CHAPTER 19

# THE PETROLEUM INDUSTRY

## CHARACTERISTICS OF THE WASTE WATER

Large quantities of waste water are discharged from all drilling areas. These types of waste water contain mostly saline water, petroleum and polluted oil to a varying extent.

Much larger amounts are discharged from the refineries themselves. The quantity varies greatly, but generally 10-20 $m^3$ of effluent are discharged for every ton of petroleum processed if the water is recycled.

The chief pollutants in the effluent are carbon hydrides and its constituents as well as suspended mineral solids, sand, inorganic acids, alkalies, salt, organic acids, sulphurous compounds and phenols are present in varying concentrations. The nature of the pollutants depends not only on the refining process but also on the quality of the crude oil. For example, some types of crude oil contain only negligible amounts of sulphurous compounds, whereas others contain more than 4%.

Table 19.1 is a typical analysis of the waste water from an oil refinery.

TABLE 19.1

Typical composition of waste water from an oil refinery

| | |
|---|---|
| pH | 6.5-8.4 |
| Alkalinity (mg/l) | 120-3000 |
| Permanganate value (mg/l) | 100-1000 |
| $BOD_5$ (mg/l) | 100-1000 |
| Organic carbon (mg/l C) | 12-650 |
| Organic nitrogen (mg/l N) | 4-10 |
| Ammonia (mg/l) | 5-80 |
| Total suspended solid (mg/l) | 150-4000 |
| Volatile suspended solid (mg/l) | 150-4000 |
| Sulphurous compounds (mg/l S) | 20-80 |

By the use of a closed-cycle cooling system or by application of air cooling instead of water cooling, it is possible to reduce the demand for water considerably.

The different types of effluent from the oil refineries are as follows:

1. Waste water from the handling of raw material and product stores, and rain water run off from the refinery area, which is polluted by oil and its components.
2. Acidic waste water containing hydrogen sulphide originating from the distillation of oil under reduced pressure.
3. Alkaline waste water from washing petroleum products with caustic soda. This waste water contains sodium sulphide, and sodium hydrogen sulphide at concentrations as high as 100 g/l.
4. Acidic waste water from washing oil products with sulphuric acid and from the processing of acid pitch.
5. Waste water containing arsenic(III)oxide up to a concentration of 10 g/l from removal of hydrogen sulphide from the produced gas.
6. Waste water containing mercaptans arising from acid pitch coking processes.
7. Waste water containing lead as sodium plumbite, $Na_2PbO_2$, are formed by removal of mercaptans from oils.

Effects of the waste water

As little as 0.5 mg/l of petroleum imparts a perceptible taste to water. The odour may be intensified by chlorination due to the formation of chlorophenol.

Naphthenic acids and their salts exert a toxic effect upon flora and fauna at about 5 mg/l. Methylmercaptan is perceptible even at 0.00025 mg/l (Gloyna et al., 1963). An unpleasant odour caused by slow hydrolysis of mercaptans may be perceptible at large distances from the discharge point. The odorous compounds in petroleum impairs the taste of fish living in the receiving streams.

A surface oil film makes it impossible to use the stream for recreational purposes since it imparts the characteristic odour of oil, damaging sporting facilities and settling on banks and beaches when the water level drops. Furthermore, the oil film prevents the water from taking up oxygen from the atmosphere. Cattle drinking water polluted with oil wastes are frequently affected by latheral diseases of the alimentary tract.

Acidic waste water can damage the material from which the sewers are constructed. Furthermore, mineral oil will disrupt the biological treatment process, since the oil forms a film which covers the medium in the percolating filter and the flocs of the activated sludge plant.

## Separation and settling

By straightforward settling it is possible to remove a substantial part of the impurities (Giles et al., 1951). Lamella separators can also be used. The top layer will consist of oil sludge and sand and organic impurities will form the bottom layer. By addition of a flocculant such as aluminium sulphate, iron(III)chloride, etc. is it possible to coagulate a substantial part of the organic matter. It will settle to a porous gelatinous sludge (Merman et al., 1949). After settling the water can be polished on a sand filter.

Instead of flocculation flotation can be used. The COD will generally be reduced 50-70% by flocculation, while by flotation it will be reduced 60-85%. However, flotation hardly can be used when the waste water contains sodium carbonate. Also foaming can prevent the flotation process.

## Biological treatment processes

After primary treatment by settling, flocculation or flotation, COD is still so high that further treatment is needed (Gloyna et al., 1969).

The activated sludge process is most often used and an adaption of the biological culture is necessary (Reno et al., 1958) and (Ludsack et al., 1960).

A flow-sheet for a total three-step treatment including separation of oil, flocculation and biological treatment is shown in Fig. 19.1.

