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**PRETREATMENT OF INDUSTRIAL WASTEWATER
FOR VOC (HYDROCARBON) REMOVAL**

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INTRODUCTION

Hydrocarbons in industrial wastewater can be troublesome both to sanitary sewer plants and to the industrial facility originating the wastewater. Some hydrocarbons are volatile and would contribute to VOC emissions from a sanitary sewer plant. In addition to being a VOC problem, too much hydrocarbon content in the incoming water would be detrimental to the health of the microbes in the sanitary plant.

The basic law covering discharges is the Clean Water Act. It was originally enacted as the Federal Water Pollution Control Act of 1972, but was amended extensively in 1977. The 1977 amendments, in conjunction with the earlier legislation, became known as the Clean Water Act. Under the terms of this Act, amended Section 402 created the National Pollutant Discharge Elimination System (NPDES) permit system. Permits for point sources including sanitary sewer plants under this system are granted by the Environmental Protection Agency (EPA) or by states with EPA approved programs. When the choice exists of either discharging wastewater effluent into a lake or stream, or to the sanitary sewer, the best choice is often the sanitary sewer. This is the method of choice because the treatment required is simpler and the requirements usually less stringent. The regulatory permit requirements are taken care of by the sanitary sewer plant and less time and expense is required to satisfy the sanitary requirements than the EPA's NPDES requirements. Sanitary sewer authorities usually require some pretreatment to preclude the possibility of large amounts of oil entering the sewer systems. Many systems for pretreatment exist and many of the most common are discussed below.

Often, the choice of pretreatment methods is dictated by the requirements of regulatory agencies. In the case of the oil reclaiming company discussed below, the necessity for low VOC emissions at the local sanitary sewer plant caused a requirement for less than 2 mg/l effluent from the reclaiming plant that mandated the use of absorbents. In one installation in Ontario, Canada, it was required that the effluent from a groundwater remediation facility be treated to drinking water standards before being discharged to a sanitary sewer plant.

HYDROCARBONS IN WATER

The hydrocarbons present in industrial wastewater can exist in one or more of several conditions. These are shown below, arranged generally in order of difficulty of removal:

- Free oil - large droplets or sheets that rise freely to the surface. This oil is easily

removed in simple gravity separators.

- Mechanically dispersed oil - fine droplets ranging from a few microns up to a few millimeters. The oil found in droplets is usually the result of some mechanical mixing of oil and water such as is found in pumping or in turbulent flow through a pipe. The oil droplets can be found in a "bell curve" of droplet sizes with some small, some large and a predominance of average size droplets. The average size will vary dependent on the amount of mixing the two liquids have undergone as well as the presence or absence of emulsion causing surfactant chemicals such as soaps or detergents. These dispersions may be removed by the use of an enhanced gravity or coalescing cartridge system.
- Chemically stabilized emulsions - droplet dispersions similar to mechanically dispersed oil, but with droplets stabilized by surface-active agents (surfactants). More surfactants or more mixing will cause a smaller average droplet size. The average droplet size is important because many separation devices are designed to capture droplets by gravity or enhanced gravity separation and if the average droplet size is smaller, the separator will have to be larger and consequently more expensive. Coalescing cartridges which rely on surface properties of the media will not be effective in removing these dispersions. Coalescing plates may be used if allowance for the very small droplet size is made.
- Oil adhering to solid particles. Can be removed by filtration or by enhanced gravity separation if the combined specific gravity is different from the water.
- Dissolved oil - either truly dissolved oil or finely dispersed droplets so small (less than 5 microns) that removal by normal physical means is impossible. The aromatic hydrocarbon Benzene has the unfortunate combination of a large solubility (about 1500 mg/l) and carcinogenic properties. Some other hydrocarbons are partially soluble as well. Dissolved oil must be removed by biological treatment, absorbents, distillation, or other non-gravity means.

REQUIREMENTS AND ANALYSIS

The requirements for pretreatment may in certain instances be very stringent, but usually range from 50 mg/l of oil to about 150 mg/l. Because most of the pretreatment devices are physical in nature and do not remove dissolved oil the analytical method of choice for determining effluent oil content is EPA Method 1660. This is an infrared spectrophotometric method and most environmental laboratories are equipped to run this analysis.

