MANAGEMENT OF TANK WASHINGS
IN MARINE AND COASTAL COMMERCE

by

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PREFACE

The original scope for this study outlined a broad area of "tank washings" to include tankers as well as barges. However, after the study was underway, it was determined that tanker operators generally followed the load-on-top policies of the companies or in some cases washed tanks at sea. On occasions when the compartments of tankers are washed, the wash water is usually routed to company-owned waste treatment facilities. In a similar manner barges washed by company-owned shipyards usually dispose of the wash water in company treatment plants. Therefore, because washwater from company manufacturing units was already being disposed of properly, in most cases, and because the amount of water generated from this activity was relatively small when compared to the total plant effluents, the emphasis for this study was directed towards the management of tank washings from commercial barge-cleaning companies.

ABSTRACT

A one-year project sponsored by the National Sea Grant College program was directed towards developing a management plan for treating and disposing of tank-cleaning wastes from barge-cleaning facilities. The study was limited to shipyards along the Texas Gulf Coast and was accomplished through a combined field survey program and laboratory effort. The majority of the background information was obtained from companies engaged in tank-cleaning, companies treating the wastewater and personnel involved in regulating tank-cleaning activities.

Presently the ten commercial companies who engage heavily in barge-cleaning activities in Texas generate between 75 and 100 million gallons of wastewater per year. Although the quantity of wastewater is relatively small compared to many other industries in the State, it is significant because of the poor quality of the wastewater and location of the cleaning companies along the major waterways of the Gulf Coast. Pollution potential from this type of wastewater is high due to oil, dissolved organic material, and extreme variations of pH.

Wastewater characteristics and present treatment methods are discussed from the results of the field and laboratory effort. A proposed system is presented designed to adequately treat the wastewater and enhance the water quality of the Texas Gulf Coast.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES (cont.)

LIST OF FIGURES

LIST OF FIGURES (cont.)

I. INTRODUCTION

Barge traffic in the United States is limited to less than 26,000 miles of inland and coastal waterways, or approximately two percent of the miles in our total national transportation system of airways, highways, waterways, pipelines and railroads. Yet, approximately 16 percent of the total weight of all goods is transported by barges illustrating the importance of barge traffic to the nation's commerce. Navigable waterways of the United States are shown in Figure 1 with 28 waterways comprising the barge transportation system (1).

Along the Texas Gulf Coast, there are approximately 450 miles of waterway (1.5% of the total) consisting primarily of intracoastal canals with a minimum depth of 12 feet (1). The Texas Gulf Coast waterways are heavily travelled by barges because this state is one of the nation's leading areas for the manufacture of petroleum products. Barges help in transporting crude oil to the refineries, move intermediate products between companies, and the eventual shipping of final products to the customers. Bulk transfer by barge is certainly not the principal transportation method but it is one of the more important methods of providing short distance delivery to many different locations that could not be economically served by pipeline or tankers.

A very important aspect of barge transportation is the cleaning and repairing of vessels. Associated with the cleaning step is the generation of highly contaminated washwater due to the residue products on the bulkheads and decks of the tanks. Therefore there is a need for adequate treatment of the wastewater prior to its being discharged to Texas waters.

The purpose of this study was to investigate the present techniques of barge washing and recommend methods for the proper disposal of the wastewater. In developing the study, the following objectives were reached:

1. to locate Texas barge-cleaning facilities,
2. investigate present washing techniques used for various types of cargoes,
3. determine quantity and quality of wastewater generated,
4. determine present wastewater treatment methods, and
5. present a proposed system capable of treating the wastewater from barge-cleaning operations.

The basic information and data for this study were collected through an intensive survey and field research effort with numerous site visits to ten barge-cleaning companies in Texas. Valuable information was also obtained from the Texas Water Quality Board, the U. S. Coast Guard, the Texas Shipyard Association and other organizations and individuals.

Figure 1: The 28 Navigable Waterways of the United States that Comprise the Barge Transportation System

II. BARGE-CLEANING FUNDAMENTALS

The map shown in Figure 2 presents the location of the ten commercial barge-cleaning companies along the Texas Gulf Coast. Most of the companies are located near the large petrochemical complexes in the Port Arthur-Beaumont-Orange area and in the Houston-Galveston-Texas City area. Three other companies are located near the lower coast in Galveston, Freeport, and Corpus Christi. In addition to the ten commercial companies there are also refineries and petrochemical plants that clean company-owned barges. However, the ten independent companies form the backbone of the barge-cleaning industry along the Texas Gulf Coast and are the firms that clean the crude and asphalt barges in addition to the so-called "clean" barges carrying products such as benzene.

Barge Cargoes Along the Texas Gulf Coast

The major products carried in barges that are frequently cleaned at Texas shipyards are summarized in Table 1. Seven of the products are either intermediates or first generation products even though they also may be sold as final products. The data are from records obtained from the commercial barge-cleaning companies for 831 barges from 1972 through 1973 (2). The records show that crude and diesel barges were cleaned in greater numbers than other product barges.

Purpose of Cleaning Barges

Although there are several reasons for cleaning barges, the most prevalent one is to prevent contamination of products from one cargo-loading to the next. For instance, a barge that previously carried diesel will need to be cleaned before it could transport alcohol. A diesel barge must be cleaned if it is to carry kerosene or gasoline. The barge owner normally attempts to restrict the types of products a barge will carry to minimize the number of times it is cleaned and thus reduce costs.

A second reason for cleaning barges is to comply with the U. S. Coast Guard certification program. If an internal inspection is necessary, the barge must be cleaned and be free of hazardous gases before it can be certified. The inspection is usually scheduled while the vessel is in for routine cleaning or repair.

A third purpose for cleaning a barge is to provide a safe environment before "hot work" (welding or cutting) is performed. To be considered safe the tank must be rendered non-explosive and non-flammable by removing flammable gases by a process called "gas-freeing". After the gas-freeing

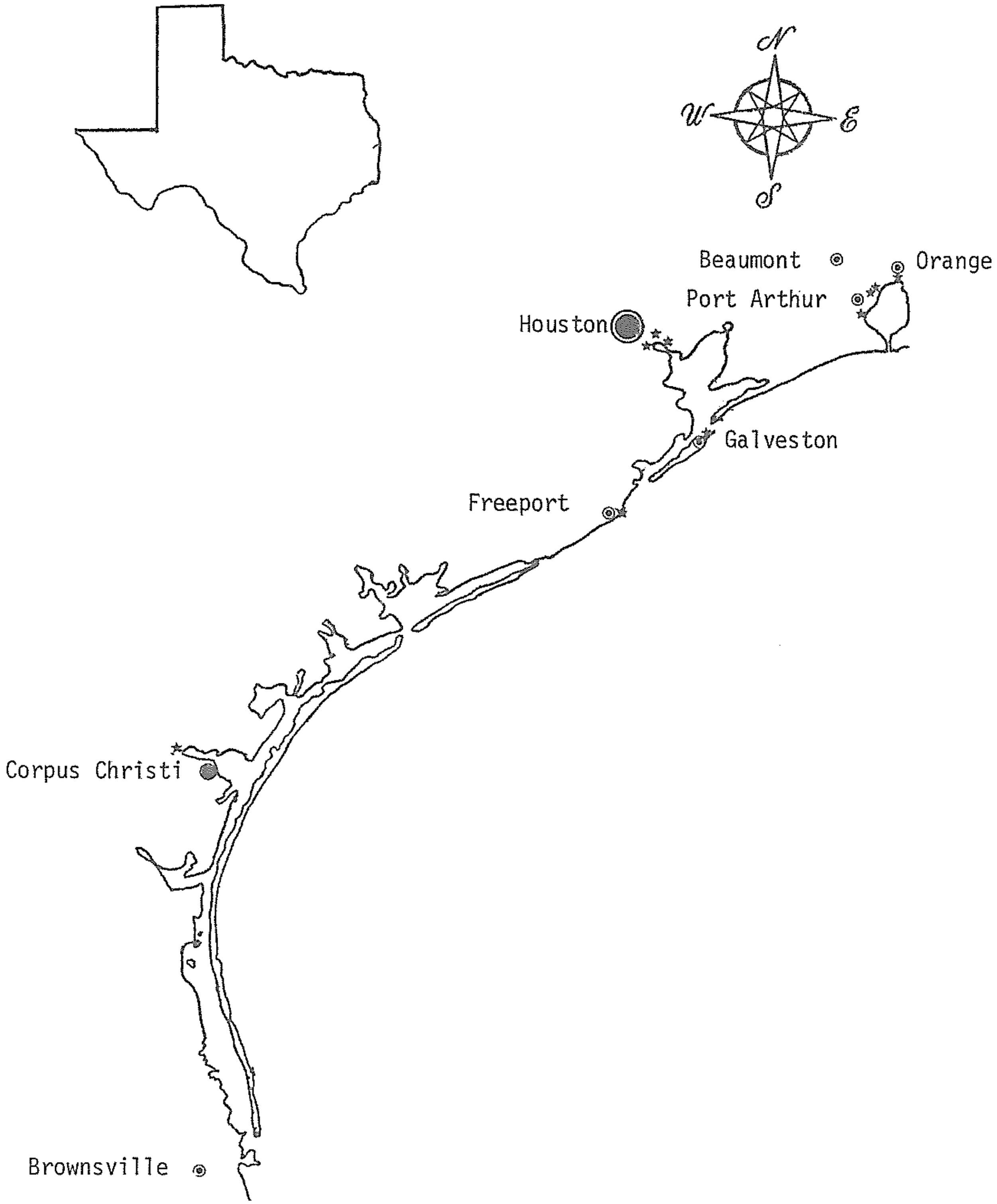

Figure 2: Location Map of the 10 Commercial Barge Cleaning Companies Along the Texas Gulf Coast

Table 1. Major Chemicals Transported by Barges Along the Texas Gulf Coast(2) Based on a Sample of 831 Barges

Chemical	Barges No.	Barges %	Refinery Step
Diesel	94	10.7	First generation, final product
Crude Oil	93	10.6	Raw material
Alcohol ($<C_5$)	64	7.7	Final product
Gasoline	45	5.1	First generation, final product
Butane (g)	39	4.4	Intermediate
Lube Oil	38	4.3	First generation
#6 Oil	33	3.7	First generation, final product
Styrene	26	2.9	Intermediate
Coke	21	2.4	Raw material
Asphalt	21	2.4	First generation, final product
126 Other Products	357	45.8	Mostly final products
Total	831	100.0	

operation, the compartments in the barge are inspected and certified safe by a registered marine chemist.

Role of the Marine Chemist at the Barge-Cleaning Facility

It is the responsibility of the marine chemist to decide whether a vessel is safe for men and safe from fire. Because lives and property are at stake the position is obviously important and the qualification requirements must be rigorously enforced. Certification of marine chemists began in 1922 by the American Bureau of Shipping. In 1962, the National Fire Protection Association (NFPA) accepted the responsibility. The NFPA serves as liaison between marine chemists, industry, and government, and acts as a clearinghouse for marine fire prevention and protection information.

A certified marine chemist must meet the following qualifications established by the NFPA (3):

1. Be 25 years of age and physically able to perform the duties of a marine chemist;
2. Be a citizen of the United States;
3. Possess an adequate education in chemistry and a thorough knowledge of the standards for the control of gas hazards on vessels to be repaired;
4. Have completed at least three years experience in chemistry or chemical engineering work subsequent to the completion of the education requirements;
5. Have completed at least six months (including not less than 300 hours actual experience under proper supervision) in shipboard work involving the testing and inspection of tank and other vessels in the application of the standards for the control of gas hazards on vessels to be repaired.

Specifically, the marine chemist enters tank vessels and with proper instruments and by visual inspection determines if the vessel is in a safe condition for men to enter and make repairs.

When the marine chemist has found a vessel to be safe, a written certificate is issued stating the condition of the vessel and listing special instructions and recommendations if necessary.

The marine chemist also acts as an advisor to the companies engaged in cleaning vessels. He deals with such problems as cleaning techniques for various cargoes, separating oil and water, treating wastewater, and proper use of safety equipment. The role of the marine chemist in barge cleaning is a vital and expanding one. Presently, there are approximately 350 certified members of the Marine Chemists' Society (2). Some are employed directly by the larger shipyards because of the number of vessels which must be cleaned and inspected. The majority, however, are in private practice, usually on call 24 hours a day.

Role of Enforcement Agencies

There are a number of governmental agencies which have legal responsibilities for barge-cleaning including the U. S. Coast Guard, the Texas Water Quality Board, the Environmental Protection Agency (EPA), and the Texas Air Control Board. Local county and city agencies may also be involved in enforcement.

The Coast Guard is charged with inspection and certification of vessel repairs. Certificates of inspection are normally issued for each barge for a two-year period. An additional inspection though not as stringent, must take place between the tenth and fourteenth month of the two-year period. The Coast Guard also has the responsibility for administering and enforcing the oil pollution laws for navigable waterways. This responsibility is divided into two groups dealing with pollution control. One group works as an oil spill prevention force charged with certifying construction plans and repairs for barges and tankers performed through the Marine Inspection Office. The second group is headed by the Captain of the Port and is responsible for investigating oil spills and performing oil spill cleanup operations (4).

The Texas Water Quality Board has authority over pollution control laws affecting navigable streams and waterways within the state. They require that any discharge of wastewater into any body of water be regulated by a waste control order that states under what conditions discharges can be made, and the limits on quantity and quality. Compliance with the order is mandatory. Any deviations from the order with respect to quality or quantity of discharge may result in fines levied against the company by the Attorney General of the State of Texas or local legal entities. An example of a waste control order for a barge-cleaning firm is shown in Table 2.

Frequently, local county and municipal organizations tend to assume the responsibility of a prosecutor when a violation occurs. The counties benefit from lawsuits they initiate by receiving one-half of any fine collected. Local regulations may at times be more stringent than state or federal standards.

The EPA also has jurisdiction for water pollution in Texas. However, because Texas is relatively more advanced than similar organizations in many other states the EPA has not occupied as great a role in water pollution control in Texas. The trend is for the Texas Water Quality Board to assume a greater share of the EPA role by combining the EPA permit with the Texas waste control order.

In addition to water pollution regulatory agencies, the Texas Air Control Board is also concerned with violations of their regulations. Probably the most frequent violation involves odor complaints from ponds or open tanks where volatile organics diffuse to surrounding areas.

Table 2. A Typical Waste Control Order Issued by the Texas Water Quality Board to a Barge-Cleaning Company[5]

Parameter	Monthly Average	24-Hour Composite (ppm)	Individual Sample
pH	6.2-8.0	6.0-8.5	6.9
Total Residue	12,000	15,000	18,000
TSS	20	25	30
VSS	15	20	25
Settleable Matter	5	7	10
BOD	20	25	30
COD	200	300	400
Oil & Grease	5	10	15
Color	40	60	80
Temperature	Ambient	Ambient	Ambient
Free Floating Oil	None	None	None

Barge-Washing Procedures

The first procedure in cleaning barges is for the resident marine chemist or gas-freeing foreman to determine the previous cargo type and what course of action to follow to render the tank hazard-free. Usually the first step in cleaning is to remove any liquid left in the compartments by pumping through the cargo lines or through a large vacuum hose placed into the tanks. Frequently, the barge may require ballasting fore or aft to gravitate the remaining cargo into one area for removal. The cargo pumped from the vessel goes to a vacuum tank. If the residual cargo was of high fuel value capable of being burned in the plant boiler, it could be stored and used as needed.

Properties to consider when salvaging products from the barges are BTU value, potential for reclaim or reuse, and limits of the storage capacity of a plant. It is impossible for the smaller firms to maintain sizable storage facilities for keeping many different products separate. However, some residual products, such as gasoline and diesel, are almost always stored for use in the shipyard. In most cases, it is uneconomical to install an incinerator for the purpose of disposing of liquid wastes. Products that cannot be used in the shipyard are usually removed by commercial disposal firms.

After the free liquid is removed, the second step is to wash the tanks by one or more methods. Cold- or hot-water washes, handwashing with hoses, and hot or cold chemical washes with caustic or a degreaser to remove oil films may be used (see Figure 3a). For crude oil or heavy fuel oil barges the liquid is stripped and hot water is used to raise the temperature of the oil to facilitate pumping. This step may take 30 minutes or more per compartment depending upon the product and its ease of removal. Throughout the washing process, vacuum pumps are constantly removing liquid from the tanks.

One time-consuming problem is how to handle material that is too heavy to vacuum from the barge. When this situation occurs, workmen must go into the tanks and shovel the material into a bucket which is pulled through the hatches. Depending on the material, this may take hours or even days. Such action may have to be taken with crude oil, creosote, coal tar, asphalt and heavy lubrication oils or greases. It is quite helpful for the barges carrying these types of materials to be equipped with heating coils to reduce the viscosity of the material. More detailed washing steps and procedures are given in Table 3 with supplemental data and explanations given in Table 4 and 5.

Once the vessel has been washed sufficiently, all that remains is to ventilate the tanks to achieve dryness and gas-free conditions. Ventilation is usually carried out by utilizing one of several types of blowers (see Figure 3b).

