

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

Petroleum refinery waste waters vary in quantity and quality from refinery to refinery. However, the wastes are readily treatable. The results of the industry survey indicate, as would be expected, that techniques for in-process control are general across the industry and the specific application of these techniques at individual plants determines their success. Local factors such as climate, discharge criteria, availability of land, or other considerations may dictate the use of different waste water treatment processes to reach an acceptable effluent. The survey has shown that although the end-of-pipe waste water treatment technologies used throughout the petroleum refining industry have a marked similarity in operational steps, a considerable variation in treatment results exist. The processes used for treating refinery waste water, however, are similar in purpose; namely--maximizing oil recovery and minimizing the discharge of other pollutants. The wastewater treatment technology described below is generally applicable across all industry subcategories.

In-Plant Control/Treatment Techniques

In-plant practices are the sole determinant of the amount of waste water to be treated. There are two types of in-plant practices that reduce flow to the treatment plant. First, reuse practices involving the use of water from one process in another process. Examples of this are: using stripper bottoms for makeup to crude desalters; using blowdown from high pressure boilers as feed to low pressure boilers; and using treated effluent as makeup water wherever possible. Second, recycle systems that use water more than once for the same purpose. Examples of recycle systems are: the use of steam condensate as boiler feedwater; and cooling towers. The reduction or elimination of a waste stream allows the end-of-pipe processes to be smaller, provide better treatment, and be less expensive. Since no treatment process can achieve 100 percent pollutant removal from the individual stream, reduction in flow allows for a smaller pollutant discharge.

Housekeeping

In addition to reuse/recycle of water streams and reduction in flows by other in-plant techniques, another effective in-plant control is good housekeeping. Examples of good housekeeping practices are: minimizing waste when sampling product lines; using vacuum trucks or dry cleaning methods to clean up any oil spills; using a good maintenance program to keep the refinery as leakproof as possible; and individually treating waste streams with special characteristics, such as spent cleaning solutions.

The use of dry cleaning, without chemicals, aids in reducing water discharges to the sewer. Using vacuum trucks to clean up spills and charging of this recovered material to slop oil tanks, reduces the discharge of both oil and water to the waste water system. The oil can also be recovered for reprocessing. Process units should be curbed to prevent the contamination of clean areas with oily storm runoff and to prevent spills from spreading widely. Prompt cleanup of spills will also aid in reducing discharges to the sewer systems. Additionally, sewers should be flushed regularly to prevent the buildup of material in the sewer, eliminating sudden surges of pollutants during heavy rains. Collection vessels should also be provided whenever maintenance is performed on liquid processing units, to prevent accidental discharges to the sewers.

Operations during turnaround present special problems. Wastes generated by cleaning tanks and equipment should be collected, rather than draining directly to the sewer. The wastes from these holding tanks should be gradually bled to the sewer, after first pretreating as necessary to eliminate deleterious effects on the waste water treatment system. An alternative method of disposal is through the use of contract carriers.

While these are not all the examples of good housekeeping practices which can be cited for refinery operations, it is evident that housekeeping practices within a refinery can have substantial impact on the loads discharge to the waste treatment facilities. The application of good housekeeping practices to reduce waste loads requires judicious planning, organization and operational philosophy.

Process Technology

Many of the newer petroleum refining processes are being designed or modified with reduction of water use and subsequent minimization of contamination as design criteria; although no major innovations in basic refining technology are anticipated. Improvements which can be expected to be implemented in existing refineries are: primarily dedicated to better control of refinery processes and other operations; elimination of marginal processing operations, and specific substitution of processes and/or cooling techniques to reduce discharge loads to waste treatment facilities. Examples of the possible changes which may be implemented include:

1. Substitution of improved catalysts which have higher activity and longer life, consequently requiring less regeneration and resulting in lower waste water loads.
2. Replacement of barometric condensers with surface condensers or air fan coolers, reducing a major oil-water emulsion source. As an alternative, several refineries are using oily water cooling tower systems, with the barometric condensers, equipped with oil separation/emulsion breaking auxiliary equipment.

3. Substitution of air fan coolers to relieve water cooling duties simultaneously reduces blowdown discharges.
4. Installation of hydrocracking and hydrotreating processes will allow generation of lower waste loadings than the units they replace. The rapid pace at which such units are being installed is exerting and will continue to exert a strong influence on the reduction of waste loadings, particularly sulfides and spent caustics.
5. Installation of automatic monitoring instrumentation, such as TOC monitors, will allow early detection of process upsets which result in excessive discharges to sewers.
6. Increased use of improved drying, sweetening, and finishing procedures will minimize spent caustics and acids, water washes, and filter solids requiring disposal.

Cooling Towers

Cooling towers eliminate large volumes of once through cooling water by passing heated water through heat exchange equipment. By recycling the cooling water many times, the amount of water used is greatly reduced. The number of times cooling water can be reused is determined by the total dissolved solids (TDS) content of the water, and the effects high dissolved solids have on process equipment. When the TDS becomes too high, scaling occurs and heat transfer efficiency decreases. The TDS level in the circulating water is controlled by discharging a portion of the steam (blowdown) from the system. The higher the allowable TDS level, the greater number of cycles of concentration and the less make-up water is required (87). Installation of cooling towers will reduce the amount of water used within the refinery by at least 90 percent (87).

There are three types of cooling towers (106); wet or evaporative, dry, and combined "wet-dry."

Evaporative Cooling Systems

Evaporative cooling systems transport heat by transfer of the latent heat of vaporization. This results in a temperature decrease of circulating water and a temperature and humidity increase of cooling air.