Many engineers and environmental personnel will refer to concentrations in parts per million (ppm) which is a volume measurement, but most analytical results are reported in milligrams / liter which is in effect a weight measurement. There is very little difference at low concentrations, but at higher concentrations the differential specific gravity may cause the mg/l to be substantially less than the ppm. The difference is due

to the specific gravity of the oil. The following equation shows the calculation for conversion:

$$\text{mg/l} = \text{ppm} \times (\text{sg of oil} / \text{sg of water})$$

Examples:

For oil of 0.85 specific gravity:

ppm = 10	mg/l = 8.5
ppm = 10000 (1% by volume)	mg/l = 850

SURFACTANTS:

Surfactants – a word contracted from surface active agents – are a class of chemicals that includes soaps and detergents. These chemicals, while very useful in plants, are very detrimental to the operations of most oil removal pretreatment systems.

Surfactants are designed to break up oil into very small droplets that will stay suspended in water and will not coalesce back into larger volumes of oil. This is the method by which soaps clean clothing – they take the skin oils off and keep them suspended in the water as it is drained.

Surfactants can be thought of as double-ended molecules where one end is soluble in the oil and the other end in water. As they encounter oil droplets, they coat the surface of the droplets (hence the term surface acting), preventing coalescence with other droplets.

Some surfactants are referred to as “quick break” detergents. These consist of molecules where the bond between the two ends of the molecules is relatively weak. This bond breaks after only a relatively short time in the water, so the detergent effect works to remove the oil from metal parts or clothing and then the molecule breaks and the oil is released so that it may be removed by a separator. While surfactants in general are not recommended, this type of surfactant is the least damaging to separator performance.

METHODS OF PRETREATMENT

Numerous methods are available to reduce the hydrocarbon content of wastewater. Some of the more common methods are discussed below. These are:

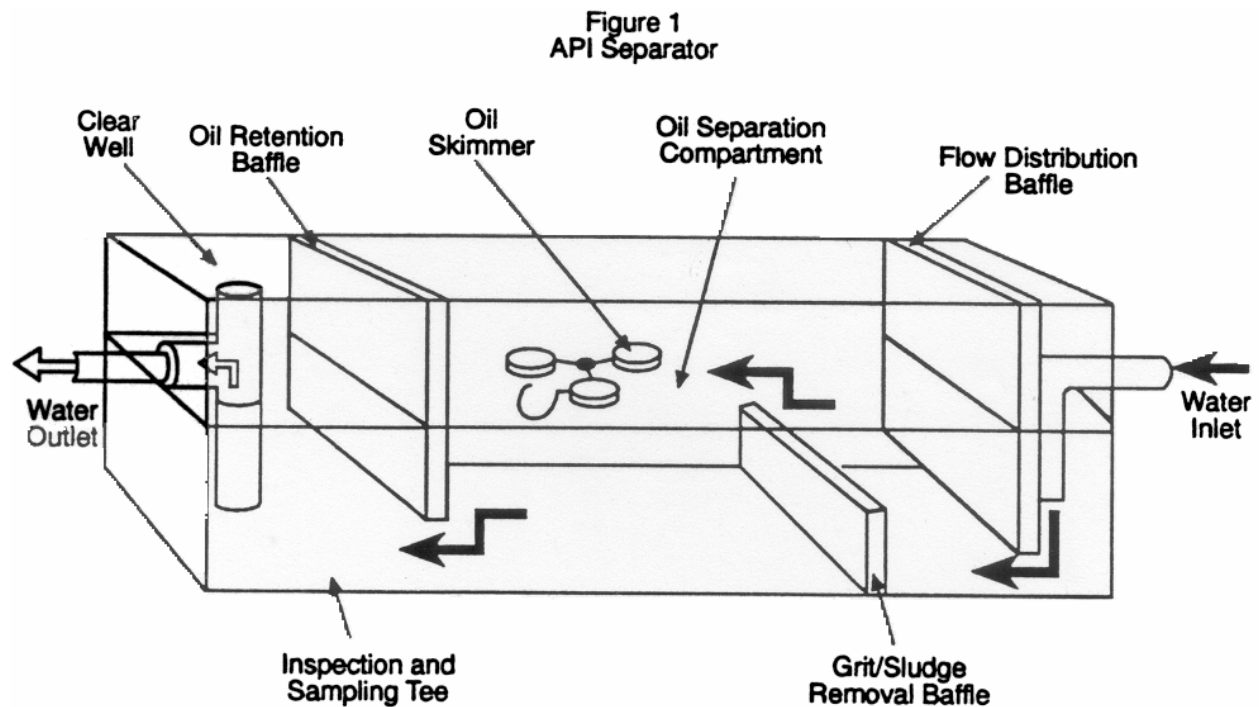
- API Separators
- Chemical flocculation
- Dissolved Air Flotation (DAF) and Induced Air Flotation (IAF)
- Coalescing Cartridge type separators
- Coalescing Plate Separators

