

Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be “used for any purpose other than private study, scholarship, or research.” If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of “fair use” that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation

Printing note: If you do not wish to print this page, then select “Pages from: first page # to: last page #” on the print dialog screen

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

Application Research on Wastewater
Reuse for Petrochemical Refining
Industry in Taiwan

By

LIH-SHYAN LEE

Thesis submitted to the Faculty of the Graduate School of
the New Jersey Institute of Technology in partial
fulfillment of the requirements for the degree of
Master of Science in Environmental Engineering

1990

Approval Sheet

Title of Thesis: Application Research on Wastewater Reuse
for Petrochemical Refining Industry
in Taiwan

Name of Candidate: LIH-SHYAN LEE
Master of Environmental Engineering,
1990

Thesis and Abstract Approved: _____
Y. C. WU
Professor
Civil and
Environmental
Department

Date

Signatures of other members
of the thesis committee

Date

Date

Date

VITA

Name : LIH - SHYAN LEE

Degree and Date to be conferred : Master of Science in
Environmental Engineering, 1990

Collegiate Institutions attended	Date	Degree	Date
Chinese Culture University, TAIWAN	67-71	B.S.	July, 71
New Jersey Institute of Technology	88-90	M.S.	Jan, 90

Major : Environmental Engineering

Abstract

Title of Thesis : Application Research on Wastewater
Reuse for Petrochemical Refining
Industry in Taiwan

Lih-Shyan Lee, Master of Science in Environmental
Engineering, 1990

Thesis Directed by Dr. Y.C. Wu

Nowadays water conservation and pollution abatement are needed to provide increasingly higher levels of treatment for industrial wastewaters.

Reducing treatment costs give us the incentive to minimize the volume of wastewater effluent. Also, the national goal of zero discharge of pollutants to the waterways by 1985 provided further incentive to minimize the flow of wastewaters.

A successful treatment of the wastewater discharged from the secondary effluent of the petroleum refinery plant to economically acceptable conditions offers a challenge to our technology.

Through this research, it is concluded that the excellent effluent water qualities produced from filtration and granular activated carbon adsorption treatment can be satisfactorily employed for cooling tower water, also the feed of manufacturing process water and boiler water supply.

Contents

	Page
I. Introduction	1
II. Significant Pollutant Parameters in Petroleum Refinery Wastewater	6
III. Literature Review on Best Available Technologies for Wastewater Reuse	13
A. Current Practices	13
1. Recycle / Reuse	13
2. At Source Pretreatment	15
3. End of Pipe Control Technologies	15
B. Case Histories	23
1. Pilot Studies for The District of Columbia	23
2. Pilot Studies of The City of Dallas's Water Reclamation research Center Demonstration Plant	26
3. Pilot Studies for Removal of Suspended Solids in Toledo Refinery Sun Oil Company of Pennsylvania	41
4. Union Carbide's Typical Petroleum Plant	44
C. EPA's Survey for The Petroleum Refinery Point Source Category	47
IV. Water Quality Standards of Reused Water	51
A. Process Water	51
B. Cooling Water	54
C. Boiler Feed Water	55
V. Construction Cost of Advanced Treatment Plants for Water Reuse	58
A. Package Gravity Filter Plants	58
B. Package Pressure Filtration Plants	60
C. Pressure Granular Activated Carbon Contactors	63
D. Granular Activated Carbon Material Cost	64
E. Multiple Hearth Granular Carbon Regeneration	66
F. Capping Sand Filters with Anthracite	68
VI. Mathematical Models	70
A. Package Gravity Filter Plants	71
B. Package Pressure Filter Plants	72
C. Pressure Granular Activated Carbon Contactors	73
D. Multiple Hearth Granular Carbon Regeneration	74
E. Furnace Hearth Area vs. Weight of GAC	75
F. Capping Sand Filter and Anthracite	76

VII. Summary and Conclusions	77
VIII. References	81
Appendix A. Picture of TAOYUAN REFINERY of Chinese Petroleum Co. TAIWAN, R.O.C	83
Appendix B. Picture of Cooling Tower at TAOYUAN REFINERY Plant	83
Appendix C. Picture of Rotating Biological Contactor at TAOYUAN REFINERY Plant	84
Appendix D. Picture of Activated Sludge Tank at TAOYUAN REFINERY Plant	84
Appendix E. Picture of Corrugated Plates Interceptor at TAOYUAN REFINERY Plant	85
Appendix F. Picture of Stablizer at TAOYUAN REFINERY Plant	85

List of Tables

	Page
1. Refinery Water Use GAL/Bbl of Crude Charge	4
2. Significant Pollutant Parameters for the Petroleum Refinery Industry	6
3. Primary Effluent Quality from Refineries	8
4. Typical Waste Loadings from Refinery Processes Typical Technology	8
5. Proposed Effluent Guidelines	9
6. Metallic Ions Commonly Found in Effluents from Petroleum Refineries	11
7. Effluent Qualities of Three-Stage Activated Sludge Treatment	24
8. Effluent Qualities in High PH Physicochemical Treatment	25
9. Effluent Qualities of Conventional Tertiary Treatment	27
10. Water Quality - Primary Effluent	29
11. Water Quality - Activated Sludge Process	31
12. Water Quality - Filtered Activated Sludge	33
13. Biological - Physical Treatment Mode	35
14. Water Quality - Chemical Treatment	37
15. Water Quality - Filtration of Chemical Treatment Effluent	37
16. Water Quality - Activated Carbon Adsorption	40
17. Suspended Solids Removal in Upflow Pilot Sand Filter at Different Flow Rates and Inlet Concentration	43
18. Upflow Filter Conditions Specified for 80% Removal of Suspended Solids	43
19. Removals of Pollutants at Each Step of a Complete Wastewater Recovery System	46

20.	Observed Refinery Treatment System and Effluent Loadings	48
21.	Typical Removal Efficiencies for Oil Refinery Treatment Processes	49
22.	Expected Effluents from Petroleum Treatment Processes	50
23.	Quality Requirements of Water at Point of Use for Petroleum Industry	52
24.	Quality Characteristics of Surface Waters That Have Been Used by The Petroleum Industry	52
25.	Quality Characteristics of Surface Waters That Have Been Used for Steam Generation and Cooling in Heat Exchangers	56
26.	Quality Requirements of Water at Point of Use from Steam Generation & Cooling in Heat Exchanger	57
27.	Conceptual Design for Package Gravity Filter Plants	59
28.	Construction Cost for Package Gravity Filter Plants	60
29.	Conceptual Design for Package Pressure Filtration Plants	62
30.	Construction Cost for Package Pressure Filtration Plants	62
31.	Conceptual Design for Pressure Granular Activated Carbon Contactors	63
32.	Construction Cost for Pressure Granular Activated Carbon Contactors	64
33.	Conceptual Design for Multiple Hearth Granular Carbon Regeneration	67
34.	Construction Cost for Multiple Hearth Granular Carbon Regeneration	67
35.	Construction Cost for Capping Sand Filter with Anthracite	69

List of Figures

	Page
1. Estimate of Rate of Withdraws of Water in U.S. for Various Purposes	2
2. Refinery Water Use	4
3. Process Flow Diagram	7
4. Refinery Effluents	9
5. Sun Oil Company - Toledo Refinery, Wastewater Reuse and Bio - Oxidation Flow Diagram	14
6. Three - Stage Activated Sludge Treatment	24
7. Physicochemical Treatment	25
8. Conventional - Tertiary Treatment	27
9. Biological - Physical Treatment Sequence	34
10. Process Flowsheet for Complete Wastewater Recovery and Recycle	45
11. Material Cost for Granular Activated Carbon	65
12. Construction Cost for Package Gravity Filter Plants	71
13. Construction Cost for Package Pressure Filter Plants	72
14. Construction Cost for Pressure Granular Activated Carbon Contactors	73
15. Construction Cost for Multiple Hearth Granular Activated Carbon Regeneration	74
16. Furnace Hearth Area vs. Weight of Granular Activated Carbon	75
17. Construction Cost for Capping Sand Filter and Anthracite	76

Introduction

A. Water supply problems

Water reuse has been practised since water was introduced for the removal of household wastes. An early and still common example is the discharge of wastewater into rivers, whence, after more or less dilution, they are abstracted for water supply downstream. The disposal of wastewater onto land, accompanied by the growing of useful crops, the venerable so-called "sewage farm", which is still being proposed now and adopted as a method for wastewater disposal.

The value of wastewater as a source is naturally expected to be high in arid and semi-arid areas of the world, but we are finding reclaimed wastewater to be a valuable resource in humid areas as well.

The data shown in Figure-1 (1) are estimates, but they do reflect the present water supply problem very well. From the data to estimate dependable supply of fresh water, which by the year of 2000 will be very close to maximum. Projected municipal, agricultural, industrial fresh water withdrawals are presented, along with the estimated fresh water withdrawals. It is of interest to noticed that in 1957 year the total fresh water use exceeded the available supply, and that by about 1980 the national water use requirements will surpass the total developable supply. The difference between water use and water supply clearly indicates the amount of water which must be reused if we as a Nation are not going to run out of water.

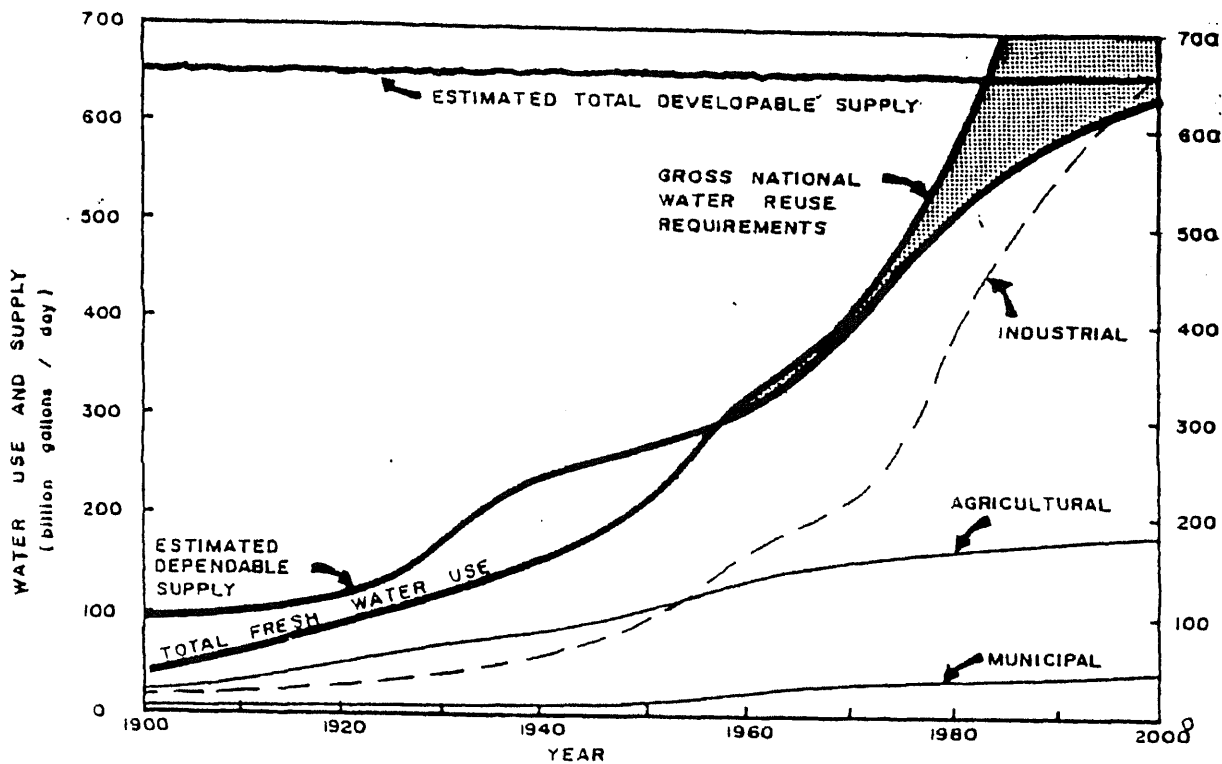


Figure-1 Estimate of Rate of Withdrawals of Water in U. S. for Various Purposes.

B. The statutes

Modern legislation which mounted the Federal effort to abate water pollution and to implement reuse and recycle technology started modestly in 1948. Each subsequent action by Congress broadened the Federal program while establishing and maintaining a major role to finance construction of wastewater water treatment facilities. It's worthy to note that the Federal Water Pollution Control Act of 1956 instituted a grants program containing prohibitions and omissions that discouraged development and use of many recycling or reuse alternatives.

The Federal Water Pollution Control Act as amended in 1972 was the first federal legislation to contain provisions that encouraged recycle and reuse. The encouragement offered in that Act was reiterated in the Clean Water Act (CWA) of 1977 and was given the added impetus of many financial incentives that encompass wastewater reuse. These financial incentives are integral factors in the innovative and alternative(I/A) technology program which places strong emphasis on recycle and reuse. The 1981 amendments to the CWA strengthened the I/A technology program and continued it through fiscal year 1985. The bill's final goal was to reach the so-called zero discharge of pollutants by 1985.

C. Industrial water need

As indicated in Figure-1 industrial water requirements represent the greatest demand on the Nation's water resources. And water needs for petroleum are categorically typical of most industries in that the majority of the water requirement is for cooling. Process use & steam production complete the major water intake balance. A graphical depiction of this water use delination is shown in Figure-2 (1).

In 1967 two surveys of refinery water use were sponsored by the American Petroleum Institute (API) to establish water effluent characteristics and reuse-recycle rates (3,4). Refinery makeup, recycle and effluent discharge

loads taken from these surveys are presented in Table-1 (3,4). However, data from one-through cooling refineries have been deleted since this practice is inconsistent with reuse. In general, the complexity of the petroleum processing progresses from the API classifications A to E and water use follows a similar pattern.

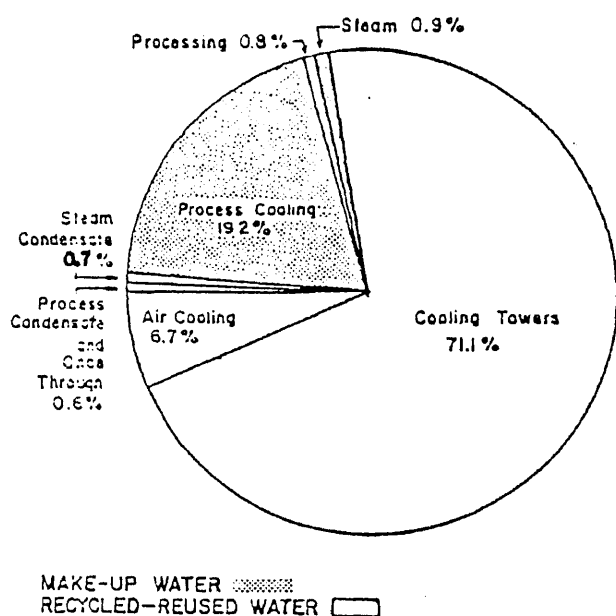


TABLE-1
Refinery Water Use (3, 4)
GAL/Bbl of Crude Charge

REFINERY CLASS	Makeup	Reuse- Recycle	Reuse Ratio	Ef- fluent
A TOPPING	81	194	2.4	13
B TOPPING & CRACKING	128	1421	11.3	24
C B PLUS PETROCHEMICALS	294	1778	6.0	42
D B PLUS LUBE OIL	320	1374	4.3	75
E C PLUS LUBE OIL	427	1923	4.5	90

NOTE: One-through cooling plants are not included.

Figure-2. Refinery Water Use.

Here it's need to distinguish between the various types of reuse, and the following is the definition of each type of reused patterns.

1. Indirect reuse

Indirect reuse of wastewater occurs when water already used one or more times for domestic or industrial purposes is discharged into fresh surface or underground waters and is used again in its diluted form.

2. Direct reuse

The planned and deliberate use of treated wastewater for some beneficial purpose, such as irrigation, recreation, landscape, industry, and recharging of underground aquifers.

3. Industrial wastewater

The spent water from industrial operations, which may be treated and reused at the plant, discharged to the municipal sewer, or discharged partially treated or untreated directly to surface waters.

4. Direct non-potable reuse

The piping of treated wastewaters directly into a water supply system that provides water for one or more non-potable purposes.

5. Indirect non-potable reuse

The abstraction of water for one or more non-potable purposes from a surface or underground source into which treated or untreated wastewaters have been discharged.

6. Direct potable reuse

The piping of treated wastewaters directly into a water supply system that provides water for drinking.

7. Indirect potable reuse

The abstraction of water for drinking and other purposes from a surface or underground source into which treated or untreated wastewater have been discharged.

Significant Pollutant Parameters in Petroleum Refinery Wastewater

Refinery wastewater characteristics vary with refinery size and process sophistication. Table-2 (5) shown the significant pollutant parameters for the petroleum refining industry. And Figure-3 (1) shows the major processes unit in the process flow diagram.