Spray ponds are an evaporative cooling system using natural air currents and forced water movement. Because of their inefficiency, spray ponds are used less in industry than cooling towers. Cooling towers have a higher efficiency because they provide more intimate contact between the air and water. As the water falls over the packing, it exposes a large contact surface area. As the water heats up the air, the air can absorb more

water. The more water evaporated, the more heat is transferred (106). Because an evaporative cooling tower is dependent on ambient temperatures and humidity, its performance is variable throughout the year. There are three types of evaporative cooling towers: mechanical draft towers; atmospheric towers, which use wind or natural air currents; and natural draft towers, which use tall stacks to move air by stack effect. Most refineries use mechanical draft towers, which have baffles, called drift eliminators, to separate entrained water from the air stream, thus reducing the amount of water carried into the air. The evaporative system is the least costly of all cooling towers.

Dry Cooling Systems

There are two types of dry air cooling systems. Either system can be used with either mechanical or natural draft cooling towers. Most refineries use mechanical draft towers on indirect condensing systems. The tubes used in dry cooling equipment have circumferential fins to increase the heat transfer area. Most tube designs have an outside to inside surface area ratio of 20:1. (106) The advantage of the dry air system is that it requires no makeup water and there is no water entrainment. Dry air cooling systems are being increasingly used to reduce the amount of water discharged to the waste water treatment plant. A disadvantage of the dry cooling process is that it has low rates of heat transfer requiring large amounts of land and uses more power than other cooling systems. The dry cooling tower is also more expensive to install than evaporative systems.

Wet-Dry Systems

The wet-dry systems use an evaporative and non-evaporative cooling tower in either series or parallel, each of which can be operated with a mechanical or natural draft tower. The series design has the evaporative cooling process preceding the dry process with respect to the air flow. This lowers the temperature of the air entering the dry process which would mean a smaller unit could be used. The problem with this method is that solids are deposited in the dry tower due to drift from the wet section. The parallel process uses a dry cooling tower upstream of the wet section, each of which has its own air supply. The two air streams are mixed and discharged, reducing the vapor plume.

Recycle/Reuse Practices

Recycle/reuse can be accomplished either by return of the waste water to its original use, or by using it to satisfy a lower quality demand. The recycle/reuse practices within the refining industry are extremely varied and only a few examples are described briefly below:

1. Reduction of once-through cooling water results in tremendously decreased total effluents.

2. Sour water stripper bottoms are being used in several refineries as make-up water for crude desalter operations. These sour water bottoms are initially recovered from overhead accumulators on the catalytic cracking units.
3. Regeneration of contact process steam from contaminated condensate will reduce the contact process waste water to a small amount of blowdown. This scheme can be used to regenerate steam in distillation towers or dilution steam stripping in pyrolysis furnaces.
4. Reuse of waste water treatment plant effluent as cooling water, as scrubber water, or as plant make-up water, reduces total make-up requirements.
5. Cooling tower blowdowns are frequently reused as seal water on high temperature pump service, where mechanical seals are not practicable.
6. Storm water retention ponds are frequently used as a source of fire water or other low quality service waters.

Many other conservation methods can be implemented, such as the use of stripped sour water as low pressure (LP) boiler make-up, and LP boiler blowdown as make-up water for crude desalting. However, these, and the other possible recycle/reuse cases outlined above must be examined by the individual refinery in light of its possible advantages/disadvantages, insofar as product quality or refining process capabilities are affected. For example, one refinery has reported that reuse of sour water stripper bottoms for desalting resulted in a desalted crude which was difficult to process downstream.

At-Source Pretreatment

Major at-source pretreatment processes which are applicable to individual process effluents or groups of effluents within a refinery are stripping of sour waters, neutralization and oxidation of spent caustics, ballast water separation, and slop oil recovery. The particular areas of application of these processes are discussed below.

Sour Water Stripping

Sour or acid waters are produced in a refinery when steam is used as a stripping medium in the various cracking processes. The hydrogen sulfide, ammonia and phenols distribute themselves between the water and hydrocarbon phases in the condensate. The concentrations of these pollutants in the water vary widely depending on crude sources and processing involved.

The purpose of the treatment of sour water is to remove sulfides (as hydrogen sulfide, ammonium sulfide, and polysulfides) before

the waste enters the sewer. The sour water can be treated by: stripping with steam or flue gas; air oxidation to convert hydrogen sulfide to thiosulfates; or vaporization and incineration.

Sour water strippers are designed primarily for the removal of sulfides and can be expected to achieve 85-99 percent removal. If acid is not required to enhance sulfide stripping, ammonia will also be stripped with the percentage varying widely with stripping temperature and pH. If acid is added to the waste water, essentially none of the ammonia will be removed. Thus, ammonia removals in sour water strippers vary from 0 to 99 percent. Depending upon such conditions as waste water pH, temperature, and contaminant partial pressure; phenols and cyanides can also be stripped with removal as high as 30 percent. The bottoms from the stripper usually go to the desalter where most of the phenols are extracted and the waste water can be sent to the regular process water treating plant. COD and BOD₅ are reduced because of the stripping out of phenol and oxidizable sulfur compounds.

The heated sour water is stripped with steam or flue gas in a single stage packed or plate-type column. Two-stage units are also being installed to enhance the separate recovery of sulfide streams and ammonia streams. Hydrogen sulfide released from the waste water can be recovered as sulfuric acid or sulfur, or may be burned in a furnace. The bottoms have a low enough sulfide concentration to permit discharge into the general waste water system for biological treatment. If the waste contains ammonia, it is neutralized with acid before steam stripping. The waste liquid passes down the stripping column while the stripping gas passes upward. Most refiners now incinerate the sour water stripper acid gases without refluxing the stripper. This converts the ammonia to nitrogen with possibly traces of nitrogen oxides. Due to the high concentrations of sulfur dioxide produced more complex processing will probably be required in the future.