API Separators

API (American Petroleum Institute) design separators may be used as pretreatment systems in situations where a large amount of oil may be expected to be present in the waste stream and it is desired to recover the oil as is particularly the case in systems treating the wastewater from petroleum refineries. API separators are designed to remove 150 micron and larger droplets and can generate effluent concentrations of oil down to about 150 mg/l (API, 1990). The API recommends a residence time in the separator of 45 minutes or more.

Since it is generally accepted that a sheen will form on the surface of the water if oil concentrations are more than 15 mg/l, and oil sheen is not acceptable under the conditions of the Clean Water Act, these separators are generally not acceptable as final treatment systems.

In a survey done by the API in 1985 (API, 1990), fewer than half of the separators were generating effluent qualities less than 100 mg/l and approximately one third were more than 200 mg/l. Please see Figure 1 below for a schematic of a typical API separator.



Chemical Flocculation

Chemical flocculation may be used to agglomerate small oil droplets into larger ones that may be removed by flotation. Disadvantages of flocculation are the cost of flocculent chemicals and difficulties in removing any excess chemicals. The largest disadvantage is the substantial amount of additional sludge produced, which since it

contains hydrocarbons may be a hazardous waste. Advantages are the low levels of hydrocarbons in the effluent water that may be attained by their use.

Dissolved Air Flotation (DAF) and Induced Air Flotation (IAF)

DAF or IAF are often used for removal of very small hydrocarbon droplets that cannot be removed by API separators. DAF designs require that compressed air be dissolved in the wastewater under pressure. When the pressure is released, very small air bubbles attach to the hydrocarbon droplets and lift them to the surface of the separator. The resulting foam or "float" is removed by a surface scraper and processed separately for recovery of the hydrocarbons. Alum or other chemicals are often used as well. Advantages of this system include effective removal of the hydrocarbons, even when present as very small droplets. Disadvantages are system cost, operating cost for compressor utilities, chemical cost, and maintenance costs for the compressors and piping systems.

Induced air floatation is similar to DAF except that the air is not actually dissolved in the water, but rather introduced in such a manner that small bubbles are produced, generating a "float" similar to that produced by DAF systems. DAF and IAF systems are considered to have high operating and maintenance costs due to air compression requirements.

Coalescing Cartridge Type Separators

Coalescing cartridges are often used as the second stage of a separator after a first stage of coalescing plates, although they are sometimes used as a primary coalescer. Coalescing cartridges are capable of producing effluent quality of 10 mg/l or less, and are suitable for use in systems where little or no solids are present. Disadvantages are plugging with solids, becoming disarmed or poisoned (becoming disabled) due to surfactants in the water stream, and expense of replacement. Generally, coalescer cartridges that have become disarmed due to surfactants must be replaced, as their efficiency cannot be recovered.

Coalescing Plate Separators

Coalescing plate separators were designed to overcome some of the disadvantages of API separators and provide separation of hydrocarbons from water streams in more compact and efficient systems. API separators are designed to remove 150 micron and larger droplets, and have effluent quality in the range of 150 mg/l, whereas coalescing plate separators may be designed to remove droplets down to 20 microns or less with effluent qualities down to 10 mg/l or less. Since oil is often present in a spectrum of small droplet sizes, the value of these separators may readily be seen as they produce relatively pure oil and do not require the use of absorbents which become waste when used.

Coalescing plate separators have the additional advantage in that the plates are not

consumables like absorbents or coalescing cartridges and will last indefinitely.

Rough estimates of API type separator sizes:

In most industrial systems, the majority of the oil will be present as either free oil or mechanical dispersions of oil. These may be treated readily by enhanced gravity systems for removal of the hydrocarbons.