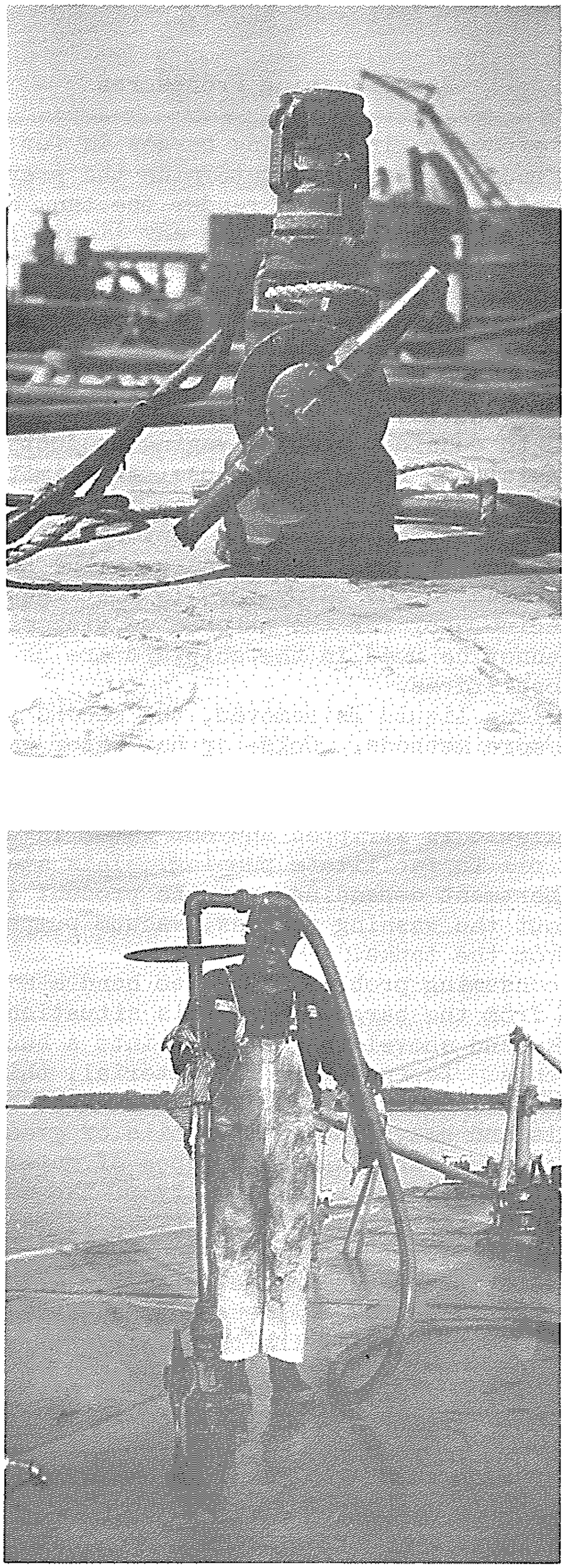

Figure 3a: Barge Washing Equipment - Butterworth Sprayers

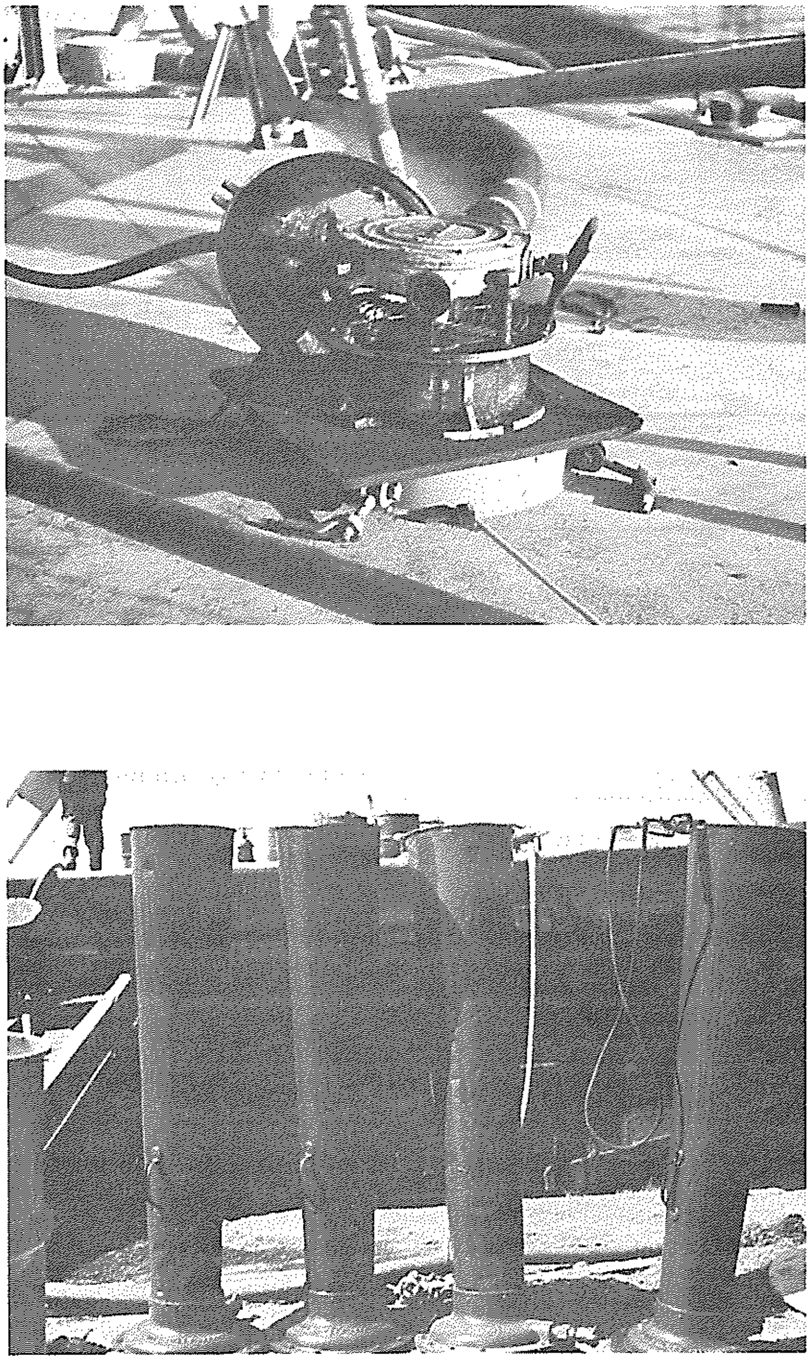

Figure 3b: Barge Ventilation Equipment - Air Eductors

Table 3. Explanation of Steps Involved in Washing a Tank Vessel Prior to Repair

Step No.	Wash Steps	Explanation
1	Strip	Remove excess cargo residue via cargo lines and/or vacuum line
2	Ventilate	Blow fresh air into tanks
3	Cold hand-wash	Wash tanks with water under high pressure using hand-held hose
4	Hand chemical wash	Wash tanks using degreaser, emulsifier, or caustic solution
5	Hot-water wash	Wash tanks using butterworth-type machine
6	Cold-water wash	(Same as #5)
7	Squeegee tanks	Clean residue from tanks using squeegee
8	Hot chemical wash	Wash tanks with butterworth-type machines using caustic or other solution
9	Muck	Bucket out residue that cannot be removed by vacuum
10	Gas-free	Remove all hazardous gases from tanks, i.e. "safe for man, safe for fire"
11	Solvent	Use solvent, such as diesel to dilute cargo

Table 4. Sequences of Washing Steps for Cleaning Various Types of Cargoes

Washing Procedures[1]

I

1. Strip
2. Cold-water wash
3. Strip
4. Hot-water wash
5. Strip
6. Ventilate
7. Gas-free

II

1. Strip
2. Hot-water wash
3. Strip
4. Ventilate
5. Gas-free

III

1. Flare cargo to atmosphere to 0 psi
2. Purge tank with nitrogen to 5 psi
3. Flare tank to 0% oxygen content
4. Repeat #3 above
5. Repeat #4 above
6. Ventilate to 0 explosiveness

IV

1. Strip
2. Cold-water wash
3. Strip
4. Ventilate
5. Gas-free

V

1. Use solvent
2. Strip
3. Hot-water wash
4. Strip
5. Ventilate
6. Gas-free

VI

1. Strip
2. Hot-water wash
3. Strip
4. Muck
5. Squeegee
6. Hot-water wash
7. Strip
8. Ventilate
9. Gas-free

VII

1. Strip
2. Cold-water wash
3. Strip
4. Hot chemical wash
5. Strip
6. Hot-water wash
7. Strip
8. Muck
9. Procedure II above

VIII

1. Cold-water wash
2. Strip
3. Chip solid material from area to be repaired
4. Bucket or wash out residue

---

[1] For explanation of each individual step refer to Table 3.

Table 5. Chemical Residues Commonly Found in Barges Prior to Cleaning; their Relative Solubility in Water and Washing Procedure for the Barge

Chemical[1]	Solubility[2]	Washing Procedure[3]
Acetic acid	∞	I
Acetic Anhydride	v	I
Acetone	s	II
Acrylonitrile	v	I
Alcohol ($\leq C_5$)	v	II
Alcohol ($> C_5$)	∞	I
Aldehydes	v-∞	I
Anhydrous ammonia (g)	v	III
Asphalt	i	VI
Benzene	i	I
Bunker C	i	I
Butadiene (g)	v-∞	III
Butane (g)	v	III
Butyl Cellusolve	v	I
Butylene oxide (g)	d	III
Carbon tetrachloride	s-∞	IV
Caustic (NaOH)	v	II
Chlorine (g)	v	III
Chlorobenzene	i	II
Chloroform (Trichloromethane)	s	I
Coal tar	i	V-VI
Chlorinated HC (e.g. Endrine)	i	II
Creosote oil	i	VI
o-Cresol, m-, p-Cresol	i	II
Crude Oil	i	VI
Cumene	i	I
Diesel	i	II
Dioxane	v	I
Dicyclopentadiene	i	I
Dripolene[4]	i	I
Ethyl benzene	i	I
Ethylene (g)	i	III
Ethylene glycol	v	II
Ethyl hexanol	v	I
Fuel Oils	i	II
Gasoline	i	II
Hexyl acetate (Methyl acryl acetate)	i	I

Table 5 (cont.)

Chemical	Solubility	Washing Procedure
Hydrochloric acid	v	IV
Hydrogen sulfide	v	N.A.
Jet fuels	i	II
Kerosene	i	II
Methyl acrylate	s	I
Methyl acrylate	s	I
Methyl chloride (g)	v	III
Methyl ethyl ketone	s	I
Methyl isobutyl ketone	v	I
Methyl methacrylate	s	I
Mineral spirits	i	II
Naptha	i	II
Napthalene (s)	i	II
Nitrogen (g)	v	III
Paraffin	i	II
Phenol	v	I
Phorone	i	II
Propane (g)	i	III
Propylene (g)	v	III
Propylene glycol	v	I
Propylene oxide (g)	v	III
Propionic acid	v	I
Soybean oil	i	VII
Styrene	i	I
Sulfur (s)	i	VIII
Sulfuric acid	v	I
Sulfur dioxide (g)	s	III
Tallow	i	II
Tetraethyl glycol	v	I
Toluene	i	I
1,1,2- Trichloroethane	s	I
Trichloroethylene	i	II
Vinyl acetate	s	I
Vinyl chloride	s	I
o-, m-, p-Xylene	i	II

Footnotes - Table 5

[1] All substances are liquids unless otherwise noted as gas (g) or solid (s).

[2] Solubility in water (2, 13):

∞: infinitely soluble
v: very soluble (>25 grams/100 ml water)
s: slightly soluble (10-24 grams/100 ml water)
i: insoluble (<10 grams/100 ml water)
d: decomposes in water

[3] Source: company records; some steps may have to be repeated. For explanation of procedure see Table 7, 8.

[4] Dripolene is composed of 50% benzene, 30% toluene and 20% xylene.

III. WASTEWATER GENERATION AND TREATMENT

The barge-washing procedure usually results in a large volume of highly contaminated emulsified water which must be stored, separated, and eventually be discarded. Lighter petrochemicals are reasonably soluble in water and provide little potential for economical reclamation although fuel oils and other heavier petroleum products, not as soluble, have a greater potential for separation from the washwater.

More wastewater of poor quality results from the water seal at the vacuum pumps. This water is used to prevent the pumps from losing vacuum when not in operation or when suction is lost at the operating end of the hose.

Wastewater Quantity

The research plan was to visit each of the 10 Texas commercial barge-cleaning companies and obtain quantity and quality data on the washwater for an extended period of time. However, during the study, it became evident that the equipment for obtaining water quantity data was not available at the shipyards. For example, only one company had a flow-measuring device located on the intake side of the washwater pump. Water flow meters were borrowed from the city of Port Arthur and the Physical Plant of Texas A&M University to determine the total flow for the washing operation. A one-inch meter was installed in a hot water-line but after a short period of time the meter stopped working because the hot water warped the hard rubber impeller in the meter. The plant meter on the cold water line did not measure the total volume of water used because of the large quantity of hot water that bypassed the cold water system.

An alternative method for measuring water volume was to measure the differential depth of wastewater pumped to the storage tanks. Unfortunately, this could be accomplished at only two companies because the other firms did not have the facilities to gauge the tanks. A second misfortune was that one of the two companies chose not to participate in the study for fear the Texas Water Quality Board would receive the information. Fortunately, the other company was willing to cooperate. Data developed for the quantity of wastewater from the one participating firm for various cargos are summarized in Table 6. The 26 barges from which the data were obtained included 14 products and over 1.2 million gallons of wastewater. These data include only a small fraction of the many products carried by barges. More significantly, the data show a wide range of wastewater generated between cargo types and between different barges carrying the same cargo. In general, approximately 10,000 gallons of washwater are produced for the clean types of cargo such as diesel fuel and

Table 6. Volume of Wastewater Generated in Cleaning of Barges Containing Various Products

Product	No. of Barges	Wastewater Generated (gal. x 10^3)
Diesel	2	9.3-76.4
Gasoline	1	9.2
Olefins	1	12.5
Aromatics	1	10.3
Acetic acid	1	16.6
Crude oil	6	39.6-176.6
Methyl acrylate	1	10.6
Methyl metharylate	4	22.2-58.4
Xylene	3	20.1-159.9
Liquid N_2 fertilizer	2	1.6-37.0
Molasses	1	24.0
Creosote	1	116.2
Isopropanol	1	19.9
Mineral spirits	1	5.2

gasoline while up to 150,000 gallons of wastewater may be required for the dirty types of cargo such as creosote and crude oil. Miscellaneous chemicals can be expected to produce about 20,000 gallons per barge cleaned.

Wastewater Quality

To determine the quality of the wastewater generated in the washing step, samples were taken from five cooperating plants. All of the samples analyzed were obtained from storage tanks after initial oil separation. Samples were obtained at levels between the surface oil layer and bottom sludge. Analyses were conducted according to Standard Methods for the Examination of Water and Wastewater (6). Results of the analyses are presented in Tables 7 and 8. The results of the water sample analyses clearly indicate the waste is generally highly contaminated and quite variable in quality. This would be expected because of the number of products carried by the barges.

Table 7 compares the data from plants 1, 2 and 3 with the data from plants 4 and 5 in Table 8. The pH ranged in value from 5.0 to 11.3 for all five plants but was often near neutral. The COD values were similar to what can be expected for petrochemical wastewater varying from 400 to 91,200 mg/l. Oil and grease concentrations ranged from 1 to 7700 mg/l with values often above what is considered compatible with biological treatment. Conductivity values ranged from 700 to 31,500 as a result of the salt water slugs that would frequently be removed from the barges. A second reason for some of the high conductivity values was that the shipyard obtained its washwater from the brackish channel at the plant.

Existing Waste Treatment Systems at Commercial Barge-Cleaning Shipyards

Of the ten commercial companies actively cleaning barges only four have disposal systems that can be described as semi-permanent. This is not to say that the other companies are in direct violation of water pollution laws. Most of the other shipyards dispose of their wastewater by having it removed by third parties using vacuum trucks as shown in Figure 4.

Sub-surface or underground waste disposal is the method used by one company as shown in Figure 5. The well is owned and operated by a trucking firm that transports waste to the site. In its broadest interpretation, subsurface waste disposal is simply the storing of waste substances beneath the surface of the ground through injection wells; thus this method is not an actual disposal system. The injection area serves only as a semi-permanent storage area that is not expected to be needed in the future. Disposal wells are not looked upon with favor by the EPA and it is expected that this

Table 7

Wastewater Characteristics From Texas Barge-Cleaning Companies (1974)

Sample Location	Plant 1				Plant 2			Plant 3				Range of Values After Gravity Separation
	Vacuum Tank			Cleaner Tank	Tank @ 3'		Tank Bottom	Holding Pond			Runoff from Pond	
Date	2/21/74	3/11	3/21	2/21	2/21	3/11	2/21	2/21	3/11	3/21	3/21	
Temp. °F	72	65	Warm	70	71	79	70	72	85	-	-	
pH	5.0	7.4	6.6	12.2	6.0	7.5	5.8	10.4	9.5	11.1	10.5	5.0-11.1
COD mg/l	2396	804	1647	11606	524	400	674	6589	91200	19622	2078	400-91200
Total Carbon ppm	-	-	2300	-	-	-	-	-	-	30000	3800	
Oil & Grease mg/l	40	1	638	65016	76.9	31.3	59.2	49.6	-	545	220	1-638
Conductivity µmhos/cm	21000	9000	7500	25500	1200	2300	1200	8700	31500	17000	10500	1200-31500

Table 7 (cont.)