Several stripping processes are available. These include: Chevron WWT; ammonium sulfate production; a dual burner Claus sulfur plant; and the Howe-Baker ammonex process. Deep well injection and oxidation to the thiosulfate are also being used, but in the future probably won't do a good enough job.

The Chevron WWT process (37) is basically two stage stripping with ammonia purification, so that the hydrogen sulfide and ammonia are separated. The hydrogen sulfide would go to a conventional Claus sulfur plant and the ammonia can be used as fertilizer.

Ammonium sulfate can be produced by treating with sulfuric acid but a very dilute solution is produced and concentrating it for sale as fertilizer is expensive. Again the hydrogen sulfide goes to a conventional Claus sulfur plant.

A dual burner Claus sulfur process is generally the answer in new plants, but adding the second burner to an existing sulfur plant is difficult. The second burner is required to handle the ammonia. A refluxed stripper is required to reduce the water vapor in the hydrogen sulfide-ammonia mixture and the line between the stripper and the Claus Unit must be kept at about 150°F to prevent precipitation of ammonium sulfide complexes.

Howe-Baker Engineers Inc. of Tyler, Texas have developed to the pilot plant stage a process they call "Ammonex". It is a solvent extraction process that basically is intended to compete with the Chevron WWT process. No commercial units have been built.

Another way of treating sour water is to oxidize by aeration. Compressed air is injected into the waste followed by sufficient steam to raise the reaction temperature to at least 190°F. Reaction pressure of 50-100 psig is required. Oxidation proceeds rapidly and converts practically all the sulfides to thiosulfates and about 10 percent of the thiosulfates to sulfates. Air oxidation, however, is much less effective than stripping in regard to reduction of the oxygen demand of sour waters, since the remaining thiosulfates can later be oxidized to sulfates by aquatic microorganisms.

The stripping of sour water is normally carried out to remove sulfides and hence, the effluent may contain 50-100 ppm of ammonia, or even considerably higher, depending on the influent ammonia concentration. Values of ammonia have been reported as low as 1 ppm, but generally the effluent ammonia concentration is held to approximately 50 ppm to provide nutrient nitrogen for the refinery biological waste treatment system (2,14,33,58).

Spent Caustic Treatment

Caustic solutions are widely used in refining. Typical uses are to neutralize and extract:

- a. Acidic materials that may occur naturally in crude oil.
- b. Acidic reaction products that may be produced by various chemical treating processes.
- c. Acidic materials formed during thermal and catalytic cracking such as hydrogen sulfide, phenolics, and organic acids.

Spent caustic solutions may therefore contain sulfides, mercaptides sulfates, sulfonates, phenolates, naphthenates, and other similar organic and inorganic compounds.

At least four companies process these spent caustics to market the phenolics and the sodium hyposulfide. However, the market is limited and most of the spent caustics are very dilute so the cost of shipping the water makes this operation uneconomical.

Some refiners neutralize the caustic with spent sulfuric from other refining processes, and charge it to the sour water stripper. This removes the hydrogen sulfide. The bottoms from the sour water stripper go to the desalter where the phenolics are extracted by the crude oil.

Spent caustics usually originate as batch dumps, and the batches may be combined and equalized before being treated and/or discharged to the general refinery waste waters. Spent caustic solutions can also be treated by neutralization with flue gas. In the treatment of spent caustic solutions by flue gas, hydroxides are converted to carbonates. Sulfides, mercaptides, phenolates, and other basic salts are converted by the flue gas stripping. Phenols can be removed and used as a fuel or can be sold. Hydrogen sulfide and mercaptans are usually stripped and burned in a heater. Some sulfur is recovered from stripper gases. The treated solution will contain mixtures of carbonates, sulfates, sulfites, thiosulfates and some phenolic compounds. Reaction time of 16-24 hours is required for the neutralization of caustic solution with flue gas.

The oxidation phase of spent caustic treatment is aimed at the sulfide content of these wastes and achieves 85-99 percent sulfide removal. In this process, sulfides are oxidized primarily to thiosulfates although in some variations there is partial oxidation of the sulfur compounds to sulfate. Oxidation processes are not applied to phenolic caustics, as phenols inhibit oxidation. It should be noted that those processes which oxidize the sulfide only to thiosulfate, satisfy half of the oxygen demand of the sulfur, as thiosulfate can be oxidized biologically to sulfate. Neutralization of spent caustics is applied to both phenolic and sulfidic caustic streams; the sulfidic caustics are also steam stripped, after neutralization, to remove the sulfides. When phenolic spent caustics are neutralized, crude acid oils or "crude carbolates" are sprung and thus removed from the waste water. The major part of the phenols will appear in the oil fraction, but a significant part may remain in the waste water as phenolates.

Fluid bed incineration is also now being used. This process was developed under an EPA demonstration grant (26) and at least two large units are under construction. Once the incinerator is started up, the sludge should provide the necessary heating value to keep the system operating. Oxidizing fuels may be required when the sludge is burnt, as ash remains in the bed of the incinerator. A constant bed level is maintained, so the sand bed originally in the incinerator is gradually replaced by the inert sludge ash (5). The gasses pass through a scrubber, so the fines and particulate matter can be recovered. The ash and fines can be landfilled. This landfill is cleaner than a sludge landfill, because there are no organic materials present to contaminate ground water or run-off.

In the past ocean dumping, deep well injection, evaporative lagoons, and simple dilution have all been used. These methods will no longer be acceptable.

Sewer System Segregation

Waste water quantity is one of the major factors that affect the cost of waste treatment facilities most directly. Water usage in the petroleum refining industry varies from less than 5 gallons of water per barrel of crude charge in the newer refineries to higher than 1000 gallons of water per barrel of crude charge in the older refineries. In order to provide efficient treatment to the wastes originating within a refinery, it is very important that segregation of concentrated waste streams be considered. Segregation of waste streams frequently simplifies waste treating problems as well as reduces treatment facility costs. Thus, treatment of highly polluted waste streams at the source can prevent gross pollution of large volumes of relatively clean waste water. Such treatment is often a more economical solution of a problem than would be possible if wastes are discharged directly to the refinery sewers. Treatment at the source is also helpful in recovering by-products from the wastes which otherwise could not be economically recovered when the wastes are combined.