Table-2

Significant pollutant parameters for the petroleum refining industry

Biochemical Oxygen Demand (BOD5)

Chemical Oxygen Demand (COD)

Total Organic Carbon (TOC)

Total Suspended Solid (TSS)

Total Dissolved Solid (TDS)

Oil & Grease (O&G)

Ammonia as Nitrogen (NH₃-N)

Phenolic Compounds

Sulfides

Chromium

Other Pollutants

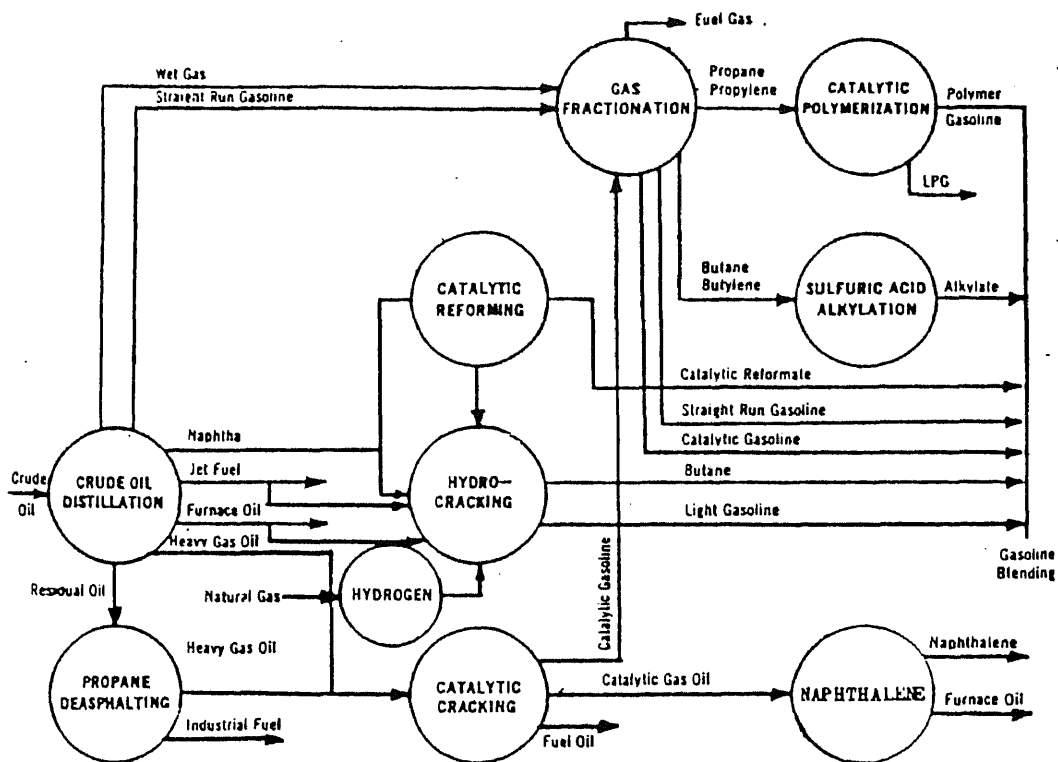


Figure-3 Process Flow Diagram.

Most refineries employ some form of primary treatment for oil recovery. Many have installed facilities to remove additional oil and suspended solids and some provide secondary and polishing steps for soluble contaminant removals. Primary refinery effluent data is presented in Table-3 (4). Untreated effluents from the refinery unit processes can be estimated from Table-4 (4). Old refineries will discharge poorer effluents and conversely newer plants would be expected to discharge less water and fewer contaminants. The use of sour water stripping as well as advanced reuse will significantly alter the values shown in the table.

TABLE - 3

Primary Effluent Quality from Refineries

REFINERY CLASSIFICATION	CONTAMINANTS, mg/l						
	GAL/Bbl Crude Throughput	BOD	COD	Oil	TDS	Sulfide	NH ₃ (N)
A	13	113	-	76	2980	2	-
B	17	326	956	64	2380	57	351
C	50	112	332	34	597	21	35
D	90	148	391	46	2100	21	40
E							Insufficient data

NOTE: Once-through cooling plants are not included.

TABLE - 4

Typical Waste Loadings from Refinery Processes
Typical Technology

FUNDAMENTAL PROCESS	WASTEWATER CHARACTERISTICS							
	FLOW GAL/Bbl	pH	BOD lb/Bbl	COD lb/Bbl	OIL lb/Bbl	H ₂ S lb/Bbl	NH ₃ lb/Bbl	TDS lb/Bbl
Crude Desalting	2.1	6.7-9.1	.003	.032	.012	.008	.009	.250
Crude Fractionation	26.	8.6	.0002	.005	.017	.001	-	.035
Catalytic Cracking	15.	8.3-9.7	.015	.018	.100	.036	.040	.090
Thermal Cracking	2.0	6.4	.001	.003	.001	.001	-	-
Hydrocracking	2.0	7.3	.002	.045	-	.002	-	.002
Hydrotreating	1.0	9.0	.010	.050	-	.002	.030	.035
Delayed Coking	1.0	8.8-9.1	-	.032	.006	-	-	.030
Reforming	6.0	7.6	-	.040	.050	.001	-	.125
Sour Condensates	3.0	4.5-9.5	.100	.200	.100	1.00	0.75	-
Alkylation	60.	8.1-12.	.001	.010	-	.010	0	.300

In addition to process effluents, other wastewater categories must be considered including storm water, ballast, sanitary wastes and utility blowdowns. It would be difficult to establish average values for ballast and storm water contributions. However, if handled properly, together they may contribute 20-50 percent of the design flow and 10-30 percent of the design BOD loading.

Because ballast normally contains high concentrations of dissolved solids, combined treatment with other refinery effluents is impractical if reuse is employed and TDS is a constraint. On the other hand, storm water, if properly

segregated, can be a valuable source of makeup water.

However, land constraints often preclude the collection and storage of all storm water for reuse.

Sources of refinery effluents are presented in Figure-4 (4). For disposal purposes, several combinations of the processes should be capable of meeting the effluent guidelines presented in Table-5 (7). The criteria are representative of currently available technology (7).

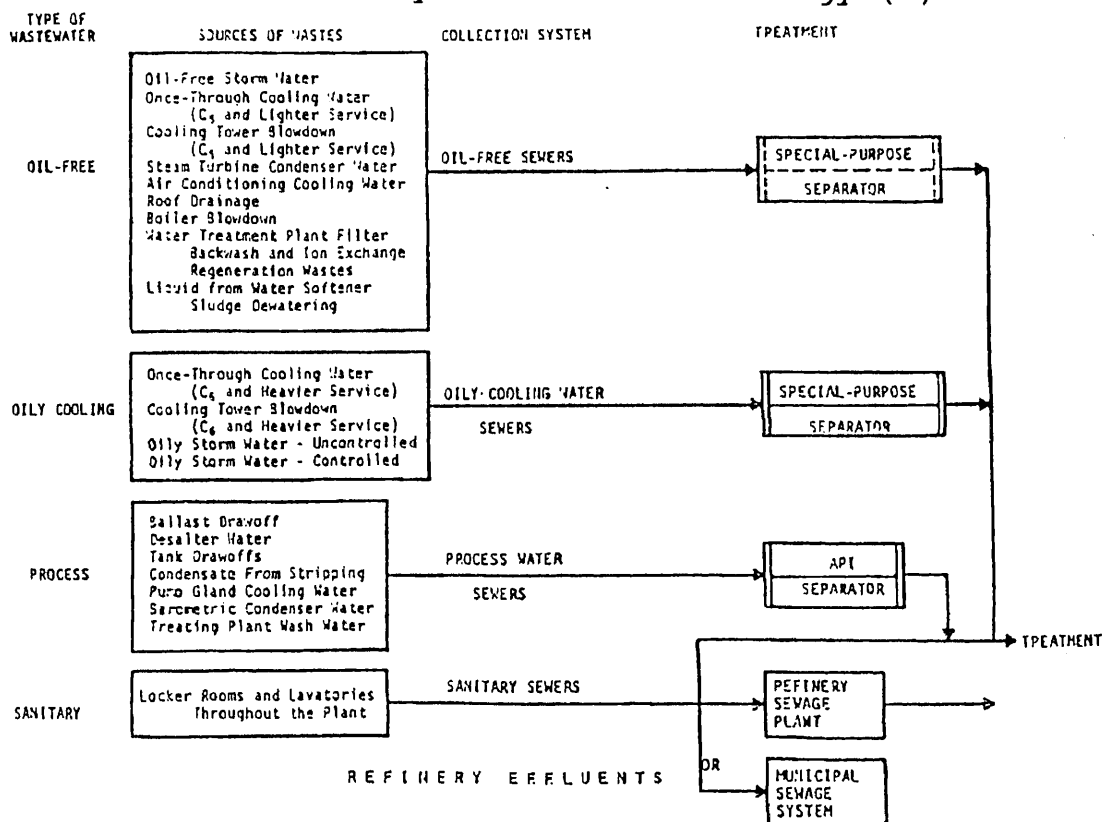


Figure-4 Refinery Effluents.

TABLE-5
Proposed Effluent Guidelines

REFINERY CLASSIFICATION	CONTAMINANTS, mg/l						
	GAL/Bbl Crude Throughput	BOD	COD	Oil	TDS	Sulfide	NH ₃ (N)
A	20	15	92	10	-	0.17	10
B	40	15	92	10	-	0.17	10
C	50	17	106	10	-	0.17	10
D	60	20	122	10	-	0.17	10
E	90	22	137	10	-	0.17	10

Typical raw waste load concentrations for each subcategory (1) are listed below:

A. Pollutants :

<u>Pollutants</u>	<u>Subcategory</u>				
	<u>Topping</u>	<u>Cracking</u>	<u>Petro-chemical</u>	<u>Lube</u>	<u>Integrated</u>
BOD5, mg/l	10 - 50	30 - 600	50 - 800	100-700	100-800
COD, mg/l	50 -150	150- 400	300 - 600	400-700	300-600
TOC, mg/l	10 - 50	50 - 500	100 - 250	100-400	50-500
TSS, mg/l	10 - 40	10 - 100	50 - 200	80 -300	20-200
O&G, mg/l	10 - 50	15 - 300	20 - 250	40 -400	20-500
NH3-N,mg/l	0.05- 20	0.5- 200	4 - 300	1 -120	1-250
Phenolic,mg/l	0-200	0 - 100	0.5 - 50	0.1 -25	0.5- 50
Sulfide,mg/l	0 - 5	0 - 400	0 - 200	0 - 40	0 - 60
Chromium,mg/l	0- 3	0 - 6	0 - 5	0 - 2	0 - 2

B. Other pollutants :

1. Total Dissolved Solids in refinery waste waters consist mainly of carbonates, chlorides, and sulfates. Median total dissolved solids concentrations for refinery effluents are 400-700 (mg/l).

2. Cyanides in water derive their toxicity primarily from undissolved hydrogen cyanide (HCN) rather than from the cyanide ion (CN⁻). Cyanide raw waste load data for the refining industry show median values of 0.0 - 0.18 (mg/l).

3. PH (Acidity & Alkalinity) value in most refinery waste water are alkaline due to the presence of ammonia and the use of caustic for sulfur removal. Cracking (thermal and catalytic) and crude distillation are the principal sources of alkaline discharges. Alkylation & polymerization utilize acid as catalyst and produce severe acidity problem.

4. Temperature is one of the most important and influential water quality characteristics. Crude desalting, distillation and cracking contribute substantial wasteloads.

5. Metallic ions in addition to chromium and zinc may be found in the refinery effluents. The major sources for their presence in waste water are from the crude itself and corrosion products. Table-6 (1) lists those metals which may be commonly found in the petroleum refinery effluents. Dissolved metallic ions create turbidity and discoloration, can precipitate to form bottom sludges, and can impart tastes to water.

Table-6

Metallic Ions Commonly Found In Effluents From Petroleum Refineries

Aluminum
Arsenic
Cadmium
Chromium
Cobalt
Copper
Iron
Lead
Mercury
Nickel
Vanadium
Zin

6. Chloride ion is one of the major anions found in water and produces a salty taste at a concentration of about 250 mg/l. Copper chloride may be used in a sweetening process and aluminum chloride in catalytic isomerization. Refinery effluents placed net chloride levels at values ranging from 57 to 712 (mg/l). The median value is 176 mg/l.

7. Fluoride ion contributes in alkylation units waste effluent. (when hydrofluoric acid is used) Optimum limits range from 0.7 to 1.2 (mg/l).

8. Phosphate comes from various forms. They range through several organic and inorganic species and are usually contributed by corrosion control chemicals. Total phosphate values are 9.49 mg/l maximum.

Literature Review on Best Available Technologies for Wastewater Reuse

A. Current Practices

1. Recycle / Reuse

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 examples of practice are described briefly below:

a. Reduction of one-through cooling water results in tremendously decreased total effluents.

b. Sour water stripper bottoms are being used in several refineries as make-up water for crude desalter operation. These sour water bottoms are initially recovered from overhead accumulators on the topping and catalytic cracking units.

c. Reuse of waste water treatment plant effluent as cooling water as scrubber water, or as plant make-up water, reduces total make-up requirement.

d. Cooling tower blowdowns are frequently reused as seal water on high temperature pump service, where mechanical seal are not practicable.

e. Regeneration of the 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.

f. Storm water retention ponds are frequently used as a source of fire water or other low quality service waters.

g. For a complete treatment system of Figure-5 (1) is a simplified flow diagram of the Toledo Refinery water system, shows the routing of fresh water supplies and the integration of water pollution abatement with conventional operating plants.

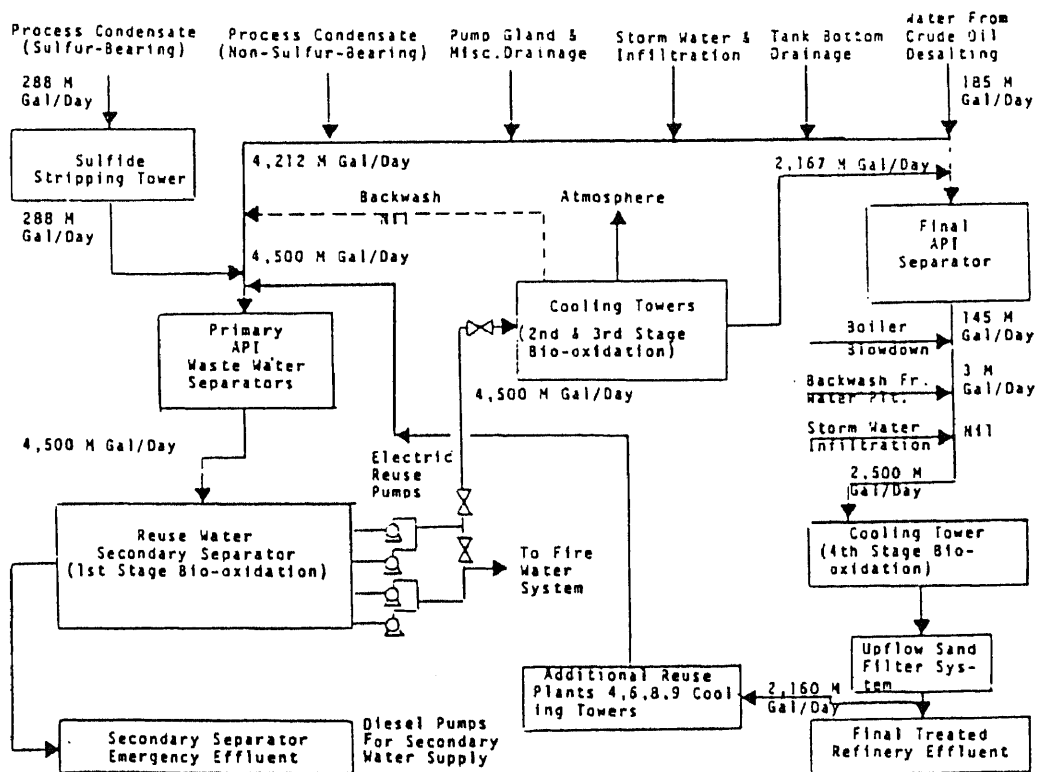


Figure-5 Sun Oil Company—Toledo Refinery, Wastewater Reuse and Bio-Oxidation Flow Diagram.

2. 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, slop oil recovery, and storm water runoff/sewer system segregation. Treatment at the source is helpful in recovery by-products from the wastes which otherwise could not be economically recovered when the wastes are combined.

3. End of Pipe Control Technologies

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. Following are the conventional effluent treatment methods:

Primary :

- Sulfide / Ammonia Stripping
- API Separators
- Tilted Plate Separators
- Liquid / Liquid Extraction
- Filtration for Oil Removal
- PH Control

Intermediate : Flotation
 Coagulation / Precipitation
 Equalization

Secondary / Tertiary : Chemical Oxidation
 Activated Sludge
 Trickling Filters
 Aerated Lagoons
 Waste Stabilization Ponds
 Filtration
 Carbon Absorption

A brief description of above treatment concepts, applicability, capacity, and process limitations in treating refinery and petrochemical wastewaters is present belowing :

a. Stripping Process

The two most prevalent pollutants found in refinery wastewaters which are susceptible to stripping are hydrogen sulfide and ammonia. These compounds result from the destruction of essentially all the organic nitrogen and sulfur compounds during desulfurization, denitrification, and hydro-treating. The use of steam within the processes is the primary source of conveyance. Phenols also may be present in these "sour water" condensates and can be stripped from solutions, although the efficiency of removal is less than that of sulfide and ammonia. Ion exchange flow sheets have also been developed for sulfide and ammonia removal.

b. Oil Removal

Gravity separation using API separators or TPS (tilted plate separators) involves the removal of materials lighter than water, such as free oils and air entrained particles, and the removal of suspended materials which are more dense than water by sedimentation. The TPS is an advanced gravity three phase separator consisting of corrugated plate modules tilted at a 45 degree angle. Although a properly designed API separator will achieve comparable efficiencies, the TPS will do it for less cost and space.

Liquid-liquid extraction is competitive with gravity separation for small streams containing high oil concentrations and few suspended solids. It is also effective for emulsions and requires no chemicals but steam is needed. Neutralization may be needed as pre-treatment depending on the feed water source. The flow consists of an extraction vessel, flash drum and coalescer filter. The end products are water and hydrocarbons.

Filtration as a pre-treatment step for oil and solids removal is a candidate system which can be used singularly or in conjunction with other oil removal systems. The advantages of filtration applied as a pre-treatment step include compactness, favorable economics and flexible operation. Dis-advantages include problems with solids stabilized oil emulsions, dirt and grit collections resulting in high operating and maintenance costs.

c. PH Control

Control of PH is commonly required in the treatment of petrochemical and refinery wastewaters as many process streams are either highly acidic or alkaline. Applications include emulsion breaking, PH control for biological treatment, corrosion control, precipitation control and coagulation.

d. Dissolved Air Flotation

Dissolved air flotation (DAF) is the most commonly used form of intermediate treatment in refineries for polishing primary effluents. Air is used to float oil and solids to the top of circular or rectangular units where the concentrated material is collected and removed. Chemicals are normally required to effect emulsion removals.