Most hydrocarbon removal systems depend on gravity or enhanced gravity separation, taking advantage of the buoyancy of the droplets.

The rising of hydrocarbon droplets in a separator is governed by Stokes's Law. This function, simply stated is shown in the following equation:

$$V_p = \frac{G}{(18 * \mu)} * (d_p - d_c) * D^2$$

Where: V_p = droplet settling velocity, cm/sec
 G = gravitational constant, 980 cm/sec²
 μ = absolute viscosity of continuous fluid(water), poise
 d_p = density of particle (droplet), gm/cm³
 d_c = density of continuous fluid, gm/cm³
 D = diameter of particle, cm

From the above it may be seen that the important variables are the viscosity of the water, the difference in specific gravity of the water and hydrocarbons, and the hydrocarbon droplet size. After these are known, the droplet rise velocity and therefore the size of separator that is required may be calculated. Stokes's Law is only valid for spherical particles or droplets and only in a laminar flow range. Laminar flow may be defined using several different Reynolds numbers, but a Reynolds Number of 500 or less is generally considered to indicate laminar flow.

Please note that because the oil present in the inlet of a separator is usually in the form of a spectrum of droplets, the following size estimate method should only be used for the roughest of estimates.

Example:

Calculate the size of a simple API gravity separator to remove oil from 100 US gpm of water, assuming a separator 36 inches wide by 36 inches in depth – length to be determined.

1. Calculate the rise rate of oil droplets with the following characteristics:

Oil droplet size: 100 micrometers (microns)
Oil Specific Gravity: 0.9 (similar to light lubricating oil in density)
Flowing Water Temperature: 55 degrees F

Note: Some typical viscosity data is provided in the table below. Data at other temperatures is available from various references.

Temperature, degrees F.	Water Viscosity, Poise
40	0.0155
45	0.0143
50	0.0132
55	0.0122
60	0.0113
65	0.0106
70	0.0099

The specific gravity of fresh water at normal plant operating temperatures is very close to one. If higher temperatures or water containing salts that would change the specific gravity are expected, the specific gravity should be measured or calculated and the correct value used in the equation.

Inserting the above data into the Stokes's Law equation, the velocity found is -0.045 cm/second or -2.68 cm/minute. The negative velocities indicate the droplet is moving up (the original work Stokes did was on solid particles falling in water).

Converting this rate to English units, the velocity of these droplets is 1.05 inches / minute.

2. Estimate the length of the separator required.

The droplets will rise according to Stokes's law at the rise rate calculated above. The droplets path will be the sum of the vectors of movement – forward because of the flow of the water and upward because of the rising of the droplets. It is therefore necessary to provide a separator large enough so that the droplets will rise to the surface before the water exits the far end of the separator.

If the droplets rise at a velocity of 1.05 inches / minute and the separator is 36 inches deep, the residence time within the separator must then be 36 inches divided by 1.05 inches per minute or 34 minutes.

The cross sectional area of the separator is 36" by 36" or a total of 9 square feet. The flow rate is 100 US gpm, which converted to cubic feet is 13.4 cubic feet per minute. Multiplying this by the residence time required gives a required volume of 456 cubic feet

and therefore a length of 50.7 feet.

There are several problems with these calculations:

- 1. While they can be used to make rough estimates they assume the validity of Stokes's Law. Stokes's Law is only valid in laminar flow, and it is impossible to be sure that laminar flow will exist in a tank of this design because the Reynolds Numbers are too high.*
- 2. The calculation also assumes that the flow occurs across the entire cross sectional area of the separator, which is not correct for larger flow areas. Flow will be expected to channel in large separators.*
- 3. The calculation is only done for a single droplet size, and except in very special circumstances the oil will exist in a spectrum of droplet sizes.*

To be sure of appropriate separation to acceptable effluent levels, it is necessary to provide some method of ensuring that the conditions for Stokes's Law are present., that flow is controlled and that the calculations account for varying droplet sizes.