In areas where water supply is limited, reduced water requirements have been incorporated into the design and operation, thereby reducing total water usage.

To minimize the size of the waste water treatment processes it is imperative polluted water only be treated. This can be guaranteed by segregating the various sewer systems. There should be a sewer carrying process and blowdown waters that are treated continuously. A polluted storm water sewer should go to a storage area from which it can be gradually discharged to the treatment facilities. A sewer system containing clean storm water can be discharged directly to the receiving water. The sanitary system should be treated separately from the process water because of the bacteria present in this stream. Once through cooling water should be kept separate because of the large volumes of water involved and the low waste loadings encountered. A connection to the treatment plant should be provided in case of oil leaks into the system.

Storm Water Runoff

An additional source of pollution from a petroleum refinery area is caused by rainfall runoff. Size and age of refinery site, housekeeping, drainage areas, and frequency and intensity of rainfall are several of the factors which compound the assignment of allowable pollutional values.

There are several measures that refiners can provide to minimize storm water loads to their treatment system after diverting all extraneous drainage around the refinery area. The major consideration is a separate storm water sewer and holding system.

By providing separate collection facilities for storm water runoff, protection is afforded the operation of the separator and ancillary treatment systems by controlling the hydraulic load to be treated. Comingling of inorganic particles with oily waste water often times produces an emulsion which is difficult to break in the oil-water separator.

Design of this facility should be based on the maximum ten-year, twenty-four-hour rainfall runoff of the refinery drainage area. Diversion of the collected storm water runoff to the oil-water separator facilities can be provided when hydraulic flows return to normal operations. In the event of excessive collection due to a high intensity storm, diversion facilities should be provided to allow for emergency bypass capability to divert the trailing edge of the runoff hydrograph (the leading edge normally contained the mass of pollutants in urban runoff investigations). An oil retention baffle and an API type overflow weir should be provided to prevent the discharge of free and floating oil.

An alternate to the separate sewer system would be the provision of a storm surge pond that would receive the polluted waters when the flow to the oil-water separator exceeded 15 percent of the normal hydraulic flow. During normal periods, the collected storm water-refinery water could then be diverted to the oil-water separator (provided process flow did not equal or exceed the units hydraulic capacity).

The major cause of pollution by storm water runoff is the lack of housekeeping within the refinery confine. Proper procedures should be encouraged to prevent the accumulation of materials which contribute to pollution due to rainfall runoff. Some of the more common preventive measures are: (1) Provide curbing around process unit pads; (2) Prevent product sample drainage to sewers; (3) Repair pumps and pipes to prevent oily losses to the surface areas; (4) Contain spilled oil from turnarounds; (5) Dike crude and product tank areas and valve precipitation to the storm water sewer.

In the event the collected water needs to be released from the storm water detention pond due to overflow, samples of the water should be monitored for; (1) Oil and Grease, (2) Organic analysis such as TOC.

Ballast Water Separation

Ballast water normally is not discharged directly to the refinery sewer system because the intermittent high-volume discharges. The potentially high oil concentrations, would upset the refinery waste water treatment facilities. Ballast waters may also be treated separately, with heating, settling, and at times filtration as the major steps. The settling tank can also be provided with a steam coil for heating the tank contents to help break emulsions, and an air coil to provide agitation. The recovered oil, which may be considerable, is generally sent to the slop oil system.

Slop Oil Treatment

Separator skimmings, which are generally referred to as slop oil, require treatment before they can be reused, because they contain an excess amount of solids and water. Solids and water contents in excess of about 1 percent generally interfere with processing.

In most cases slop oils are easily treated by heating to 190°F for 12 to 14 hours. At the end of settling, three definite layers exist: a top layer of clean oil; a middle layer of secondary emulsion; and a bottom layer of water containing soluble components, suspended solids, and oil. In some cases, it is advantageous or even necessary to use acid or specific chemical demulsifiers to break slop oil emulsions. The water layer resulting from acid and heat treatment has high BOD and COD, but also low pH, and must be treated before it can be discharged.

Slop oil can also be successfully treated by centrifugation or by precoat filtration using diatomaceous earth as the precoat.

Gravity Separation of Oil

Gravity separators remove a majority of the free oil found in refinery waste waters. Because of the large amounts of reprocessible oils which can be recovered in the gravity separators, these units must be considered an integral part of the refinery processing operation and not a waste water treatment process. The functioning of gravity-type separators depends upon the difference in specific gravity of oil and water. The gravity-type separator will not separate substances in solution, nor will it break emulsions. The effectiveness of a separator depends upon the temperature of the water, the density and size of the oil globules, and the amounts of characteristics of the suspended matter present in the waste water. The "susceptibility to separation" (STS) test is normally used as a guide to determine what portion of the influent to a separator is amenable to gravity separation.

The API separator is the most widely used gravity separator. The basic design is a long rectangular basin, with enough detention time for most of the oil to float to the surface and be removed. Most API separators are divided into more than one bay to maintain laminar flow within the separator, making the separator more effective. API separators are usually equipped with scrapers to move the oil to the downstream end of the separator where the oil is collected in a slotted pipe or on a drum. On their return to the upstream end, the scrapers travel along the bottom moving the solids to a collection trough. Any sludge which settles can be dewatered and either incinerated or disposed of as landfill.

The gravity separator usually consists of a pre-separator (grit chamber) and a main separator, usually rectangular in shape,

provided with influent and effluent flow distribution and stilling devices and with oil skimming and sludge collection equipment. It is essential that the velocity distribution of the approach flow be as uniform as possible before reaching the inlet distribution baffle.

