

भारतीय मानक मसौदा

पेट्रोलियम रिफाइनिंग उद्योग के अपशिष्टों के उपचार और निपटान के लिए गाइड

(पहला पुनरीक्षण)

Draft Indian Standard**GUIDE FOR TREATMENT AND DISPOSAL OF EFFLUENTS OF
PETROLEUM REFINING INDUSTRY**

(First Revision)

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FOREWORD

(Formal clause shall be added later)

There are a number of oil refineries in India engaged in crude refining, both imported and indigenous. Large quantities of water are used in refining processes, cooling purpose, power plant etc., in this industry. The effluents from the refineries if discharged untreated, may pose a serious threat to the environment.

A waste treatment system is an essential part of every petroleum refinery installation. This should be considered during the development, selection and design stages of new refineries or of any major modifications of existing facilities in refineries. Further, importance should be given for recycling wastes after treatment within the refinery itself. Its waste control facilities should also be reshaped to meet the needs of process modernization and changing demands on water resources. Consequently, a waste control system is not a static thing and its day-to-day operation should not be expected to remain constant. The design of a waste treatment system should be one which is adaptable to needs that vary with production rates and to overloads that result from emergency conditions.

The objective of this guide is to provide basic information on methods of treatment of effluents of oil refineries and to make definite recommendations for treatment of these effluents in India. This guide

does not seek to provide detailed information on the designing or operation of an effluent treatment plant. Further, the methods recommended have been selected taking into consideration the practicability of their adoption by the industry. As and when more information and data are available, this guide will be revised.

Over the period of last 40 years since the standard was originally published, several new units have come in refinery configuration and the effluent composition has also changed. Hence, need was felt to revise characteristics of composite oil refinery waste water.

IS 10044 was originally published in 1981. During this first revision, characteristics given in table 1 have been revised based on current practices. Suitable modifications in various sub-clauses under treatment clause have also been done as per present scenario. This revision has been taken up in order to bring out the standard in the latest style and format of the Indian Standards.

1 SCOPE

This standard covers the methods of treatment and disposal of effluents of petroleum refineries.

2 SOURCES AND CHARACTERISTICS OF EFFLUENTS

2.1 Sources

2.1.1 The major water pollutant in refinery operations is oil, besides chemicals that may be formed during treatment of petroleum products by chemical processes for removal of undesirable constituents.

2.1.2 The effluents may be classified under the following five categories:

- a) Effluent free from oil and dissolved organic material;
- b) Effluent accidentally contaminated with oil;
- c) Effluent continuously contaminated with oil but not contaminated with other soluble organic material;
- d) Process effluent; and
- e) Sanitary and domestic effluent.

2.1.2.1 *Effluents free from oil and dissolved organic material* — These originate from:

- a) Boiler blow-down,
- b) Water treatment plant effluent, and
- c) Storm water from oil-free areas.

2.1.2.2 *Effluents accidentally contaminated with oil* — These originate from:

- a) Storm water from tank farms; and
- b) Blow-down from circulating cooling water system.

2.1.2.3 *Effluents continuously contaminated with oil but free from soluble organic material* — These originate from:

- a) Storm water from oil processing areas, and
- b) Ballast water.

2.1.2.4 *Process effluents* — These originate from:

- a) Desalter,
- b) Condensate from steam stripping operations,
- c) Pump gland cooling water,
- d) Barometric condenser water containing emulsions, and
- e) Wash water from treating plants.

2.1.2.5 *Sanitary and domestic effluents* — These originate from:

- a) Toilets, and

b) Canteen.

2.2 Characteristics — General characteristics of the composite oil refinery wastewater (before treatment) are likely to be as given in Table 1 (*see also 3.1*).

3 EFFECTS OF POLLUTION

3.1 The principal public health hazard caused by untreated refinery effluents is pollution of water courses and land with toxic chemical compounds such as oil, hydrogen sulphide, ammonia, mercaptans, phenol, cyanides, fluorides, acids, alkalis, chromates, and traces of heavy metals.