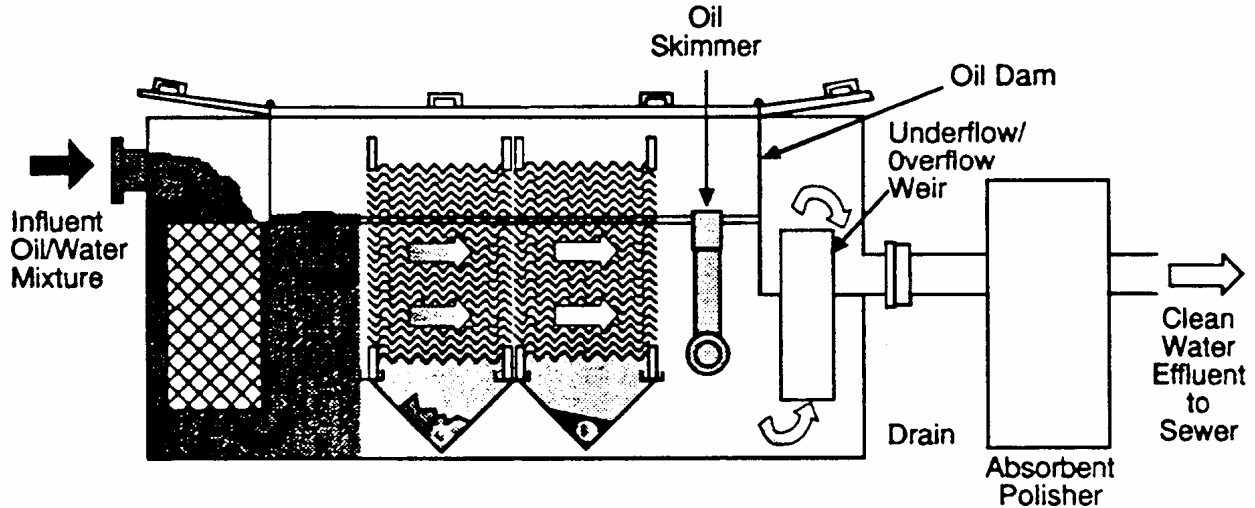
Insertion of coalescing plates in the system is a good way of ensuring both of the first problems above are overcome. The coalescing plates ensure laminar flow and constitute an excellent flow distribution baffle. In addition, the closely spaced plates – often ¼” or ½” spacing – reduce the rise distances for the droplets dramatically and allow much better efficiency in much smaller equipment.

EXAMPLES OF PRETREATMENT SYSTEMS

Oil Reclaiming Facility

An oil reclaiming company, processors of used lubricating oil, utilizing approximately 750 m³/year (200,000 gal per year) in Minnesota was required by local regulators to provide wastewater pretreatment down to 2 mg/l to meet VOC requirements as a precondition to obtaining an operating permit. The system installed utilizes a multiple angle separator with a wood pulp-based absorbent downstream. A schematic of the system is shown in Figure 2 below. The separator effluent is not normally tested, but exhibits no slick (which would indicate less than 15 mg/l). Effluent from the absorbent bed meets the requirements of the sanitary sewer plant. The system has successfully operated for several years, with flow rate depending on the plant throughput and water content of the inlet oil.