Coagulation-precipitation is often included in the DAF flow sheet. The conventional system utilizes a rapid mix tank followed by slow agitation of the mixture in a flocculation basin and finally solids separation is accomplished by sedimentation or flotation. Reactor-clarifiers may be used which contain the flow sheet in one package unit.

e. Equilization

Biological processes as well as physical-chemical systems operate more effectively if the composition and volume of wastewater feed is relatively constant. Refinery

effluents normally do not conform to these requirements and some form of attenuation is needed.

f. Chemical Oxidation

Chemical oxidation, raising the oxidation level of a substance or reducing its BOD and COD, can be accomplished using the primary oxidizers oxygen, ozone, permanganate, chlorine, or chlorine dioxide. Catalytic oxidation offers a practical means of oxidizing small volumes of concentrated organic waste which are not susceptible to other forms of treatment.

Gaseous or dissolved oxygen is used both as a stripping agent for such gases as carbon dioxide, hydrogen sulfide, methane, and other low boiling organic compounds as well as for chemical oxidation. Air oxidation is used for sulfide oxidation as well as for removal of divalent forms of iron and manganese. The oxidation of iron, however, is strongly PH-dependent.

Heavy oils should be eliminated from the waste prior to oxidation since pilot plant studies indicate that five percent oil could decrease the oxidation rate by 50 percent. Ozone is an oxidizing agent used for phenols, cyanides, and unsaturated organics destruction since it is a considerably stronger oxidizing agent than chlorine.

Permanganate oxidation has been and is being used in treating water to remove taste, odor, iron and manganese, but is not generally used for the specific removal of BOD.

Chlorine has been applied in oxidizing phenol and cyanides in petrochemical wastes. The oxidation of phenols, however, must be carried to completion to prevent the release of chlorophenols which can cause objectionable odors and tastes in drinking water even at very low concentrations.

g. Biological Treatment

Biological treatment is the most widely accepted form of secondary treatment for refinery wastewaters. This method is usually the most economical approach for reducing the toxicity, organic content and objectionable appearance of refinery effluents. The first forms of biological treatment were ponds where some organic removal was accomplished under either aerobic or anaerobic conditions. The trickling filter was also used to some degree although it is now used primarily for pre-treatment. In the trickling filter biological slimes coating rock or synthetic media remove dissolved organics in the presence of air.

Aerated lagoons and activated sludge systems employ suspended biological growths in the presence of dissolved oxygen supplied by mechanical aerators or diffused air. The activated sludge system includes a clarifier for maintaining a large population of organisms within the system through recycle while clarifying the effluent. The aerated lagoon offers only a straight flow-through regime.

h. Filtration

Filtration, having been used for years as a polishing step in treating water for domestic use, is finding application as an effluent treating polishing process. More filtration polishing can be anticipated in the future for industrial treatment facilities as effluent criteria are becoming more stringent and filter units can easily be adapted to existing biological systems. Moreover, a filtration step is usually required before carbon adsorption polishing units can be put on line.

Filtration is particularly applicable for polishing an activated sludge or extended aeration plant receiving refinery or petrochemical wastewaters, as much of the effluent organic material is in suspended or colloidal form. Slip stream filtration of cooling tower recycle is also common.

Gravity filters using the downflow or upflow modes of operation are generally used for effluent polishing, although pressure filtration may offer some advantages as part of a tertiary treatment system.

i. Carbon Adsorption

Although the carbon adsorption process has not been widely used in the field of refinery and petrochemical wastewater treatment to date, preliminary pilot work and limited experience indicates selected applicability.

The efficacy of utilizing carbon adsorption for the treatment of refinery and petrochemical wastewaters at any

point in a process sequence can be determined only after a thorough investigation using continuous flow pilot systems has been performed. The technical and economic justification for including carbon adsorption as a treatment process in a refinery or petrochemical complex must, therefore, be predicated on pilot plant simulation, particularly in the absence of case histories and full scale operational experience.

Consideration for utilization of the carbon adsorption process includes biological-carbon series treatment, carbon-biological series treatment, and carbon adsorption as a total process. Each of these applications requires primary treatment for the removal of oily substances and suspended matter using gravity separators and, in some instances, dissolved air flotation. Of the applications indicated, the series biological-carbon treatment scheme will probably be most prevalent in the immediate future.

In the process soluble organics are adsorbed by carbon particles contained in a column or in a mixed suspension. Once the carbon has been extracted it is removed and transferred to a furnace where the organics are combusted and the regenerated carbon is then reused.

B. Case Histories

1. Pilot Studies for The District Of Columbia

With the availability of the biological pilot plant in late 1969 (8), the work at the pilot plant evolved into a detailed evaluation of the some basic treatment approaches for C, P, and N removal. Described as the following :

(1). Three-stage activated sludge treatment

The process design data (Heidman et al. 1975) developed for the District of Columbia's three-stage activated sludge treatment system Figure-6 (8) included :

- a. Chemical requirements (alum, FeCl_3), lime, methanol.
- b. The BOD5 removal rates and the kinetics of nitrification & denitrification for sizing the bio-reactor.
- c. The settling and thickening characteristics and solids production for design of clarifiers and sludge wasting and recycle systems.
- d. The sludge handling characteristics.

This system with mineral addition reliably provided high quality water as indicated in Table-7 (8). The residual of BOD5, COD, P, and N in all the effluents were average of data from 10 months of continuous operation. The addition of carbon adsorption, although not required for the discharge standard, reduced COD to 5 mg/l and thus produce final effluent qualities of 5 mg/l of COD, 0.15 mg/l of P, and 1.4 mg/l of N.

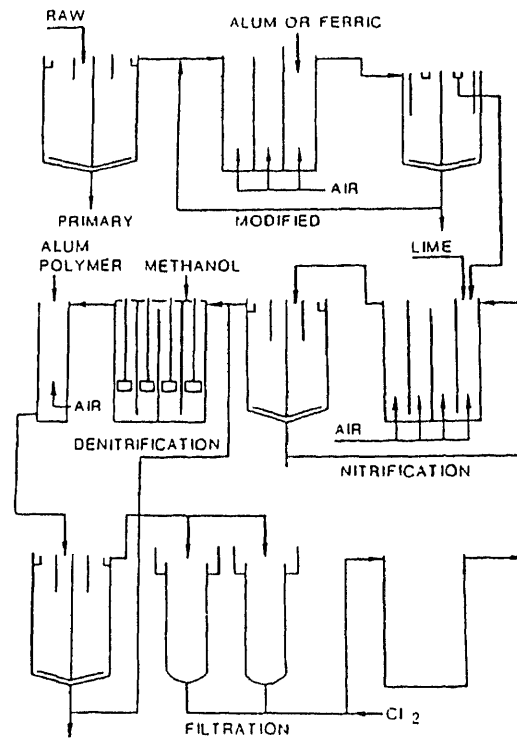


Figure-6 Three-stage activated sludge treatment.

Table-7
Effluent Qualities of Three-Stage Activated Sludge Treatment

Treatment	Amount of effluent ^a (mg/liter)			
	BOD	COD	Total P	Total N
Primary	99.2	231	6.8	23.6
Aeration	23.6	64.3	1.5	16.7
Nitrification	15.9	22.4	0.87	13.5
Denitrification	9.0	26.7	0.46	2.1
Filtration	2.7	15.9	0.15	1.4

^aEffluent qualities through the filtration stage are averages from 10 mo of continuous operation.

(2). High PH Physical-chemical Treatment

This system representative of the second basic approach to advanced wastewater treatment, in Figure-7(8) is the process flow chart and the physi-chemical system produced water of excellent quality as stated in Table-8(8). The residuals of BOD₅, COD, and P in all the effluents were averages of data from 10 months of continuous operation.

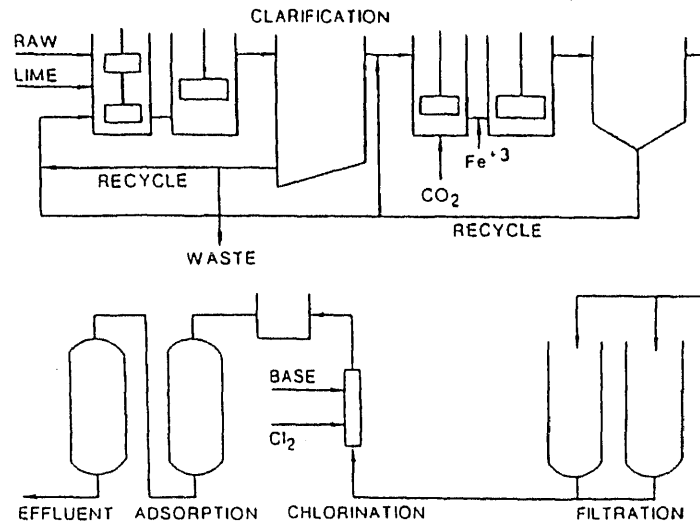


Figure-7 Physicochemical treatment.

Table-8
Effluent Qualities in High pH Physicochemical Treatment

Treatment	Amount of effluent (mg/liter) ^a				
	BOD	COD	Total P	Total N ^b	
				Cl ₂	Ion exchange
Raw	129	307	8.4	22	23
Clarification	24	55	0.27	15	17
Filtration	20	49	0.18	14	16
N removal	—	—	—	2.6	3
Carbon adsorption	6	15	0.13	2.5	2

^aEffluent qualities for BOD, COD, and total P represent 10 mo of continuous operation.

^bEffluent concentrations for N represent typical efficient operating performance for continuous operation of chlorination and selective ion exchange.

(3). Conventional Tertiary Treatment

Conventional tertiary treatment was continuously operated with the exception of nitrogen removal (10 months). During the study, air stripping of ammonia was operated for 4 months short pilot studies on breakpoint chlorination of filtered secondary effluent without chemical clarification were performed later.

The Figure-8 (8) shows the flow chart of this treatment. And the effluent qualities of Table-9 (8) are BOD5, COD, and P in the conventional tertiary treatment also represented averages of data from 10 months of continuous operation. Nitrogen removals and the effluent qualities after chlorination represented the typical operation. Nitrogen removal with breakpoint chlorination required a complex control system. But efficiency was basically independent of seasonal and wastewater variations except for ammonia content.

2. Pilot Studies Of The City of Dallas's Water Reclamation Research Center Demonstration Plant

The data presented here were obtained from two parallel treatment sequences being operated at the City of Dallas's Water Reclamation Research Center Demonstration Plant(1). This project was sponsored by EPA for the purposes of studying the removal of various metals and viruses through different wastewater treatment processes.

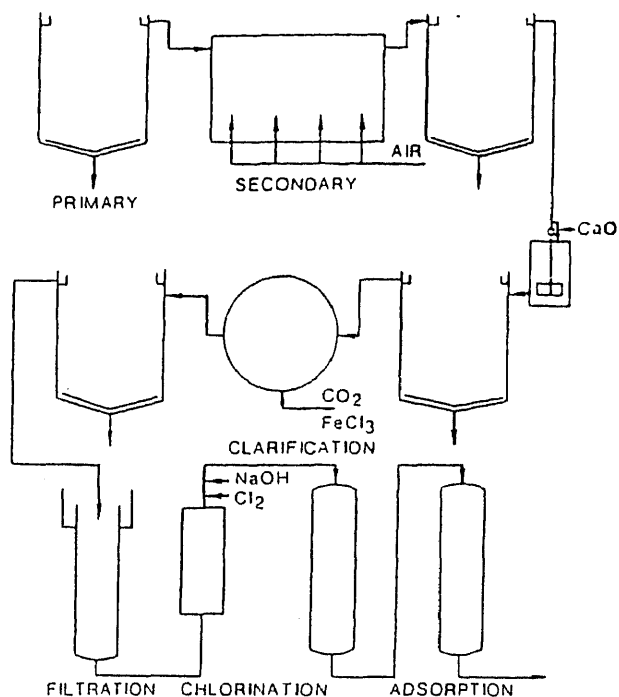


Figure- 8 Conventional-tertiary treatment.

Table-9
Effluent Qualities of Conventional Tertiary Treatment

Treatment	Amount of effluent ^a (mg/liter)			
	BOD	COD	Total P	Total N
Raw	129	307	8.4	22
Secondary	19.7	59	6.7	17
Clarified	4.2	22.7	0.34	15
Filtered	3.3	21.7	0.14	14
Chlorinated	—	—	0.14	3

^aThe filtered effluents for BOD, COD, and P represent 10 mo of continuous operation. Nitrogen removals represent typical results of short pilot tests.

Participating organizations included also the City of Dallas, and Texas A&M University which had responsibility for research direction.

(1). Treatment Method I :

The biological-physical treatment includes the following unit processes mode in series:

treatment mode in series :

- a. Screening and degritting
- b. Primary sedimentation
- c. Completely mixed activated sludge
- d. Multi-media filtration
- e. Disinfection

(2). Treatment Method II :

The biological-chemical-physical treatment includes the following unit processes mode in series:

- a. Screening and degritting
- b. Primary sedimentation
- c. Completely mixed activated sludge
- d. Chemical treatment
- e. Multi-media filtration
- f. Activated carbon adsorption
- g. Disinfection

(I). Results of Method I Treatment :

(a) Primary Effluent

Water quality data for primary effluent are given in Table-10 (8). It should be clear that certain water quality parameters will vary widely from city to city. In fact all parameters can be expected to vary over a large range. In particular hardness and alkalinity are functions of geographical location, antecedent precipitation, and discharges into the collection system.

Primary effluents were certainly not high quality, but they were amenable to certain industrial reuse applications. Primary effluent can be used in a limited way as cooling water, and in the lumber industry. In addition, primary effluent can be used by the primary metals industry for quenching, hot rolling, and gas cleaning.

Table-10 Water Quality – Primary Effluent

<u>Parameter</u>	<u>mg/l</u>
TDS	516
TSS	88
BOD	157
COD	326
Total P	13.1
Total N	32.3
NH ₃ - N	21.9
Org. N	10.2
NO ₂ & NO ₃ - N	0.2
Turbidity	—
SO ₄	191
SiO ₂	18.7
Ca	39
Mg	5.3
Fe	1.05
Mn	0.067
Hardness	165
Alkalinity	235
Fecal Coliforms per 100 ml	6 × 10 ⁶
MPN per 100 ml	15 × 10 ⁷
Total Count per ml	150 × 10 ⁵

(b) Activated Sludge Effluent

Activated sludge effluents were in general of moderate quality, and as such they were suitable for several industrial applications. In some instances the industry may need to practice a minimum of pretreatment prior to using the effluent as a process water. Depending upon the operational mode of the biological system, the form of the nitrogen compounds and the alkalinity of the effluent will vary considerably. If the process is being operated to nitrify, the alkalinity will be reduced through the activated sludge process and the ammonia will be converted to nitrate nitrogen. The alkalinity decrease will be about 7.1 mg/l per mg/l of ammonia converted to nitrate nitrogen. If the process is operated under relatively high organic loading (non-nitrifying), the ammonia and alkalinity will be largely unaffected.

Activated sludge effluents have reuse application in the lumber industry, for cooling water, in the petroleum industry, and for quenching, hot rolling and gas cleaning in the primary metal industry. In addition the cement industry can utilize activated sludge effluents as process water, as can the paper industry (for mechanical pulping) if the iron and manganese values are low enough to avoid the problems of color and staining. Activated sludge effluent quality is given in Table-11 (8).

TABLE-11
Water Quality – Activated Sludge Process
(September 1972)

<u>Parameter</u>	<u>Raw Wastewater</u>	<u>A.S. Effluent</u>	<u>Efficiency %</u>
TSS	264	9	96.6
BOD ₅	251	9	96.4
COD	606	45	92.6
TOC	250	14	94.4
Total P	14.0	9.4	32.9
NH ₃ - N	22.1	1.5	93.2
Org. N	15.7	3.8	75.8
NO ₂ & NO ₃ - N	0.2	15.7	—
Total N	38.0	21.0	44.7
SO ₄	191	125	34.7
Ca	39	37	5.1
Mg	5.3	5.0	6.0
Fe	1.05	0.3	71.4
Mn	0.067	0.050	25.4
SiO ₂	18.7	—	—
Fecal Coliform per 100 ml	6 × 10 ⁶	3 × 10 ⁴	99.5
MPN per 100 ml	15 × 10 ⁷	10 × 10 ⁵	99.3
TPC per ml	150 × 10 ⁵	91 × 10 ³	99.4

(c) Filtered Activated Sludge Effluent

The water quality for filtered activated sludge effluent is presented in Table-12 (8). In general, the water was of good physical quality since the great bulk of the suspended solids had been removed. The only remaining organics are mostly to be found in the soluble form, and only a small portion of these were biodegradable, indicating that they were not likely to promote the growth of slime-forming organisms. The biological quality of the water was not good without chlorination. Fecal coliforms, total coliforms, and total bacterial counts were all high without chlorination, However, after disinfection the biological quality of water was excellent. The type of chlorine residual will depend to a great extent on the operation of the activated sludge process. If complete nitrification is not occurring, there will be almost no chance of obtaining a free chloride residual (hypochlorous acid), the residual will be a chloramine, the type, depending upon the PH of the effluent. If nitrification is complete a free residual can be obtained in most cases and the biological quality should approximate the data given below:

Fecal coliforms per 100 ml=0

Coliform bacteria per 100 ml=0

Total bacteria per ml=10

Due to the relatively high quality of the effluent, considerable industrial reuse can be realized including use

by the primary metals industry (quenching, hot rolling, gas cleaning, cold rolling, and some rinse waters), the petroleum industry, the lumber industry, as cooling water, the paper industry (mechanical pulping), and the leather industry (tanning processes).