TABLE 1 GENERAL CHARACTERISTICS OF COMPOSITE OIL REFINERY WASTE WATER

(Clause 2.2)

Sl. No.	Characteristic	Range of Value
1	Free Oil, mg/l	1500 to 15000
2	Emulsified Oil, mg/l	150 to 1000
3	Sulphides (as H ₂ S) and mercaptans, mg/l	10 to 40
4	Phenolic compounds (as C ₆ H ₅ OH), mg/l	5 to 20
5	Biochemical Oxygen Demand (5 days at 20 °C), mg/l	350 to 1500
6	Suspended Solids, mg/l	500 to 3500
7	pH value	7.5 to 10.5
8	Chemical Oxygen Demand, mg/l	1000 to 4500
9	Total Kjeldahl Nitrogen (TKN), mg/l	60 to 170
10	Ammoniacal Nitrogen	30 to 95

NOTE — Cyanides and ammonia may be present in the waste water from refineries where cracking process is practiced.

3.1.1 Acids and alkalis are toxic to aquatic life and inhibit self-purification of water courses. Fluorides cause dental fluorosis and dental caries which affect teeth, joints and bones. Presence of hydrogen sulphide, mercaptans and phenol produce disagreeable odour in water and, at the same time, increases biochemical oxygen demand of water. Oils, which are difficult to biodegrade, form a thin film over water surface, causing unsightly appearance and interfere with the natural process of aeration and photosynthesis, and also cause fire hazards.

4 TREATMENT

4.1 Oil-free waste waters should never contain oil and, hence, they may bypass certain sections of the waste treatment facilities depending on other characteristics such as Suspended solids, BOD,

COD etc. If all parameters are within Minimal National Standards (MINAS), they may discharge directly into the refinery outfall line after decontamination through gravity separators or surge ponds to take care of accidental contamination (see 2.1.1.2), (facilities should be provided for oil removal). If there are other characteristics which need correction, then such waste water can be routed through suitable treatment facility for Minimal National Standards (MINAS) compliance (such as secondary treatment etc., as required).

4.2 The general treatment methods to handle wastewaters from refinery operations are as follows.

4.2.1 Primary Treatment — It consists of free oil removal. Oil removal is also affected by in-plant processes like stripping and extraction. Further, removal of oil from the wastewater is carried out principally in two stages — the first stage featuring gravity separation and the second stage floatation with or without addition of chemicals/coagulants (see 4.2.2). Gravity separation is meant for removal of separable free oil.

4.2.1.1 Oily effluents originating from various sources in the refinery are collected in a sump and routed to an oil separator for removal of free oil. Oil separators are designed considering hydraulic load, density and viscosity of the oil and diameter of oil globules. A brief description of a typical API oil separator (see Fig. 1) is given below.

The API separator mainly consists of an inlet bay, a middle or a separator bay and an outlet bay. The inlet bay contains sluice gates for commissioning or decommissioning the individual bays of the separator. It contains a vertical hanging baffle to retain the oil and also arrangement to collect the separated oil.

The middle or separator bay is the place where remaining portion of the oil is separated by reducing the velocity, so that the water becomes almost quiescent. The separated oil is retained in the middle bay by another vertical hanging baffle situated at the end of this bay and the collected oil is skimmed by a skimmer provided near this baffle. A flight scraper provided in the middle bay brings oil to the skimmer for its removal and also at the same time pushes the sludge collected at the bottom to the sludge pit or hopper for periodic removal.

The outlet bay contains a weir over which the oil-free water flows out for further treatment. Oil content in the effluent after the API separator is normally less than 100 mg/l in water.

4.2.1.2 It is very important that the oily effluent be sent to a primary oil removal basin and to the API or gravity separators by means of gravity flow. Pumps, especially centrifugal type, should be avoided to minimize formation of oil emulsion with water which would call for additional chemical method for its removal. Where pumping of oily effluent is essential after the primary oil removal basin, screw type or diaphragm type pumps should be used.