Wastewater Characteristics - 1

	Plant 1				Plant 2			Plant 3				Range of Values After Gravity Separation
	Vacuum Tank			Cleaner Tank	Tank @ 3'		Tank Bottom	Holding Pond			Runoff from Pond	
Total Solids mg/l	31143	6755	5624	22663	1262	1616	1282	9654	25427	14250	8610	1262-31143
Total Fixed mg/l Solids	25473	5524	4692	17484	918	1307	936	8606	18394	11986	7568	918-25473
Total Volatile mg/l Solids	5627	1231	932	5179	344	308	346	1048	7033	2264	1042	308-7033
% Volatile Solids	18	18	17	23	27	19	27	11	28	16	12	11-28
Total Suspended mg/l Solids	350	134	394	6375	130	73	130	245	2696	78	186	73-2696
Total Fixed Suspended mg/l Solids	205	113	90	935	0	23	0	30	1672	46	136	0-1672
Total Volatile Suspended mg/l Solids	145	21	304	5440	130	50	130	215	1024	32	50	21-1024
% Volatile Suspended Solids	41	16	77	85	100	68	100	88	38	41	27	16-100
Total Dissolved mg/l Solids	30793	6621	5230	16288	1132	1542	1152	9409	22731	14172	8424	1132-30793

Table 8

Wastewater Characteristics From Texas Barge-Cleaning Companies

	Plant 4			Plant 5						Range of Values After Grav. Sep.
	Holding Tank		Con-crete Basin	After Oil-Water Separation		After Oxidation Pond		Effluent Discharge		
Date	3/14/74	3/28/74	3/14/74	3/14/74	3/28/74	3/14/74	3/28/74	3/14/74	3/28/74	
Temp. ^{o}F	73	72	64	91	84	68	79	67	66	
pH	11.1	8.4	11.3	6.5	7.0	7.05	7.2	--	9.0	6.5-11.3
COD mg/l	67864	2323	19561	818	4094	317	677	263	612	818-67864
Total Carbon ppm	8000	2500	5700	260	3500	140	890	150	590	260-8000
Oil & Grease mg/l	7732	109	443	140	198	57.2	--	18.1	20	109-7732
Conductivity μmhos/cm	4900	10000	5200	700	950	3000	2400	3900	3250	700-10000

Table 8 (cont.)

Wastewater Characteristics - 2

	Plant 4			Plant 5						Range of Values After Gravity Separation
	Holding Tank		Con-crete Basin	After Oil-Water Separation		After Oxidation Pond		Effluent Discharge		
Total Solids mg/l	6318	7720	3330	1174	694	2308	1674	2050	1922	604-7720
Total Fixed Solids mg/l	2950	7048	2590	1000	512	1762	1406	1838	1692	512-7048
Total Volatile Solids mg/l	3368	672	740	174	92	546	268	212	230	92-3368
% Volatile Solids	53	9	22	15	15	24	16	10	12	9-53
Total Suspended Solids mg/l	2564	164	68	104	132	130	188	24	30	68-2564
Total Fixed Suspended Solids mg/l	656	142	22	38	88	48	160	8	22	22-656
Total Volatile Suspended Solids mg/l	1908	22	46	66	44	82	28	16	8	22-1908
% Volatile Suspended Solids	74	13	68	63	33	63	15	76	27	13-74
Total Dissolved Solids mg/l	3754	7556	3262	1070	472	2178	1486	2026	1892	1070-3754

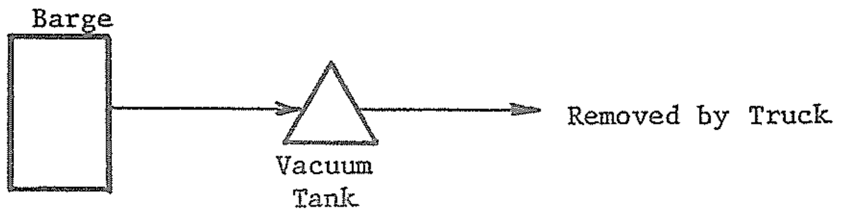

Figure 4: All of Wastewater and Residue Product Removed by Third Party

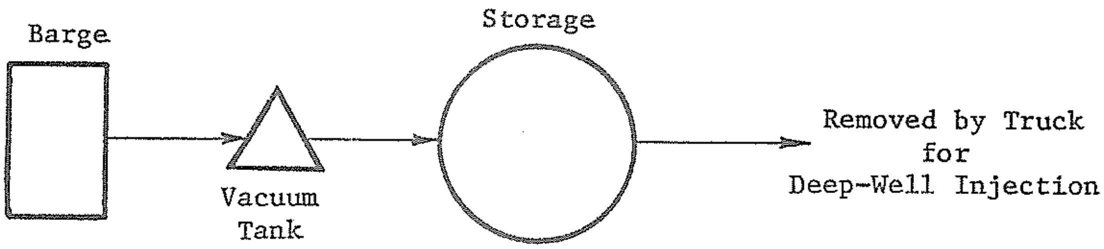

Figure 5: Deep Well Injection of Wastewater Used by a Texas Barge Cleaning Firm

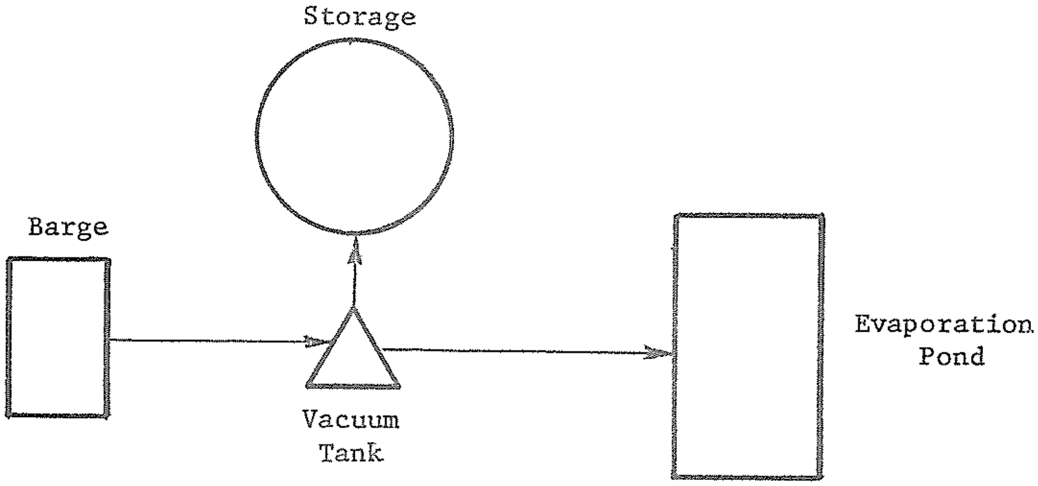

Figure 6: Evaporation Pond Used by a Texas Barge Cleaning Firm

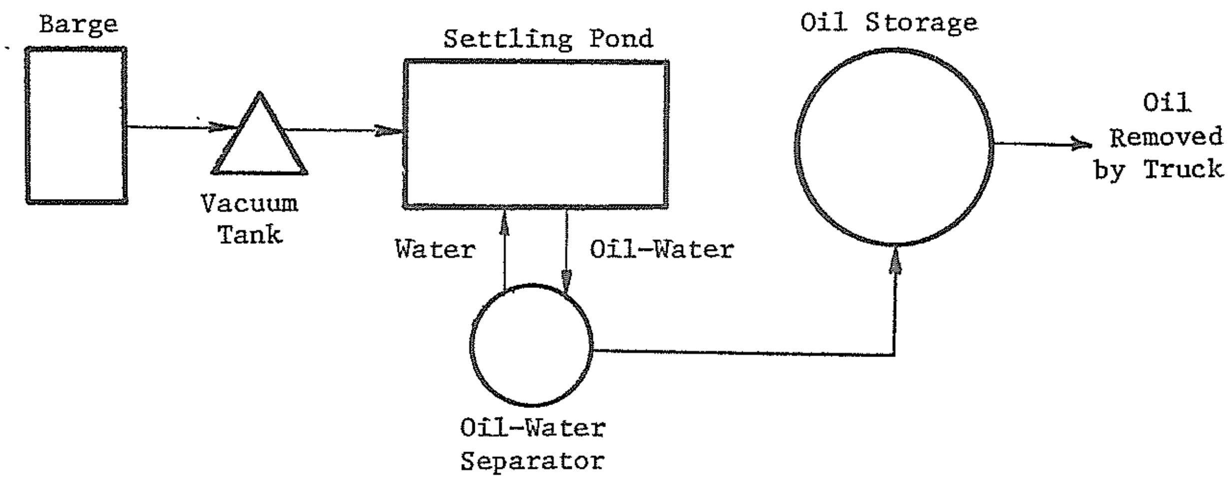

Figure 7: Evaporation-Settling Pond System Used by a Texas Barge Cleaning Firm

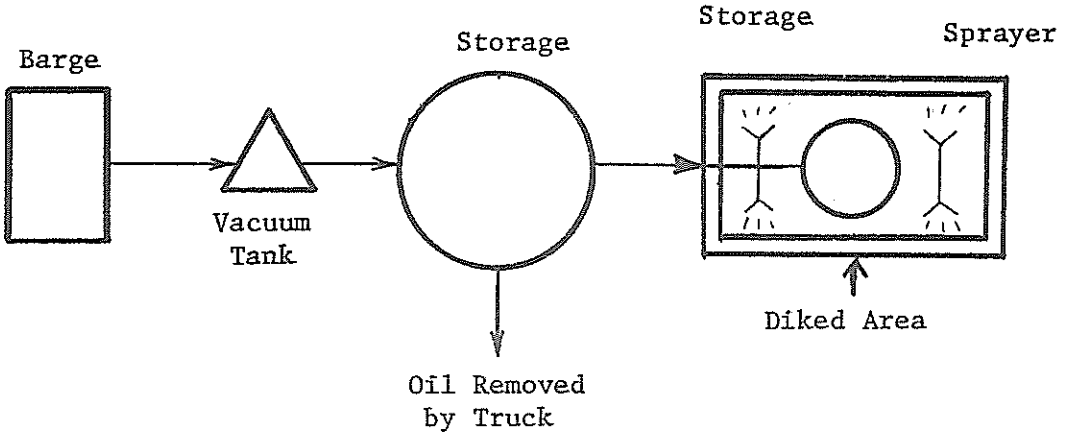

Figure 8: Evaporation-Spray System Used by a Texas Barge-Cleaning Firm

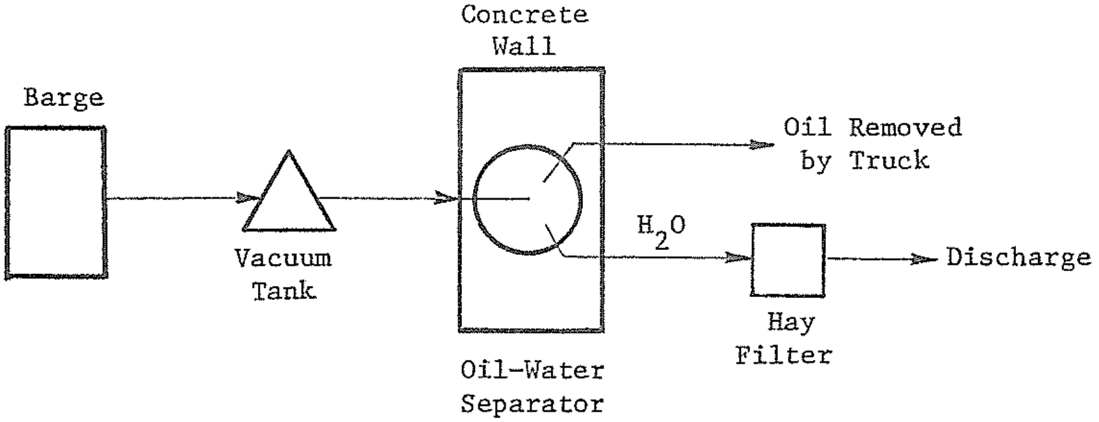

Figure 9: Oil-Water Separator Followed by a Hay Filter Used by a Texas Barge Cleaning Firm

method will be approved only for unique circumstances in the future.

Another consideration is that deep-well injection may not be the most economical solution to the problem. The costs of a deep well may be $25 per foot of depth depending on the geographical area. An additional $100,000 or more is needed for surface equipment to inject the waste which may cost 15-30 cents per gallon per day. Aside from the actual investment and injection costs, the possibility of chemical recovery is lost (7).

The deep-well disposal site used by one of the barge-cleaning companies is located on the Texas Gulf Coast and owned by a vacuum trucking company. The location is particularly suitable for injection wells because of thick layers of saltwater-bearing rock. Since extensive petroleum drilling activities have occurred along the coast the subsurface geology is also well known. The limits of the existing injection well and plans for future use could not be determined.

A third waste disposal system in use is an evaporation pond. This system has been approved by the Texas Water Quality Board and is shown in Figure 6. The advantage of this system is that there are no discharges except to the atmosphere. To work properly, however, evaporation ponds must be kept clear of oil which could reduce evaporation to an ineffective level. Oil must be removed through the use of an oil-water separator. A second important factor is the rainfall-evaporation differential in the location of the pond. Another factor to be considered is the permeability of the soil which must prevent seepage of the waste into the groundwater. If the soil is too permeable, plastic lining can be placed at the bottom of the pit. An evaporation pond is an effective method for reducing the volume of waste with a miminum energy requirement providing the above restrictions are met.

Two other companies are equipped for some form of evaporation system as shown in Figures 7 and 8. The system in Figure 7 uses a settling pond to permit evaporation and probably seepage. This plant is in the process of developing a new treatment system. The system shown in Figure 8 uses a series of sprayers in a diked area to evaporate the water. This method is expected to be of very limited value with most of the water leaving the system by unknown means rather than by evaporation.

One of the companies has been separating its oil from the water by gravity separation tanks and permitting the water to flow back into the river through a hay filter. This system is shown in Figure 9. Although this system was more straightforward than others the resulting water quality needed to be improved. This company is also in the process of upgrading its wastewater treatment system (Figure 9).

The most complicated system in service is a biological chemical system shown in Figure 10. It has been in operation since early 1974 and was the first biological system designed for a barge-cleaning facility in Texas. The cargo residue, which has significant fuel value, is stored and then is burned in one of several boilers. These boilers employ a sprayer-type arrangement to break the waste liquid into small particles for combustion. Materials and washwater that are undesirable for incineration are pumped through a series of ponds for oil-water separation. Separation is

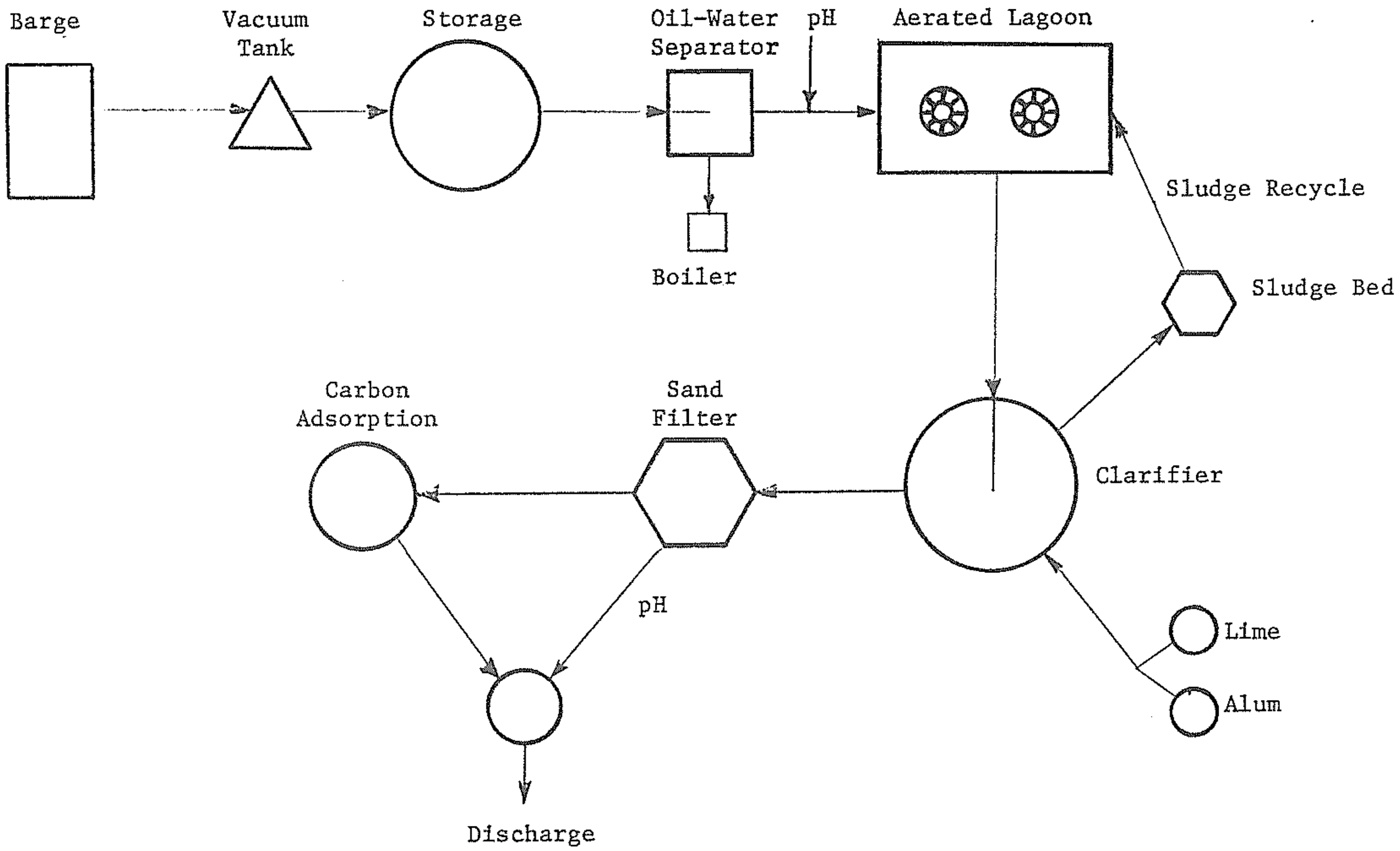

Figure 10: Complete Biological-Chemical Treatment System Used by a Texas Barge-Cleaning Firm

facilitated in one pond by using steam-heated coils to break emulsions (5). After passing through two ponds of approximately one-eigth acre each, the wastewater moves through two smaller ponds which remove most of the remaining separated oil. Another pond with heating coils receives all the oil separated from the other ponds. From this pond, the oil is pumped to the boilers for incineration. Usually, this oil consists of heavy crudes, fuel oil, lubrication oil, and heating oil, all of which are easily separated from the water.