TABLE -12
Water Quality - Filtered Activated Sludge
(September 1972)

<u>Parameter</u>	<u>Influent (mg/l)</u>	<u>Effluent (mg/l)</u>	<u>Percent Reduction</u>
TSS	9	2	77.8
BOD ₅	9	1	88.9
COD	53	37	30.2
Total P	9.4	8.9	5.3
Total N	21.0	20.6	1.9
NH ₃ - N	1.5	1.3	13.3
Org. N	3.8	3.0	26.7
NO ₂ & NO ₃ - N	15.7	16.3	-
Turbidity (JTU)	3.3	2.5	24.2
SO ₄	125	121	3.2
Ca	37	38	-
Mg	5.0	5.0	0.0
Fe	.3	.12	60
Mn	.050	.041	18
Alkalinity	235	70	-
Hardness	165	-	-
Fecal Coliform per 100 ml	3 × 10 ⁴	46 × 10 ³	-
MPN per 100 ml	10 × 10 ⁵	28 × 10 ⁴	72.0
TPC per ml	91 × 10 ³	65 × 10 ³	28.6

(d) Biological-physical treatment mode

The biological - physical treatment sequence is shown diagrammatically in Figure-9 (8), and a summary of the final product water quality and total efficiency is given in Table-13 (8). While screened and degrittred raw wastewater may have some industrial applications, it generally has too much settleable and organic matter to make it of any practical use, and for certain public health and aesthetic reasons its use should preferably be avoided.

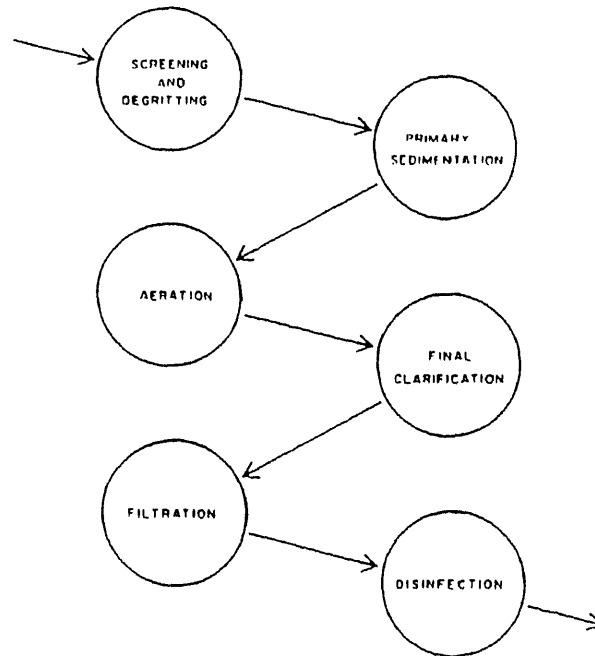


Figure-9 Biological-Physical Treatment-Sequence.

Table-13

Biological-Physical Treatment Mode
(Average-Aug./Sept./Oct. 1972)

<u>Parameter</u>	<u>Raw Wastewater</u>	<u>AWT Effluent</u>	<u>% Removal</u>
TSS	284	4	98.6
BOD5	239	2	99.2
COD	588	33	94.4
TOC	211	15	92.9
NH3-N	22.5	2	91.1
Org.N	15.1	2.8	80.4
NO2 & NO3-N	0.2	11.6	-
P	13.9	8.7	37
Total N	37.7	16.4	56.5
PH	-	7	-
Turbidity	-	1.6	-
SO4	191	121	36.6
Ca	39	38	2.6
Mg	5.3	5	6
Fe	1.05	0.12	88.6
Mn	0.067	0.041	38.8
SiO2	18.7	NA	-
Alkalinity	235	70	70.2
Hardness	165	-	-
Fecal Coliform			
per 100 ml	6×10^6	0	100
MPN per 100ml	15×10^7	0	100
TPC per ml	150×10^5	10	99.99+

(II). Results of Method II Treatment :

(a) Chemical Treatment Effluent

The influent of this treatment method is from the activated sludge unit outlet, and the water quality characteristics of the effluent from a chemical treatment process will obviously depend on the chemicals being used to accomplish coagulation / flocculation. In the case of lime treatment with recarbonation a net reduction in the hardness and the alkalinity is possible. The Dallas facility did not have recarbonation facilities at the time the present data were collected and, as a result, the final PH value was generally in excess of 11.5 with the attendant high alkalinity and hardness. In the event alum was being used as the primary coagulant an increase in sulfates will occur, the amount depending on the feed required to get good treatment.

Water quality criteria for chemical treatment effluent are given in detail in Table-14 (8). Since the water is of high quality, it has considerable application as a process water for industry. High-lime treatment is successful in eliminating coliform bacteria, ova, cysts, and high biological forms, as well as bacterial viruses. Biological quality is excellent when high lime treatment has been employed eliminating the need for disinfection unless a residual is desired. Industry reuse applications are listed below:

TABLE -14
Water Quality - Chemical Treatment
(September 1972)

<u>Parameter</u>	<u>Influent (mg/l)</u>	<u>Effluent (mg/l)</u>	<u>Percent Reduction</u>
TSS	9	9	0
BOD ₅	9	1	88.9
COD	45	23	48.9
Total P	10.3	0.1	99.0
Total N	21.0	21.0	0
NH ₃ - N	1.5	1.6	-
Org. N	3.8	2.5	34.2
NO ₂ & NO ₃ - N	15.7	16.9	-
Turbidity (JTU)	3.4	1.6	52.9
SO ₄	125	119	5
Ca	37	140	-
Mg	5.0	.6	88
Fe	.3	.23	23
Mn	.05	.008	84
Fecal Coliform per 100 ml	3 × 10 ⁴	0	100
MPN per 100 ml	10 × 10 ⁵	.1	99.99+
TPC per ml	91 × 10 ³	4	99.99+

TABLE-15
Water Quality - Filtration of Chemical Treatment Effluent
(September 1972)

<u>Parameter</u>	<u>Influent (mg/l)</u>	<u>Effluent (mg/l)</u>	<u>Percent Removed</u>
TSS	9	3	66.7
BOD ₅	1	1	0
COD	23	23	0
Total P	0.1	0.1	0
Total N	21.0	20.8	1.0
NH ₃ - N	1.6	1.5	6.25
Org. N	2.5	2.1	16.0
NO ₂ & NO ₃ - N	16.9	17.2	-
Turbidity (JTU)	1.6	0.7	56.3
SO ₄	119	109	8.4
Ca	140	133	5.0
Mg	.6	.4	33.3
Fe	.23	.08	65.2
Mn	.008	.005	37.5
Fecal Coliform per 100 ml	0	0	-
MPN per 100 ml	.1	.1	0.0
TPC per ml	4	4	0.0

- a. Lumber industry
- b. Cooling water
- c. Petroleum industry
- d. Primary metals industry (quenching, hot rolling, gas cleaning, cold rolling, and some rinsing)
- e. Paper industry (mechanical pulping, unbleached product process water)
- f. Cement / Chemical industry
- g. Leather industry(tanning processes)

(b) Filtered Chemical Treatment Effluent

Water quality for a filtered chemical treatment effluent are given in Table-15 (8). The water quality at this point in the processing is excellent, with the only major contaminant in the process flows being the nonbiodegradable soluble organic chemical species. The only real water quality problem that are likely to be encountered at this stage are color and foaming, resulting from the organic compounds that remain in solution. The industrial uses that can be made of this water include the following:

- a. Lumber industry
- b. Cooling water
- c. Petroleum industry
- d. Primary metals industry
- e. Paper industry
- f. Cement / Chemical industry

(c) Activated Carbon Adsorption Effluent

The water quality at this point in the treatment of unit processes is excellent, all of the major contaminants have been removed. After disinfection the final effluent will meet the specific criteria of the U.S. Public Health Service Drinking Water Standards. As such, the water is suitable for almost all industrial water use applications.

There is one constraint to the use of the final product water-those industries requiring potable water for their processing, which includes the food processing industry and the bottled and canned soft drink industry. While the effluent satisfies the Drinking Water Standards in terms of meeting the criteria, it does not meet the logical of the Standards. The use of a wastewater as a potable water has never been considered as the "most desirable source which is feasible." Much more research needs to be completed before the production of a potable water can be guaranteed and produced on a consistent basis.

Water quality of the activated carbon effluent is given in Table-16 (8). The industrial uses that can be made of this high quality water include the same eight industries as for the chemical treatment effluent.

TABLE-16
 Water Quality – Activated Carbon Adsorption
 (September 1972)

<u>Parameter</u>	<u>Influent (mg/l)</u>	<u>Effluent (mg/l)</u>	<u>Percent Removed</u>
TSS	3	2	33.4
BOD ₅	1	1	0
COD	24	12	50
Total P	0.1	0.0	100
Total N	20.8	19.8	4.8
NH ₃ - N	1.5	1.8	—
Org. N	2.1	1.6	23.8
NO ₂ & NO ₃ - N	17.2	16.4	4.7
Turbidity (JTU)	0.7	0.2	71.4
SO ₄	109	99	10.1
Ca	133	123	7.5
Mg	.4	.4	0.0
Fe	.08	.05	37.5
Mn	.005	.006	—
Fecal Coliform per 100 ml	0	0	—
MPN per 100 ml	.1	0	100
TPC per ml	4	7	—

3. Pilot Studies for Removal of Suspended Solids in
Toledo Refinery Sun Oil Company of Pennsylvania (1)

In 1971, a four-month study was initiated to evaluate seven pilot units in the removal of suspended solids from the fourth stage of bio-oxidation effluent. Included in the evaluation were three filters, two air-flotation units, and two microstrainers.

Microstrainers proved to be unsuitable for this application. Polyester fabric in 3, 5, & 10 micron opening, and stainless steel fabric in 15, 23, & 35 micron opening removed only approximately 50 percent of the suspended solids in the best case.

Induced air flotation showed unacceptable results, even at extremely high polyelectrolyte dosage. Pressurized air flotation was piloted at raw water rate of 0.67 to 1.8 gallons per minute per square foot. Recycle rate varied from 2.7 to 1.0 gallon per minute of recycle per gallon of feed. Removal performance was much better than in the induced-air flotation unit.

A pilot upflow sand filter was installed to determine suspended solids removal efficiency when charging effluent from the fourth stage of bio-oxidation. The filter was two feet in diameter and contained four inches of 1-1/4 to 1-1/2 inch gravel, ten inches of 3/8 to 5/8 inch gravel, 12 inch of 6 to 10 mesh sand, and approximately five feet of 12 to 20 mesh sand. The unit was supplied with the necessary

equipment to make the pilot operation fully automatic.

In the test runs, the filters was operated in the range of 4.5 to 6.4 gal/min/sq.ft. with an air scour. Typical suspended solids removal trends at varying flow rates and inlet concentrations are listed in Table-17 (1). Average removal was 88 percent at the 4.5 gallons, and 84 percent at 6.4 gallons.

COD reduction through the filter was in the 50 percent range. TOC removal followed a similar pattern. Limited data reflected good removal of trace oil and phosphorus. The capacity of the filter was found to be four to five pounds of dry solids per sq.ft. of filter area. This capacity would permit operating cycles as long as 24 hours.

The upflow filter system is guaranteed to remove 80 percent by weight of the suspended solids present in colloidal dispersion without use of chemical additives. Flow rate is 4 to 12 gpm per sq. foot, at an average total flow of 2000 gpm and maximum flow of 3000 gpm. All the guarantee criteria are listed in Table-18 (1).

Table-17

Suspended Solids Removal in Upflow Pilot Sand Filter at Different Flow Rates And Inlet Concentrations

<u>Flow Rate</u> <u>GPM/Sq.Ft.</u>	<u>Suspended Solids PPM</u> <u>Inlet</u>	<u>Suspended Solids PPM</u> <u>Outlet</u>	<u>Removal Efficiency %</u>
4.5	48	10	79
4.5	46	7	85
4.5	36	2	94
4.5	32	2	94
6.4	42	7	83
6.4	52	14	73
6.4	38	2	95

Table-18

Upflow Filter Conditions Specified for 80% Removal Of Suspended Solids

	<u>Min.</u>	<u>Avg.</u>	<u>Max.</u>
Flow, GPM/Sq.Ft.	4		12
Flow, GPM(Total)		2000	3000
Temperature (°F)	50		80
Suspended Solids, PPM	55	117	200
Total Organic Carbon, PPM	40		60
Oil, PPM	15	50	200

4. Union Carbide's Typical Petrochemical Plant

A thorough survey 1972 (1) of water usage in one of Union Carbide's integrated, multi-product petrochemical facilities represented a water conservation program in this particular plant.

There are six different classes of water usage, each with a different quality requirement. That is cooling water, potable water, service water, boiler feed water, and process reagent water.

To produce recovered water suitable for recycle as process or boiler feedwater, three types of contaminants must be removed :

- a. Dissolved organic substances (as BOD or COD)
- b. Suspended solids (organic and inorganic)
- c. Dissolved (primarily inorganic) solids

For recycle as service water, only the first two steps would probably be required. Figure-10 (1) is a schematic flowsheet of a complete wastewater purification system such as will be required to meet "zero discharge" effluent standards or to provide high purity water for recycle. This system will involve :

- a. Maximum reduction of waste loads at sites.
- b. Primary clarification.
- c. Biological treatment.
- d. Coagulation, flocculation, and filtration for complete removal of suspended solids.

- e. Equipment for sludge conditioning, dewatering, and incineration.
- f. Activated carbon adsorption, with thermal regeneration of carbon.
- g. Demineralization in ion exchange or reverse osmosis facilities.
- h. Deep-well disposal of waste brine.

Table-19 (1) is a summary of contaminant removals projected for each step of the recovery system shown in Figure-10.

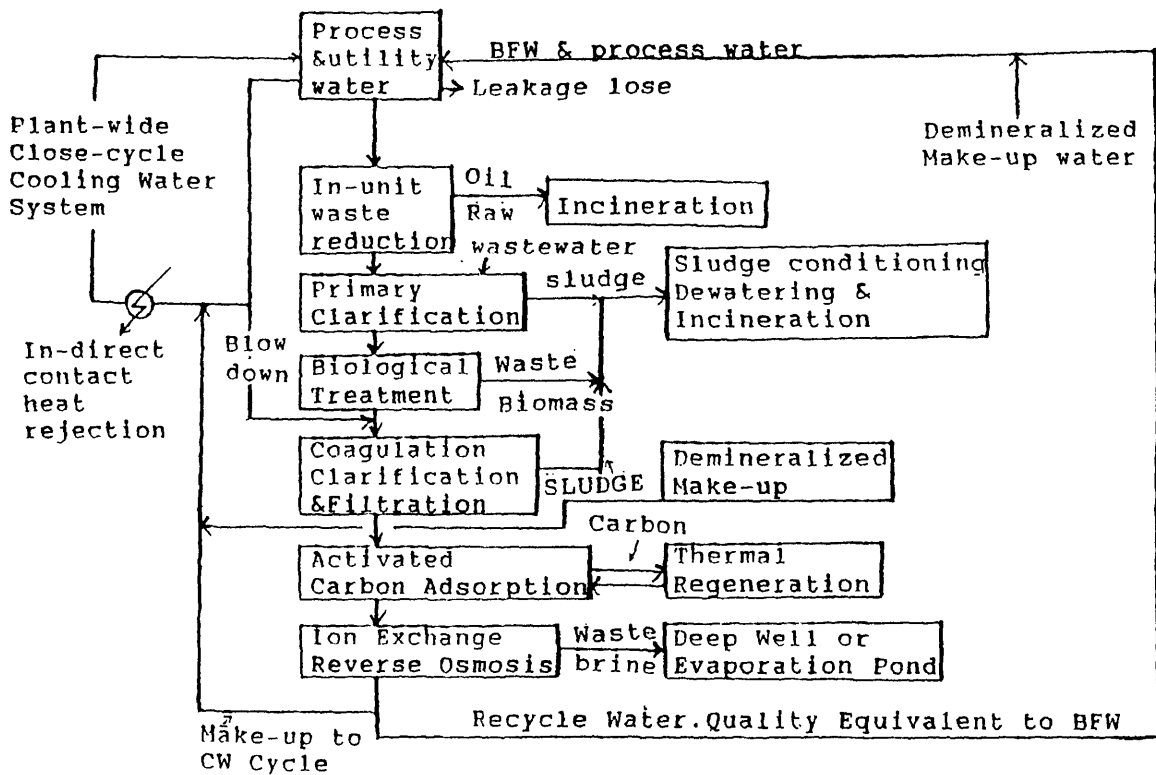


Figure-10 Process Flowsheet for Complete Wastewater Recovery and Recycle.

TABLE -19

Removals of Pollutants at Each Step of a Complete Wastewater Recovery System

<i>Process Step</i>	<i>BOD^a</i>		<i>COD^a</i>		<i>TSS</i>		<i>TDS</i>	
	<i>% Removed</i>	<i>Remaining mg/l</i>	<i>% Removed</i>	<i>Remaining mg/l</i>	<i>% Removed</i>	<i>Remaining mg/l</i>	<i>% Removed</i>	<i>Remaining mg/l</i>
Raw Wastewater	-	1400	0	2700	-	NA	-	NA
In-Unit Waste Reduction	(b)	-	(b)	-	(b)	-	(b)	-
Primary Clarification	10	1260	20	2160	?	?	0	NA
Biological Treatment	93	85	72	599	gain	80	0	2000
Coagulation, Clarification, Filtration	0	85	0	599	97	2	?	<2000
Activated Carbon Adsorption	75	21	70	180	-	1	0	<2000
Undefined COD Removal Step	(b)	~ 0	(b)	~ 5	-	1	0	<2000
Ion Exchange or Reverse Osmosis	0	0	0	~ 5	-	1	98	50

NOTES: BOD = biochemical oxygen demand; COD = chemical oxygen demand; TSS = total suspended solids; TDS = total dissolved (Inorganic solids)

^a BOD and COD are total values for raw wastewater; soluble fractions at all other points.