Another type of separator finding increasing employment in refineries is the parallel plate separator. The separator chamber is subdivided by parallel plates set at a 45° angle, less than 6 inches apart. This increases the collection area while decreasing the overall size of the unit. As the water flows through the separator the oil droplets coalesce on the underside of the plates and travel upwards where the oil is collected. The parallel plate separator can be used as the primary gravity separator, or following an API separator.

Further Removal of Oil and Solids

If the effluent from the gravity separators is not of sufficient quality to insure effective treatment before entering the biological or physical-chemical treatment system, it must undergo another process to remove oils and solids. Most refineries use either clarifiers, dissolved air flotation units or filters to reduce the oil and solids concentration. Each of these processes has also been used to treat the effluent from a biological system.

Clarifiers

Clarifiers use gravitational sedimentation to remove oil and solids from a waste water stream. Often it is necessary to use chemical coagulants such as alum or lime to aid the sedimentation process. These clarifiers are usually equipped with a skimmer to remove any floating oil. Clarifiers used after a biological system normally do not have skimmers as there should be no floating oils at that point. The sludge from the clarifiers is usually treated before final disposal.

End-of-Pipe Control Technology

End-of-pipe control technology in the petroleum refining industry relies heavily upon the use of biological treatment methods. These are supplemented by appropriate pretreatment to insure that proper conditions, especially sufficient oil removal and pH adjustment, are present in the feed to the biological system. When used, initial treatment most often consists of neutralization for control of pH or equalization basins to minimize shock loads on the biological systems. The incorporation of solids removal ahead of biological treatment is not as important as it is in treating municipal waste waters.

One of the initial criteria used to screen refineries for the field survey, was degree of treatment provided by their waste water treatment facilities. Therefore, the selection of plants was not based on a cross-section of the entire industry, but

rather was biased in favor of those segments of the industry that had the more efficient waste water treatment facilities. Table 26 indicates the types of treatment technology and performance characteristics which were observed during the survey. In most of the plants analyzed, some type of biological treatment was utilized to remove dissolved organic material. Table 27 summarizes the expected effluents from waste water treatment processes throughout the petroleum refining industry. Typical efficiencies for these processes are shown in Table 28.

During the survey program, waste water treatment plant performance history was obtained when possible. This historical data were analyzed statistically and the individual plant's performance evaluated in comparison to the original design basis. After this evaluation, a group of plants was selected as being exemplary and these plants were presented in Table 26. The treatment data in Table 28 represent the annual daily average performance (50 percent probability-of-occurrence).

There were enough plants involving only one subcategory to make the interpretation meaningful. In preparing the economic data base, however, all the waste water treatment plant data were analyzed to develop a basis for subsequent capital and operating costs.

The treatment data from the exemplary plants referred to previously were analyzed to formulate the basis for developing BPCTCA effluent criteria. The effluent limitations were based on both these treatment data, other data included in Supplement B, and other sources as discussed in Section IX. These effluent limitations were developed for each subcategory individually and thus no common treatment efficiency was selected as being typical of the petroleum refining industry for use in the BPCTCA effluent limitations. A brief description of the various elements of end-of-pipe treatment follows.

Equalization

The purpose of equalization is to dampen out surges in flows and loadings. This is especially necessary for a biological treatment plant, as high concentrations of certain materials will upset or completely kill the bacteria in the treatment plant. By evening out the loading on a treatment plant, the equalization step enables the treatment plant to operate more effectively and with fewer maintenance problems. Where equalization is not present, an accident or spill within the refinery can greatly affect the effluent quality or kill the biomass (R7, R20).

The equalization step usually consists of a large pond that may contain mixers to provide better mixing of the wastes. In some refineries the equalization is done in a tank (55, R29). The equalization step can be before or after the gravity separator but is more effective before as it increases the overall efficiency of the separator. However, care must be taken to prevent anaerobic decomposition in the equalization facilities.

Observed Refinery Treatment System and Effluent Loadings

TABLE 26

SUBCATEGORY	A	B	B	B	B	B	C	C	C	D	D	E
Type of Treatment Refinery Observed Average Effluent Loadings Net-kg/1000 m3 of feedstock (1b/1000 bbl of feedstock)	OP R32	AL-PP R18	AL-F R27	E-DAF-AS R26	OP R26	DAF,AL,PP R7	DAF,AS R20	DAF,AS R8	DAF,AL,PP R23	E,TF,AS R24	E,AS R28	DAF,AS,PP R25
BOD5		8(2.8)	8.0(4.4)	5.9(2.1)	10(3.6)	3.7(1.3)	13(4.6)	2.7(0.95)	2.6(0.91)	7.4(2.6)	14(5.0)	17.5(6.2)
COD	-----	39(13.8)	68(24)	96(34)	71(25.0)	39(13.8)	67(23.5)	-----	54(19)	57(20)	136(48)	320(113)
TSS	-----	-----	25(8.7)	34(12)	8.5(3.0)	4.2(1.5)	13.6(4.8)	8.5(3.0)	7(2.5)	12(4.3)	38(13.5)	36(12.7)
O&G	2.0(0.7)	2.3(0.8)	9(3.2)	4.0(1.4)	-----	2.8(1.0)	6.5(2.3)	-----	-----	4(1.4)	7.2(2.55)	22(7.7)
NH3-N	-----	-----	-----	-----	4.8(1.7)	0.14(0.05)	4.5(1.6)	-----	2(0.7)	1.2(0.44)	-----	2.3(0.8)
Phenolic Compounds	0.14(0.05)	0.003(0.001)	0.4(0.145)	0.37(0.13)	0.05(0.018)	0.0006(0.002)	0.06(0.023)	-----	-----	0.17(0.06)	-----	0.017(0.005)
Sulfide	0.03(0.009)	-----	0.2(0.07)	0(0)	0.03(0.010)	0.014(0.005)	0.05(0.018)	-----	-----	-----	-----	0.20(.07)