Without any additional pre-treatment except neutralization, the wastewater flows into an oxidation pond. At this point the wastewater contains from 50-150 mg/l oil. (Although the amount of oil entering a biological system is not fully agreed upon, one study conducted for the American Petroleum Institute stated that oily content should be less than 75 mg/l and preferably below 50 mg/l (9)). Mechanical aerators provide the necessary means for oxygen transfer and the hydraulic retention time is approximately five days. Wastewater is pumped from the aerated lagoon to a coagulation-sedimentation basin. Here, aluminum sulfate and calcium hydroxide are added. Sludge is removed from the bottom to a sludge pond while the supernatant from the clarifier is passed through a sand filter. A carbon adsorption column is available for further treatment when needed. Prior to discharge, the water is again neutralized.

Chemical and Biological Treatability Investigations

To determine what could be expected from chemical and biological treatment of barge-cleaning wastewater, a representative commercial shipyard was selected for study. Samples were taken from the shipyard for use in the tests and compared to earlier data shown in Table 9.

Table 9 presents seven characteristics of single wastewater grab samples obtained at intervals starting September 1972 through January 1974. As with the data from other companies these data show exterme variation in pH, ranging from 5.0 to 11.5. Chloride and total residue concentrations are often high due to the influence of brackish water from leaking barges. The low values for suspended solids indicate that the high organic concentrations are probably petroleum products dissolved and emulsified in the wastewater.

Three representative samples of wastewater were obtained at approximately monthly intervals from the gravity-settling tanks at the shipyard starting April 23 through June 19, 1974. The characteristics of these samples are presented in Table 10. By comparing the data in Tables 9 and 10, it is observed that the samples taken for the study are fairly representative of the wastewater over the last two years.

Chemical Pretreatment Tests:

Because a pretreatment unit capable of primary sedimentation and/or

Table 9

Characteristics of Wastewater From One Shipping Company

Date	pH	Color APHA Units	Chloride Cl^-	COD mg/l	BOD_5 mg/l	Total Residue mg/l	Total Suspended Solids mg/l	Volatile Suspended Solids mg/l
9-30-72	6.8	50	16,458	735	352	29,536	24	24
10- 9-72	7.0			835	56	1,819	52	36
12-14-72	11.3	200	2,184	4,158	784	4,930	29	18
1- 5-73	6.9	480	580	2,600	864	1,523	102	102
1-30-73	8.3	560	1,880	3,800	1,280	12,995	140	121
2- 6-73	9.7	560	1,000	1,804	1,200	3,818	9	8
2- 7-73	8.5	240	2,280	1,030	800	3,420	40	26
2-16-73	9.3	70	3,520	2,458	760	6,757	6	4
2-23-73	8.4	40	4,888	962	404	7,655	14	10
3- 7-73	5.3	120	3,337	3,636	740	6,740	55	23
3-19-73	6.6	35	794	4,536	3,260	1,574	11	8
3-27-73	7.4	160	2,020	13,072	7,500	5,026	70	49
4- 5-73	7.8	120	5,450	888	500	9,153	34	24
4-24-73	6.8	140	3,520	4,116	3,300	6,868	14	11
5-14-73	5.0	140	658	11,424	7,500	3,650	125	104
5-16-73	5.4	960	917	6,297	5,200	3,057	163	114
5-29-73	5.0	960	714	7,400	5,260	3,125	29	19
7- 9-73	5.2	160	7,536	1,800	756	12,615	34	27

Table 9 (cont.)

Date	pH	Color APHA Units	Chloride Cl^-	COD mg/l	BOD_5 mg/l	Total Residue mg/l	Total Suspended Solids mg/l	Volatile Suspended Solids mg/l
7-30-73	5.0	160	382	1,280	1,080	1,108	65	39
8-29-73	6.2	320	5,750	1,313	482	10,427	56	50
10-15-73	9.5	960	5,985	10,000	7,450	13,022	240	220
10-15-73	11.5	800	2,925	4,400	3,200	1,142	76	60
10-31-73	5.0	120	3,330	734	475	5,937	25	18
11-13-73	7.1	240	9,990	2,000	1,250			60
1-15-74	8.0	120	735	2,678	2,470	19,619	17	5
Average	7.3	320	3,600	3,760	2,280	7,020	62	50
High	11.5	960	16,500	13,100	7,500	19,600	240	220
Low	5.0	35	380	730	60	1,108	6	4

Table 10

Wastewater Characteristics of Samples Used in Treatability Study

Run number	1	2	3
Date obtained	4-23-74	5-20-74	6-19-74
pH	8.1	10.7	12.0
COD, mg/l	1350	4440	911
Oil and grease, mg/l	78	6603	32
Salinity, ppt	2.5	8.0	18.5
Total Kjeldahl Nitrogen, mg/l	38	--	35
Total Ortho phosphate, mg/l	0.5	1.0	2.5

chemical coagulation-precipitation is often considered desirable upstream of a biological unit that must accept oily wastes, several tests were conducted to determine the efficiency of COD removal by chemical addition. The study was performed on the wastewater collected May 20, 1974. This wastewater was very dark-colored with over 600 mg/l oil and grease. The coagulants used in this study were alum, ferrous sulfate and ferrous chloride. Each chemical was added to beakers containing one liter of wastewater using standard jar test procedures. After chemical addition the wastewater was fast-mixed for three minutes, slow-mixed for 25 minutes, and allowed to settle for 45 minutes before obtaining samples for COD analysis.

Results shown in Figures 11 through 14 indicate that the reduction of COD was small to negligible with the coagulants used. During the study it was noted that a heavy floc would form with or without chemical addition when the pH of the wastewater was reduced to near 7.0. Although all coagulants would aid in settling the floc, thereby imparting a significantly improved appearance to the wastewater, the majority of the COD remained dissolved and was not removed with the floc. Although the floc will form during the neutralization step and would be removed in a biological unit, it is recommended that the floc be removed upstream of the biological unit, should one be required, to decrease the tendency for the mixed liquor to contain a high percentage of inorganic floc.

Biological Treatability Results:

Two methods were considered regarding the manner in which to conduct the study. The first method was to obtain daily samples of the wastewater to simulate an inplace treatment unit while the second method was to obtain a few representative samples and to better define the treatment kinetics with a fairly constant quality feed. Because the wastewater quality would change drastically from one barge to the next, it was decided to take the second approach and to define in detail the treatability characteristics of three separate representative samples.

The first sample was obtained on April 23, 1974 with the characteristics as shown in Table 10. The COD was 1,350 mg/l, oil and grease 78 mg/l and salinity of 2.5 ppt. Because of the low nutrient concentrations, nitrogen and phosphorus were added as ammonium di-phosphate. Seed organisms were obtained from the mixed liquor of a petrochemical-activated sludge plant. A mixture of soil was added that had been obtained from near the gravity separation tanks at the shipyard. The activated sludge units were permitted to acclimate for over a period of two weeks until the filtered COD and mixed liquor suspended solids concentration became stabilized.

Four 12-liter reactors were utilized in this study based on the original design by T. D. Reynolds and promoted by Eckenfelder. The reactors were operated as complete-mix no sludge recycle units. Wastewater feed was stored in a 50-liter container that was kept well-stirred. The wastewater was metered to each of the four reactors by variable speed, positive displacement pumps. Because the units were complete-mix, no recycle, the flow rate from each pump set the mean cell retention time or sludge age in each unit. Throughout the