^b That portion of the BOD and COD not removed in the other steps must be removed by a combination of in-unit waste load reductions and an undefined step following the activated carbon adsorbers.

C. EPA's Survey for The Petroleum Refinery
Point Source Category April 1974 (5)

Table-20 (5) 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. Typical efficiencies for these processes are shown in Table-21 (5). And the Table-22 (5) summarizes the expected effluents from waste water treatment processes throughout the petroleum refining industry.

Observed Refinery Treatment System and Effluent Loadings

Table-20

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 (lb/1000 bbl of feedstock)	OP	AL-PP	AL-F	E-DAF-AS	OP	DAF,AL,PP	DAF,AS	DAF,AS	DAF,AL,PP	E,TF,AS	E,AS	DAF,AS,PP
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)
Oil	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(0.07)

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-21

Typical Removal Efficiencies for
Oil Refinery Treatment Processes

PROCESS	PROCESS INFLUENT	REMOVAL EFFICIENCY, %							
		BOD ₅	COD	TOC	BS	OIL	PHENOL	AMMONIA	SULFIDE
1. API Separator	Raw Waste	5-40	5-30	NA	10-50	60-99	0-50	NA	NA
2. Clarifier	1	30-60	20-50	NA	50-80	60-95	0-50	NA	NA
3. Dissolved Air Flotation	1	20-70	10-60	NA	50-85	70-85	10-75	NA	NA
4. Filter	1	40-70	20-55	NA	75-95	65-90	5-20	NA	NA
5. Oxidation Pond	1	40-95	30-65	60	20-70	50-90	60-99	0-15	70-100
6. Aerated Lagoon	2,3,4	75-95	60-85	NA	40-65	70-90	90-99	10-45	95-100
7. Activated Sludge	2,3,4	80-99	50-95	40-90	60-85	80-99	95-99+	33-99	97-100
8. Tricking Filter	1	60-85	30-70	NA	60-85	50-80	70-98	15-90	70-100
9. Cooling Tower	2,3,4	50-90	40-90	10-70	50-85	60-75	75-99+	60-95	NA
10. Activated Carbon	2,3,4	70-95	70-90	50-80	60-90	75-95	90-100	7-33	NA
11. Filter Granular Media	5-9	NA	NA	50-65	75-95	65-95	5-20	NA	NA
12. Activated Carbon	5-9 plus 11	91-98	86-94	50-80	60-90	70-95	90-99	33-87	NA

NA - Data Not Available

Table-22
Expected Effluents from Petroleum Treatment Processes

PROCESS	PROCESS INFLUENT	EFFLUENT CONCENTRATION, mg/L							
		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
2. Clarifier	1	45-200	130-450	NA	25-60	5-35	10-40	NA	NA
3. Dissolved Air Flotation	1	45-200	130-450	NA	25-60	5-20	10-40	NA	NA
4. Granular Media Filter	1	40-170	100-400	NA	5-25	6-20	3-35	NA	NA
5. Oxidation Pond	1	10-60	50-300	NA	20-100	1.6-50	0.01-12	3-50	0-20
6. Aerated Lagoon	2,3,4	10-50	50-200	NA	10-80	5-20	0.1-25	4-25	0-0.2
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
8. Trickling Filter	1	25-50	80-350	NA	20-70	10-80	0.5-10	25-100	0.5-2
9. Cooling Tower	2,3,4	25-50	47-350	70-150	4.5-100	20-75	.1-2.0	1-30	NA
10. Activated Carbon	2,3,4	5-100	30-200	NA	10-20	2-20	<1	10-140	NA
11. Granular Media Filter	5-9	NA	NA	25-61	3-20	3-17	0.35-10	NA	NA
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

A - Data Not Available

Water Quality Standards of Reused Water

A. Process Water

For process water requirements, refiners use treated or untreated cooling water, public water supplies, or ground water. Of the total water intake by refineries, about 84% is secured from surface supplies, 7% from ground water, and the remaining 9% from public water supplies.

The primary treatment of water for process use is for suspended solids and turbidity removal. Some washing operations are normally provided with water of about 10 mg/l or less suspended solids. However, there are many refineries that do not treat process water.

The quality characteristics of waters that have been treated by existing processes to produce waters acceptable for process use (report of the National Technical Advisory Committee to the Interior Water Quality Criteria) are given in Table-23 (10). The surface water quality requirements for use are given in Table-24. From U.S. Department of the Interior, Office of Water Research and Technology, OWRT/RU-79/1, 1979. We get the water quality criteria for cooling and boiler feed use as following :

TABLE - 23: Quality Requirements of Water at Point of Use for Petroleum Industry

[Unless otherwise indicated, units are mg/l and values that normally should not be exceeded. Quality of water prior to the addition of substances used for internal conditioning.]

Characteristic	Concentration	Characteristic	Concentration
Silica (SiO ₂)----	(¹)	Nitrate (NO ₃) --	(¹)
Iron (Fe) -----	1	Dissolved	
Calcium (Ca) --	75	solids -----	1,000
Magnesium		Suspended	
(Mg) -----	30	solids -----	10
Total sodium and potassium		Hardness	
(Na, K) -----	(¹)	(CaCO ₃) -----	350
Bicarbonate		Noncarbonate	
(HCO ₃) -----	(¹)	hardness	
Sulfate (SO ₄)----	(¹)	(CaCO ₃) -----	70
Chloride (Cl)----	300	Color, units -----	(¹)
Fluoride (F) ----	(¹)	pH, units -----	6.0-9.0

¹ Accepted as received (if meeting total solids or other limiting values); has never been a problem at concentrations encountered.

NOTE.—Application of the above values should be based on Part 23, ASTM book of standards (1), or APHA Standard methods for the examination of water and wastewater.

TABLE - 24¹ Quality Characteristics of Surface Waters That Have Been Used by the Petroleum Industry

[Unless otherwise indicated, units are mg/l and values are maximums. No one water will have all the maximum values shown.]

Characteristic	Concentration	Characteristic	Concentration
Silica (SiO ₂)----	50	Chloride (Cl)---	1,600
Iron (Fe) -----	15	Fluoride (F)----	1.2
Calcium (Ca) --	220	Nitrate (NO ₃) --	8
Magnesium		Dissolved	
(Mg) -----	85	solids -----	3,500
Total sodium and potassium		Suspended	
(Na, K) -----	230	solids -----	5,000
Bicarbonate		Hardness	
(HCO ₃) -----	480	(CaCO ₃) -----	900
Sulfate (SO ₄)----	570	Color, units -----	25
		pH, units -----	6.0-9.0

NOTE.—Application of the above values should be based on Part 23, ASTM book of standards (1), or APHA Standard methods for the examination of water and wastewater.

Water Quality Criteria for
Cooling and Boiler feed Use

Parameter	Cooling Water		Boiler Feed Water
	Once-through	Recirculation Make-up	
Alkalinity	500	350	350
Aluminium	b	0.1	5
Bicarbonate	600	24	170
Calcium	200	50	b
Chloride	600	500	b
Copper	b	b	0.5
COD	75	75	5
Hardness	850	650	350
Hydrogen Sulphide	-	b	b
Iron	0.5f	0.5	1
Magnesium	b	b	b
Manganese	0.5	0.5	0.3
Nitrogen-Ammonia (asN)	b	b	0.1
Oil	no floating	-	-
Organics, CTE	g	b	1
MBAS	b	b	1
Oxygen, dissolved	present	b	2.5
pH, units	5.0 - 8.3	b	7.0-10.0
Silica	50	50	30
Suspended Solids	5 000	100	10
Total Dissolved Solids	1 000	h	700
Sulphate	680	200	b
Temperature °C	b	b	b
Zinc	b	b	b

Notes:

- b Accepted as received
- f 0.5 mg/l iron and manganese
- g No floating oil
- h Effluent TDS values are typically in the range 500 to 800 mg/l.

B. Cooling Water

One-through cooling waters should be reasonably free of suspended matter which may clog or settle out in the system and of excessively heavy contamination with living organism. A few specific limitations which have been suggested, and which are equally applicable to open recirculating systems, are that the turbidity be below 50 ppm, iron or manganese below 0.5 ppm, and sulfides (as H₂S) below 5 ppm.

For open recirculating systems, the water must be treated to keep it reasonably noncorrosive and non-scale-forming, as well as free from slime and algae growths. It is generally considered good practice to limit the total dissolved solids to not over 2000 ppm in circulating waters of large cooling towers so as to minimize galvanic corrosion in the equipment.

Closed circulating cooling water systems rarely have sufficient makeup to create serious scale problems, but corrosion is fairly common. For this reason it is desirable to maintain a minimum of 200 ppm sodium chromate in such waters with a PH in the 7.0 to 8.5 range. Suspended matter, particularly abrasive suspended matter, can damage circulating pumps and should also be minimized.

C. Boiler Feed Water

Specific standards of concentration for the various constituents in boiler water can be more readily established, although these will still vary considerably with operating pressure, construction, and type of operation of the boiler. Quality requirements of makeup water should be free of any suspended matter. For some cases require low dissolved oxygen in the makeup water. With chromate-treated boilers, water-treatment standards range from 500 ppm sodium chromate, which provides ample protection under conditions of good control, to 2000 ppm sodium chromate as recommended for general use by the Steel Boiler Institute. Table-25 (10) shows the quality characteristics of surface waters that have been treated by existing processes to produce waters acceptable for boiler makeup and cooling. Table-26 (10) shows quality requirements for both boiler-feed water and cooling water at point of use.

TABLE-25¹ Quality Characteristics of Surface Waters That Have Been Used for Steam Generation and Cooling in Heat Exchangers

[Unless otherwise indicated, units are mg/l and values are maximums. No one water will have all the maximum values shown.]

Characteristic	Boiler makeup water			Cooling water			
	Industrial		Electric utilities	Once through		Makeup for recycling	
	Low and medium pressure 0 to 700 psig	High pressure 700 to 1,500 psig	High pressure > 1,500 psig	Fresh	Brackish ²	Fresh	Brackish ²
Silica (SiO ₂)	150	150	150	50	25	150	25
Aluminum (Al)	3	3	3	3	(³)	3	(³)
Iron (Fe)	80	80	80	14	1.0	80	1.0
Manganese (Mn)	10	10	10	2.5	0.02	10	0.02
Copper (Cu)	(³)	(³)	(³)	(³)	(³)	(³)	(³)
Zinc (Zn)	(³)	(³)	(³)	(³)	(³)	(³)	(³)
Calcium (Ca)	(³)	(³)	(³)	500	1,200	500	1,200
Magnesium (Mg)	(³)	(³)	(³)	(³)	(³)	(³)	(³)
Ammonia (NH ₃)	(³)	(³)	(³)	(³)	(³)	(³)	(³)
Bicarbonate (HCO ₃)	600	600	600	600	180	600	180
Sulfate (SO ₄)	1,400	1,400	1,400	680	2,700	680	2,700
Chloride (Cl)	19,000	19,000	19,000	600	22,000	500	22,000
Nitrate (NO ₃)	(³)	(³)	(³)	30	(³)	30	(³)
Phosphate (PO ₄)	(³)	(³)	50	4	5	4	5
Dissolved solids	35,000	35,000	35,000	1,000	35,000	1,000	35,000
Hardness (CaCO ₃)	5,000	5,000	5,000	850	7,000	850	7,000
Acidity (CaCO ₃)	1,000	1,000	1,000	(³)	(³)	200	(³)
Alkalinity (CaCO ₃)	500	500	500	500	150	500	150
pH, units	(³)	(³)	(³)	5.0-8.9	5.0-8.4	3.5-9.1	5.0-8.4
Color, units	1,200	1,200	1,200	(³)	(³)	1,200	(³)
Organics:							
Methylene blue active substances	1	2	10	1.3	(³)	1.3	1.3
Carbon tetrachloride extract	100	100	100	(³)	(³)	100	100
Chemical oxygen demand (O ₂)	100	100	500	(³)	(³)	100	200
Odor	(³)	(³)	(³)	(³)	(³)	(³)	(³)
Hydrogen sulfide (H ₂ S)	(³)	(³)	(³)	(³)	4	(³)	4
Dissolved oxygen (O ₂)	(³)	(³)	(³)	(³)	(³)	(³)	(³)
Temperature, F	120	120	120	100	100	120	120
Suspended solids	15,000	15,000	15,000	5,000	250	15,000	250

¹ Brackish water—dissolved solids more than 1,000 mg/l by definition 1963 census of manufacturers.

² Accepted as received (if meeting total solids or other limiting values); has never been a problem at concentrations encountered.

³ Zero, not detectable by test.

⁴ No floating oil.

NOTE.—Application of the above values should be based upon analytical methods in Part 23, ASTM book of standards (1) or APHA Standard methods for the examination of water and wastewater.

TABLE - 26 Quality Requirements of Water at Point of Use for Steam Generation and Cooling in Heat Exchangers

(Unless otherwise indicated, units are mg/l and values that normally should not be exceeded. No one water will have all the maximum values shown.)

Characteristic	Boiler feed water				Cooling water			
	Quality of water prior to the addition of substances used for internal conditioning				Once through	Makeup for recirculation		Brackish ¹
	Industrial			Electric utilities		Fresh	Brackish ¹	
	Low pressure 0 to 150 psig	Inter- mediate pressure 150 to 700 psig	High pressure 700 to 1,500 psig	1,500 to 5,000 psig				
Silica (SiO ₂)	30	10	0.7	0.01	50	25	50	25
Aluminum (Al)	5	0.1	0.01	0.01	(*)	(*)	0.1	0.1
Iron (Fe)	1	0.3	0.05	0.01	(*)	(*)	0.5	0.5
Manganese (Mn)	0.3	0.1	0.01	(*)	(*)	(*)	0.5	0.02
Calcium (Ca)	(*)	(*)	(*)	(*)	200	420	50	420
Magnesium (Mg)	(*)	(*)	(*)	(*)	(*)	(*)	(*)	(*)
Ammonia (NH ₃)	0.1	0.1	0.1	0.7	(*)	(*)	(*)	(*)
Bicarbonate (HCO ₃)	170	120	48	(*)	600	140	24	140
Sulfate (SO ₄)	(*)	(*)	(*)	(*)	680	2,700	200	2,700
Chloride (Cl)	(*)	(*)	(*)	(*)	600	19,000	500	19,000
Dissolved solids	700	500	200	0.5	1,000	35,000	500	35,000
Copper (Cu)	0.5	0.05	0.05	0.01	(*)	(*)	(*)	(*)
Zinc (Zn)	(*)	(*)	(*)	(*)	(*)	(*)	(*)	(*)
Hardness (CaCO ₃)	20	(*)	(*)	(*)	850	6,250	130	6,250
Free mineral acidity (CaCO ₃)	(*)	(*)	(*)	(*)	(*)	(*)	(*)	(*)
Alkalinity (CaCO ₃)	140	100	40	(*)	500	115	20	115
pH, units	8.0-10.0	8.2-10.0	8.2-9.0	8.8-9.2	5.0-8.3	6.0-8.3	(*)	(*)
Color, units	(*)	(*)	(*)	(*)	(*)	(*)	(*)	(*)
Organics:								
Methylene blue active... substances	1	1	0.5	(*)	(*)	(*)	1	1
Carbon tetrachloride ... extract	1	1	0.5	(*)	(*)	(*)	1	2
Chemical oxygen demand (O ₂)	5	5	0.5	(*)	75	75	75	75
Dissolved oxygen (O ₂)	2.5	0.007	0.007	0.007	(*)	(*)	(*)	(*)
Temperature, F	(*)	(*)	(*)	(*)	(*)	(*)	(*)	(*)
Suspended solids	10	5	(*)	(*)	5,000	2,500	100	100

¹ Brackish water—dissolved solids more than 1,000 mg/l by definition 1963 census of manufacturers.

² Accepted as received (if meeting total solids or other limiting values); has never been a problem at concentrations encountered.

³ Zero, not detectable by test.

⁴ Controlled by treatment for other constituents.
* No floating oil.

NOTE.—Application of the above values should be based on Part 23, ASTM book of standards (1), or APHA Standard methods for the examination of water and wastewater.

Construction Cost of Advanced Treatment Plants for Water Reuse

Based on the previous technology evaluation, We know the efficiency of each unit process wastewater treatment methods. Before we decide which process will be adopted for the wastewater reuse; First, we must compare the cost of different treatment processes and find the most economical one which we will applied. Here are the examples of the construction cost of the reuse of secondary effluent wastewater treatment plants.

The construction cost was based on U.S. EPA developed report in AUG.1979 (11) and which consisted of the following eight principal components :(1) excavation and site work (2) manufactured equipment (3) concrete (4) steel (5) labor (6) pipe and valve (7) electrical equipment & instrumentation (8) housing.

A. Package Gravity Filter Plants

Cost estimates were developed and proceeded by a 1-hr detention basin. The capacity range utilized was 150 to 1400 gpm for filtration rates of 2 and 5 gpm/sq.ft. and a media depth of 30 inch. Conceptual designs for the cost estimates are presented in Table-27 (11). The contact basin removes rapidly settling materials such as sand and silt that could hamper the operation of the filters, and it also provides additional time for coagulant dispersion and flocculation.

Cost estimates are for filter vessels that are open-top, cylindrical steel tank sized to permit shop fabrication and over-the road shipment. The plants are complete, including filter vessels, mixed media, piping, valves, controls, electrical system, back wash system, surface wash system, chemical feed system, raw water pumps, 1-hr detention pre-filter contact basin, backwash / clearwell storage basin, building, and the other ancillary items required for a complete and operable installation. The estimated construction costs for filtration rates of 2 and 5 gpm/sq.ft. are shown in Table-28 (11).

