WATER POLLUTION CONTROL IN PETROLEUM REFINERIES IN THE UNITED STATES

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ABSTRACT

The principal use of water by the petroleum refining industry in the United States of America is in the refining branch itself, and the present paper is concerned with problems arising from this use of water, and some of the measures being taken by the industry to solve these problems. The compilation of the *Manual on Disposal of Refinery Wastes* is briefly alluded to, and the importance of recirculation indicated. It is reported that cooling accounts for 97 per cent of total refinery water requirements. The use of air coolers is growing rapidly in the USA. It may well be more effective and more economical to segregate waste waters by classes and treat each class separately. Next, the use of dissolved air flotation for removal of suspended solids and oils is considered, followed by comments on ponding. Some biological treatments are briefly described, with notes on application. Examples of waste water treatment in new refineries are given, paying attention to the effects of recent legislation to control deterioration of the environment. Difficulty is likely to arise at any stage where particles have the same density as the water into which they are introduced. In future, processes will be redesigned still further to improve re-use of circulating water and reduce water usage from outside sources, coupled with more and more air cooling stages.

The petroleum industry in the United States has been concerned with water use and the subsequent handling and treatment of waste water for many years. In the late 1920's, a group known as the Committee on Disposal of Refinery Wastes was formed in the Division of Refining of the American Petroleum Institute (API) to deal specifically with waste water treatment in refineries. The committee's scope was later expanded to include all pollution problems inside the refinery fence.

One of the important continuing contributions of this committee has been the compilation of a *Manual on Disposal of Refinery Wastes*. The various volumes which make up the Manual are kept up to date by periodic revisions. In 1969, a completely rewritten *Manual on Liquid Wastes* was published, combining former Volumes I and III and adding new data. The titles of the volumes are as follows:

Volume on *Liquid Wastes*
Vol. II, *Waste Gases and Particulate Matter*
Vol. IV, *Sampling and Analysis of Waste Water*
Vol. V, *Sampling and Analysis of Waste Gases and Particulate Matter*
Vol. VI, *Solid Wastes*

The petroleum industry uses very large quantities of water. The principal use of water by the industry is in the refining branch. Other operations such as the transportation of crude oil and products and marketing do not use significant amounts of water. Some water is used in the producing branch for drilling wells and operation of natural gasoline plants, but the amount is small in relation to that used in refineries.

I will confine my remarks to the problems arising from the use of water by the refining segment of the petroleum industry in the United States and some of the measures being taken by the industry to solve these problems.

It is estimated that US petroleum refineries have a gross water use of 16.7 billion gallons a day. However, the water intake to refineries is only 3.6 billion gallons a day. This indicates a substantial re-use or recirculation of water and extensive conservation of intake water from external sources.

Of the 3.6 billion gallons, roughly half is fresh water with the balance being either brackish or salt water.

The day of the once-through use of water in petroleum refining is becoming a thing of the past. This is particularly true in new installations, and in refineries which have undergone major revamping or modernization programmes. Reduction in water use has been accomplished by changes in process design of refinery operating units to improve heat transfer, by the use of air cooling of process streams, and by water re-use or recirculation.

In late 1967, API conducted a survey in order to secure representative data on the waste water treatment and control practices of oil refineries in the US. The survey report was issued in September, 1968.

Of the 260 refineries operating in the 48 contiguous states, replies to the questionnaire were received from 171 refineries representing approximately 93 per cent of domestic capacity. Some 39 relatively small asphalt, lubricating oil blending, and specialty plants responded but were subsequently deleted from the overall tabular comparisons due to fragmentary data and because they did not represent typical crude oil processing operations. The remaining 132 reporting refineries had a total crude oil capacity of 9 050 000 BPDC, representing some 87 per cent of US capacity.

Our industry recognizes that the extent of downstream processing complexity, as well as the nature of the crude oil processed, has a significant impact on the character and quantity of contaminants entering a given refinery waste water system.

Catalytic cracking, octane upgrading processes, lubricating oil processing and petrochemical processes all increase the waste load potential of the system. After due consideration of a number of factors, the refinery processing classification system shown in *Table 1* was used in the survey.