4.2.1.3 Stripping — Stripping is another physical method. It is done with the aid of steam to remove gases like hydrogen sulphide, mercaptans and ammonia and to some extent phenol and free cyanides.

4.2.1.4 Extraction — Extraction is yet another physical method which is used to remove phenolic compounds in refinery operations. In this process, solvents like tricresyl phosphates and mixed organic esters are used for extraction of phenol from wastes. Use of petroleum fractions or crude oil is also made for extraction in some of the refineries.

4.2.2 Secondary Treatment Methods — The secondary treatment methods may be classified as follows:

- a) Physical Method
- b) Chemical method, and
- c) Biological method.

4.2.2.1 Physical Method—The main purpose of deploying physical separation as a secondary treatment method is to remove free oil left over from primary treatment processes to the maximum extent possible by simple physical means, without use of chemicals dosing. In this way, the clean-up process is made more environment-friendly & typically, saves on cost also.

- a. *Use of oil skimmers*— An oil skimmer is a device that is designed to remove oil and other contaminants from effluent water. The effluent is collected in a tank over which the device is installed. The device works by bringing a synthetic fabric in form of a belt, drum or disk in contact with the water surface. The fabric repels water but absorbs oil and swells up. The fabric slowly moves to the extraction section of the equipment where the fabric is squeezed/scraped tightly. The oil absorbed in the fabric along with a little water) gets released and is collected for disposal. The skimming belt/drum/disc keeps moving & again comes in contact with the effluent and the cycle continues. It is a continuous slow-speed operation with no chemicals usage, low energy and maintenance requirement device.
- b. Dissolved Air Flotation (DAF) System— DAF systems are designed to remove low density suspended solids or particles formed after chemical coagulation which have low density. DAF also removes fat, oils and greases (O&G) from wastewater by injecting air under pressure into the recycle stream of wastewater from the clarified effluent from DAF which mixes with incoming wastewater in an internal contact chamber . The dissolved air converts to micron-sized bubbles attached to Oil & Grease and rise to the surface, A surface skimmer can remove the floating sludge. DAF requires lower footprint than other physical /chemical treatment processes.

4.2.2.2 Chemical method — The main purpose of a chemical method is to remove emulsified oil with addition of flocculating agents and also to remove suspended solids and toxic substances, thereby conditioning the effluents for further treatment by biological method. Sedimentation is normally employed to remove suspended solids after chemical treatment. Various chemical methods available may be further classified under the following four categories:

- a) Neutralization method,
- b) Precipitation and clarification method,
- c) Chemical oxidation method, and
- d) Regeneration method.

a) *Neutralization* — Neutralization methods are applied to many types of refinery wastes as primary treatment. The wastes considered here are:

- 1) *Dilute acid or alkaline wastes from various refining processes and from water treatment plant* — Neutralized to produce a neutral effluent.
- 2) *Spent caustic solution* — Neutralized with either spent acid or acidic stack gases.
- 3) *Sulphuric acid sludges* — Neutralized with alkaline wastes
- 4) *Spent catalyst* — Neutralized with spent caustic wastes.
- 5) *Hydrofluoric acid wastes*—Neutralized with caustic soda solution.

b) *Precipitation and clarification method* — Precipitation method is used in the treatment of several types of refinery wastes such as:

- 1) *Spent caustic solutions* — Acidic oils in caustic are precipitated by neutralization.
- 2) *Sulphide water* — Precipitated with iron salts.
- 3) *Solutions of sulphonates* — Precipitated by the addition of lime.