Table-27

Conceptual Design for
Package Gravity Filter Plants

<u>Plant Capacity(gpm)</u>		<u>Filter Vessels</u>				
<u>2gpm/ft²</u>	<u>5gpm/ft²</u>	<u>Number of Units</u>	<u>Area (ft²)</u>	<u>Diameter (ft)</u>	<u>Total Area(ft²)</u>	<u>House Area(ft²)</u>
152	380	2	38	7	76	1,800
200	500	2	50	8	100	1,800
316	790	2	79	10	158	1,800
678	1,695	3	113	12	339	3,600

Table-28

Construction Cost for
Package Gravity Filter Plants

<u>Cost Category</u>	<u>Plant Flow Rate (gpm)*</u>			
	152 & 380	200 & 500	316 & 790	678 & 1,695
Excavation & site work	\$1,140	\$1,510	\$1,660	\$2,800
Manufactured Equipment	37,130	40,310	53,040	95,480
Concrete	20,670	28,090	30,740	50,350
Labor	13,340	14,330	17,290	27,040
Pipe & Valves	8,910	11,810	12,380	26,870
Elec. & Instr.	26,070	32,450	48,580	84,800
Housing	57,830	57,830	57,830	115,660
Subtotal	165,090	186,330	221,520	403,000
Miscellaneous & Contingency	24,760	27,950	33,230	60,450
Total	189,850	214,280	254,750	463,450

*Lower capacity represents a filtration rate of 2 gpm/sq.ft.
Higher capacity represents a filtration rate of 5 gpm/sq.ft.

B. Package Pressure Filtration Plants

Pressure filters are available from many manufactures with either rapid sand, dual-media or mixed-media filter beds. Unit can be either totally automatic or manual in operation.

Construction costs were developed of capacities ranging between 1000 gpd to 0.5 mgd, for filtration rates of 2 and 5 gpm/sq.ft. and a media depth of 30 inch. Conceptual

designs for the plants are shown in Table-29 (11). All units are skid mounted, completely self-contained, and include a single vertical pressure vessel with internal, automatic control valves, filter supply pump, filter media (mixed), backwash pump, and control panel. Included with each unit are two chemical feed units including tank, mixer, and chemical feed pump. Finished water is discharged to an at-grade storage tank/clearwell, which is not included in the cost estimate. Backwash water is pumped from the storage tank by an end suction centrifugal pump. The filter supply pump is also an end suction centrifugal pump and requires a flooded suction. The filter units are designed for automatic operation. Backwash is initiated by excessive headloss or by elapsed operating time. Surface wash is obtained from a separate pump or from a pressure distribution system through a backflow preventer. Estimated construction costs are presented in Table-30 (11).

Table-29

Conceptual Design for
Package Pressure Filtration Plants

<u>Plant</u> <u>2gpm/ft²</u>	<u>Capacity(gpm)</u>		<u>Filter</u> <u>Area</u> <u>(ft²)</u>	<u>Filter</u> <u>Diameter</u> <u>(ft)</u>	<u>Vessels</u> <u>Total</u> <u>Area(ft²)</u>	<u>House</u> <u>Area(ft²)</u>
	<u>5gpm/ft²</u>	<u>Number</u> <u>of Units</u>				
7	17	1	3.14	2	3.14	300
28	70	1	12.6	4	12.6	480
70	170	1	34.2	6.5	34.2	896
140	350	1	64	9	64	1,080
158	393	1	79	10	79	1,500
226	565	1	113	12	113	1,800

Table-30

Construction Cost for
Package Pressure Filtration Plants

<u>Cost Category</u>	<u>Plant Flow Rate (gpm)*</u>			
	<u>170</u>	<u>350</u>	<u>565</u>	<u>694</u>
Excavation & Site Work	\$ 210	\$ 230	\$ 798	\$ 980
Manufactured Equipment	39,110	58,350	81,947	100,670
Concrete	1,170	1,380	1,375	1,690
Labor	11,620	17,340	18,739	19,620
Piping & Valves	1,170	1,490	19,235	23,630
Elec. & Instru.	10,680	14,970	16,348	20,080
Housing	28,790	34,700	53,699	65,970
Subtotal	92,750	128,460	192,706	233,334
Miscellaneous & Contingency	13,910	19,270	28,906	33,290
Total	106,660	147,730	221,612	266,624

*Capacity represents a filtration rate of 5 gpm / sq.ft.

C. Pressure Granular Activated Carbon Contactors

Construction costs were based on the basis of a 7.5min detention time, an activated carbon loading rate of 1 gpm/ ft of carbon, a bed depth of 5 ft, and a hydraulic loading rate of 5 gpm/sq.ft. Conceptual designs are presented in Table-31 (11).

Table-31

Conceptual Design for Pressure Granular Activated Carbon Contactors

<u>Plant</u> <u>gpm</u>	<u>Flow</u> <u>gpd</u>	<u>Flow Rate</u> <u>gpm/ft²</u>	<u>Carbon Columns</u> <u>area(ft²)</u>	<u>Columns</u> <u>Dia.(ft)</u>	<u>Total Carbon</u> <u>Vol(ft³)/wt.lb</u>	<u>House</u> <u>(ft²)</u>
175	250,000	5.1	34	6.5	170/4,420	375
350	500,000	5.5	64	9	320/8,320	450
432	622,037	5.5	79	10	395/10,270	880
622	895,733	5.5	113	12	565/14,690	1,260
694	1000,000	5.5	157	10x2	785/20,410	1,750

The costs are based on the use of cylindrical, pressurized, downflow steel contactors conforming to the ASME code for pressure vessels designed for a working pressure of 50 psi. Tank have a skirt base and are furnished with inlet and outlet nozzles, a nozzle-style underdrain system, access manholes, manual ball or butterfly valves, differential pressure gauge, and an initial charge of activated carbon. The units are designed

for manual operation. A supply and backwash pump designed for flooded suction application is furnished skid-mounted with the activated carbon columns. Construction cost are shown in Table-32 (11).

Table-32

Construction Cost for
Pressure Granular Activated Carbon Contactors

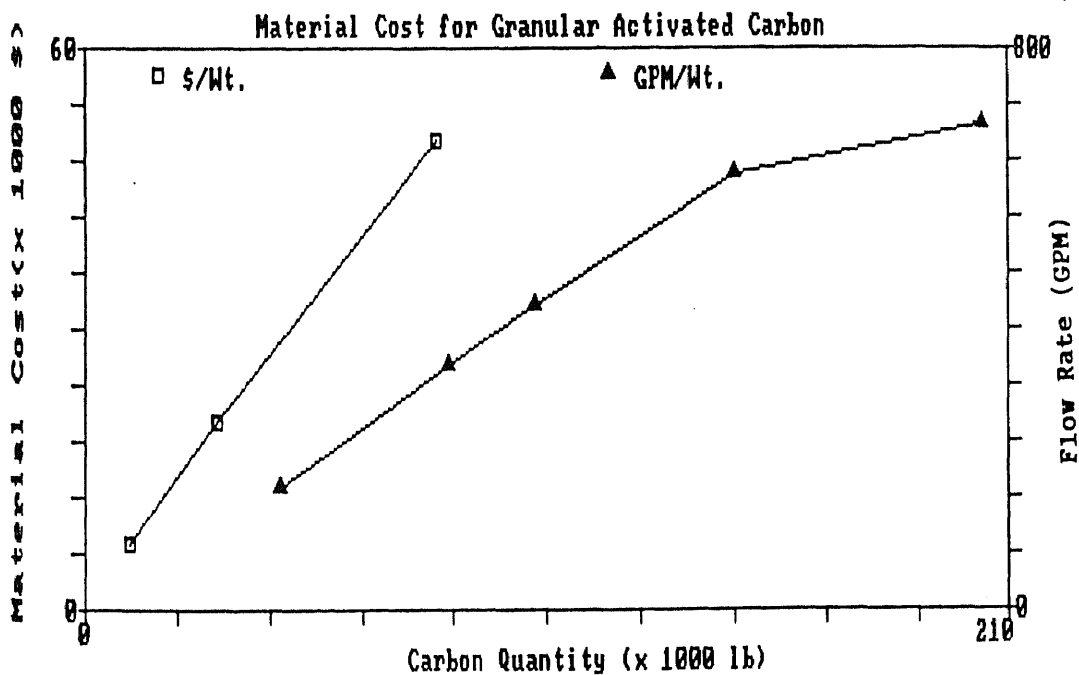
<u>Cost Category</u>	<u>Plant</u>		<u>Flow</u>		<u>Rate (gpm)</u>	
	<u>175</u>	<u>350</u>	<u>622</u>	<u>694</u>		
Excavation & Site work	\$ 80	\$ 80	\$ 475	\$ 530		
Manufactured Equipment	14,600	27,100	43,993	49,010		
Concrete	580	700	1,962	2,190		
Steel			1,012	1,130		
Labor	9,500	13,000	7,616	8,500		
Pumps, Pipes & Valves	6,400	8,800	13,664	15,250		
Elec. & Instru.	1,100	1,300	14,004	15,630		
Housing	10,300	11,400	29,165	32,550		
Subtotal	42,560	62,380	112,513	124,790		
Miscellaneous & Contingency	6,380	9,360	168,770	18,720		
Total	48,940	71,740	129,390	143,510		

D. Granular Activated Carbon Material Cost

Virgin carbon is generally purchased in 2-ft bags for quantities of 40,000 lb and less, with larger quantities transported in bulk by rail. Cost were developed for

purchase and placement of virgin carbon in a contactor. These costs may be used for either pressure or gravity carbon contactors to obtain the complete cost of the carbon contactor. The curve may also be used to determine the cost of makeup carbon to replace carbon lost during contactor operation and carbon regeneration. The cost curve is presented in terms of pounds of carbon, and a density of 26 lb/ft³ may be used to convert between volume and weight. Figure-11 presents a cost curve for purchase, delivery, and placement of virgin carbon.

Figure-11



E. Multiple Hearth Granular Carbon Regeneration

Granular activated carbon (GAC) is effectively regenerated in multiple hearth furnaces by exposure to properly and closely controlled conditions of temperature, oxygen, and moisture content of the atmosphere within the furnace. During the process, adsorbed organics are oxidized and driven off, restoring the adsorptive properties of the activated carbon. The multiple hearth furnace is a cylindrical, refractory-lined shell carrying a series of fired refractory hearths located one above the other. A revolving insulated central shaft and attached radial rabble arms move the material across the hearth directing material alternately outward or inward as material drops from one level to the next. The required size of this furnace is a function of the required frequency of regeneration, the carbon dosage used, the allowable hearth loading of the furnace, and anticipated downtime. Construction costs for a series of single furnace with various hearth areas. Conceptual designs for multiple hearth furnaces used in the cost estimates are shown in Table-33. The cost include the basic furnace, center shaft drive, furnace and cooling fans, spend carbon storage and dewatering equipment, auxiliary fuel system, exhaust scrubbing system, regenerated carbon handling system, quench tank, steam boiler, control panel, and instrumentation. Construction cost for a complete carbon regeneration furnace are presented in Table-33.

Table-33

Conceptual Design for
Multiple Hearth Granular Carbon Regeneration

Effective Hearth (sq.ft.)	Hearth Area	carbon Wt* lb/Day	Furnace Configuration		No.Hearths	Building area (sq.ft.)
			I.D. ft.- in.			
27		1,215	30"		6	750
37		1,665	30"		6	750
147		6,615	39"		6	900
359		16,155	10'-6"		5	1,200
732		32,940	14'-6"		6	1,800
1,509		67,905	20'-0"		6	2,400

*Use a hearth carbon loading 40 to 50 lb/sq.ft./day
& regen. cycle 6 days.

Table-34

Construction Cost for
Multiple Hearth Granular Carbon Regeneration*

<u>Cost Category</u>	<u>Furnace Hearth Area (ft²)</u>				
	<u>27</u>	<u>37</u>	<u>47</u>	<u>359</u>	<u>732</u>
Manufactured Equip.	\$220.6	\$275.8	\$519.8	\$647.1	\$1,039.6
Labor	117.7	147.1	273.2	346.8	557.1
Pipe and Valves	8.3	8.3	8.3	14.5	23.5
Elec.& Instru.	8.3	8.4	8.4	9.2	14.9
Housing	109.7	109.7	124.2	175.1	245.8
Subtotal	464.7	549.3	934.9	1,192.8	1,880.9
Miscellaneous & Contingency	69.7	82.4	140.1	178.9	282.1
Total	534.4	631.7	1,074.1	1,371.6	2,163.0

*Number in the table x \$1000 is the real value.

F. Capping Sand Filters With Anthracite

A popular technique for increasing the capacity of existing rapid sand filter installations involves removing the top 6 to 12 in. of sand and replacing it with anthracite coal. The coarser coal permits suspended solids penetration into the filter bed, allowing operation of the filter beds at higher flow rates and for longer periods between backwash. In many situations, this modification can effect a 30 to 50 percent increase in capacity and a reduction in wash water usage.

Cost data were assuming the removal of 12 in. of sand and replacement with 12 in. of anthracite coal for total filter bed areas ranging from 350 to 70,000 sq.ft. The costs include labor for removing the sand from the filter and disposing of it on-site, material and freight costs for anthracite coal, and installation labor. The labor costs were assuming that sand removal from filters smaller than 3,500 sq.ft. would be accomplished by manual labor. For larger filters, manual labor was supplemented with mechanical equipment. Construction costs are summarized in Table-35 .

Table-35

Construction Cost for
Capping Sand Filter With Anthracite

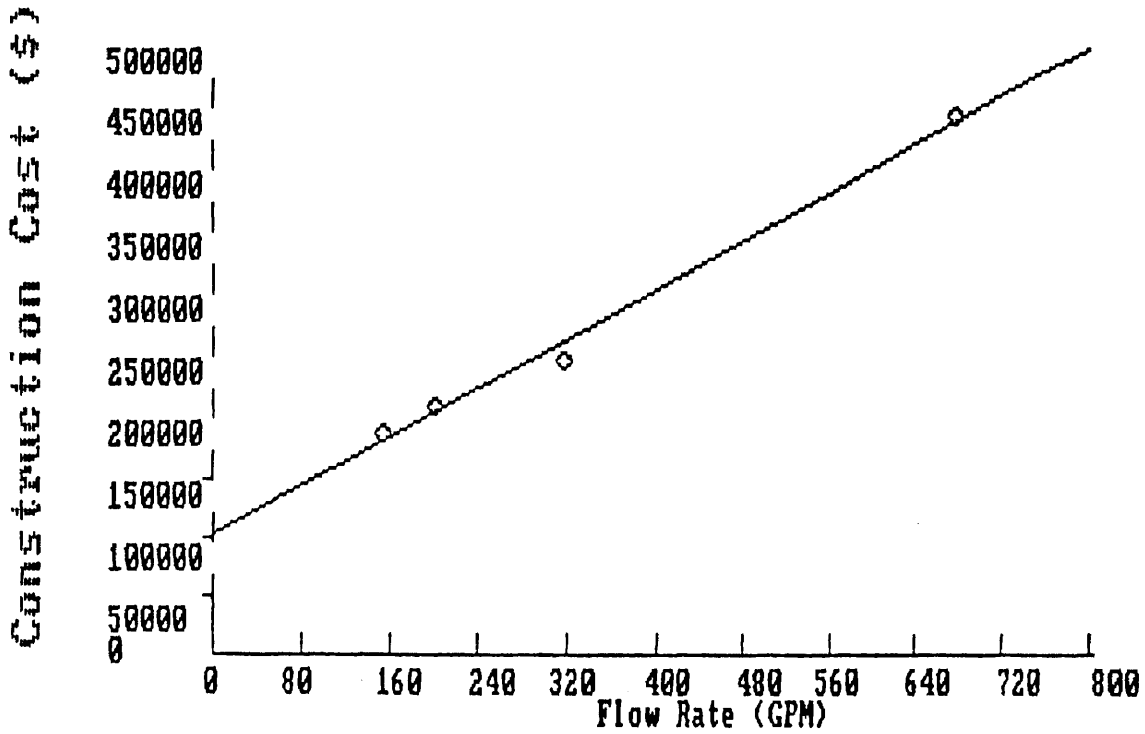
<u>Cost Category</u>	<u>Filter Area (sq.ft)</u>				
	<u>100</u>	<u>150</u>	<u>250</u>	<u>350</u>	<u>1750</u>
Material	\$238	\$596	\$993	\$1,390	\$6,940
Labor	113	283	471	660	2,140
Subtotal	351	879	1,464	2,050	9,080
Miscellaneous & Contingency	53	132	220	310	1,360
Total	404	1,011	1,684	2,360	10,440

Mathematical Models

From the information given above, We can plot the wastewater flow rate in gallon per minute (GPM) as the abscissa, the construction costs in U.S. Dollars as the ordinate, and find the relationship between these two parameters. Now it is found that this relation model is nearly linear. The following charts are effective and easy for us to estimate the alternative treatment construction cost when sizing the waste water reuse plants of the petroleum refinery secondary effluents :

1. Figure-12 Construction cost for package gravity filter plants
2. Figure-13 Construction cost for pressure filter plants
3. Figure-14 Construction cost for pressure granular activated carbon contactors
4. Figure-15 Construction cost for multiple hearth granular activated carbon regeneration
5. Figure-16 Multiple furnace hearth area vs. weight of granular activated carbon
6. Figure-17 Construction cost for capping sand filter and anthracite