Table 1. Refinery processing classification system

Category	*Processing scheme*
A	Topping (atmospheric and/or vacuum distillation)
B	Topping plus catalytic cracking
C	Topping, plus catalytic cracking plus petrochemicals
D	Integrated (topping plus catalytic cracking plus lubrication oil processing)
E	Integrated plus petrochemicals

After classifying each responding refinery into one of the five complexity categories, each reply was evaluated and classified by type of waste treatment employed.

Waste treatment categories were established as shown in *Table 2*.

Table 2. Waste treatment categories

Primary treatment	Gravity separation
Intermediate treatment	Chemical flocculation Air flotation—without chemicals Air flotation—with chemicals Filtration
Biological treatment	Activated sludge Trickling filter Stabilization ponds—with aerators Stabilization ponds—without aerators Oxidation in cooling towers

Table 3 shows a breakdown of the total number and total capacity of refineries in each of the five complexity categories.

Table 3. Processing categories vs. crude capacities

Category	*No. of refineries reporting*	*Crude capacity* (BPCD)	*% of total US crude capacity*
A	15	317000	3.0
B	70	2921000	27.9
C	20	2002000	19.2
D	18	2142000	20.5
E	9	1668000	16.0
	132	9050000	86.6

A breakdown by type of waste treatment is shown in *Table 4*.

Table 4. Breakdown of capacity by type of waste treatment

	Crude capacity (BPCD)	*% of US Capacity*
Primary treatment only	3446000	33.0
Intermediate treatment	1171000	11.2
Biological treatment	4433000	42.4
	9050000	86.6

Utilizing the survey data, representing 87 per cent of US refining capacity and extrapolating for the balance of unreported refineries, the estimated overall total refinery effluent contaminant loadings, following waste treatment, are as shown in *Table 5*.

Table 5

Contaminant	*Pounds per day*
BOD	800000
COD	2500000
Oil	360000
Phenol	55000
Suspended solids	500000

The results of this survey indicated that on an average, cooling accounts for 97 per cent of total refinery water requirements. The average total requirement is 45 barrels of water per barrel of crude charged.

It is significant that 46 per cent of the refineries reported some use of air cooling of process streams. Air cooling was used most extensively by refineries with complex operations including petrochemical operations. A number of refineries used air cooling to fill over 20 per cent of their total cooling requirement. The use of air coolers is growing rapidly in the US.

Of the water used for steam generation and processing (3 per cent), 1.7 per cent is supplied by raw water and 0.9 per cent is supplied by steam condensate and process condensate. The remaining 0.4 per cent is from miscellaneous re-use.

The re-use of process condensate, although small in proportion, may be quite important in terms of pollution control. This water usually contains ammonia, sulphides and phenols. The ammonia and sulphides are normally removed by steam stripping before water re-use. The phenols are often substantially removed by the re-use process, such as extraction by crude oil in desalters, or by biological oxidation in cooling towers. Forty-seven per cent of refineries reported re-use of process condensate.

Experience has taught that, in general, each class of waste water (process, cooling, sanitary) can be treated more effectively, and frequently more economically, when treated individually rather than in admixture with other classes of waste water. Although the provision for separate drainage systems may be impractical in some cases, special efforts are usually made to segregate and treat sanitary waste waters separately.

Practically all refineries have some form of primary treatment of waste waters. The majority have an API gravity-type oil and water separator to remove oil and suspended solids. Those refineries that do not have standard API separators generally have earthen basin separators with skimming devices to accomplish the same purpose.

After primary treatment the methods of treatment referred to as intermediate and biological treatment in *Table 2*, and commonly referred to as secondary treatment, vary widely.

A method of intermediate treatment carried out by many refiners is air flotation. Extensive work has been carried out during the past two decades on the use of dissolved air flotation for removal of suspended solids and oils. The process utilizes the action of extremely fine bubbles of air being released from the solution immediately following a reduction in pressure. The need for this process has been demonstrated by the ineffectiveness of gravity separation in removing oil-solids agglomerates whose densities closely approach or equal that of water. The air flotation process assures an average density of these agglomerates substantially below that of water. Air flotation does not supplant gravity separation but in series is useful as an additional clarification step.

One of the most prevalent forms of treatment is ponding. Ponding involves the retention of waste water in a relatively large earthen basin for a sufficient period of time to separate the suspended matter from the water. After the bulk of the oil and the readily separable solids have been removed by primary treatment, ponding will further reduce the oil content, suspended solids, sulphides and biochemical oxygen demand. Some of the smaller refineries have ponds with holding times up to 180 days. The big drawback to ponding as a means of treatment is the land requirement for such installations. However, holding time can be greatly reduced by the use of mechanical aeration.

