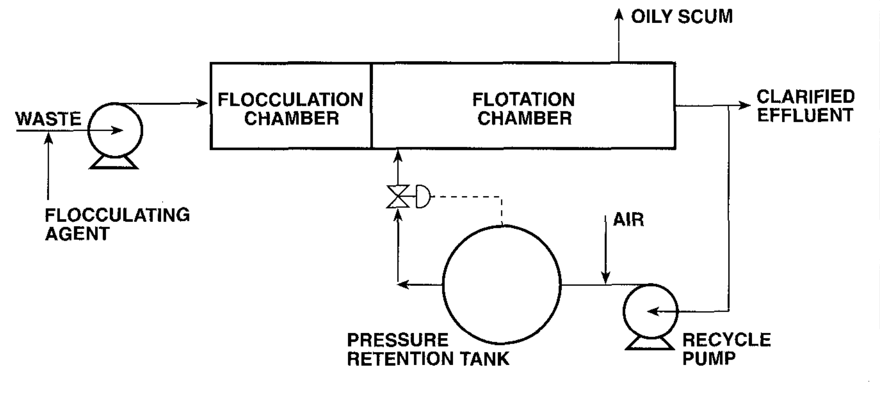


Figure 4: Recycle-Flow Air Flotation

Centrifugal Separators

In this technique, the more dense water phase is moved to the outer region rotating volume of fluid. The lighter oily materials collect near the vortex and are subsequently removed. This requires that the oil-collecting mechanism must be designed to remove a small column of oil at the center line if it is to be effective in oil-in-water emulsions. The maximum benefit of centrifugal forces is realized at the outer radial regions, apart from the small column of separated oil. For these reasons, centrifugal separators have found limited use in the treatment of oil-in-water emulsions, but have found widespread use in the treatment of water-in-oil emulsions. A modification of the basic centrifuge, which incorporates parallel plates to provide laminar flow regions, has been found effective in treating dispersed oil. Effluent qualities averaging 50 to 70 parts per million (ppm) of oil are reported.

Emulsification

Processes used to break oil/water emulsions include chemical, electrical, and physical methods. Chemical methods are in widest use. The electrical process is directed toward emulsions containing mainly oil, with small quantities of water. Physical emulsion breaking methods include heating, high speed centrifugation, and precoat filtration. Chemical treatment of an emulsion destabilizes the dispersed oil droplets or chemically binds or destroys any emulsifying agents present. Chemical demulsifying processes include acidification, coagulation, salting out, and demulgation with organic cleaving agents.

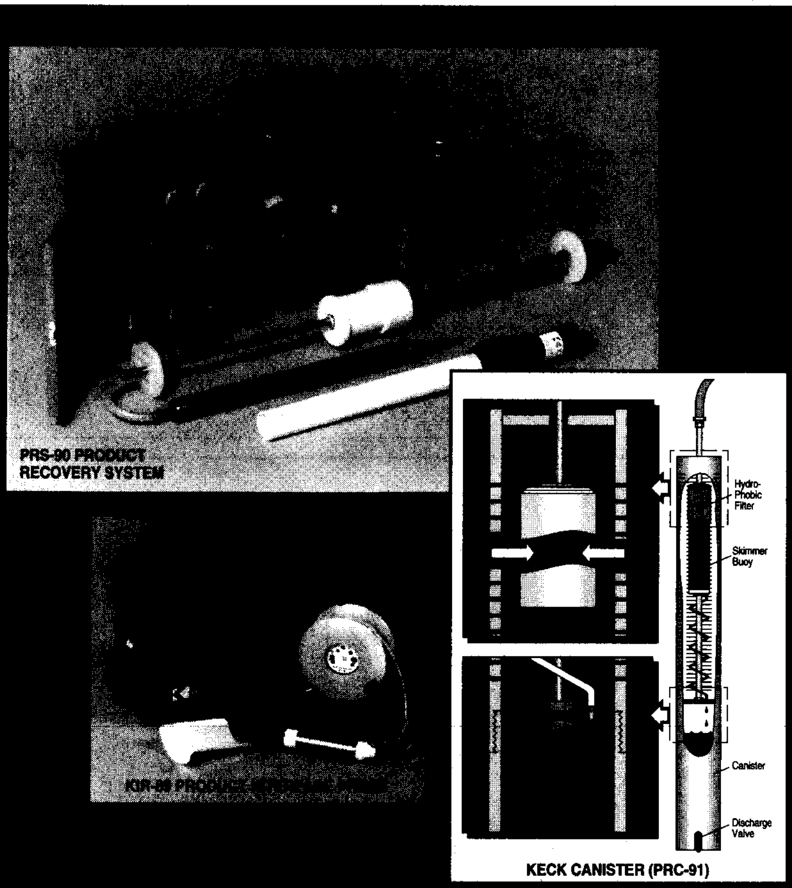
Acids generally cleave emulsions more effectively than coagulant salts, but are more expensive and the resultant wastewater must be neutralized after the separation. Salting out of an emulsifier is achieved by adding large quantities of an inorganic salt, thereby increasing the dissolved solids content of the water phase. Coagulation with aluminum or iron salts is generally effective, and is in common use even though the resultant hydroxide sludges are difficult to dewater, and limit the reusability of the recovered oil.

Organic demulgators are extremely effective demulsifying agents, but are generally very expensive and specialized. Two modes of operation include adding a specific chemical agent with sufficient properties to neutralize any other charges that inhibit coalescence, or chemically reacting with and/or breaking down the specific chemical species causing the emulsification. Chemical demulgators are normally considered only if effective in low concentrations, due to their cost, and in many cases, their toxicity at higher concentrations. Demulsification is normally followed by sedimentation or flotation for removal of the destabilized oil.