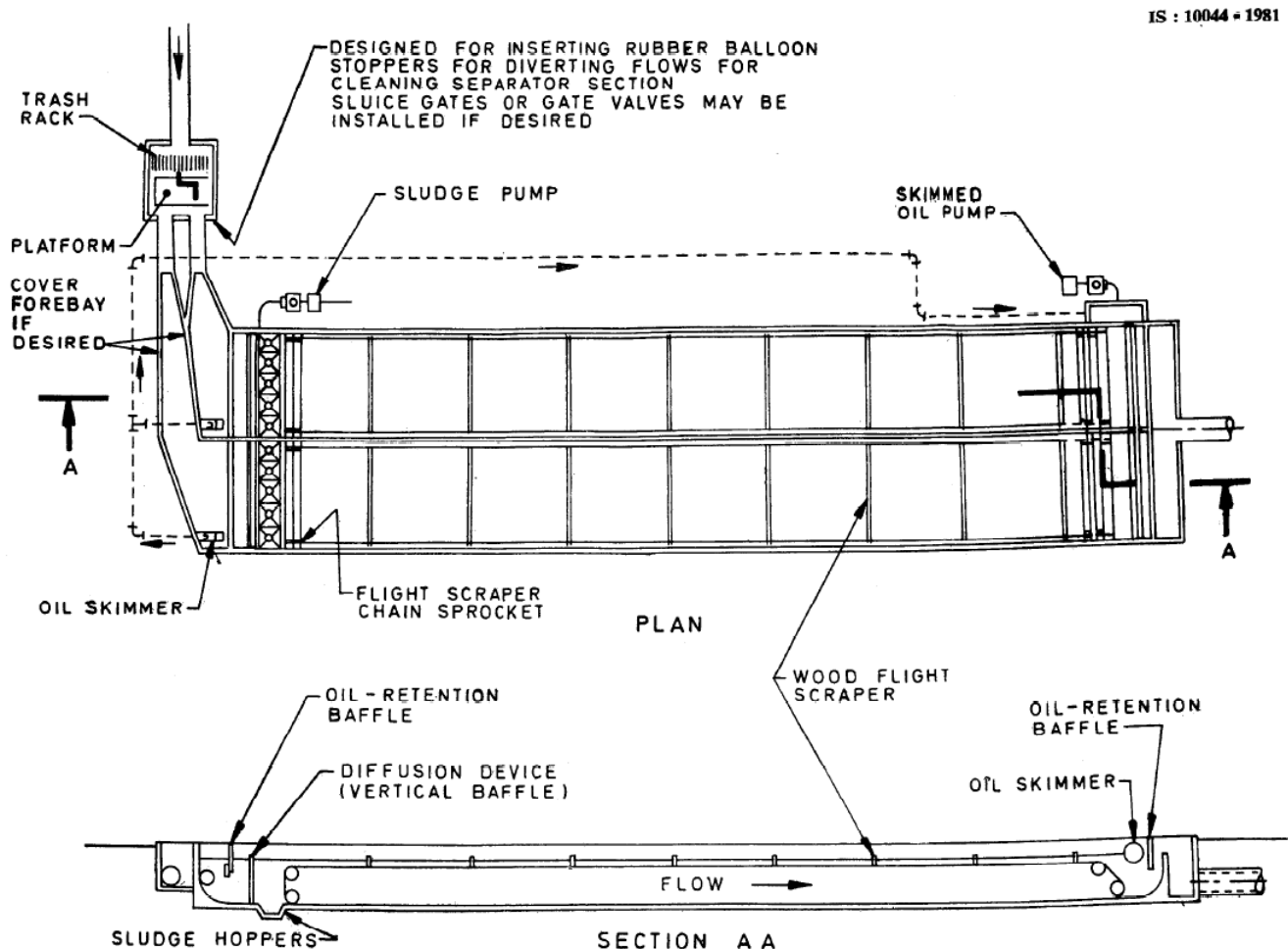


FIG. 1 API OIL-WATER SEPARATOR

- 4) *Chromates from cooling water* — Reduced to trivalent with ferrous sulphate, sulphur dioxide or hydrogen sulphide and precipitated with lime as chromium hydroxide.

c) *Chemical oxidation method* — This method may be used for:

- 1) Treatment of phenols and cyanides in wastes; and
- 2) Combustion of certain wastes.

d) *Regeneration method* — Production of spent caustic solutions is reduced by the regeneration of a chemical like monoethanolamine, which is used to absorb hydrogen sulphide and mercaptans. It is regenerated by steam stripping for further use.