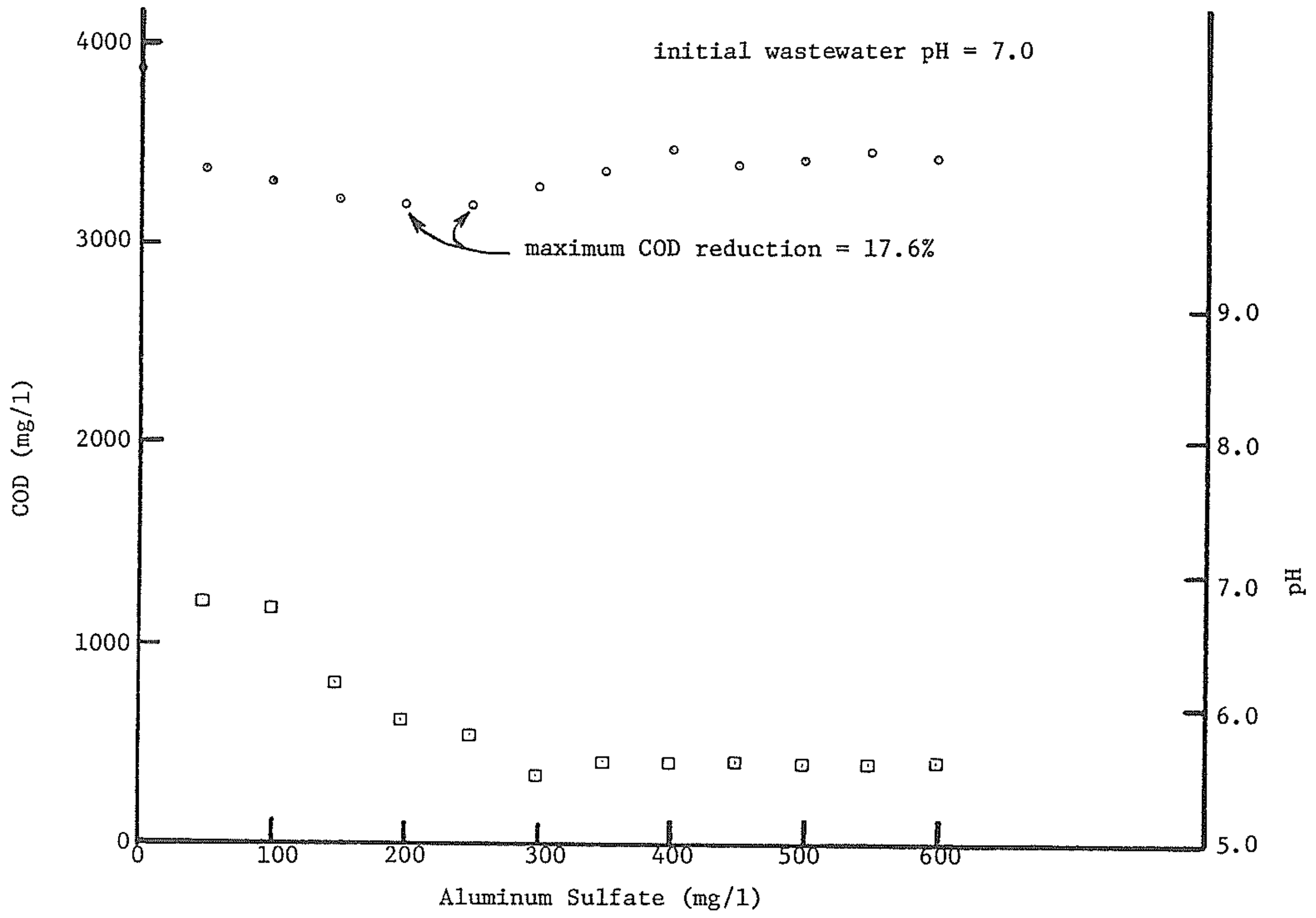

Figure 11: Chemical Treatment of Barge-Cleaning Wastes with Alum at pH = 7

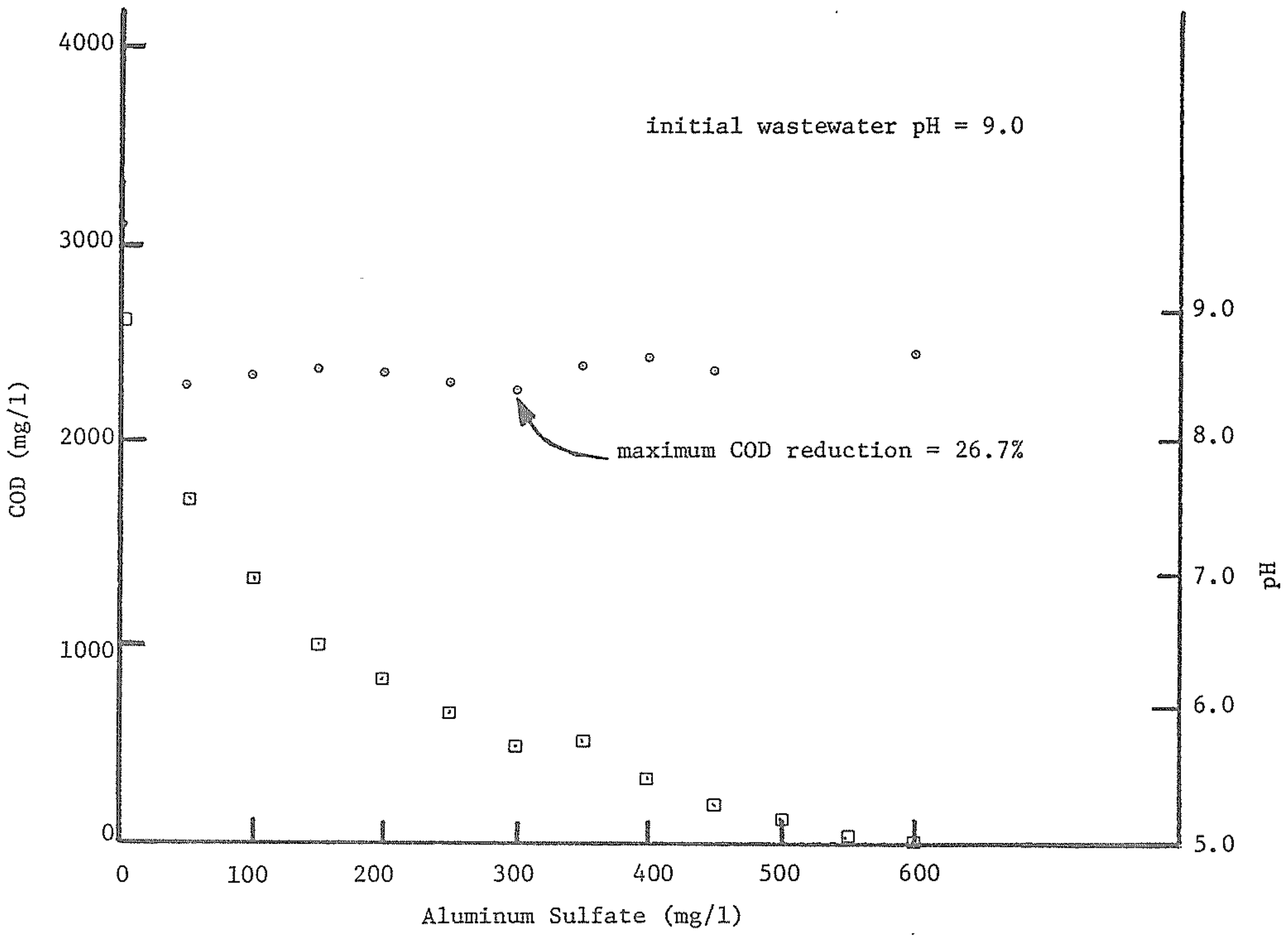

Figure 12: Chemical Treatment of Barge-Cleaning Wastes with Alum at pH = 9.0

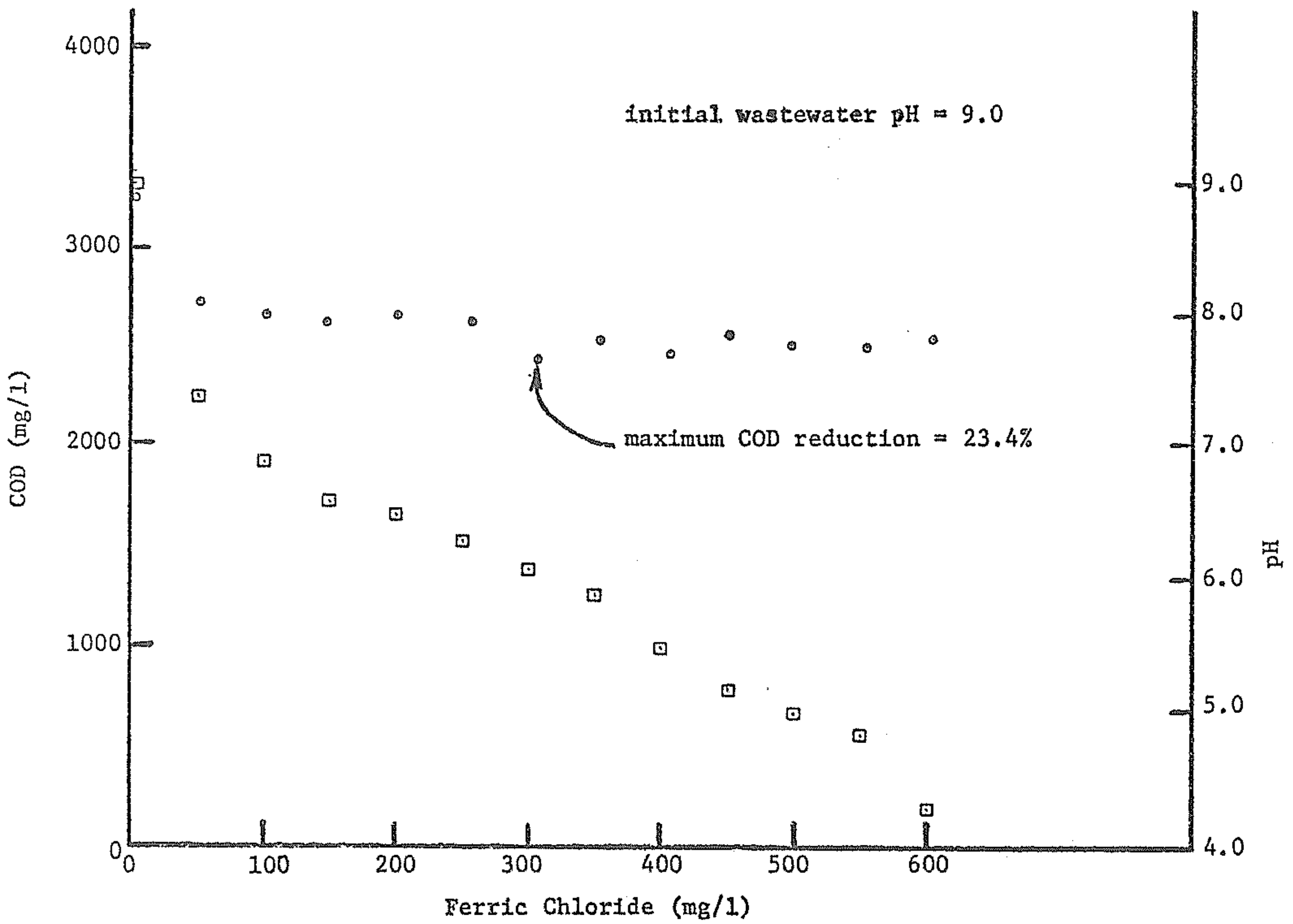

Figure 13: Chemical Treatment of Barge-Cleaning Wastes with Ferric Chloride

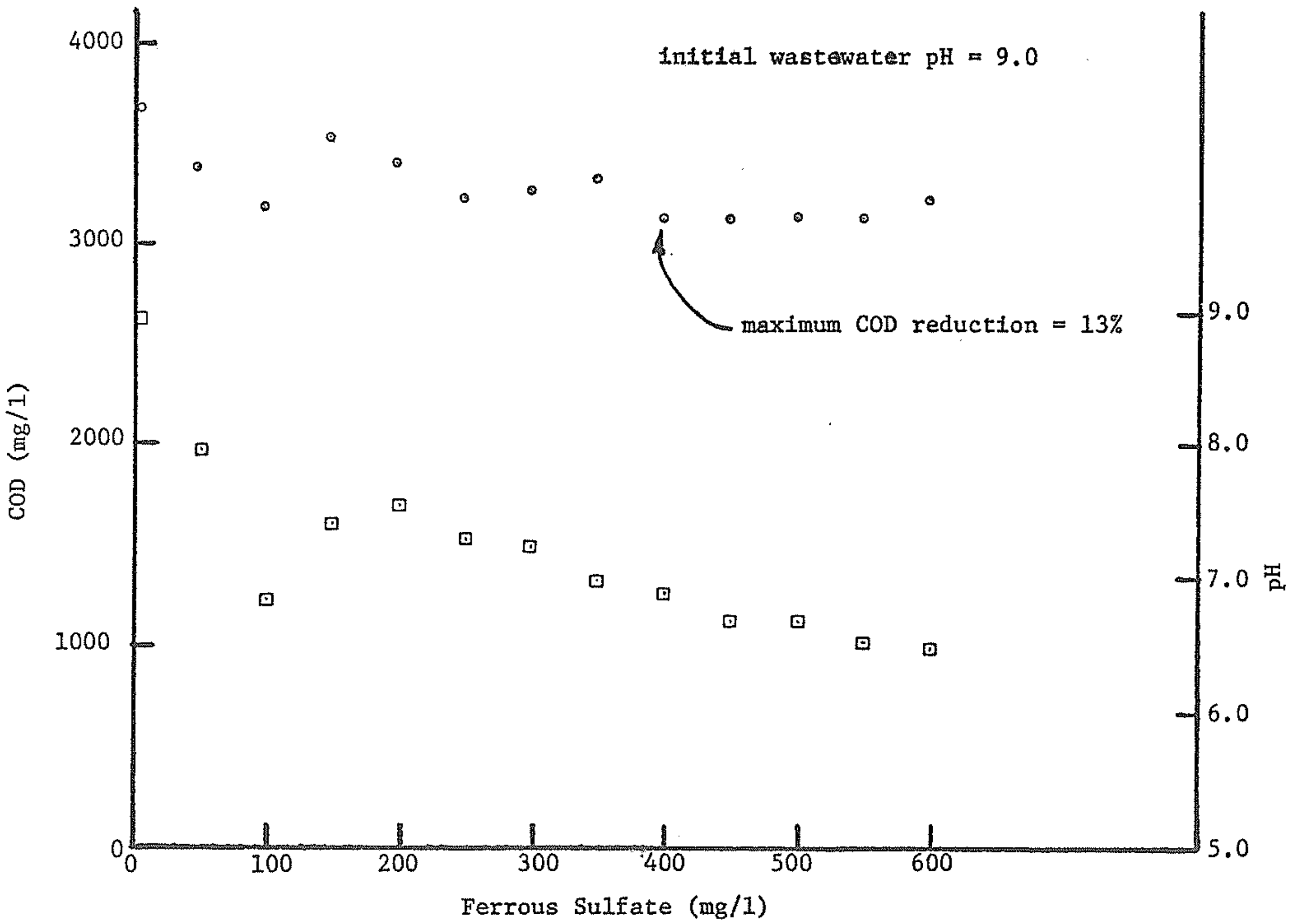

Figure 14: Chemical Treatment of Barge-Cleaning Wastes with Ferric Sulfate

study, the sludge ages for the four units were maintained at one, two, four and eight days.

The pH of each reactor was checked at least twice each day to maintain a range between 6.5 and 7.0. Dissolved oxygen concentrations were checked with a YSI DO meter and the level maintained at 2.0 mg/l or more. The pumping rate for the feed required frequent calibration to maintain the proper sludge age in each unit. A photograph of the reactors is shown in Figure 15.

Figure 16 shows the filtered COD remaining versus sludge age indicating a significant reduction of COD for the waste of greater than 90 percent with a sludge age of about three days.

Figure 17 shows the relationship between the reciprocal of the sludge age and the substrate removal rate q, for the purpose of obtaining the sludge growth rate coefficient Y and endogenous respiration coefficient k_d. The cell growth coefficient of 0.31 agrees well with data from most other studies but the sign of the endogenous respiration coefficient proved to be positive rather than negative. This could have been caused by the rate of carryover to the reactor and additional inorganic floc formation within the reactor at a greater rate than the decay of cells within the reactor. Figure 18 presents the relationship between substrate removal rate and filtered COD. The COD values were adjusted by approximately 75 mg/l to account for the refractory COD in the waste.

The second biological treatability study was conducted using the same methods as in the first test. The wastewater sample was collected on May 20, 1974 and contained a higher concentration of COD and oil and grease than the first waste. The average BOD_5 for the second waste was 1960 mg/l.

Figure 19 shows the remainder of filtered COD versus sludge age. A significantly slower rate of degradation compared to the first waste is observed. A sludge age of 1 1/2 days would decrease the filtered COD by only 50 percent compared to approximately 85 percent for the first sample.

The growth rates for samples I and II were essentially the same, Figure 20, with a very small but negative endogenous separation coefficient. The substrate removal rate coefficient K was significantly smaller, Figure 21, than expected. A comparison of the kinetic values is presented in Table 11.

A third test was attempted using the wastewater from June 19, 1974, described in Table 10. Although COD and oil and grease concentrations were lower compared to the first and second wastewaters, the salinity was much higher, i.e. 18.5 ppt. The third wastewater was slowly blended with the second wastewater to minimize salinity effects. However, the salt concentration was too great and killed the populations in all four reactors.

Summary of Treatability Study:

The treatability study showed that the representative wastewater samples are biologically treatable providing the pH is near neutral, nutrients are added and the salinity is not too high. Kinetic data developed during this study can be used to design a biological treatment unit but the probability of frequent upsets caused by slugs of saline water raise a question as to the feasibility of a biological process for this type of wastewater.