Footnotes: AL-aerated lagoon
AS-activated sludge
DAF-dissolved air flotation
E-equalization
F-filtration
OP-oxidation pond
PP-polishing pond
TF-trickling filter
A-Topping
B-Cracking
C-Petrochemicals
D-Lube
E-Integrated

TABLE 27

Expected Effluents from Petroleum Treatment Processes

PROCESS	PROCESS INFLUENT	EFFLUENT CONCENTRATION, mg/L								REFERENCES
		BOD ₅	COD	TOC	SS	OIL	PHENOL	AMMONIA	SULFIDE	
1. API Separator	Raw Waste	250-350	260-700	NA	50-200	20-100	6-100	15-150	NA	7,13,30,41,49,59
2. Clarifier	1	45-200	130-450	NA	25-60	5-35	10-40	NA	NA	34,48a,49
3. Dissolved Air Flotation	1	45-200	130-450	NA	25-60	5-20	10-40	NA	NA	13,29,32,48a,49
4. Granular Media Filter	1	40-170	100-400	NA	5-25	6-20	3-35	NA	NA	17,41,48a,48
5. Oxidation Pond	1	10-60	50-300	NA	20-100	1.6-50	0.01-12	3-50	0-20	18,22,23,31,42,48a, 49,55,75,R18
6. Aerated Lagoon	2,3,4	10-50	50-200	NA	10-80	5-20	0.1-25	4-25	0-0.2	31,39,42a,48a,49, 55,59,R7,R23,R26
7. Activated Sludge	2,3,4	5-50	30-200	20-80	5-50	1-15	0.01-2.0	1-100	0-0.2	13,24,27,30,34,35, 42,48a,49,60,69,72 R8,R20,R24,R25,R27 R28,R29
8. Trickling Filter	1	25-50	80-350	NA	20-70	10-80	0.5-10	25-100	0.5-2	18,30,42,48a,49,
9. Cooling Tower	2,3,4	25-50	47-350	70-150	4.5-100	20-75	.1-2.0	1-30	NA	33,41
10. Activated Carbon	2,3,4	5-100	30-200	NA	10-20	2-20	<1	10-140	NA	17,21,27,48,48a,49, 53,62a
11. Granular Media Filter	5-9	NA	NA	25-61	3-20	3-17	0.35-10	NA	NA	17,48,54
12. Activated Carbon	5-9 and 11	3-10	30-100	1-17	1-15	0.8-2.5	0-0.1	1-100	0-0.2	17,21,27,48,48a,49, 53,62a

A - Data Not Available.

TABLE 28

Typical Removal Efficiencies for Oil Refinery Treatment Processes

PROCESS	PROCESS INFLUENT	REMOVAL EFFICIENCY, %								REFERENCES
		BOD ₅	COD	TOC	SS	OIL	PHENOL	AMMONIA	SULFIDE	
1. API Separator	Raw Waste	5-40	5-30	NA	10-50	60-99	0-50	NA	NA	7,13,30,41,49,59
2. Clarifier	1	30-60	20-50	NA	50-80	60-95	0-50	NA	NA	34,48a,49
3. Dissolved Air Flotation	1	20-70	10-60	NA	50-85	70-85	10-75	NA	NA	13,29,32,48a,49
4. Filter	1	40-70	20-55	NA	75-95	65-90	5-20	NA	NA	17,41,48a,49
5. Oxidation Pond	1	40-95	30-65	60	20-70	50-90	60-99	0-15	70-100	18,22,23,31,42,48 49,55,75,R18
6. Aerated Lagoon	2,3,4	75-95	60-85	NA	40-65	70-90	90-99	10-45	95-100	31,39,42,48a,49, 55,59,R7,R23,R26
7. Activated Sludge	2,3,4	80-99	50-95	40-90	60-85	80-99	95-99+	33-99	97-100	13,24,R7,30,34,35 42,48a,49,60,69,72 R8,R20,R24,R25,R2 R28,R29
8. Trickling Filter	1	60-85	30-70	NA	60-85	50-80	70-98	15-90	70-100	18,30,42,48a,49
9. Cooling Tower	2,3,4	50-90	40-90	10-70	50-85	60-75	75-99+	60-95	NA	33,41
10. Activated Carbon	2,3,4	70-95	70-90	50-80	60-90	75-95	90-100	7-33	NA	17,21,27,48,48a,49 49,53,62a
11. Filter Granular Media	5-9	NA	NA	50-65	75-95	65-95	5-20	NA	NA	17,48,54
12. Activated Carbon	5-9 plus 11	91-98	86-94	50-80	60-90	70-95	90-99	33-87	NA	17,21,27,48,48a, 49,53,62a

NA - Data Not Available

Dissolved Air Flotation

Dissolved air flotation consists of saturating a portion of the waste water feed, or a portion of the feed or recycled effluent from the flotation unit with air at a pressure of 40 to 60 psig. The waste water or effluent recycle is held at this pressure for 1-5 minutes in a retention tank and then released at atmospheric pressure to the flotation chamber. The sudden reduction in pressure results in the release of microscopic air bubbles which attach themselves to oil and suspended particles in the waste water in the flotation chamber. This results in agglomerates which, due to the entrained air, have greatly-increased vertical rise rates of about 0.5 to 1.0 feet/minute. The floated materials rise to the surface to form a froth layer. Specially designed flight scrapers or other skimming devices continuously remove the froth. The retention time in the flotation chambers is usually about 10-30 minutes. The effectiveness of dissolved air flotation depends upon the attachment of bubbles to the suspended oil and other particles which are to be removed from the waste stream. The attraction between the air bubble and particle is a result of the particle surface and bubble-size distribution.