4.2.2.3 Biological method — This is intended to remove the biodegradable organic substances and toxic substances like phenol. Biological treatment also reduces the residual oil after primary treatment (but the oil is not recoverable). The biological method of treating the wastewater is done by application of conventional methods like trickling filter, activated sludge process and low cost waste treatment methods like aerated lagoon and oxidation pond. Trickling filters can tolerate oil up to 100 ppm, whereas activated sludge process can tolerate oil up to 25 ppm. Presence of oil in oxidation ponds retards reaeration. Besides oil, biological treatment methods are influenced by BOD, toxic substance like chromium, lead, nickel, hydrogen sulphide, etc, temperature, pH and nutrients.

- a) *Activated sludge process* — The activated sludge process is an aerobic biological treatment process in which wastewaters are treated with microorganisms that are suspended uniformly within a reaction tank into which oxygen is introduced by mechanical means. The microorganisms are maintained in the reaction tank by recycling activated sludge which is formed by the microorganisms in the process. Essentially, the organic matter is removed from the wastewaters by synthesis and oxidation. An aerobic environment is necessary to maintain the proper microbial balance in the system. The basic process consists of a aeration tank followed by a sedimentation tank. The activated sludge removed from the sedimentation tank is recycled to the aeration tank to maintain a high concentration of activated sludge. The activated sludge will continue to build up until it is necessary to 'waste', or discard, some of the excess. In most activated sludge systems, sludge wasting is carried out on a continuous basis at a relatively low rate. Activated sludge forms naturally and does not need any special seeding for proper development.
- b) *Trickling filters* — The trickling filter is a bed of broken stone or coarse aggregate. It also consist of plastic media, Raschig rings. A bed is from 1 m to 3 m deep and may be either rectangular or circular. It may be deeper when plastic packing is used. Fixed or moving sprinklers distribute the wastewater over the surface of the bed. A gelatinous film of slime composed of aerobic organisms develops on the surface of the aggregate. As the wastewater trickles over the film, both dissolved and suspended organic matter is removed by adsorption. The adsorbed matter is oxidized by the organisms in the slime during their metabolic processes. Air flows through the filter by convection, thereby providing the oxygen needed to maintain aerobic conditions. The oxidized wastewater from the filter is clarified

in a sedimentation tank before discharge into a watercourse. The microbial film that develops on the surface of the rocks is responsible for removing the organic materials from solution.

- c) *Oxidation and stabilization ponds and aerated lagoons* — The oxidation pond is a popular type of biological waste treatment system where land is plentiful. Fundamentally, the oxidation pond depends on the bacteria to aerobically stabilize the organic wastes added to the pond. In heavily loaded ponds, a certain amount of the stabilization occurs anaerobically rather than aerobically.

The oxygen for the bacteria is supplied by surface transfer from the air and from the metabolism of algae that grow in the pond. The production of oxygen by algae occurs only as a result of synthesis of cellular protoplasm. Thus, as the algae produce oxygen in synthesizing algae protoplasm, the bacteria utilize the oxygen in synthesizing bacterial protoplasm. The net effect of this process is the production of organic matter in the oxidation pond. In hard-water areas, more organic matter is produced than stabilized. The important relationship, which permits the oxidation pond to produce a more stable effluent than influent, is that the rate of degradation of cellular protoplasm is very slow compared to the rate of degradation of organic matter for synthesis of cellular protoplasm. Also, many of the microorganisms settle out in the pond and are not removed in the effluent. The organic loading on the oxidation pond is limited by the oxygen transfer capacity. A broad, shallow pond with considerable surface agitation, caused by wind action will have a high rate of oxygen transfer. A small pond with little exposed surface area will be able to handle a relatively low organic load per unit of surface area. Although the tendency is to construct a single pond, there are some areas that require at least two ponds. The dual ponds tend to reduce short-circuiting and permit retention of floating organics in the first pond. The second pond is usually very lightly loaded in comparison to the first pond and may build up a sufficiently large animal population during the warmer months to remove most of the algae and produce a clearer effluent.