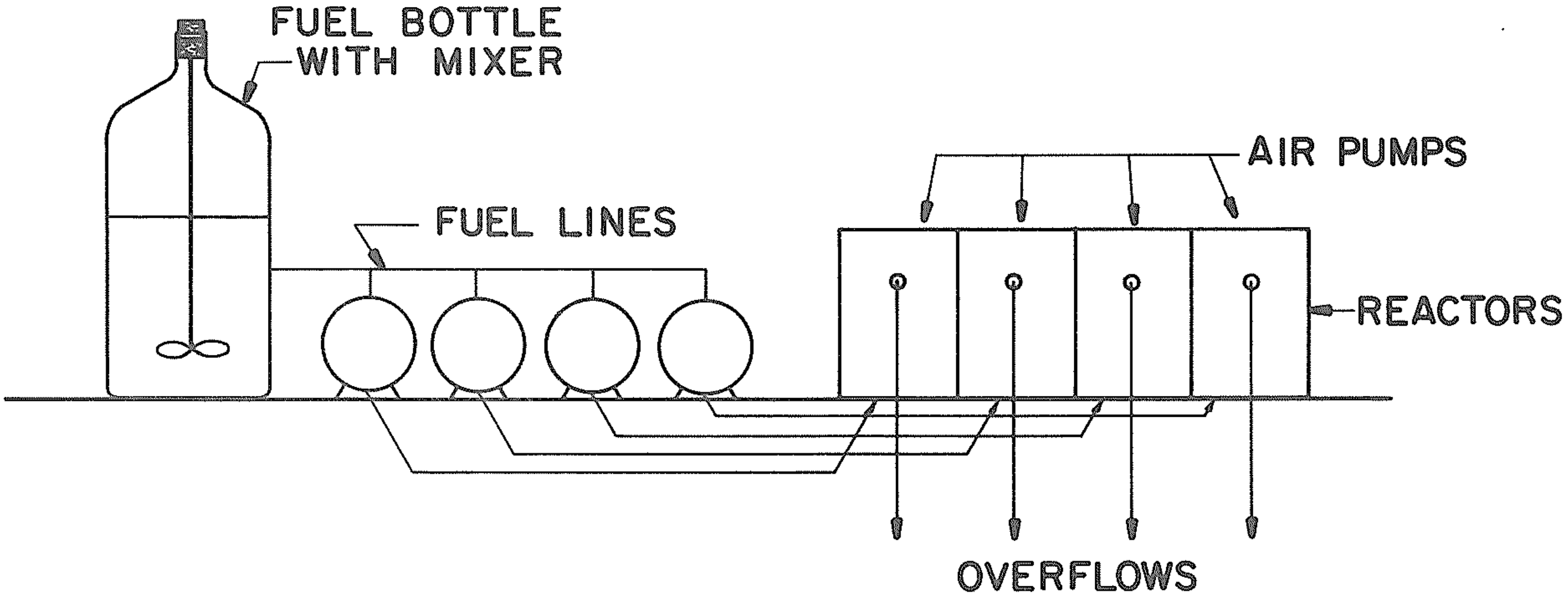

Figure 15: Biological Reactors, Feed Bottle, Pumps and Air System Used in Study

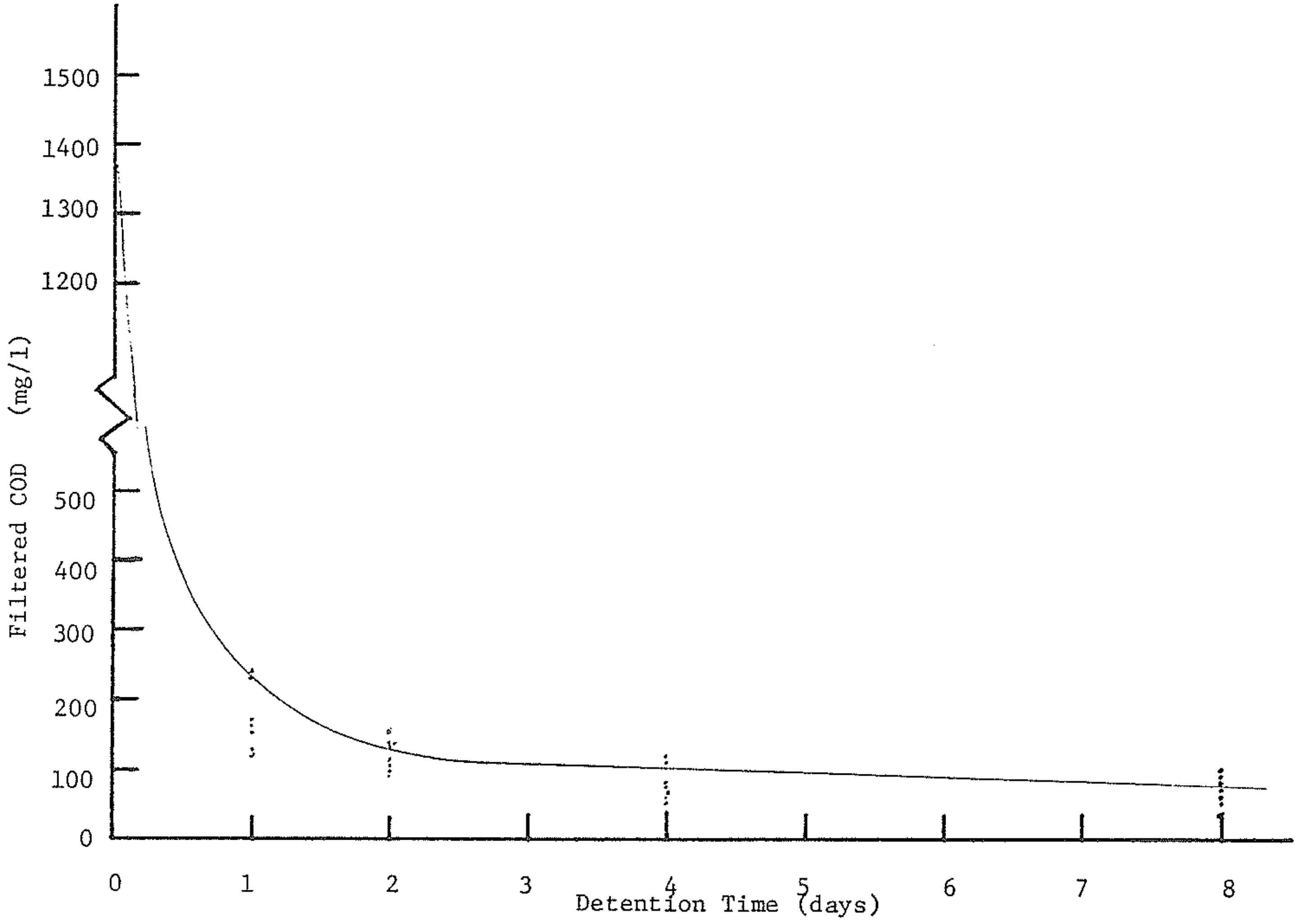

Figure 16: Filtered COD Versus Sludge Age in Days for 1st Sample

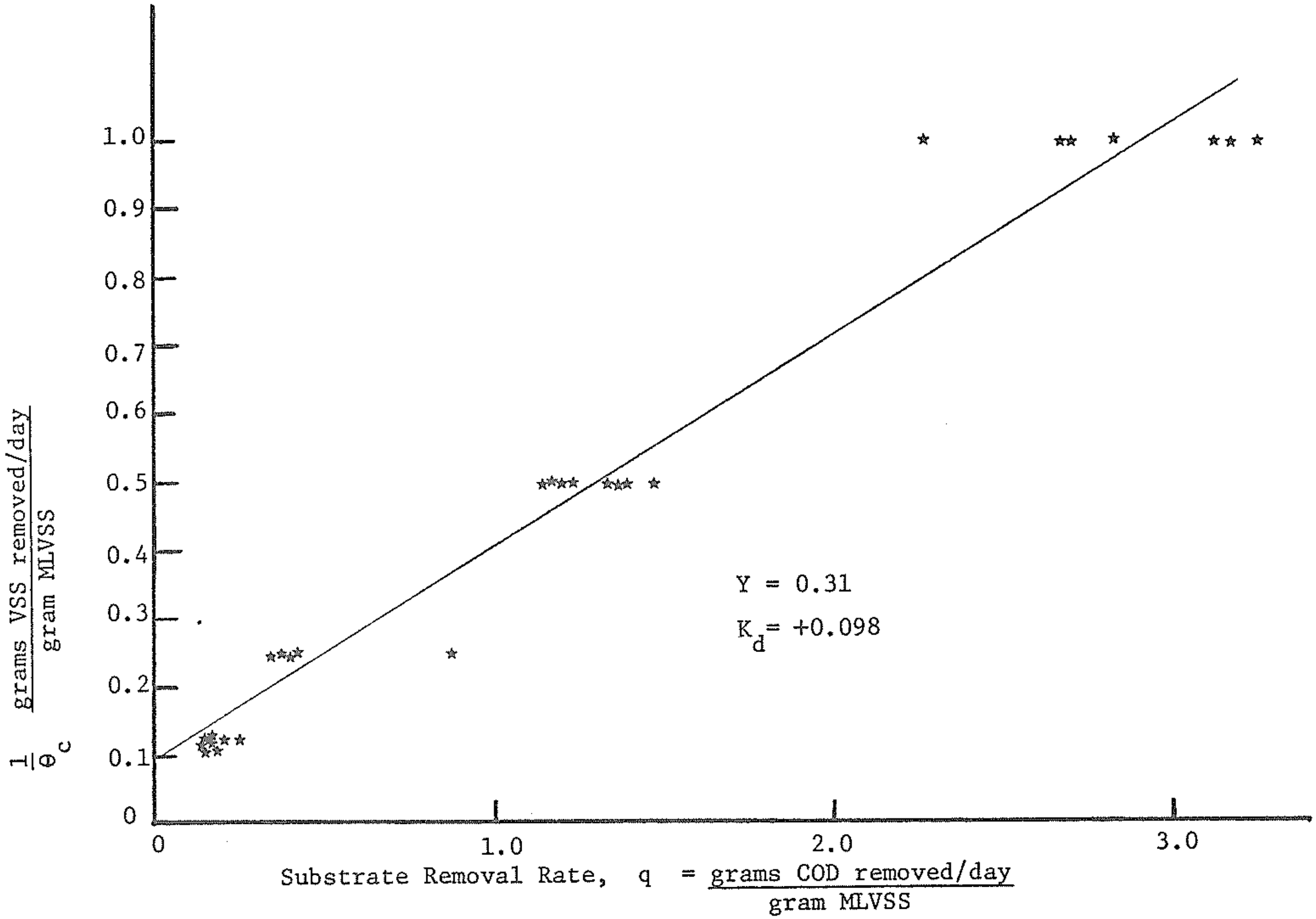

Figure 17: 1/Sludge Age Versus Substrate Removal Rate for 1st Sample

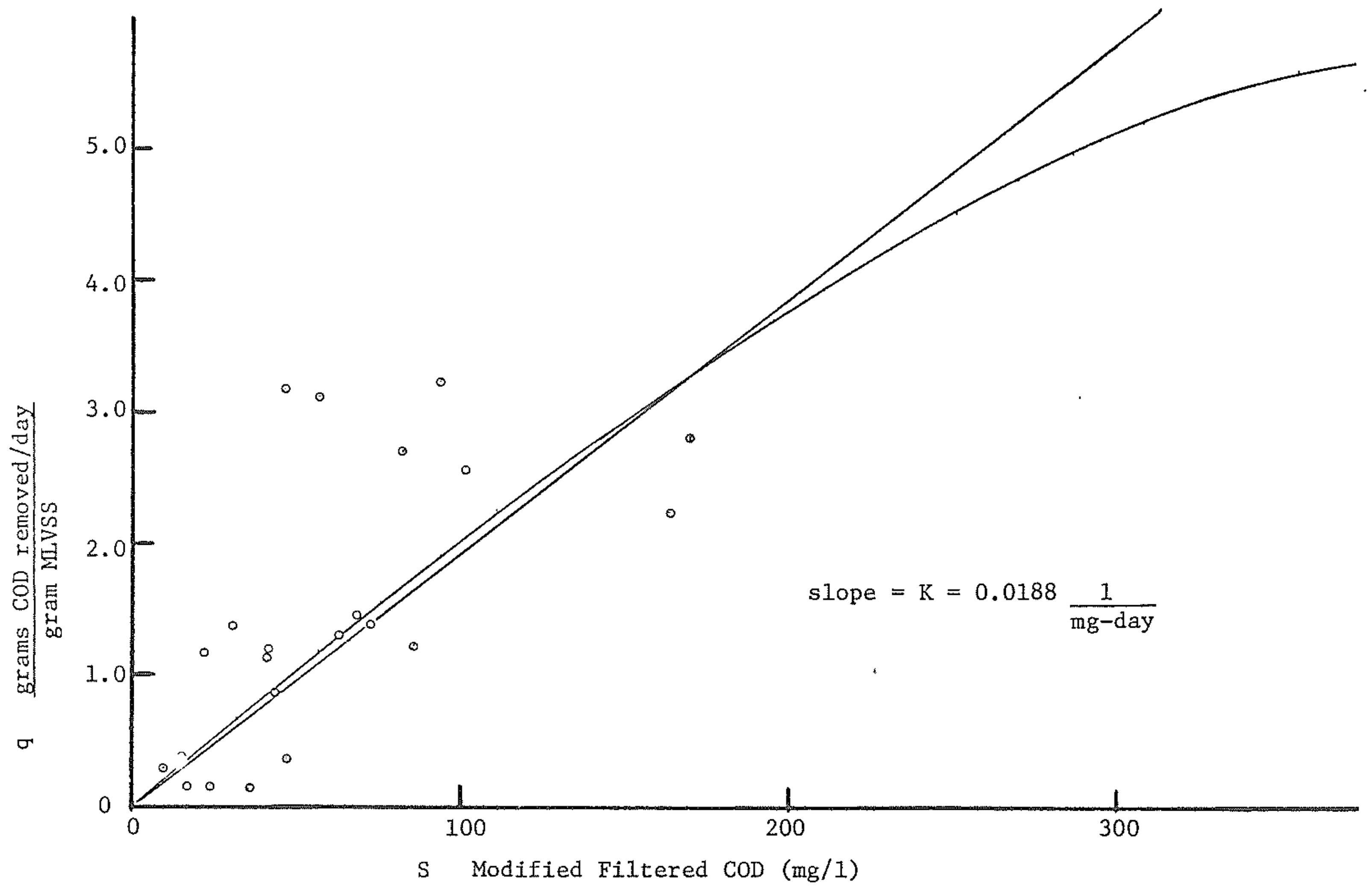

Figure 18: Substrate Removal Rate Versus Filtered COD for 1st Sample

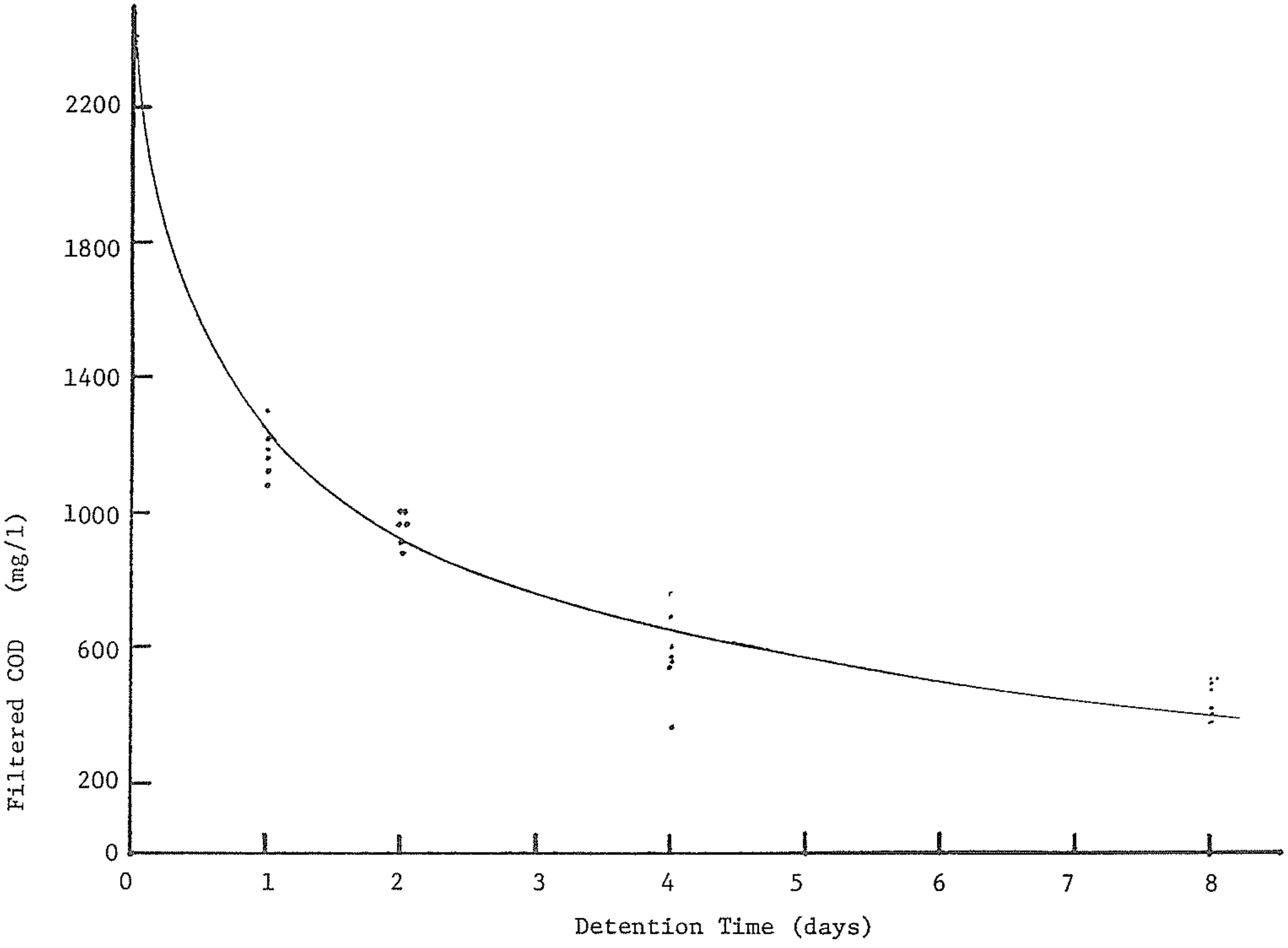

Figure 19: Filtered COD Versus Sludge Age in Days for 2nd Sample

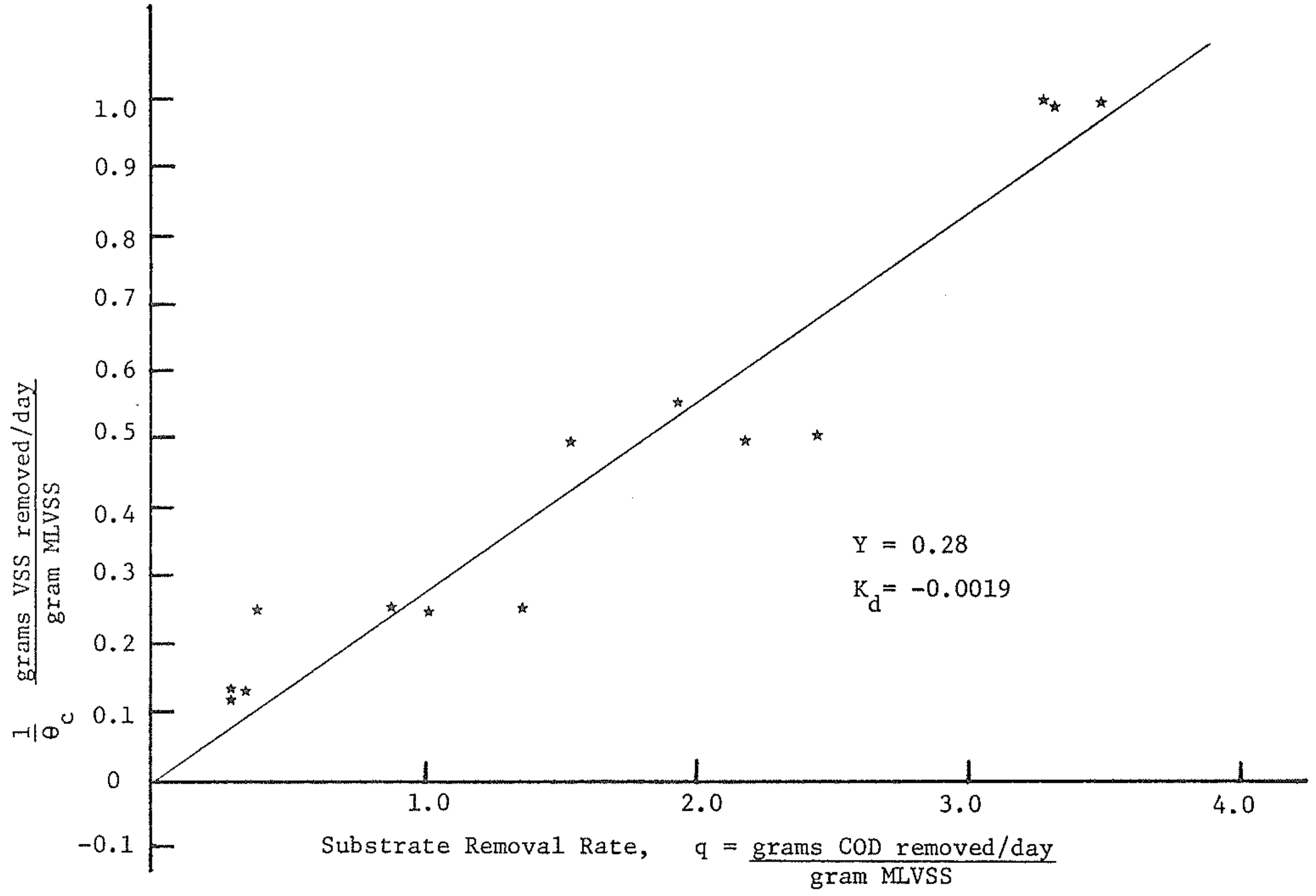

Figure 20: 1/Sludge Age Versus Substrate Removal Rate for 2nd Sample

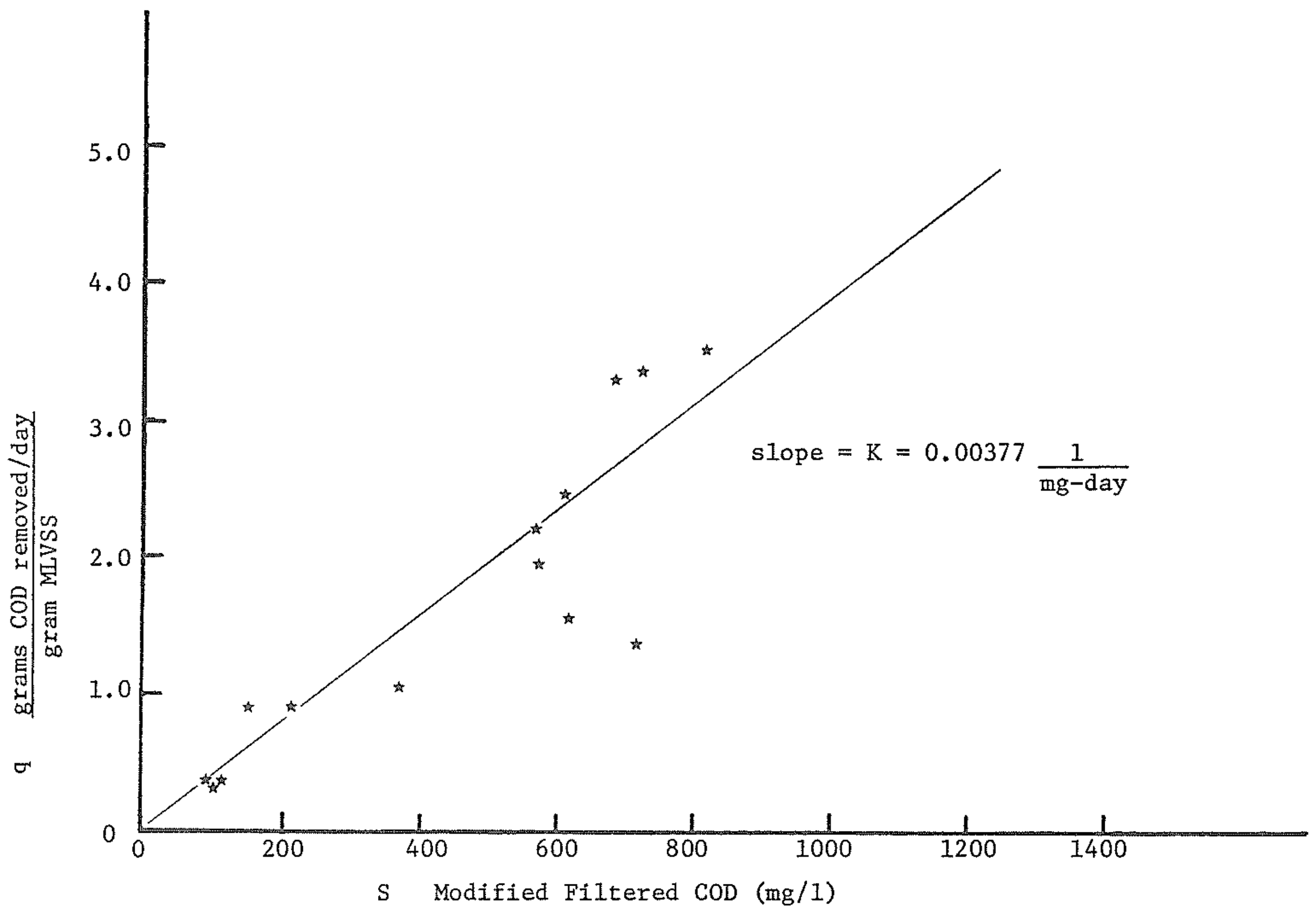

Figure 21: Substrate Removal Rate Versus Filtered COD for 2nd Sample

Table 11

Comparison of Kinetic Values

Waste Sample	Y	K_d	K
1	0.31	+0.098	0.0188
2	0.28	-0.002	0.0038

Assuming that total residue concentrations above 10,000 mg/l would cause an upset, the frequency of occurrence estimated from data in Table 1 indicates that an upset may occur 24 percent of the time. With additional time required to recover from an upset following a salinity slug, a biological unit could be out of service much of the time.

IV. TREATMENT AND DISPOSAL OF BARGE-CLEANING WASTES

The most important aspect of any proposed waste treatment improvement for the barge-cleaning industry would be some form of waste segregation. Segregation would not necessarily be required on a product basis, but rather on the basis of families of products with similar properties. More attention must be given to the properties of residues left in the tanks and how to effectively take advantage of different properties. This type of treatment system would include additional storage facilities for waste oils in many instances and would add some expense to the operation. However, the savings should outweigh the initial expense of constructing the storage facilities.

Initial separation of residual products would be based on solubility of each chemical in water. Solubility data is given in Table 5 for the more commonly transported chemicals. Additional information may be found in other references (3,10). A simple separation of solubles and insolubles should take place at this point. Since there are degrees of solubility, the routing of the wastes can be based on other factors such as fuel utility and biodegradability.