One of the most important methods of secondary treatment of refinery effluents is biological treatment. One method of biological treatment used today is the activated sludge system. This is an aerobic biological treatment process in which the micro-organisms are suspended throughout the reaction tank and air is introduced into the system by mechanical means. The concentration of active sludge organisms is high and the holding times relatively short, compared with treatment in natural or mechanically aerated ponds.

A biological filter, commonly called the trickling filter, is one of the most widely used aerobic systems for the treatment of industrial wastes. However, in the petroleum refining industry, activated sludge systems and aerated ponds are somewhat more prevalent. Trickling filters are sometimes used in front of activated sludge plants because they can handle shock loads. Recent studies with activated sludge systems have shown that the completely mixed activated sludge systems are not readily upset by heavy organic loadings and with collection basins to level out shock loads, the trickling filter is not needed.

All of the standard, time-tested methods of water treatment are used in purification of refinery wastes, such as coagulation, flocculation, filters of all sorts and activated carbon as an absorption agent to remove organic compounds not responsive to clarification or biological treatment.

The newer, or third stage, treatment process such as dialysis, electrodialysis and ion exchange are not yet in commercial use in refineries. However, many refiners are experimenting with these systems and other processes and they will be undoubtedly incorporated in future designs.

Also, at least one refinery is using chemical coagulation and removal of the coagulated material by air flotation as tertiary or third stage treatment.

EXAMPLES OF WASTE WATER TREATMENT IN NEW REFINERIES

I would like to discuss briefly how some of these processes are put together in some of our newer refinery installations. One such refinery was designed to meet the stringent air and waste water quality standards of the San Francisco

Bay area. This refinery's processing scheme would put it in Category 'B'.

Minimum use of water was a basic concept in the design of this 'grass-roots' refinery. To conform to this concept, re-use of water was planned to the extent practical, air cooling was maximized and the use of once-through water avoided. Approximately 70 per cent of the cooling accomplished by utilities is done by air cooling. This resulted in a refinery effluent volume of 22 gallons per barrel of crude throughput. While minimum use of water usually is desirable, it does present problems where regulations on effluent discharges are specified as concentration limits and not as quantity limits. A flow diagram of this refinery's waste water treating system is shown in *Figure 1*.

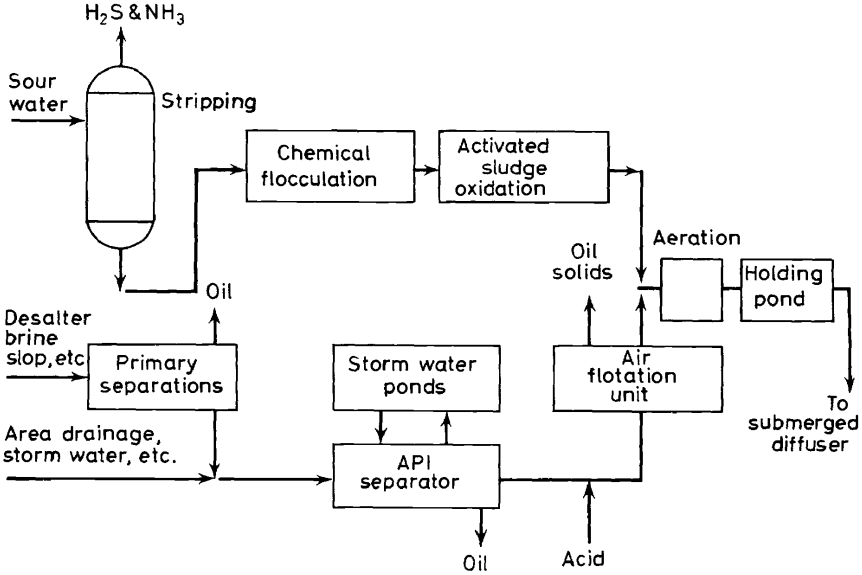

Figure 1.

The refinery has two sewer systems. One system is the general sewer system for the refinery and care is taken to avoid inclusion of water containing contaminants of the nature that would interfere with meeting the required effluent qualities.