Table 19.2 summarizes the analytical data for such a three-step treatment. The data are from an oil refinery with reduced water consumption. The analytical data for the different treatment methods must be compared with the stated maximum concentrations for discharge of waste water to the sea:

1. Carbon hydrides: less than 10 mg/l.
2. Phenols: less than 5 mg/l.
3. pH: between 6 and 8.

According to Hovious et al. (1973) an approximate reduction of 50% in the COD can be obtained by using an anaerobic lagoon step in the treatment of petrochemical wastes.

Anaerobic treatment of the waste water from the petroleum industry can be carried out without any pretreatment.

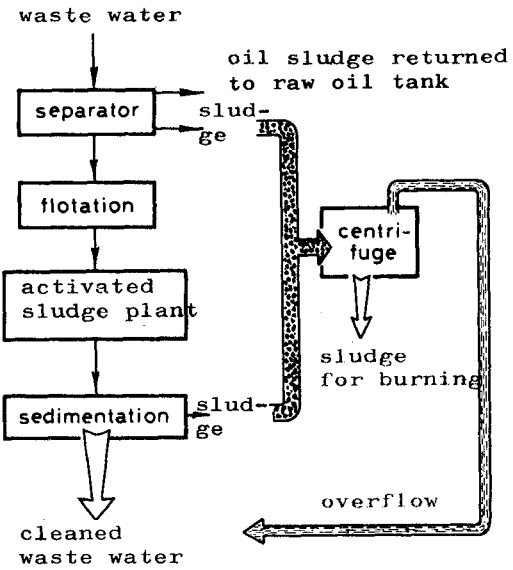


Fig. 19.1. Flow-sheet for a total three-step treatment of waste water from an oil refinery.

TABLE 19.2

Analytical data for waste water from an oil refinery after a three-step treatment

| | Untreated water | After separator | After floc-culation | After biolo-gical treatment |
|---|---|---|---|---|
| $BOD_5$ | 860 | 680 | 200 | 20 |
| COD | 1880 | 1600 | 400 | 40 |
| S | 40 | 36 | 12 | 0 |
| Phenol | 180 | 170 | 64 | 0.5 |

Other treatment methods

If further treatment after the biological treatment or after flocculation is required, adsorption on activated carbon offers a good possibility.

Studies with 93 petrochemicals adsorbed simply by activated carbon show that as the molecular weight increases and polarity, solubility and degree of branching decreases, the extent to which pure components are adsorbed by the activated carbon increases rather predictably.

Of the classes of compounds studied, the aromatic compounds could most easily be adsorbed by the activated carbon, because of their relatively low solubility in aqueous solutions. Functionality was seen to have a substantial effect, which was interrelated with the solubility and polarity. For the straight chain compounds the relative adsorption to carbon for compounds of less than four carbon atoms was
undissociated organic acids > aldehydes > esters > ketones > alcohols > glycols.

For compounds with more than four carbon atoms the alcohols were less readily adsorbed.

Adsorption from certain two-component systems was found in isothermal test to be fairly predictable from single-component data. However, data from four-component systems indicate that only about 60% of the anticipated adsorption was realized probably because competition from adsorption sites and mutual solubility effects are not negligible at this level.

Adsorption results from three continous systems indicated that greater than 80% of the ultimate equilibrium capacity was attained as measured in isothermal tests with the pure compounds and mixtures.

The refractory organic compounds in industrial waste water are often aromatic compounds such as aromatic acids. A substantial part of these compounds can be removed by adsorption on aluminium oxide. Naphthalene derivatives are adsorbed readily by aluminium oxide.

The adsorption capacity to aluminium oxide increases with an increasing number of acidic groups.

Extraction of phenols has long been carried out in the treatment of refinery wastes where the phenols are extracted by a light oil refinery stream or by a solvent such as benzene (American Petrol Institute, 1969).

Ghosh (1975) has studied a new process for the removal of oil from dilute aqueous emulsions. This process may find application in the treatment of oil in industrial wastes. It is especially suitable for the treatment of residual hazes caused by finely dispersed oil. In principle two dissimilar metals in contact with each other and submerged in a conducting aqueous medium will form an electrochemical cell. This voltaric cell develops an electric field by which negatively charged oil droplets move to the anodic areas. Electrodeposition of oil droplets takes place on the anodic surfaces.

Ultra-filtration is an alternative to the usual chemical flocculation and coagulant system, followed by dissolved air flotation if soluble oil waste needs to be treated.

Kohn (1976) has reported the recovery and removal of organic acids by extraction with tri-n-octyl-phosphine oxide. This compound has the ability to separate from water both organic and inorganic chemicals, that are poorly if at all separated by conventional solvents.

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