If the soluble material is kept free of water and separate from insoluble products, its value as a fuel and as resale material is greatly enhanced. Separation of soluble organic chemicals from water involved expensive equipment which would make efficient recovery impractical. The burning of various wastes in the same boiler can be accomplished even though it can be a dangerous operation. As was described previously this is presently being done by one company (2). If the material in the wastewater is readily degradable by microorganisms, it can be released into the treatment system. On the other hand, resistant and/or known toxic substances must be routed through a storage system to be released slowly into the biological treatment unit at a level noninhibitory to the microorganisms. Without prior experience, the plant operator cannot be sure what is going to upset his system. After many months of operation, however, the operator should have catalogued enough information to determine which substances can be treated in a given system. A schematic showing the routing of wastes and possibilities for disposal is shown in Figure 22.

A list of compounds known to be resistant to biological treatment is presented in Table 12. Some precautions should be taken and provisions made for handling these wastes. It must be remembered that the list of compounds in Table 12 is not all-inclusive. Some of the compounds, such as the cresols, would cause problems because they are disinfectants and are meant to be resistant

Table 12. Some Compounds Generally Resistant to Biological Degradation

Compound	Formula	Reference
Ethers		
Diethyl ether	$C_2H_5OC_2H_5$	13
Methyl phenyl ether	$CH_3OC_6H_5$	4, 13
Ethylene glycol diethyl ether	$(CH_2OC_2H_5)_2$	4, 13
Diethyl carbitol	$(C_2H_5OCH_2CH_2)_2O$	4, 13
Tetraethylene glycol	$CH_3O(CH_2)_2O(CH_2)_2\ {}_2O$	4, 13
Dioxane	$CH_2CH_2OCH_2CH_2O$	4, 13
Ethylene chlorohydrin	$CL(CH_2)_2OH$	3
Isoprene	$H_2C:C(CH_3)HC:CH_2$	3
Ketones		
Diethyl ketone	$C_2H_5COC_2H_5$	13
Methyl isobutyl ketone	$CH_3COCH(CH_3)C_2H_5$	13
Methyl n-amyl ketone	$CH_3COC_5H_{11}$	13
Methyl phenyl ketone	$CH_3COC_6H_5$	13
Morpholine	$OC_2H_4NHCH_2CH_2$	3
Oils	Fuel, heat, crude, etc.	3
Vinyl compounds		
Acetyl vinyl ketone	$CH_2:CHCOCH_3$	14, 17
Acrolein	$CH_2:CHCHO$	14, 15
Acrylic acid	$CH_2:CHCOOH$	16
Vinyl acetate	$CH_2:CHOCHOCH_3$	16
Methyl methacrylate	$CH_2OCOC(CH_3):CH_2$	16
Styrene	$C_6H_5CH:CH_2$	16
Benzene sulfonates		
n-Propyl benzene sulfonate	$C_3H_7C_6H_4SO_3Na$	18
sec-Propyl benzene sulfonate	$C_2H_4(CH_3)C_6H_4SO_3Na$	18
n-Butyl benzene sulfonate	$C_4H_9C_6H_4SO_3Na$	18
sec-Butyl benzene sulfonate	$C_3H_6(CH_3)C_6H_4SO_3Na$	18

Table 12 (cont.)

Compound	Formula	Reference
t-Butyl benzene sulfonate	$(CH_3)_3CC_6H_4SO_3Na$	18
t-Amyl benzene sulfonate	$C_2H_5(CH_3)_2CC_6H_4SO_3Na$	18
t-Dipropene benzene sulfonate	$C_6H_{13}C_6H_4SO_3Na$	18
Selected hydrocarbons		
Mineral oil	$C_nH_{(2n + 2)}$	19, 20, 21
Benzene	C_6H_6	22
Ethyl benzene	$C_2H_5C_6H_5$	22
n-Propyl benzene	$C_3H_2C_6H_5$	22
n-Butyl benzene	$C_4H_9C_6H_5$	22
t-Butyl benzene	$C_6H_5C(CH_3)_3$	22
Tertiary aliphatic alcohols		
t-Butanol	$C(CH_3)_3OH$	22, 23
t-Amyl alcohol	$C_2H_5C(CH_3)_2OH$	24
Phenols		
Creosols (o, m, p)	$C_6H_4(CH_3)OH$	25
Catechol	$C_6H_4(OH)_2$	26
Trichlorophenols	$C_6H_2OH(Cl_3)_3$	3

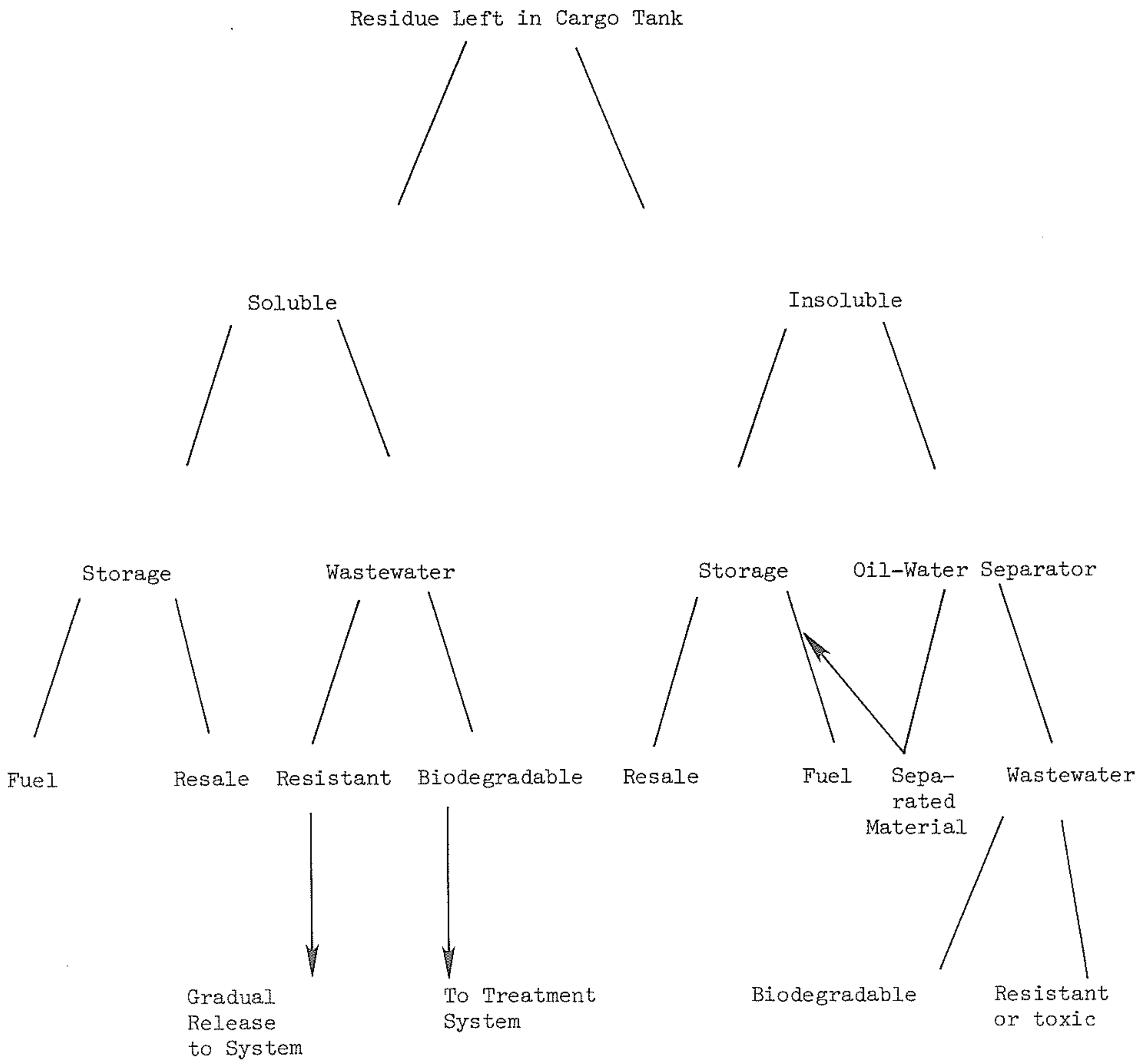

Figure 22: Schematic Representing Residue and Wastewater Routing

to biological attack. The chemical structures of some of the tertiary alcohols contain a carbon without direct hydrogen linkage and may not be available for metabolism. Compounds such as ethers with the C-O-C linkage generally show substantial resistance to treatment. In the vinyl group, methyl vinyl ketone was highly resistant. The formation of higher molecular weight polymers may decrease treatability (11). Mills and Stack suggest that molecular weights in the 250- to 600-range are borderline between resistance and availability on a molecular size basis (12).

Providing the waste is biodegradable, the key to successful biological treatment is acclimation of the seed microorganisms. It would be impractical, however, to acclimate the organisms to more than 150 products encountered by barge-cleaners. For this reason, the logical course of action is to prevent the treatment system from being overloaded by resistant or toxic compounds. The only way to avoid killing the microorganisms or rendering the system ineffective is to keep a record of how different compounds affect a given treatment system.

Treatment Systems for Consideration

Treatment of wastewater regardless of source is accomplished through certain basic unit processes. These process units must be placed in proper sequence to attain the desired level of treatment. The sequence of the units depends on the characteristics of the wastewater. For instance, an oil-water separator is not normally needed in treating municipal waste. Likewise, a biological oxidation unit may not be the most feasible method to treat all industrial wastes.

The barge-cleaning activity is a batch-type cleaning process producing a quality and quantity of wastewater which fluctuates greatly. Consequently, equalization must be provided to normalize flow because most downstream process units require continuous operation. As an example of volume requirements, the water usage for washing some barges requires over 100,000 gallons. As the size of the equalization storage increases, a corresponding reduction in fluctuation of water quality occurs. Storage facilities must be adequate but should not be overdesigned because tanks or ponds are expensive and require space.

After flow equalization, neutralization by pH adjustment is generally desirable. The pH change may aid in breaking emulsions and will be required prior to chemical and biological treatment.

Following neutralization the wastewater should be treated with a gravity-type separator or air-flotation unit equipped with sludge rakes or sludge pumps to remove settled matter from the bottom and oil from the top. According to the American Petroleum Institute the ability of a separator to function satisfactorily depends on type and state of oil in the waste stream, characteristics of the carrier liquid, and the design and size of the unit (27). Probably the most-used gravity oil-water separator is the so-called "API Separator", the design of which is a direct result of a series of projects conducted by the University of Wisconsin under the sponsorship of the

American Petroleum Institute. The basic design is a rectangular multichannel unit allowing for at least a one-hour detention time with a horizontal velocity not exceeding two feet per second.

Removal of oil from the waste stream must be effective to prevent clogging of sand filters and coating of microorganisms in subsequent units. Oil content should not exceed 100 ppm and preferably be as low as 50 ppm in order for bacteria to settle properly. According to one reference the oily material introduced into a biological system is almost immediately adsorbed on the biological floc (28). Higher levels of oil are not necessarily toxic to the bacteria but tend to coat them and consequently reduce their settling properties.

Reduction of organic matter in the waste can be accomplished by physical means such as activated carbon chemical coagulants, or by biological means. A combination of unit processes may be desirable for maximum reduction of organic matter.

Sand filters are useful because of their versatility. For example, they can be used immediately after oil-water separation and as pretreatment before biological treatment. They can also be applied after coagulation-sedimentation to remove unsettled floc and other impurities, or they can be placed at the end of the system for final polishing. The most common type is the rapid sand filter which operates at rates of 2.5-10 gpm/ft^2-day.

Action by a rapid sand filter in removing solids is quite complex and consists mainly of straining, flocculation, and sedimentation. A number of theories have been advanced in recent years to describe the mechanisms by which suspended matter is removed. Tchobanoglous has listed some nine removal mechanisms (29). Some of the mechanisms are related to physical parameters such as grain size while others refer to the chemical and surface characteristics of the suspended matter and filter bed. Sand filters have been successfully employed for final treatment of ballast water. In this instance it is preceded only by an oil-water separator and is particularly effective for filtering wastewater with a high oil content (27).

Chemical coagulation involves the addition of a coagulant and possibly a coagulant aid. Coagulants are compounds which enhance the precipitation of suspended and colloidal matter in water and wastewater, thereby producing a clarified effluent. The major reasons for chemical coagulation of waters are removal of colloids and precipitation of cations (22). At times it becomes necessary to help the precipitation process by adding coagulant aids. Some of the most popular coagulants and coagulant aids are listed in Table 13.

Coagulation of the suspended matter in the waste is followed by floc formation in which the smaller particles agglomerate forming larger particles of greater density. These larger particles settle at a faster rate than the smaller ones. The actual settling velocity is a function of size and density. Once the floc has formed, it must be left to settle under quiescent conditions in a sedimentation tank. Retention time in the clarifier is usually two hours. This process results in forming a sludge that must be removed and disposed of by incineration, land-fill, or other means.

Biological systems used to treat wastes are primarily modifications or improvements upon natural assimilative systems. The methods are acceptable for treating industrial wastes but are considerably more complex than methods -

Table 13. Chemical Coagulants and Coagulant Aids Used in Wastewater Treatment, and pH Ranges Required for Suitable Floc Formation

Coagulant	Formula	Optimum pH Range
Aluminum Sulfate (Alum)	$Al_2SO_4 \cdot 18H_2O$	4-7
Ferrous (Copperas) Sulfate + Lime	$FeSO_4 \cdot 7H_2O + Ca(OH)_2$	>9.5
Chlorinated Copperas-Ferrous Sulfate + Chlorine		3.5-7.0, >8.5
Ferric chloride	$FeCl_2$	3.5-7.0, >8.5
Ferric Sulfate	$Fe_2(SO_4)_3$	3.5-7.0, >8.5
Sodium aluminate	$NaAlO_2$	
Lime	CaO	>10
Coagulant Aids		
Activated silica	SiO_2	
Polyelectrolytes		
Clay		

used to treat municipal wastewater. For instance, extensive pretreatment may be required. Since natural means are used in reducing organic content, toxicity, and objectionable appearance, biological treatment is usually the most economical method for treating industrial wastewater. Probably the three most widely used biological systems are activated sludge, trickling filter or towers, and oxidation ponds or aerated lagoons.

The first biological process to be discussed is the activated sludge process. It is a continuous process whereby aerobic microorganisms are mixed with wastewater. After the microorganisms have metabolized the organic matter in the waste, they are separated in a clarifier. A portion of the concentrated sludge is recycled and mixed with additional waste. The operation of the system is based on the production and maintenance of an environment favorable for optimal microbial growth. Impurities and toxic compounds must be removed or kept at non-inhibitory levels before activated sludge treatment will give satisfactory effluents. High concentrations of suspended solids will reduce overall efficiency and should be kept at less than 125 mg/l (20). Colloidal matter, especially, must be reduced by coagulation before activated sludge treatment, and with the oil content of the waste stream not exceeding approximately 75 mg/l (26). Although the completely mixed activated sludge system has the advantage that it does tend to dampen slug loads, equalization and neutralization are highly desirable. In fact, they are usually essential. One toxic or highly concentrated waste alone is sufficient to wipe out the entire microbial population. A final clarification unit is required to separate the sludge from the effluent. Activated sludge systems are usually more expensive to install than other systems but they generally produce a higher quality effluent.

Trickling filters consist mainly of a bed containing stones or other media on which a biological slime adheres and grows. The wastewater is usually distributed over the bed by a rotary spray powered by jets of water sprayed in a backward direction. As the wastewater flows over the slime, organics and oxygen diffuse into the slime, thereby undergoing oxidation to CO_2, water, and metabolic by-products. Trickling filters have been used in industrial waste treatment systems for removing surges of organic loading, acting much like an equalization tank, in this respect, prior to activated sludge systems or aerated lagoons. They rarely meet stringent effluent quality standards by themselves (30). The usual treatment efficiencies range from 75-90% removal.

Aerated lagoons are basins, 6-12 feet in depth, containing an environment conducive to the growth of aerobic organisms. Oxygen is supplied by mechanical aeration or through diffusers. Reduction of BOD is a function of detention time, temperatire, nature of the waste, and suspended biological solids concentration. Although aerated lagoons are relatively inexpensive to construct and maintain, they require more land than most other systems. This disadvantage has to be weighed against the value of the land for other purposes. In addition, the turbulence created by mechanical aeration or diffusers is often insufficient to maintain all solids in suspension.

A Proposed Treatment System

It is recognized that a number of technically feasible schemes can be developed that will treat the typical wastewater generated by barge-cleaning operations. However, several logical steps which would probably be assembled would include segregation, gravity separation, equalization-neutralization, pretreatment, treatment, final polishing and recycle. An example of this type of system is presented in Figure 8.

Residue products can be pumped from the vacuum tanks to one of at least three segregation tanks to be held for resale, used in plant boilers and equipment, and held for bleeding back to the treatment system. The third tank would be used for those products that, because of their resistance to biological degradation or toxicity, should be diluted with the normal wastewater prior to treatment.

Washwater would be routed to one of at least two gravity oil separation tanks, with each tank capable of storing one day's washwater. The tanks should be operated alternately allowing up to 24 hours for gravity separation of the dissolved and emulsified oil from the washwater. Each tank should be constructed with a swing-line to permit removing oil from the surface for return to the segregation tanks.

Once each day washwater could be charged to the neutralization-equalization tank. The purpose of this unit would be to add acid or base to neutralize the pH and to add coagulants if required. The tank should be equipped with a mixer for rapid equalization to keep the solids from settling in the tank.