Figure 2
Oil Reclaiming Facility
Water Pretreatment

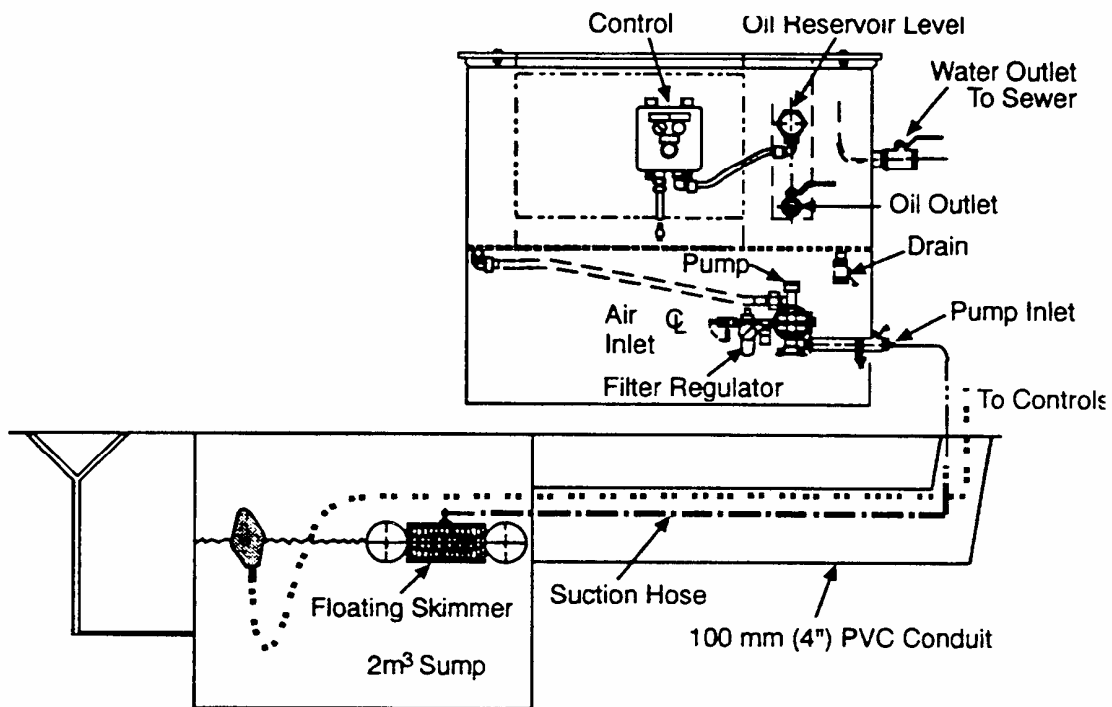


Auto Maintenance Floor Washing Water

A major US auto company was interested in developing a standard design for dealer maintenance shops that involved use of a thorough separation device to separate any oil that might be contained in floor washing water and ensure that it not be directed to the sanitary sewers in the community.

Since the flow was relatively low and a positive assurance against the oil being allowed into the sewers was desired, a system was designed consisting of a series of floor drains directed to a "dead end" sump of 2 m³ (500 gal.) capacity. Please see Figure 4 for a schematic of this design.

Figure 4
Auto Maintenance
Floor Washing Water



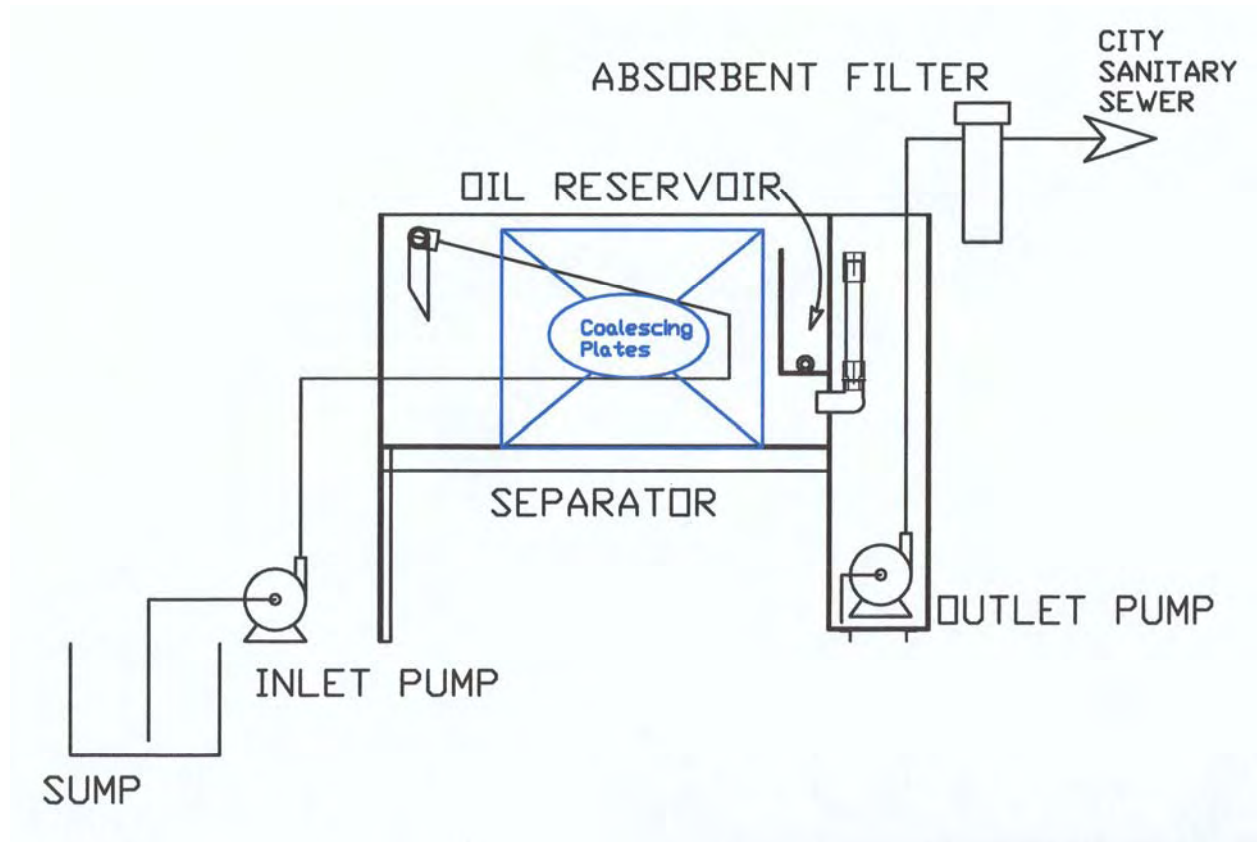
The hydrocarbon removal is by a plate separator with a flow capacity of 6 l/min. (1.6 gpm) and is provided with an automatic operating/control system.