The flow from this system is treated in an API separator. Dual channels are provided in the separator each with capacity for normal dry season flow. During periods of heavy rainfall, inflow in excess of efficient separation capacity is diverted automatically to a detention pond designed to handle one day's accumulation with maximum expected rainfall.

The API separator has a preseparator section with trash and sludge removal facilities and two floating rotary drum skimmers for oil removal. The main two separator channels are equipped to remove sludge and oil. Some difficulty has been encountered with adherence of oil to particulate matter, resulting in the formation of particles having the same density as the water, and an air flotation unit is now being installed following the separator to remove these materials. The water stream from the air flotation unit then enters a holding pond, the entering area of which is equipped with fixed mechanical aerators.

The second sewer system handles waste streams containing such impurities as phenolic compounds, sulphides, ammonia and thiocyanates. These waste streams go to one of two sour water-stripping systems, one to handle water with high ammonia content and the other to handle water that is essentially ammonia free. The stripped sour waters are treated in a flocculation unit to remove suspended matter and oil.

The clarified water from the flocculation unit flows to an activated sludge plant built as two units, each with a capacity for the normal flow. With the units operated in parallel retention time ranges up to twenty hours, the units are of a completely mixed type, and sludge is withdrawn periodically to a gravity thickener to maintain the solids density at a desired level.

The outflow from the aeration sections passes through sedimentation chambers which have a volume equal to that of the oxidation zone. The clarified water from the sedimentation chambers flows to the aeration section of the holding pond where it joins with the effluent from the air flotation unit.

The re-aerated water is held in the pond for an average of three days. Bacteriological action continues during this period. Facilities are available to skim any oil that might collect. The water is pumped periodically through a jet disperser submerged in the estuary. The water is discharged about a third of the time on ebb tides only, and tidal action and high pumping rates contribute to rapid dilution of the effluent.

I have given an example of the processing train for waste water in a refinery operating on a salt water estuary. Another example of employing modern techniques is a new refinery operating in the Chicago area whose source of water is the Chicago Sanitary and Ship Canal. The canal is a badly polluted body of water at the present time.

This new plant replaces several oil refineries which had operated in the Middle West. This refinery would fall into Category 'C'.

In the design of the new refinery waste water system, advantage was taken of the physical characteristics of the refinery site. There were several quarries on the property fed by artesian water. The water in these quarries was pumped out and the quarries sealed. The one quarry is now used as a storm water holding basin which has the capacity of holding a four-inch rainfall occurring within a 24-hour period. The outfall from the storm water holding basin is returned to either the inlet or outlet of the API separator treating the process water.

The flow diagram of the refinery's treating plant is shown in *Figure 2.*

A second quarry is used as a holding basin for treated waste water and it has a capacity of 16 million gallons. For flexibility of operations the outflow of the holding basin can be returned to the canal as effluent, or can go to the storm water holding basin, from where it can be returned to the waste water treating system.

In the actual water cycle in the refinery, water is pumped from the canal and treated to reduce hardness by a cold lime process. The boiler feed-water is treated by hot lime and zeolite. The bulk of the cold lime treated water goes to a 50000 gpm cooling tower as make-up.

The oily waste water from refinery operations goes to a standard API two-bay oil–water gravity separator equipped with rotary drum skimmers in the inlet section for primary oil removal.

The effluent from the API separator flows to an equalization tank where it is mixed with sewage from the sanitary sewage system and water from the storm water holding pond, if this water is not returned to the inlet of the API separator because of oil contamination.

The water outfall from the equalization tank goes to a sedimentation tank to remove solids and suspended matter. From the sedimentation tank the effluent is pumped to two parallel activated sludge tanks maintained at 90° Fahrenheit to promote maximum bacteriological action. The retention time is six hours.

The effluent from the bio ponds goes to a final clarifier where lime is used as a coagulant. The waste water then is pumped and chlorinated en route to the third quarry which is used as a treated waste water holding basin. If the quality of the waste water in the holding basin is satisfactory, it is pumped through two multicone aerators and returned to the canal.