Figure-12 Construction Cost Package Gravity Filter Plants



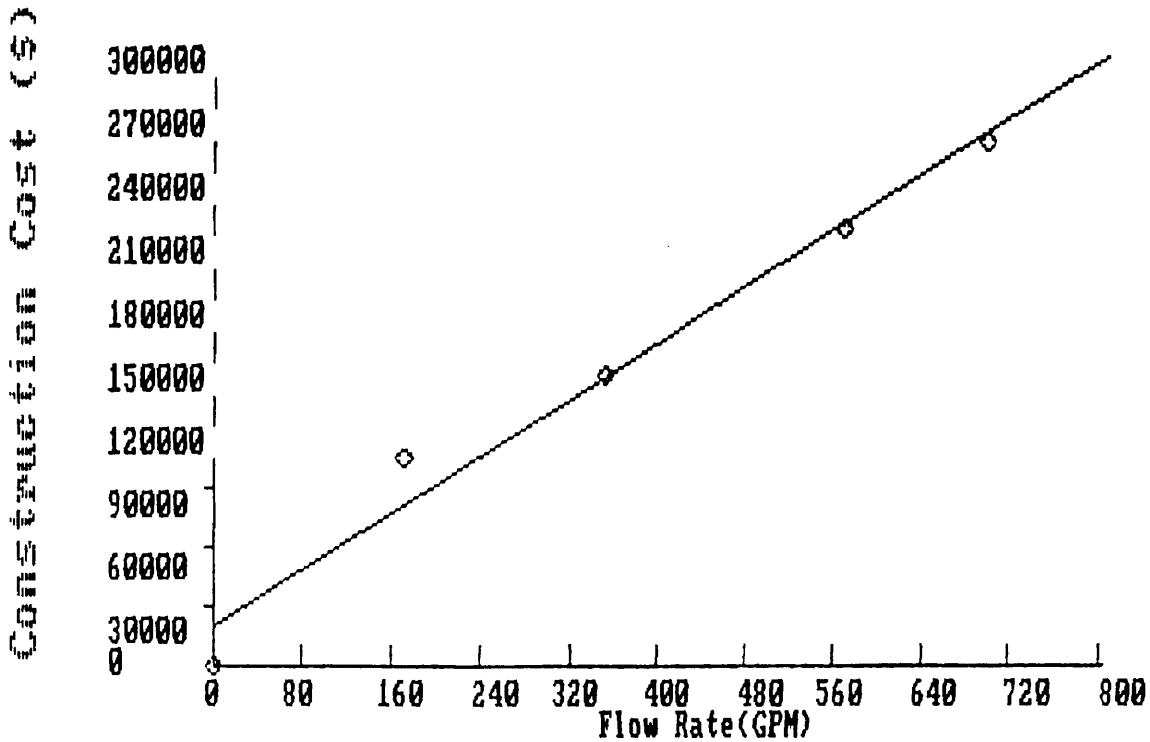
Construction Cost Package Gravity Filter Plants

POINT	X	Y
1	152	189850
2	200	214280
3	316	254750
4	678	463450

Slope = 523.0492 +/- 30.00266
 Intercept = 104576.5 +/- 12360.04
 Correlation = .9967258
 Calculated on points 1 TO 4

Equation :
 $Y = 523.05 X + 104576.5$

Figure-13 Construction Cost for Pressure Filter Plants



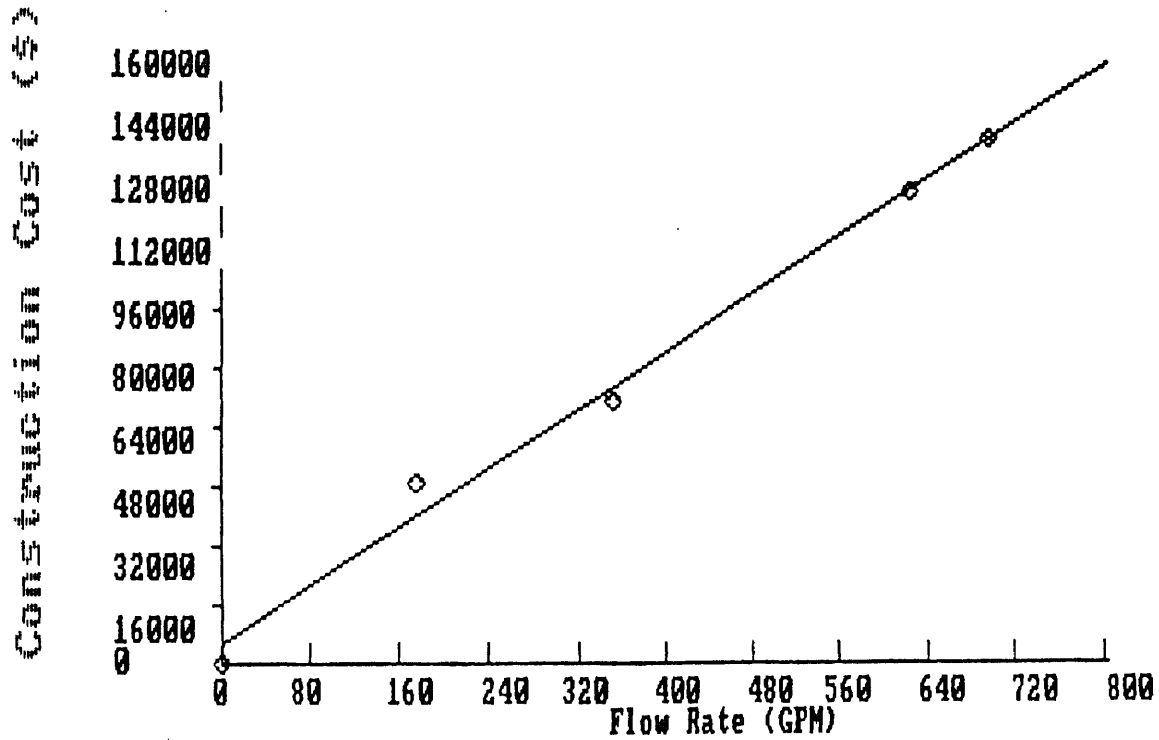
Construction Cost for Pressure Filter Plants

POINT	X	Y
1	0	0
2	170	106660
3	350	147730
4	565	221612
5	694	266624

Slope = 362.8619 +/- 33.28428
 Intercept = 19418.94 +/- 18807.62
 Correlation = .9876132
 Calculated on points 1 TO 5

Equation :
 $Y = 362.9 X + 19418.94$

Figure-14 Construction Cost for Pressure GAC Contactors



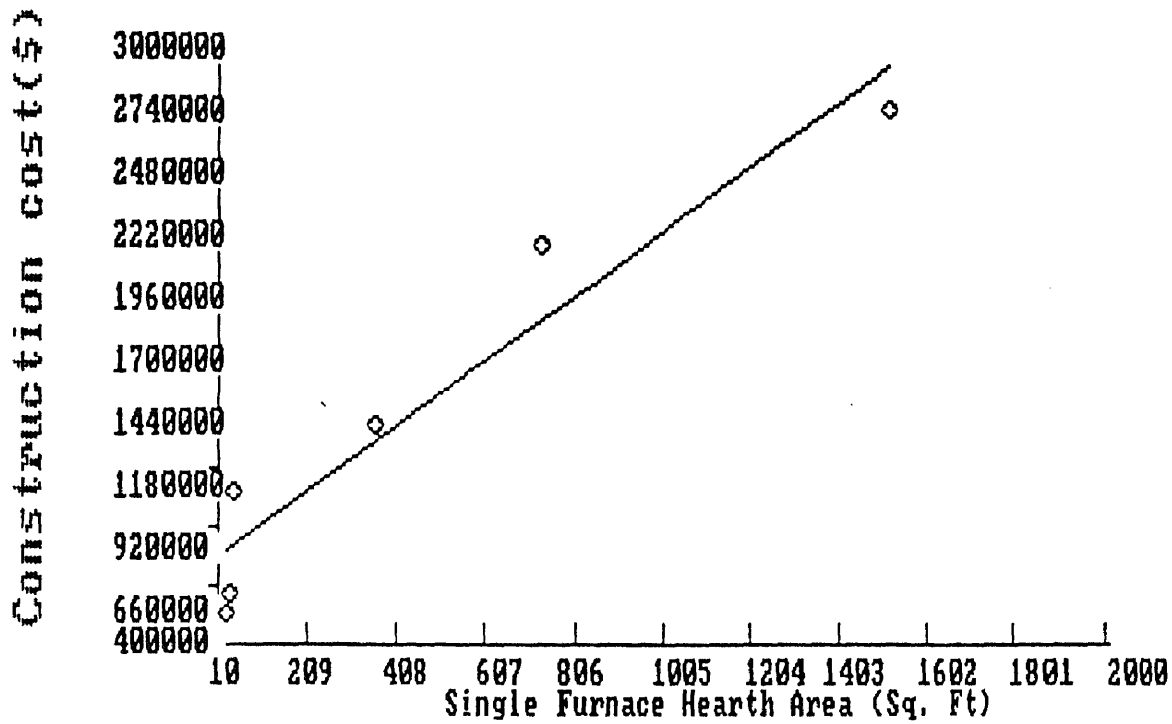
Constructio Cost for Pressure GAC Contactors

POINT	X	Y
1	0	0
2	175	48940
3	350	71740
4	622	129390
5	694	143510

Slope = 200.2214 +/- 10.58668
 Intercept = 4994.5 +/- 6207.341
 Correlation = .9958326
 Calculated on points 1 TO 5

Equation :
 $Y = 200.22 X + 4994.5$

Figure-15 Construction Cost Multiple Hearth GC Regeneration



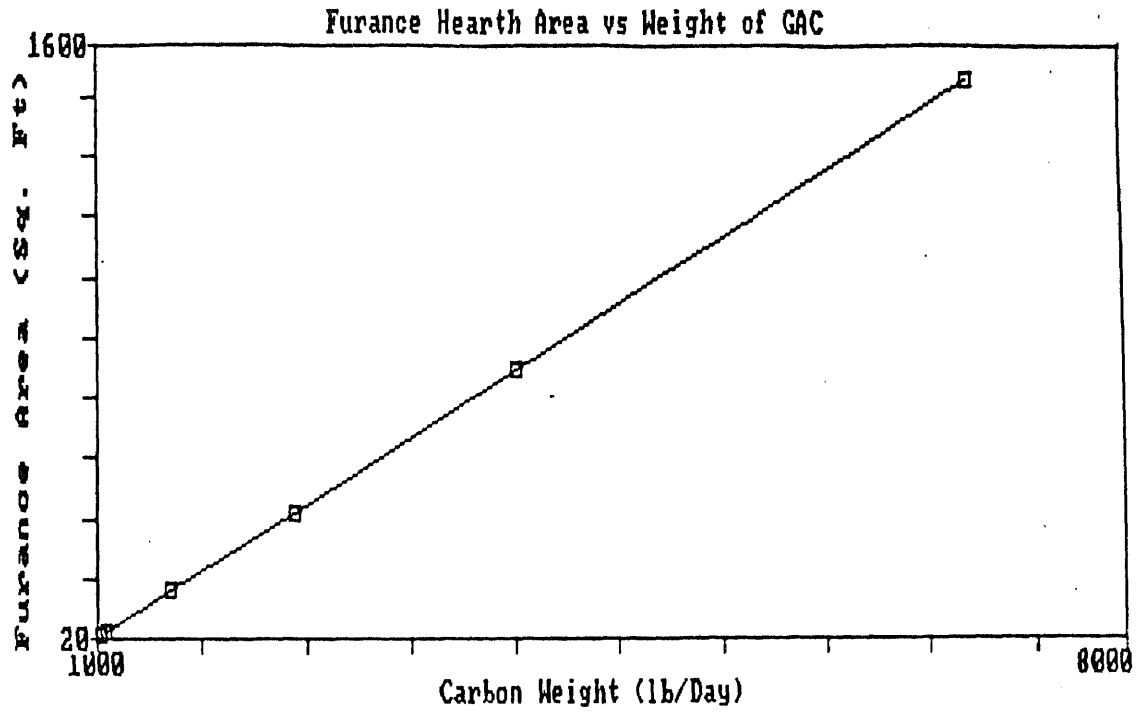
Construction Cost Multiple Hearth GC Regeneration

POINT	X	Y
1	27	534370
2	37	631720
3	47	1074110
4	359	1371670
5	732	2163020
6	1509	2782230

Slope = 1450.196 +/- 214.0619
 Intercept = 770939.6 +/- 280835.3
 Correlation = .9590791
 Calculated on points 1 TO 6

Equation :
 $Y = 1450.196 X + 770939.6$

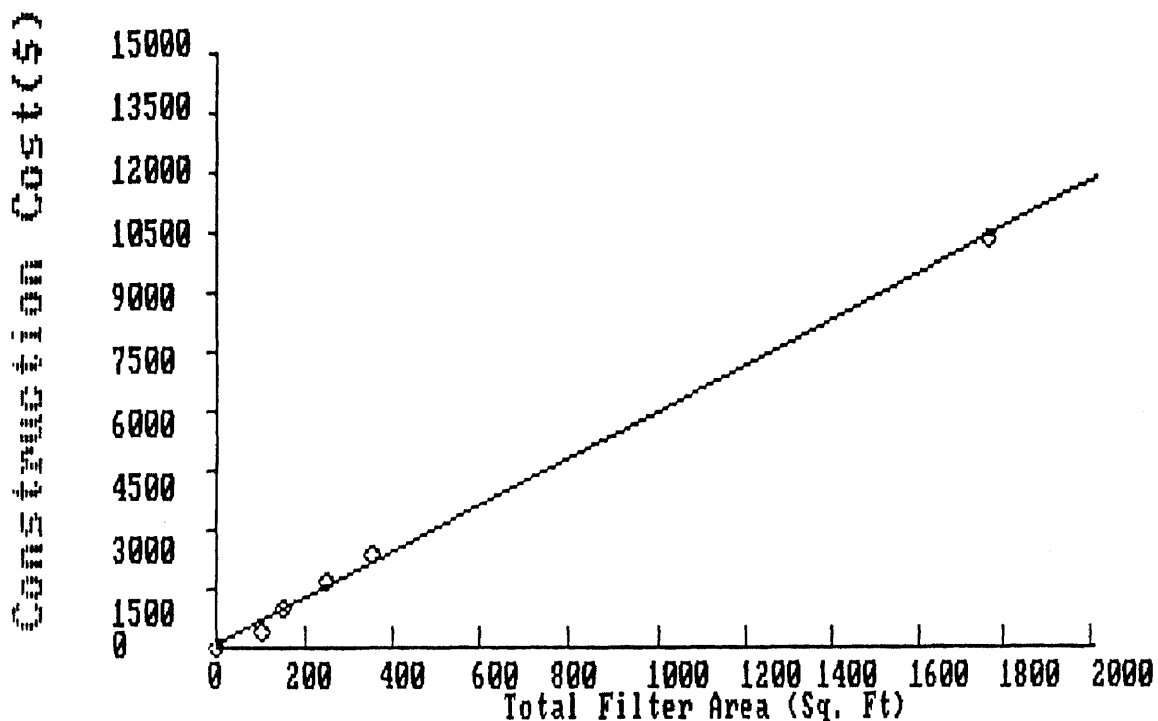
Figure-16



POINT	X [*]	Y
1	1215	27
2	1665	37
3	6615	147
4	16155	359
5	32940	732
6	67905	1509

* Carbon weight use a hearth carbon loading of 40 to 50 lb/sq.ft. per day

Figure-17 Construction Cost Capping Sand Filter & Anthracite



Construction Cost Capping Sand Filter & Anthracite

POINT	X	Y
1	100	404
2	150	1011
3	250	1684
4	350	2360
5	1750	10440

Slope = 5.934425 +/- .1496977
 Intercept = 93.89922 +/- 207.8589
 Correlation = .9990468
 Calculated on points 1 TO 5

Equation :
 $Y = 5.934 X + 93.899$

Summary and Conclusions

The advanced wastewater treatment processes can be used to improve the secondary effluent water quality for wastewater reuse through additional processes in the treatment sequence.

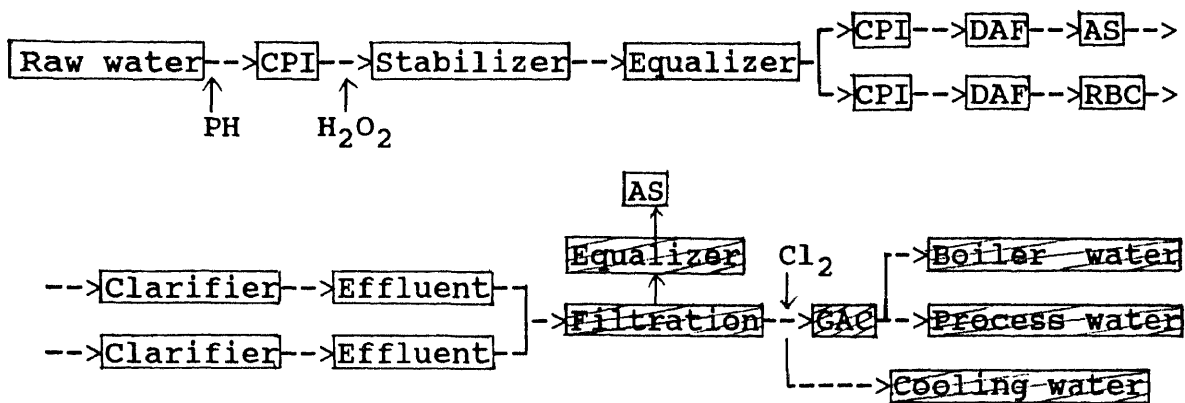
Two major concerns in treating refinery secondary effluent for reuse are the removal of organics and suspended solids. Reduction in organic matters, normally expressed by BOD, COD, or TOC, and suspended solids is required. Biological treatment followed by coagulation, filtration, and activated carbon adsorption is the typical scheme used to treat industry wastewaters for reuse when high quality water is required. But the activated carbon adsorption process can be expensive and require large amounts of energy if frequent regeneration cycles are necessary.

When wastewater reuse is concerned, the following major factors will influence unit process selection :

1. Influent wastewater characteristics
2. The effluent quality required
3. Sludge handling
4. Process compatibility and reliability
5. Cost

Since the cost of treatment increases with each additional process in the treatment sequence, the user should select the minimum water quality required for the reuse purpose and thus minimize the size of the treatment plant and the cost of the treatment.