Oxidation ponds have been used to treat the entire plant wastes as well as to polish the effluent from other biological waste treatment processes.

Although oxidation ponds have been constructed for refinery wastes, very few data are available on their operation. Retention periods in oxidation ponds range from a little more than 1 day up to 90 days. For the most part, the reduction in organic matter is a function of the retention period and effluent concentration. Generally, the entire plant wastes are treated in the oxidation ponds, so that the organic concentration applied is quite low. The net result is a low rate of microbial metabolism, and a long period of retention is required for organic reduction. As a rule, simple oxidation ponds are ineffective if the holding time is less than 7 days.

Oxidation ponds for refinery may employ surface aeration units in the first stage to permit loadings at 10 times the conventional oxidation pond loadings. Conventional lagoons may be used as a second-stage treatment for producing a high quality effluent. This system has been termed the 'aerated lagoon' system. One of the major problems with oxidation ponds is emulsions which block sunlight penetration and prevent algae growth. Normal oxidation pond operation is retarded until the emulsion is broken by bacterial metabolism. The low rate of bacterial metabolism in the absence of oxygen requires a large pond volume to break the emulsion.

4.2.3 Tertiary Treatment Method — Tertiary treatment can consist of Ultrafiltration, Clariflocculator(s), Pressure Sand Filters, activated carbon filtration process, reverse osmosis, ozonation etc. which are effective in removal of the taste, TDS, odour and organics from biologically treated waste waters. However, these methods are extremely costly. Many of the refineries prefer to use oxidation ponds after biological treatment to serve as tertiary treatment. This is one of the cheapest methods of treatment where enough land is available. A general plan for the sources, the collection, the treatment and the disposal of refinery liquid wastes is shown in Fig. 2.

4.2.4 Treated liquid wastes which satisfy the permissible standards as stipulated by State Pollution Control Board / Central Pollution Control Board are predominantly reused within the refinery premises and balance only discharge to water bodies as consented by statutory authorities.

5 POLLUTION CONTROL PRACTICES

5.1 In waste control, preventive methods other than treatment should be used for reducing the amount of polluting wastes. New techniques should be tried with the aim of lowering treatment costs. The preventive measures can be studied under the following headings:

5.1.1 Pollution Control Measures — These may include:

- a) Provision of separate drainage and sewer systems to prevent pollution of large volumes of clean water by small volumes of dirty water;
- b) Segregation of waste water streams may be done, so that non-oily chemical wastes and oily process wastes are collected and treated separately;
- c) Following water conservation measures at refinery will reduce both water supply and cost of waste treatment:

Installation of air cooled exchangers and cooling towers; pump gland cooling water to serve as cooling tower blow-down and use of oily water emulsion from barometric condenser; and stripped sour water and phenolic waste water as make-up water for desalter.

5.1.2 Process Design Modifications — These may include:

- a) Acid sludge or spent clay disposal problems may be eliminated by replacing acid treatment or clay treatment of lubricating oil with propane deasphalting or with hydrofinishing process.
- b) Substitution of continuous process for batch processes.
- c) Use of processes which include regeneration of chemicals used for hydrogen sulphide and mercaptan removal may avoid problems associated with disposal of caustic wastes.
- d) Use of downgraded chemicals is economical for both process and waste control. Fresh caustic used for washing light hydrocarbon streams is used for gasoline treating.
- e) Use of methods for conversion of hydrogen sulphide to elemental sulphur.