A level switch in the sump turns the system feed pump on and off as necessary. When the pump is operating, oil is automatically separated from the water and comes to the surface of the separator where it is skimmed off into an integral oil tank. An alarm system in the separator actuates a "service separator" light located remotely in the building to alert the operator to drain and recycle the collected oil. Cleaned effluent water from the system flows directly to the sewer by gravity.

Quick Lubrication Facility Water

A local franchisee of a chain of quick lubrication facilities wished to install a system for removal of hydrocarbons from the pit under the oil change facilities because the particular pit suffered an inflow of ground water from the neighboring hillside during and after a rain event. Local authorities required treatment of the water before it was pumped into the sanitary sewer because of contamination. The system was to be automatic, highly efficient, and meet the requirements of the local environmental authorities. The system designed included a small integral air diaphragm pump to pump the water into the separator, coalescing plates to remove most of the oil, and an oil reservoir to capture the oil removed by the plates. Downstream of this treatment, the unit is provided with an integral clear well, and a pump (the previous sump pump,

relocated) pumps through a final absorbent filter downstream to the sewer. Normally the final filter would not be required, but the regulators wanted the absolute minimum discharge oil content.



Surfactant Manufacturing Plant

A large North American industrial surfactant (soaps and detergents) manufacturing plant had difficulty meeting the standards of the local sanitary sewer plant, often substantially exceeding the allowable effluent oil content. The effluent stream is not large, only 30 US gpm and a system was in place to attempt to remove the hydrocarbons in the effluent. The system installed was a below-ground simple gravity settler with a skimming device.

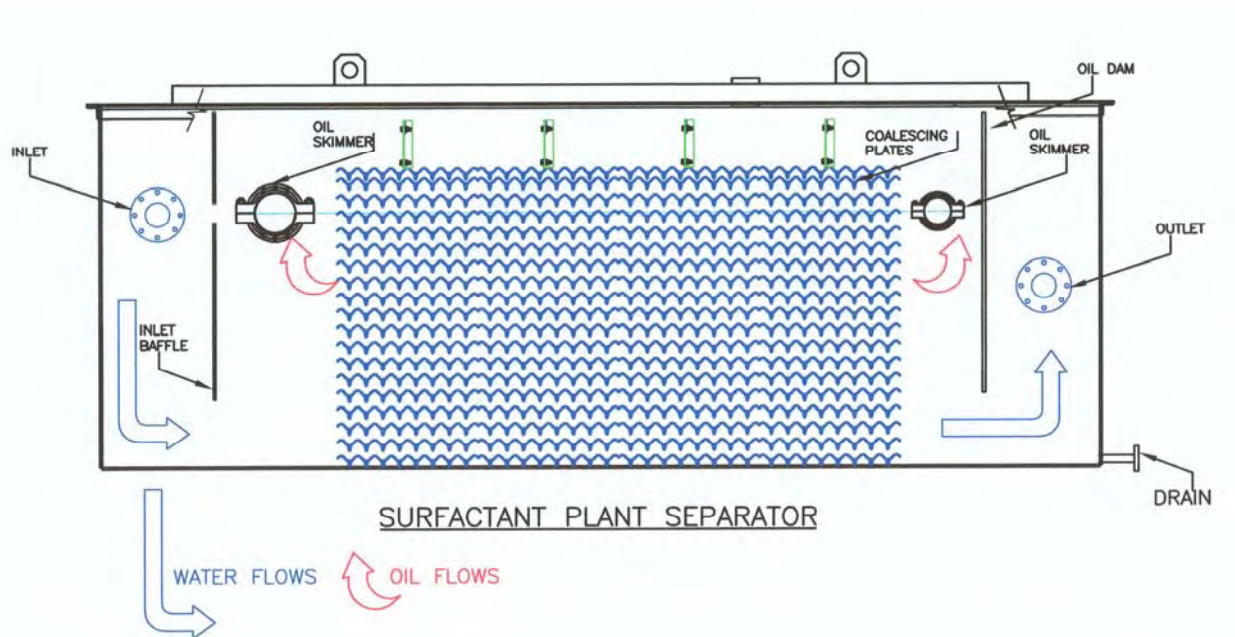
Because the existing system was not performing well and the effluent was out of compliance, it was expected that some of the surfactants being produced in the facility were entering the wastewater stream and causing a very small average oil droplet size. This small droplet size would not be removed by the system, causing the effluent oil to be more than allowed.