Chemical flocculating agents, such as salts of iron and aluminum, with or without organic polyelectrolytes, are often helpful in improving the effectiveness of the air flotation process and in obtaining a high degree of clarification.

Dissolved air flotation is used by a number of refineries to treat the effluent from the oil separator. Dissolved air flotation using flocculating agents is also used to treat oil emulsions. The froth skimmed from the flotation tank can be combined with other sludges (such as those from a gravity separator) for disposal. The clarified effluent from a flotation unit generally receives further treatment in a biological unit, prior to discharge. In two refineries, dissolved air flotation is used for clarification of biologically treated effluents (29).

Oxidation Ponds

The oxidation pond is practical where land is plentiful and cheap. An oxidation pond has a large surface area and a shallow depth, usually not exceeding 6 feet. These ponds have long detention periods from 11 to 110 days.

The shallow depth allows the oxidation pond to be operated aerobically without mechanical aerators. The algae in the pond produce oxygen through photosynthesis. This oxygen is then used by the bacteria to oxidize the wastes. Because of the low loadings, little biological sludge is produced and the pond is fairly resistant to upsets due to shock loadings.

Oxidation ponds are usually used as the major treatment process. Some refineries use ponds as a polishing process after other treatment processes.

Aerated Lagoon

The aerated lagoon is a smaller, deeper oxidation pond equipped with mechanical aerators or diffused air units. The addition of oxygen enables the aerated lagoon to have a higher concentration of microbes than the oxidation pond. The retention time in aerated lagoons is usually shorter, between 3 and 10 days. Most aerated lagoons are operated without final clarification. As a result, biota is discharged in the effluent, causing the effluent to have high BOD₅ and solids concentrations. As the effluent standards become more strict, final clarification will be increasing in use.

Trickling Filter

A trickling filter is an aerobic biological process. It differs from other processes in that the biomass is attached to the bed media, which may be rock, slag, or plastic. The filter works by: 1) adsorption of organics by the biological slime 2) diffusion of air into the biomass; and 3) oxidation of the dissolved organics. When the biomass reaches a certain thickness, part of it sloughs off. When the filter is used as the major treatment process, a clarifier is used to remove the sloughed biomass.

The trickling filter can be used either as the complete treatment system or as a roughing filter. Most applications in the petroleum industry use it as a roughing device to reduce the loading on an activated sludge system.

Bio-Oxidation Tower

The bio-oxidation tower uses a cooling tower to transfer oxygen to a waste water. API (112) has called the bio-oxidation towers a modified activated sludge process, as most of the biomass is suspended in the wastewater. Results from refineries indicate it is a successful process to treat portions or all of a refinery waste water (80, 81, 92).

Activated Sludge

Activated sludge is an aerobic biological treatment process in which high concentrations (1500-3000 mg/L) of newly-grown and recycled microorganisms are suspended uniformly throughout a holding tank to which raw waste waters are added. Oxygen is introduced by mechanical aerators, diffused air systems, or other means. The organic materials in the waste are removed from the aqueous phase by the microbiological growths and stabilized by biochemical synthesis and oxidation reactions. The basic activated sludge process consists of an aeration tank followed by a sedimentation tank. The flocculant microbial growths removed in the sedimentation tank are recycled to the aeration tank to maintain a high concentration of active microorganisms. Although the microorganisms remove almost all of the organic matter from the waste being treated, much of the converted organic matter remains in the system in the form of microbial cells. These

cells have a relatively high rate of oxygen demand and must be removed from the treated waste water before discharge. Thus, final sedimentation and recirculation of biological solids are important elements in an activated sludge system.

Sludge is wasted on a continuous basis at a relatively low rate to prevent build-up of excess activated sludge in the aeration tank. Shock organic loads usually result in an overloaded system and poor sludge settling characteristics. Effective performance of activated sludge facilities requires pretreatment to remove or substantially reduce oil, sulfides (which causes toxicity to microorganisms), and phenol concentrations. The pretreatment units most frequently used are: gravity separators and air flotation units to remove oil; and sour water strippers to remove sulfides, mercaptans, and phenol. Equalization also appears necessary to prevent shock loadings from upsetting the aeration basin. Because of the high rate and degree of organic stabilization possible with activated sludge, application of this process to the treatment of refinery waste waters has been increasing rapidly in recent years.

Many variations of the activated sludge process are currently in use. Examples include: the tapered aeration process, which has greater air addition at the influent where the oxygen demand is the highest; step aeration, which introduces the influent waste water along the length of the aeration tank; and contact stabilization, in which the return sludge to the aeration tank is aerated for 1-5 hours. The contact stabilization process is useful where the oxygen demand is in the suspended or colloidal form. The completely mixed activated sludge plant uses large mechanical mixers to mix the influent with the contents of the aeration basin, decreasing the possibility of upsets due to shock loadings. The Pasveer ditch is a variation of the completely mixed activated sludge process that is widely used in Europe. Here brushes are used to provide aeration and mixing in a narrow oval ditch. The advantage of this process is that the concentration of the biota is higher than in the conventional activated sludge process, and the wasted sludge is easy to dewater. There is at least one refinery using the Pasveer ditch type system.

The activated sludge process has several disadvantages. Because of the amount of mechanical equipment involved, its operating and maintenance costs are higher than other biological systems. The small volume of the aeration basin makes the process more subject to upsets than either oxidation ponds or aerated lagoons.

As indicated in Table 25, the activated sludge process is capable of achieving very low concentrations of BOD₅, COD, TSS, and oil, dependent upon the influent waste loading and the particular design basis. Reported efficiencies for BOD₅ removal are in the range of 80 to 99 percent.