5.1.3 Local Pretreatment or Disposal

5.1.3.1 In general, it is advantageous to treat or dispose of concentrated and unusual wastes locally. Treatment of highly polluted waste streams at the sources can prevent gross pollution of large volumes of

relatively clean waste water. Such treatment is a more economical solution to the problem than discharging directly into the refinery sewers. For example:

- a) Stripping ammonia and hydrogen sulphide condensate before discharging into sewer.
- b) Neutralizing the spent caustic waste before discharging into sewer.

5.1.4 *Operation Control Measures*

5.1.4.1 Operating procedure has a significant effect on waste control. However, control practices should have the interest and support of management, process supervisors and operators. A waste control group or a qualified supervisor may be appointed who should be responsible for the quality of wastewater that leaves the refinery. In addition, the following should be practised:

- a) The group or supervisor, with the aid of the refinery laboratory should maintain a complete record of data concerning sources, characteristics and quantities of all wastes and wastewater streams. These data should be reported periodically.
- b) Operating departments should be held responsible for their own discharges or wastewater. They should advise the control group or supervisor of each special discharge they intend to make, so that precautions can be taken to prevent adverse effects.
- c) Both management and control group should be informed of any process changes or new sewer connections. Current accurate maps and plans of all waste disposal facilities should be maintained.
- d) Close, and cooperative relations between the operating and waste control group personnel are essential for successful waste control.
- e) Waste control group should make all the employees conscious of waste problems by continually reminding them of the problems through booklets or leaflets.