A new above-ground system was installed, provided with a very large amount of coalescing plates so that very small droplets would be removed. The new system was installed upstream of the old system for convenience of installation. Almost immediately upon installation problems arose with the new system and it was subsequently

discovered that not only was there a large amount of small droplets of the light hydrocarbon present (the hydrocarbon the system was designed for) but also a large quantity of heavy hydrocarbon that was not suspected at the time of the design. Because the coalescing plates operate equally well separating heavy liquids downward as separating light liquids upward, the separator successfully removed the heavy liquid as well as the light liquid.

The source of the heavy liquid was traced to a process upset that periodically happens, so it was necessary to design for this case as well as the original design. Instrumentation was added to the system to notify the operators in the event of a heavy oil event and a system for manually removing the heavy oil if present was installed.

The system is currently operating well within the requirements of the local sanitary sewer authority, and the captured oil can be reused or recycled. The sketch below shows the design of this system. Please note that the oil flows through the oil skimmers into an integral oil tank, not shown, and that a water overflow weir (also not shown) controls the oil-water interface level.



HOW TO AVOID PITFALLS IN SPECIFYING A PRETREATMENT SYSTEM

Start by finding out just what all of the requirements are for the local sanitary sewer plant in all parameters including flow, oil content and content of other contaminants that would be allowed.

Check the system chosen to perform the pretreatment to ensure it will handle all possible performance requirements and still provide acceptable effluents. Ensure suitable sample points are available to take effluent samples to check effluent quality

and train operators in sample taking procedures.

Ensure that surfactants are not in use in the plant so as to avoid disarming the pretreatments system. If surfactants are necessary, try to both minimize their use and change to quick-break types.

Provide for environmentally safe disposal of captured oil and/or used coalescer cartridges.

SUMMARY

Air emissions standards for evaporation of VOCs from wastewater treatment ponds and sanitary sewer plants are becoming more stringent. Many of the troublesome compounds are hydrocarbon in nature and their presence in the sanitary sewer plant is the result of inadequate pretreatment of industrial wastewater streams.

Numerous methods are available for pretreatment of industrial water streams; only a few of them are listed above. Generally the best treatment method for any wastewater stream must be chosen by review of the available options and costs.

Criteria for choice of options should be:

- Effectiveness of treatment
- Simplicity and reliability of operation
- Minimum consumable use
- Minimum production of sludge and used filter/absorbent cartridges
- Minimum energy use
- Governmental/regulatory requirements

The best and most cost effective method is usually the simplest that will still provide adequate pretreatment.

After the choice of pretreatment system is made and the equipment installed, it is necessary to do a study to determine whether the system as installed is providing satisfactory results. This usually consists of taking a series of effluent samples for analysis, but additional data may be required. Consult the sanitary sewer authority to determine what the personnel there believe is adequate proof that the system installed is meeting their needs. Long term monitoring will also probably be required.

REFERENCE

API (1990) Publication 421 - Design and Operation of Oil-Water Separators, American Petroleum Institute, Washington, D.C.