Physical-Chemical Treatment

Physical-chemical treatment refers to treatment processes that are non-biological in nature. There are two types of physical-chemical processes; those that reduce the volume of water to be treated (vapor compression evaporators, reverse osmosis, etc.), and those that reduce the concentration of the pollutants (activated carbon).

Physical-chemical (P-C) processes require less land than biological processes. P-C processes are not as susceptible to upset due to shock loading as are biological processes. Another advantage of P-C is that much smaller amounts of sludge are produced.

Flow Reduction Systems

Flow reduction systems produce two effluents, one of relatively pure water and one a concentrated brine. The pure water stream can be reused within the refinery resulting in a smaller effluent flow. The brine is easier to treat as it is highly concentrated. Both of the processes described herein have been demonstrated on small flows only and at present the costs involved are extremely high (45, 52, 93).

In the vapor compression evaporator the waste water flows over heat transfer surfaces. The steam generated enters a compressor where the temperature is raised to a few degrees above the boiling point of the waste water. The compressed steam is used to evaporate more waste water while being condensed. The condensed steam is low in dissolved solids. The major process costs are the costs of electrical power, which is approximately \$1.0/1000 gallons of clean water (93).

The reverse osmosis process uses high pressures (400-800 psig) to force water through a semi-permeable membrane. The membrane allows the water to pass through, but contains the other constituents in the waste water. Currently available membranes tend to foul and blind, requiring frequent cleaning and replacement. Until this problem is corrected, reverse osmosis is not a practicable process. The operating cost for a reverse osmosis unit is approximately 20-30¢/1000 gallons (45, 95).

Granular Media Filters

There are several types of granular media filters: sand, dual media, and multimedia. These filters operate in basically the same way, the only difference being the filter media. The sand filter uses relatively uniform grade of sand resting on a coarser material. The dual media filter has a coarse layer of coal above a fine layer of sand. Both types of filters have the problem of keeping the fine particles on the bottom. This problem is solved by using a third very heavy, very fine material, (usually garnet) beneath the coal and sand.

As the water passes down through a filter, the suspended matter is caught in the pores. When the pressure drop through the

filter becomes excessive, the flow through the filter is reversed for removal of the collected solids loading. The backwash cycle occurs approximately once a day, depending on the loading, and usually lasts for 5-8 minutes. Most uses of sand filters have been for removing oil and solids prior to an activated carbon unit. There is one refinery that uses a mixed media filter on the effluent from a biological system. Granular media filters are shown to be capable of consistently operated with extremely low TSS and oil effluent discharges, on the order of 5-10 mg/L.

Activated Carbon

The activated carbon (AC) process utilizes granular activated carbon to adsorb pollutants from waste water. The adsorption is a function of the molecular size and polarity of the adsorbed substance. Activated carbon preferentially adsorbs large organic molecules that are non-polar.

An AC unit follows a solids removal process, usually a sand filter which prevents plugging of the carbon pores. From the filter the water flows to a bank of carbon columns arranged in series or parallel. As the water flows through the columns the pollutants are adsorbed by the carbon, gradually filling the pores. At intervals, portions of the carbon are removed to a furnace where the adsorbed substances are burnt off. The regenerated carbon is reused in the columns, with some makeup added, because of handling and efficiency losses.

Activated carbon processes currently have only limited usage in the refining industry. However, there are new installations in the planning construction stages. The increasing use of activated carbon has occurred because activated carbon can remove organic materials on an economically competitive basis with biological treatment. Activated carbon regeneration furnaces have high energy requirements.

Sludge Handling and Disposal

Digestion

Digestion is usually used preceding the other sludge concentration and disposal methods. The purpose of digestion is to improve the dewatering of the sludge. Digestion can occur aerobically or anaerobically. During digestion, bacteria decompose the organic material in the sludge producing methane, carbon dioxide and water. At the end of the digestion process, the sludge is stable and non-decomposable.

Vacuum Filtration

The various vacuum filters, usually a revolving drum, use a vacuum to dewater the sludge. The revolving drum type has a vacuum applied against a cloth. The water passes through the cloth and returns to the influent of the treatment plant. The sludge remains on the drum until it is scraped off with a knife.

Centrifugation

Centrifugation uses high speed rotation to separate sludge and water. The heavier sludge moves to the outside and is conveyed to one end, where it is collected for final disposal. The water flows out the opposite end and is returned to the treatment plant.

Sludge Disposal

From any waste water treatment plant, the sludge must be disposed of. The methods used are landfilling, landfarming, barging to sea, and incineration.

Landfilling

A landfill operation requires a large amount of land. Before landfilling, the sludge should be digested to avoid odor problems. The sludge is disposed of in an excavation site. After each batch is disposed of, it is covered with a layer of earth. When the site is filled to capacity it is covered with a thick layer of earth.

The largest problem of industrial landfills is the pollution to ground and surface waters by leaching. Leaching occurs when water percolates through the landfill. As it drains through the landfill site, the water carries with it dissolved and suspended solids and organic matter. This water can then contaminate underground or surface streams it comes in contact with.

Incineration

Incineration is gradually complementing landfills as a method of sludge disposal. The principal process is fluid bed incineration. In this process, a bed of sand is preheated with hot air to 482-538°C (900 - 1000°F). Torch oil is then used to raise the bed temperature to 649 - 705°C (1200 - 1300°F). At this point waste water sludge and/or sludge is introduced and the torch oil is stopped. The solid products of combustion remain in the bed which is gradually withdrawn to maintain a constant bed height. Eventually, the bed will be composed of only ash.

The sludge fed to the incinerator usually contains inorganic as well as organic material. However, the sludge must contain a minimum amount of organics to maintain the combustion process. One refinery (26) suggests a minimum of 1,930,000 cal/cu m (29,000 Btu/gal) of sludge heating value is necessary to maintain the combustion process.