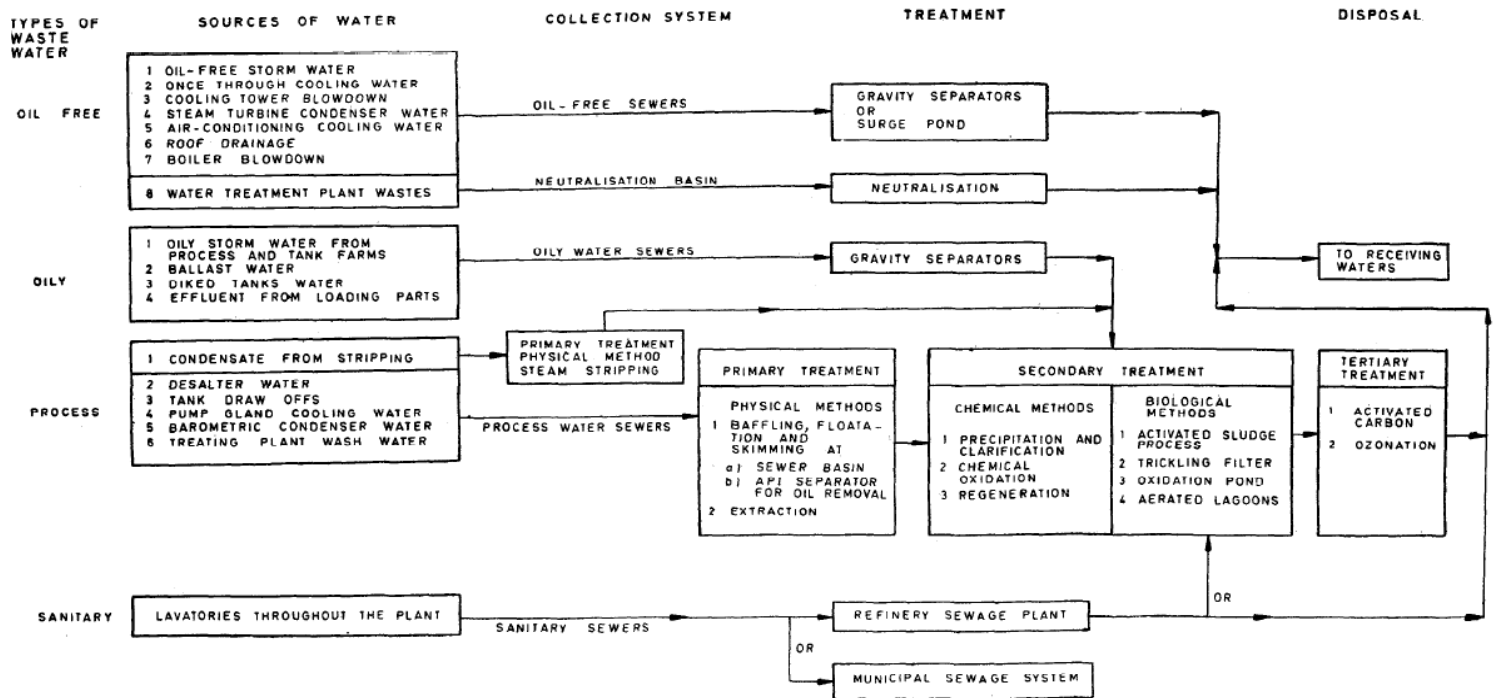


FIG. 2 GENERAL PLAN FOR THE TREATMENT AND DISPOSAL OF EFFLUENTS OF PETROLEUM REFINING INDUSTRY

5.1.5 Periodic Inspections — Periodic inspection of the waste system is essential as preventing oil and other polluting wastes from getting into plant sewers is preferable to the heavy expenditure of both money and efforts necessary to remove them.

5.1.6 Good House-keeping — Good house-keeping should be emphasized. Apparently, it can be attained by instilling the proper attitude in operating personnel and then it can be maintained by periodic inspection.

6 DESIGN OF COLLECTING SYSTEMS

6.1 Refinery collection or drainage systems should be constructed, so that waters subject to contamination by oil do not drain directly into adjoining properties or into adjacent surface waters. Drainage lines should be laid out so that the oil-contaminated wastes flow by gravity to the oil-water separators. Pumping of oil-water mixtures tends to form emulsions and should be avoided. If pumping cannot be avoided before separation of at least the bulk of the oil, pumps specially designed to minimize emulsification should be used.

6.2 Accurate maps and plans of the drainage systems, separators, catch basins, and other facilities should be maintained to show all details of the original installation, as well as any changes or additions.

6.3 Intakes to storm water sewers should be provided with adequate sediment chambers. As a precautionary measure, separate storm sewers should be provided with water-sealed connections.

6.4 Drainage systems for cooling and process wastewaters should be provided with water-sealed intakes at every point where wastewaters enter in order to prevent hydrocarbon vapours, present in the sewer system, from escaping into process areas. When process wastewater contains quantities of sediment, suitable inlet catch basins should be provided.

6.5 Sewer systems should be provided with manholes and junction boxes to permit ready access. These openings are necessary to permit gaging and cleaning of sludge accumulations to maintain the full capacity

of the sewer system. Access points are also needed for sampling and visual observation when the sources of oil or other waste material are to be determined.

6.6 In general, all branch or lateral sewers should be isolated from main sewers by the use of suitable water seals and manholes. This prevents the travel of hydrocarbon vapours from one section of the system to another and confines to a limited area any fire or explosion that might occur. To prevent trapping oil layers, manholes in refinery areas should usually be provided with water-sealed inlets and open outlets. In specific locations where trapped outlets are to be installed, the outlets should be provided with vents to prevent syphoning and vapour locks. Properly designed vents should be provided to vent hydrocarbons safely from manholes of sewer systems handling light hydrocarbons. Failure to do so may create a fire hazard at ground elevation. Vents should be installed at manholes where a pressurized sewer is converted to gravity sewer. Vents should be discharged in areas that are remote from furnaces or other permanent sources of ignition; they should not be located near operating platforms or air intakes, and they should be high enough to disperse vapours safely. Furthermore, vents should be distinctly marked. Indiscriminate venting may create hazards if the design permits air to be sucked into the system, thereby diluting a safety-rich atmosphere to one that is potentially explosive.

6.7 It is clear that the design considerations for venting and sealing or trapping refinery waste drainage systems differ from engineering practice for sanitary sewage systems. Safety precautions to prevent an explosive condition and/or the spread of fire are paramount design requirements in a refinery drainage system.