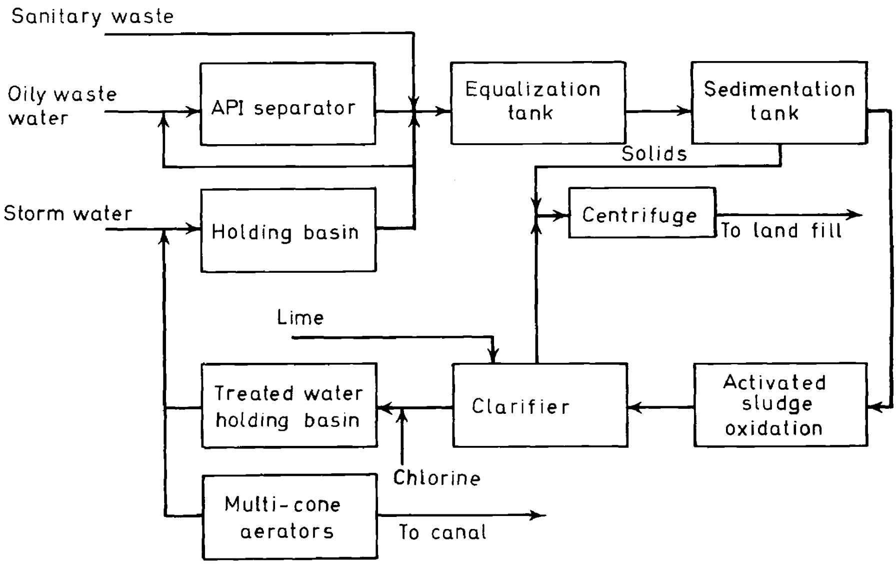

Figure 2.

Of particular interest in this operation is the fact that the old refinery on this location, now shut down, processed some 50000 barrels of crude oil per day and required 70 million gallons of water, equivalent to approximately 33 barrels of water per barrel of crude. The new refinery processes approximately three times as much crude per day but uses only 6 million gallons of water, or approximately 1 barrel of water per barrel of crude.

This dramatic decrease in water used is due primarily to water recirculation, very extensive use of air cooling of process streams, and to integration or close-coupling of the process units.

Not shown in *Figure 2* due to lack of space, is the sour water system. Process waters contaminated by sulphides, ammonia and phenols are sent to steam strippers before going to the secondary treatment system.

One problem with this type of operation is eventual disposition of organic and lime sludges. At the present, they are thickened, centrifuged, and hauled away to land fill area. In the future, other methods of disposal will probably become necessary.

DEVELOPING TRENDS

A review of these two new refinery waste water treating systems indicates a clear trend for future developments in refinery waste water treatment. There will be a concerted effort to further reduce water usage in petroleum refining operations. This will be accomplished by process design changes using close-coupling between various process units to eliminate the need for intermediate cooling and storage. It will be done by re-use of water to a far greater extent than is now being employed, and by increased use of air cooling.

The American Petroleum Institute is currently sponsoring a research project to develop a mathematical model for refinery water management which, it is hoped, will enable individual refiners to determine the optimum utilization of water in their refineries. Each individual refinery could insert its own particular parameters into the model and be guided by the answers. It is too early to predict how successful this project will be, as the model when developed will require considerable testing. Those working on this project are convinced that it will prove to be a most useful tool.

Although water use will be reduced, there will still be some discharge to be handled. We believe that many of the new 'third-stage' processes for treating effluents will be improved and the cost of constructing and operating these processes will be lowered.

The role that the Federal Government is playing in developing new, unique or improved techniques for controlling effluent discharges from industrial waste sources is an important one.

The objective of the Federal Water Quality Administration's industrial research and development programme is to develop and demonstrate the required technology to achieve the specified degree of pollution control by least-cost methods for all significant sources of pollution. These objectives are carried out by the grant mechanism whereby the FWQA offsets the risk portion of the yet unproven techniques. About ten such projects of considerable interest to the petroleum industry are going forward under this programme.

CONCLUDING REMARKS

Growing concern during the sixties over the quality of our environment led to the passage of the Water Quality Act of 1965. The act required the states to develop, within a time schedule, water quality standards for the nation's interstate waters.

The impact of the act on both industry and on cities has been substantial. The oil industry has stepped up its annual rate of capital investment in water pollution control facilities over the past five years and we expect this trend to continue for some years to come.

In all too many instances, the assimilative and restorative capacities of our water resources have been overtaxed or overburdened by the waste loadings imposed by community sewage, by industry and by agricultural activities. The task ahead is a formidable one. It will be costly—it will take time, but it must be done.