



Pretreatment of Industrial Wastewater for VOC Removal

An Online Continuing Education Course for Engineers

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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 It was originally enacted as the Federal Water Pollution Control Act of 1972, but was amended extensively in 1977.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:

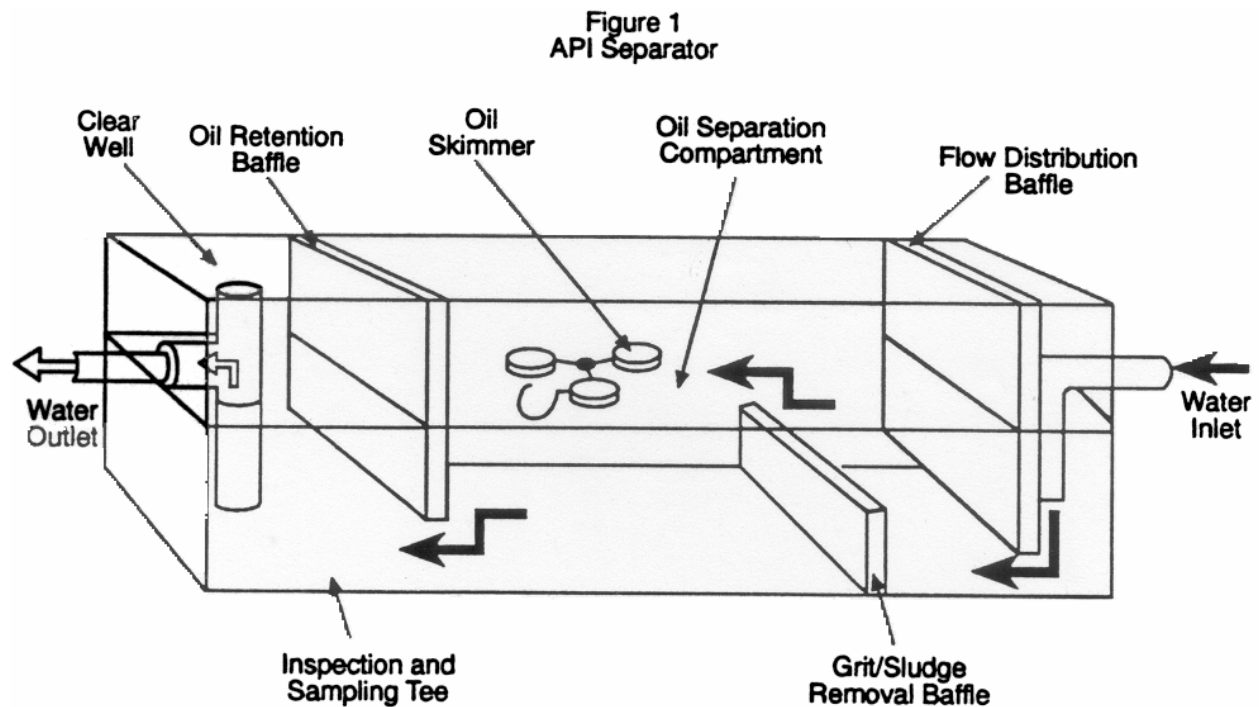
- API Separators
- Chemical flocculation
- Dissolved Air Flotation (DAF) and Induced Air Flotation (IAF)
- Coalescing Cartridge type separators
- Coalescing Plate Separators

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 and the water is collected separately for recovery of the hydrocarbons. The float is usually dewatered as well.

Advantages of DAF and IAF are that they can be used, even when the wastewater is highly turbid, and they require a lower capital cost for compressors and piping than other methods.

Induced air flotation (IAF) is a variation of dissolved air flotation (DAF) in which the air is dissolved in the wastewater under pressure. When the pressure is released, the air bubbles attach to the hydrocarbon droplets and lift them to the surface of the separator. IAF systems are often used for wastewater with high suspended solids content. They require less space than DAF systems.

Coalescing

Coalescing separators are a first stage of oil-water separation. Coalescing separators are suitable for applications where plugging is a concern. They use surfactant cartridges to improve efficiency.

Coalescing

Coalescing separators are a first stage of oil-water separation. They are designed to remove 150 micron and larger droplets from water streams in more compact applications. They are designed to remove 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