Technically it is possible to reuse the effluent of wastewater treatment plant at Taoyuan Refinery. A typical process flow diagram of the Taoyuan wastewater treatment system is discussed as follows :



*AS : Activated Sludge

BFW : Boiler Feed Water

CPI : Corrugated Plates Interceptor

DAF : Dissolved Air Flotation

GAC : Granular Activated Carbon

RBC : Rotating Biological Contactor

□ : Existing

▨ : Proposed

Based upon the secondary effluent wastewater quality of the Taoyuan Refinery plant (70,000 to 100,000 Barrel Per Stream Day) in Taiwan, it is clear that only removal of suspended solids and organics by filtration method is adequate to produce the satisfactory water quality for cooling tower makeup water. As a result of the addition of granular activated carbon contactors to polish the filtration effluent water will produce the water quality

excellent for boiler feed water or process water supply.

Expected Wastewater Quality And Treatment Efficiency at TAOYUAN REFINERY Plant

<u>Parameter</u>	<u>Raw water</u>	<u>Secondary</u>	<u>Expected</u>		<u>Expected</u>	
	<u>(459GPM)</u>	<u>Effluent</u>	<u>Filtration</u>	<u>Performance</u>	<u>GAC</u>	<u>Performance</u>
	mg/l	mg/l	eff.%	conc. mg/l	eff.%	conc. mg/l
BOD5	80-105	35	60	14	95	0.7
COD	170-335	20-100	50	10-50	90	1-5
TSS*	132-200	20-70	85	3-10	75	0.75-2.5
O & G*	23-100	2-6	80	0.4-1.2	85	0.06-0.18
Phenol	1.3-1.4	0.8	15	0.68	95	0.03
PH	6-8	6-8				

* TSS : Total Suspended Solids. O & G : Oil and Grease

The high costs of the GAC process is the deterrents to the wide spread application. It is possible that the cooling tower makeup water can be obtained by using only filtration of the secondary effluent wastewater. However, as wastewater discharge limitations become increasingly restrictive, more sophisticated treatment process will be required. Under such conditions, GAC process maybe economical competitive.

The potential for large scale direct potable reuse of any wastewaters in the future is low due to undefined potentially adverse health effects resulting from long term exposure to low concentration trace materials. Non-potable reuse of industrial wastewaters has an average potential in areas with costly or limited water supplies.

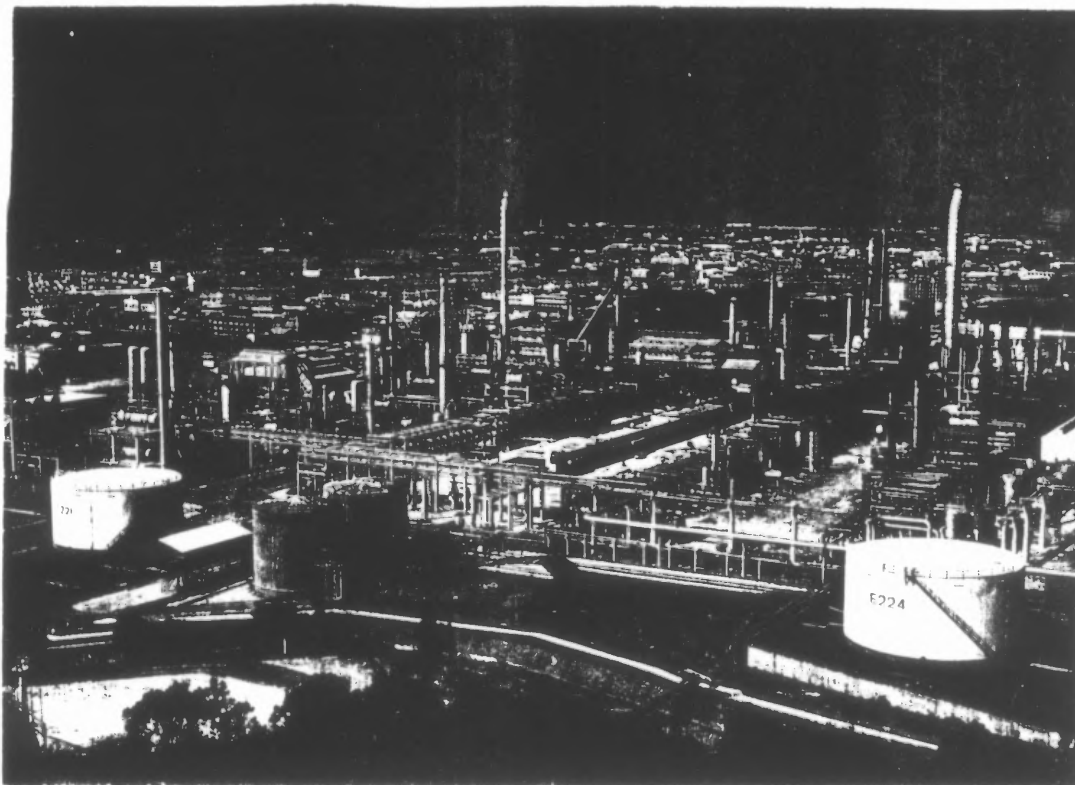
Non-potable reuse would be accomplished via the dual distribution systems for the other application such as landscape irrigation, gulf course irrigation, road construction, and home toilet flushing.

References

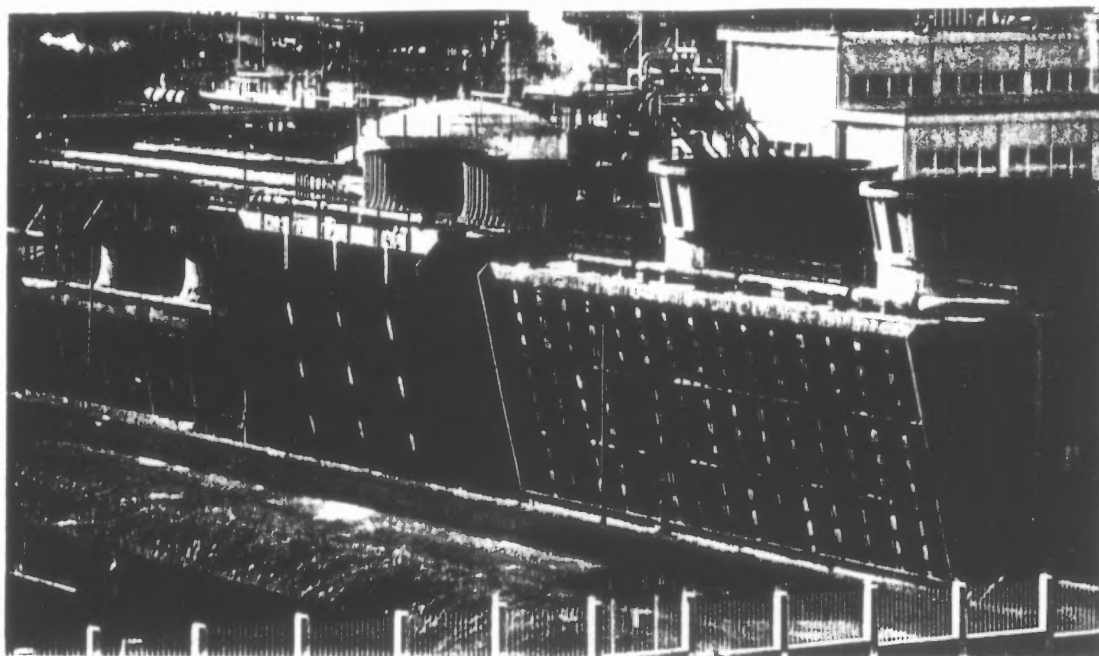
1. Lawrence K. Cecil, Complete Water Reuse, National Conference on Complete Water Reuse, April 23-27, 1973
2. Warren Viessman Jr. & Mark J. Hammer, Water Supply and Pollution Control, 4th edition, Harper & Row Publishers, New York, 1985
3. Committee for Air and Water Conservation API, 1960 Domestic Refinery Effluent Profile, Sept. 1968
4. Committee on Disposal of Refining Wastes, Div. of Refining API, Petroleum Industry Refinery Water Reuse Survey, Aug. 1968
5. EPA, Washington DC, Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Petroleum Refining, EPA-440/1-74-014a April, 1974
6. M. Anis Ai-Layla & Shamin Ahmad & E. Joe Middlebrooks, Water Supply Engineering Design, Ann Arbor Science Publish Inc. 1977
7. Petroleum Refinery Industry, Effluent Limitation Guidance for the Reuse Act Permit Program, 1972
8. Hillel I. Shoval, Water Renovation and Reuse, Academic Press. Inc. 1977
9. W.S. Holden, Water Treatment and Examination, Williams and Wilkins Company, 1970
10. Report of the National Technical Advisory Committee to the secretary of Interior, Water Quality Criteria, 1968
11. EPA, Washington DC, Estimating Water Treatment Costs, Volume 1,2,3, EPA-600/2-79-162 a,b,c, Aug. 1979
12. American Water Works Association, Future of Water Reuse Proceedings, Volume 1,2,3, Aug. 26-31, 1984, San Diego, Ca
13. American Water Works Association, Future of Water Reuse Proceedings, Volume 1,2,3, Aug. 23-28, 1981, Washington DC
14. National Conference on Complete Water Reuse, 2nd. Water's Interface with Energy, Air and Solids, Chicago, 1975

15. Proceedings of the International Symposium organized by the Institute of Civil Engineers, Reuse of Sewage Effluent, Oct. 30-31, 1984, Thomas Telford, London
16. Roger E. Kasperson and Jeanne X. Kasperson, Water reuse and the Cities, University Press of New England Hanover, New Hampshire, 1977
17. Proceedings of the 1983, 1984, 1985, 1986 Specially Conference, Environmental Engineering, American Society of Civil Engineers, New York
18. Mark J. Hammer, Water and Wastewater Technology, 2nd edition, John Wiley And Son, 1986
19. Harold E. Babbitt and James J. Doland and John L. Cleasby, Water Supply Engineering, Sixth edition, McGraw-Hill Book Co. 1971
20. Water Pollution Control Federation Journal, Granular Media Filtration of Secondary Effluent, 50, Volume 2, 9 1978
21. Water Pollution Control Federation Journal, Filtration Techniques in Tertiary Treatment, Volume 42, April 1970
22. API Proceedings, API Refinery Effluent Survey Summary and Analysis, Volume 48, 1968

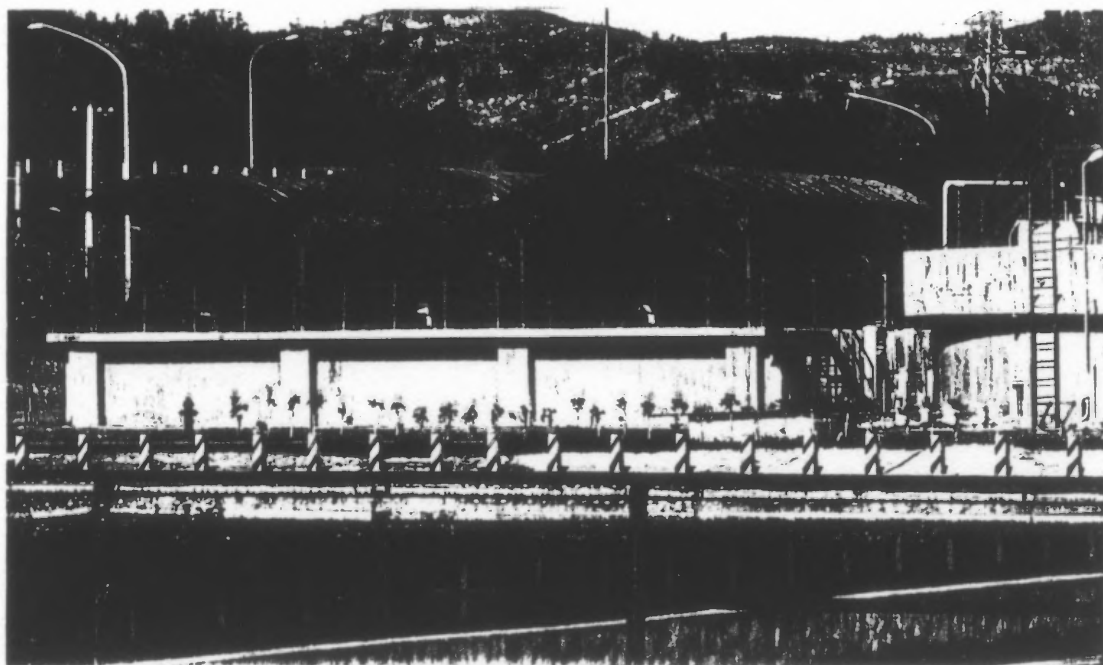
Appendix A. Picture of TAOYUAN REFINERY of Chinese Petroleum Co. TAIWAN, R.O.C



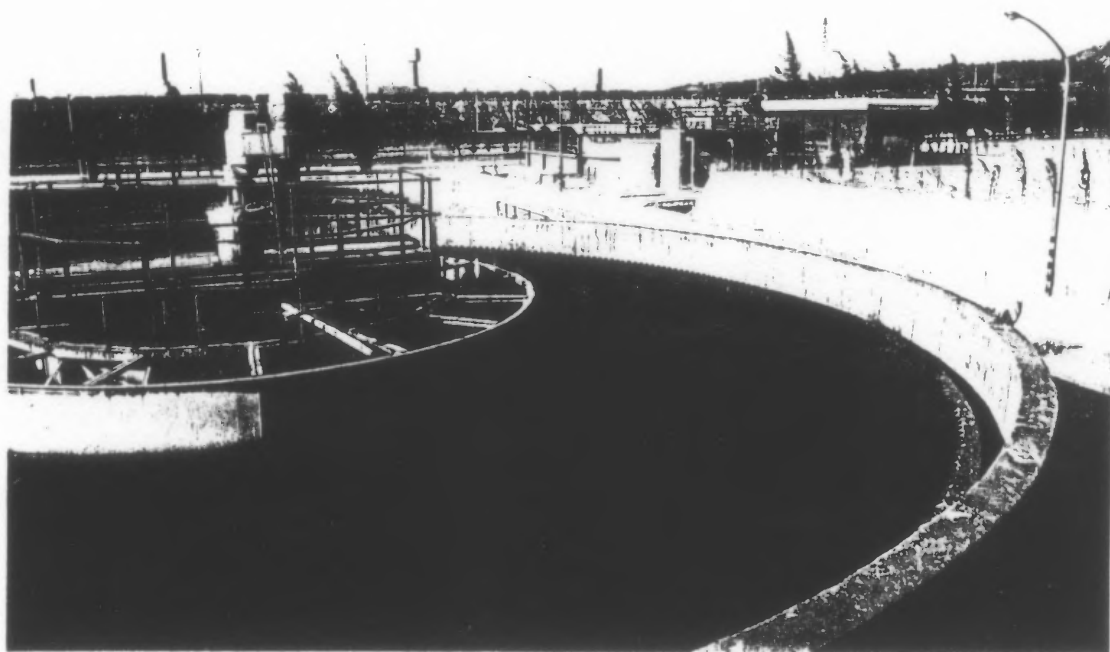
Appendix B. Picture Of Cooling Tower at TAOYUAN REFINERY Plant



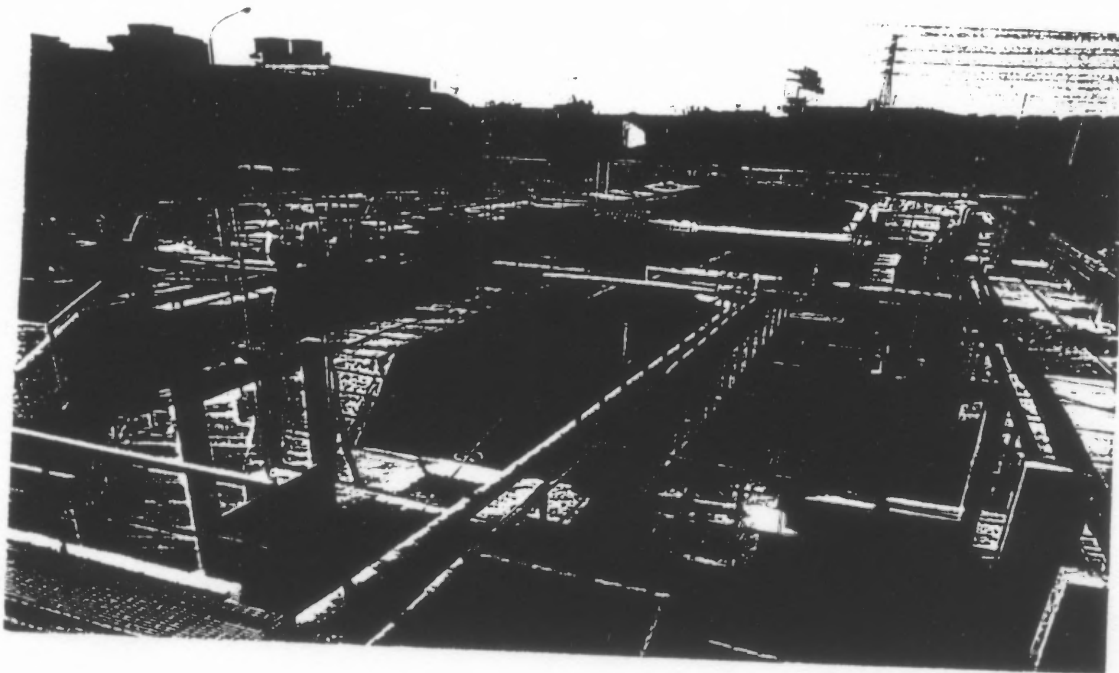
Appendix C. Picture of Rotating Biological Contactor
at TAOYUAN REFINERY Plant



Appendix D. Picture of Activated Sludge Tank
at TAOYUAN REFINERY Plant



Appendix E. Picture of Corrugated Plates Interceptor
at TAOYUAN REFINERY plant



Appendix F. Picture of Stabilizer at TAOUYAN REFINERY
plant