Breaking the emulsion into separate surface active properties tends to alter the surface wetting properties of the coalescing fibers, which usually lends to "poisoning" of the media. In addition, the effectiveness of the system depends, among other things, on the mechanical forces of the influent passing through the filter. If the volume and/or force of the pumping is too great, the oil droplets tend to be prematurely carried into the mainstream flow, and are insufficient in size to gravity-separate from the effluent. Despite these drawbacks, filter coalescers are quite effective. The effluent quality achievable with such devices is in the range of 1 to 50 ppm oil depending on the surfactant content, loading condition, and oil type.

Coalescing media used for oil separation vary in the materials used and the effective pore size. In some coalescing media, a fibrous material such as nylon or propylene is wound about a rigid spool to form a cartridge. The tighness of the wrap and the fiber diameter largely control the effective porosity for these devices. Other coalescing media incorporate the use of tightly woven or tightly wrapped sheets of fiberglass. Since coalescing media does tend to plug with particulates, less costly pleated-paper type elements are often used as coalescing media or as prefiltration media.

Reticulated polyurethane foams have come into use as coalescing media.



These foams are natural sorbents, are light in weight, are relatively inexpensive, and can be molded in such a manner as to readily control effective pore size. In most cases, the separators incorporating coalescence are designed for the replacement of the media once it is poisoned, plugs, or otherwise fails.

The geometry and orientation of coalescing elements in separator devices varies from one design to another. Most manufacturers use long, relatively small-diameter cartridges of a standard size, and stack these in parallel to handle the required throughput. Several stages of these groupings operating in series are often used to achieve a greater degree of removal and to act as a built-in backup. The media is normally installed vertically or horizontally, depending upon the design. Horizontal orientation normally decreases the effective oil droplet rise height. However, this design is normally more difficult and time consuming to service since the entire vessel must be completely drained before opening.

Biotechnology

The treatment of dissolved oils and other types of chemically stabilized emulsions that cannot be destabilized by chemical additions can pose serious problems. Biological treatment with acclimated microorganisms is generally effective in degrading much of this material, and is commonly used in petroleum refineries and rendering plants. However, the systems are only effective if suitable pretreatment and high dilution can be achieved. Too much oil is a problem in biological systems because it is adsorbed by the microorganisms faster than it can be metabolized.

In trickling filters, oil tends to coat the microbial surfaces and reduce the transfer of more readily oxidizable organics. In activated sludge systems, the adsorbed oil tends to impair sludge settling charttacteristics. Resulting sludge losses may be so high as to reduce the microbial level in the system enough to cause reduced efficiency and possible system failure.

The microbial metabolism of oil is limited by the low solubility of oil, the chemical configuration of oil molecules, and the microbial surfaces. Trickling filters can treat oil concentrations of up to 100 ppm with no effect. Activated sludge systems show no effect if the oil concentration is kept less than 25 ppm. Biologically treated effluents typically contain less than 10 ppm of oil.

Selection of the optimum biological waste treatment process for a particular waste is complex. Many factors are involved, including economics, land availability, and effluent quality required. Bench-scale testing is also useful in determining the toxic limit of the oily contaminant. It should be realized, however, that the oxygen transfer rates and the sludge separation/return efficiencies in pilot systems are higher than the rates in a full-scale system and must be compensated for in scale-up.

Carbon Adsorption

Carbon adsorption has been used extensively as a means of removing trace quantities of oil. Treatment requires a suitable means of regenerating the carbon. Methods that have been addressed include steam, hot water, organic solvents, and pyrolysis. Treatment by carbon adsorption also generally requires a large capital investment for carbon inventory and regeneration equipment and has, therefore, not found widespread use in oil separation where high concentrations are involved.

Ultrafiltration

Ultrafiltration is based on the sieving

action of a polymeric membrane controlling the flow of molecules larger than the membrane pores. Applied pressure is used to increase the flux of the liquid across the membrane. The membranes tend to foul with particulates and the flux therefore decreases. The fouling is normally removed by back flushing and/or detergent washing. Reverse osmosis is similar to ultrafiltration in that an applied pressure forces the water through the membrane against a concentration gradient, while oil is retained due to the small size of the membrane pores. However, in reverse osmosis, the pore sizes are smaller and the applied pressures are significantly higher. These treatments can be used to produce essentially oil-free effluents, but require large capital investment and have high operating costs.

In selecting the appropriate separator equipment, the specifics of the oily waste problem should be carefully studied. The characteristics of the oily water mixture should be determined after all reasonable water management techniques have been instituted. Typical characteristics that should be determined include the oil and bulk fluid densities, the oil rise velocity, the oil droplet size distribution, the presence of emulsifying agents, and the suspended solids content and distribution. Every effort should be made to treat the waste in its most concentrated form and to prevent contamination with particulates and chemical emulsifiers. Low shear positive displacement pumps should be used to prevent shear of the fluid. If the oil is present in quantities greater than roughly 1 percent, gravity separation or similar methods should be used to achieve bulk separation. If chemical emulsions are present, they should be treated before contacting coalescer media. De-emulsifying agents should be evaluated by jar testing. Prefiltration should be used to increase coalescer life when applicable.

It may be necessary to install a separation system for a specific separation problem. In such cases, the available off-the-shelf components can be added together in series to meet the requirements of the specific situation. A separation system may well consist of gravity separation, emulsion breaking, flocculation assisted air flotation, prefiltration, and filter-coalescence. ❑