The washwater would be directed to a pretreatment unit which could consist of an API type separator or an air flotation unit. Because of the back-type flow and the relatively small volume of water requiring treatment it would probably be more economical to provide an API separator. The separator should be capable of surface skimming and sludge removal. Surface skimmings should be rerouted to the segregation units. Waste sludge could be routed to a tank for land-fill disposal.

Because of the relatively small reduction in COD from chemical treatment, it is desirable for a biological unit to follow the API separator. This unit could be a complete-mix, aerated lagoon facility depending on the availability of the land at the plant. Sludge waste must be provided which could be removed by vacuum tank to a commercial disposal pit.

A sand filter should follow the biological system to remove any suspended matter that would carry over from the clarifier. At least two filters must be provided so that one unit would be in service while the second unit is being backwashed. Backwash water could be recirculated from the recycle washwater tanks and discharged to the influent end of the biological unit or to the equalization-neutralization tank. The system should be flexible so that backwash water could be directed to either point.

Effluent from the sand filter should be directed to a washwater recycle tank for re-use. An effluent blowdown would be provided to prevent buildup of salt concentration in the recycled washwater. Effluent quantity- and quality-monitoring must be provided according to state and EPA regulations. A freshwater makeup line must also be provided to account for any loss in washwater from the effluent.

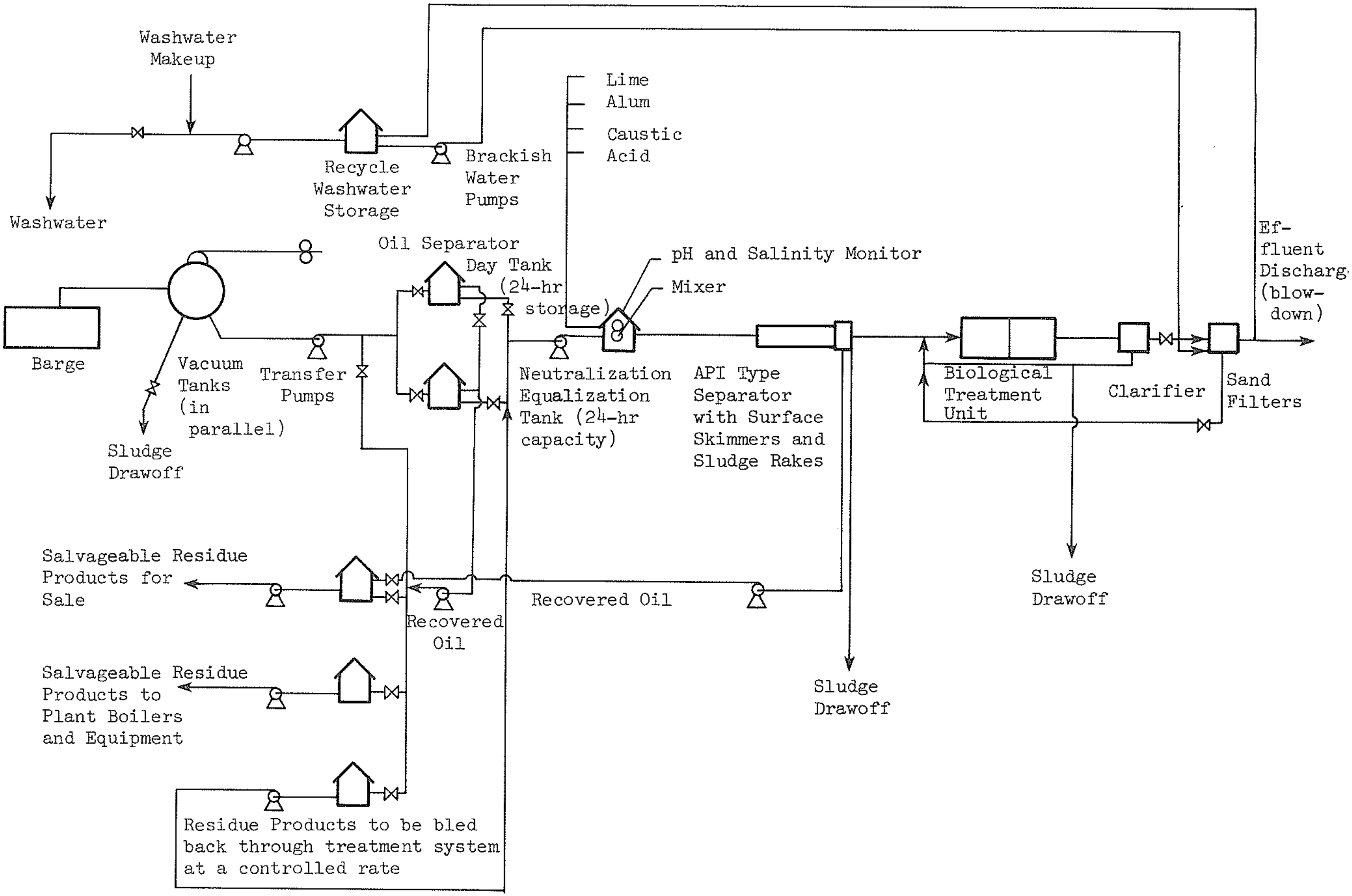

Figure 23: Proposed Treatment System for Barge-Cleaning Companies

In summary, the system proposed in Figure 23 and described in the text is not the only system that will treat the washwater from barge-cleaning operations. However, the system should work reasonably well if: 1) bypass-piping is provided around each unit, 2) effluent from each unit can be recirculated back to the head of the system for retreatment, 3) dual units are provided for each step in case of breakdown, and 4) operation personnel are properly trained to understand and operate the system.

An Alternate Means of Financing Waste Disposal Systems

An alternate available to commercial shipyards who would rather not be in the business of treating washwater would be to investigate the services available through the Texas river authorities. The river authorities, as governmental agencies of the State of Texas, have been given powers by the Legislature to perform the waste treatment functions for industry. For example, the Sabine River Authority, in Orange, has made the following policy guidelines relating to wastewater treatment (31):

A. The Authority can finance, construct and operate waste treatment facilities for industrial and commercial concerns under negotiated contractual agreements. The Authority can finance these facilities on a contract basis by fund advances from the customer, or by issuance and sale of Authority revenue bonds under contract agreement with the customer to guarantee bond amortization, issue costs and other related expenses.

B. The Authority will also enter into contract agreements to operate new waste treatment facilities, whether constructed and owned by Authority or by the customer, or to operate existing facilities, non-Authority financed, on the basis of actual operating costs plus administrative charges.

This policy offers an excellent opportunity for smaller industries to form a cooperative or to act separately with a river authority. A list of the authorities having jurisdiction over river basins emptying into the Gulf of Mexico is given in Appendix D.

V. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions were drawn from this study:

1) There are ten companies along the Texas Gulf Coast actively engaged in commercial barge-cleaning and repairing. Most of the firms are relatively small-service companies owned and operated by families. All are located near the large petroleum refinery areas along the coast.
2) The quantity and quality of wastewater generated from cleaning barges is highly variable. In general, approximately 10,000 gallons of wastewater results from the cleaning of barges that carry such products as diesel fuel and gasoline with up to 150,000 gallons of wastewater from cleaning creosote and crude cargo barges. Barges carrying miscellaneous chemical cargoes require about 20,000 gallons of water to clean the barge.
3) Treatability tests on two washwater samples indicate that the waste is amenable to biological treatment providing the pH is neutralized and nutrients added. However, a biological process could be upset by frequent slugs of highly saline water.

The following recommendations are made for consideration by barge-cleaning firms:

1) It is suggested that barge-cleaning procedures be modified to include washwater segregation. This will increase the amount of product that can be salvaged as well as water use.
2) It is suggested that a treatment system be constructed that would meet or exceed the capabilities of the proposed system described in this text. The units include gravity separation, equalization-neutralization, pretreatment, treatment, polishing and recycle.
3) The barge-cleaning companies should investigate the economic feasibility for regional waste treatment facilities and for contracting the services through river authorities or similar entities.

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APPENDIX A

Table C-1. Wash Procedures for Change of Cargo

FROM TO	Acrylonitrile	Benzene	Butane	Caustic	Creosote	Crude oil	Cumene	Diesel	Ethyl benzene	Ethyl dichloride	Fish oil	Fuel oil	Fuel oil	Gas (natural)	Gasoline	Jet fuel	Kerosene	Lube oil	Methanol	Mineral spirits	Monene	Process oil	Resinol	Rubber solvent	Styrene	Toluene	Vinyl acetate	Xylene
Acetic anhydride										IV																		
Acrylonitrile																												XI
Asphalt																		XII										
Benzene		III					I					III							XII						III			
Chlorinated HC						IX																						
Cresylate																						X						
Crude oil						VI						VI	II															
Cumene							III																		VII			
Diesel		XI																XII										
Dripolene																					IX		VII					
Ethyl benzene																									VII			
Ethyl hexanol							VII																	XI				
Ethylene glycol							XI																					
Fertilizer (liquid)																										VI		
Fish oil																												
Fuel oil											IV							II										
Gas (natural)														II														
Gasoline								III								IV	VI											
Glycol							X																					
Glycol (waste)							XI																					
Jet fuel															IX											II		
Kerosene																II	II											
Lube oil		X		IV														IV									VI	
Methylene chloride																										VII		
Mineral spirits																				I								
Naphtha	V																											
Plasticizer							X																					
Propanol																			VII									
Propylene oxide			VIII																									
Styrene		VII					VII		III										XI		VII							
Toluene					VII																							
Trichloroethane						IX																						
Xylene		VII																									VII	

Washing Procedures for Change of Cargo

I

1. Strip free liquid
2. Blow-dry to LEL

III

1. Strip free liquid
2. Blow-dry

V

1. Strip free liquid
2. Store cargo residue
3. Store cargo residue
4. Hot water butterworth
5. Strip washwater
6. Clean and dry

VII

1. Cold water butterworth rinse
2. Strip free liquid
3. Store cargo residue
4. Hot water butterworth
5. Strip washwater
6. Clean and dry

IX

1. Hot water butterworth
2. Strip washwater
3. Hot chemical butterworth wash
4. Strip washwater
5. Cold water butterworth rinse
6. Dry

XI

1. Hand-wash
2. Strip free liquid
3. Store cargo residue
4. Hot water butterworth
5. Strip washwater
6. Hand-wash
7. Strip washwater
8. Dry

II

1. Drain cargo lines
2. Squeegee, if necessary
3. Strip free liquid

IV

1. Hot water butterworth
2. Strip washwater
3. Clean and dry

VI

1. Hot water butterworth
2. Strip washwater
3. Ventilate
4. Bucket out residue
5. Clean

VIII

1. Flare tanks and lines to 0 psi
2. Purge with nitrogen to 0% oxygen reading
3. Repeat 1 and 2
4. Hot water butterworth
5. Ventilate to dryness
6. Purge with nitrogen to 3% O_2

X

1. Cold water butterworth rinse
2. Strip free liquid
3. Store cargo residue
4. Hot water butterworth
5. Strip washwater
6. Ventilate
7. Gas-free

XII

1. Cold water butterworth rinse
2. Strip free liquid
3. Store cargo residue
4. Hot water butterworth
5. Strip washwater
6. Hot chemical butterworth wash
7. Strip washwater
8. Cold water butterworth rinse
9. Clean and dry

APPENDIX B

Barge-Cleaning Companies Along the Texas Gulf Coast

Company and Contact	Address	Location	Wastewater Treatment Facilities
Channel Shipyard Co. M. E. Rushing	999 S. Lynchberg Road Baytown (713) 424-5581	1/4 mile up San Jacinto River from Lynchberg Ferry	Storage tanks, transports to refinery
Gulfco, Inc. Charles Tanner	Route 2, Box 448-P41 Freeport (713) 233-7401	Surfside, mile 393 Intercoastal Waterway	Evaporation ponds
Gulfport Shipbuilding Co. J. L. Weakley	West End Lakeshore Dr. Port Arthur (713) 982-5781	Mile 286 WHL on Sabine Neches Waterway	Oil-water separation, aerated lagoon, coagulation, sand filter, carbon adsorption, pH adjustment
Kelso Shipbuilding Wayne Pace	P.O. Box 268 Galveston (713) 744-5341	Mile 355 WHL	Barge storage, transports via truck to injection well
Levingston Shipbuilding Co. G. A. Duchamp	P.O. Box 968 Orange (713) 883-3521	On Sabine River off mile 266.1 WHL	Gasfreeing facility on Louisiana side of Sabine River
Neches Intersection Shipyard Co., Inc. S. W. Liggett	P.O. Box 3465 Old Yacht Club Road Port Arthur (713) 982-5721	Mile 277 WHL Sabine Neches Waterway	Oil-water separation, coagulation, sand filters, pH adjustment
Platzer Shipyard E. W. Platzer	P.O. Box 9788 Houston (713) 453-7251	Greens Bayou off Houston Ship Channel	Oil-water separation, storage tanks, sells recovered oil

Company and Contact	Address	Location	Wastewater Treatment Facilities
Rincon Shipyard, Inc. W. R. Miller	P.O. Box 9315 Corpus Christi (512) 883-5741	Mile 538.1 WHL	Storage Tanks
Southwestern Barge Fleet Service, Inc. H. T. Hilliard	P.O. Box 845 Highlands (713) 452-7521	1 3/4 mile up San Jacinto River	Storage tanks, evaporation sprayer system
State Welding and Marine Co. Chester Slay, Sr.	Industrial Road Port Arthur		Facility under construction

APPENDIX C

Various Chemical Cargoes Transported by Barges

Compound	No. of Barges	Compound	No. of Barges
Acetic acid	14	Calcium chloride	1
Acetic anhydride	1	Carbitol	1
Acetone	1	Carbon tetrachloride	1
Acrylonitrile	9	Caustic	8
Aldehydes (mixed)	1	Caustic (spent)	5
Ammonia (anhydrous) (g)	5	Cellusolve	6
Aromatic gasoline	13	Chlorinated HC	1
Aromatic oils	1	Chlorine (g)	1
Asphalt	21	Chlorobenzene	1
Benzene	13	Chloroform	1
Bright stock	2	Coal	6
Bunker C	3	Coal tar	18
Butadiene (g)	39	Coke	21
Butane (g)	4	Creosote Oil	5
Butanol	4	Cresol (o, m, p)	1
Butyl acetate	1	Crude oil	93
Butyl aldehyde	3	Cumene	4
Butyl cellusolve	5	Decyl alcohol	1
Butyl glycol	1	Diesel fuel	94
Butylene (crude)	2	Dioctyl pthalate	1
Butylene oxide	1	Dioxane	1
C-4, -5 products	4	Dicyclopentadiene	1

Compound	No. of Barges	Compound	No. of Barges
Diethylene triamine	1	Hydrochloric acid	2
Dripolene	14	Hydrogen sulfide	1
Ethanol	19	Isobutanol	4
Ethyloxytil glycol	2	Isodecanol	31
Ethyl acetate	3	Isopentane (g)	1
Ethyl amine	10	Isophorone	2
Ethyl benzene	13	Isooctanol	1
Ethyl hexane	1	Isopropanol	15
Ethyl hexanol	16	Isoraffinate	1
Ethyl hexyl alcohol	2	Jet fuels	2
Ethyl hexyl pthalate	2	Kerosene	13
Ethylene (g)	1	Liquid fertilizers	1
3-Ethylene-4-amine	1	Lubrication oil	38
Ethylene diamine	4	Methanol	18
Ethylene dichloride	1	Methoxy triglycol acetate	2
Ethylene glycol	14	Methyl acrylate	2
Fish oil	1	Methy amyl acetate	2
Flexol	1	Methy amyl alcohol	3
Formic acid	1	Methy amyl ketone	1
Fuel oils	36	Methyl cellusolve	4
Gasoline	45	Methyl chloride (g)	5
Glycol (waste)	2	Methyl ethyl ketone	5
Heating oil	6	Methyl isobutyl ketone	4
Hexane (crude)	3	Methylmethacrylate	1

Compound	No. of Barges	Compound	No. of Barges
Mineral spirits	2	Sulfuric acid	9
Monoethanolamine	1	Sulfur dioxide (g)	1
Naphthol	13	Tallow	1
Naphthalene (s)	4	Tergitol	2
Natural gas (g)	1	Tetraethylene glycol	2
Niox polyols	1	Toluene	12
Nitrogen	1	Trichloroethane	2
Paraffin	8	Trichloroethylene	2
Pentaldehyde	1	Triethylene triamine	1
Perchloroethylene	1	Valeraldehyde	2
Phenol	2	Vinyl acetate	13
Potash	1	Vinyl chloride	1
Process gas	1	Xylenes (o, m, p)	5
Propane (g)	1		
Propanol	5		
Propionaldehyde	6		
Propionic acid	1		
Propylene (g)	9		
Propylene glycol	6		
Propylene oxide (g)	1		
Soda ash	3		
Soybean oil	3		
Styrene	26		
Sulfur (s)	7		

APPENDIX D

River Authorities and Other Organizations That Control Activities Along Rivers in Texas That Empty Into the Gulf of Mexico

John W. Simmons, General Manager
SABINE RIVER AUTHORITY OF TEXAS
P.O. Box 579
Orange, Texas 77630
(713) 883-9334

J. D. Nixon, General Manager
LOWER NECHES VALLEY AUTHORITY
7805 North 11th Street
Beaumont, Texas 77706
(713) 892-4011

William A. Elmore, General Manager
NECHES RIVER CONSERVATION DISTRICT
P.O. Box 387
Lufkin, Texas 75901
(713) 632-7795

Ralph Irvine, General Manager
UPPER NECHES RIVER MUNICIPAL WATER AUTHORITY
P.O. Box
Athens, Texas
(214) 876-2430

David Brune, General Manager
TRINITY RIVER AUTHORITY OF TEXAS
P.O. Box 5786
Arlington, Texas 76011
(817) 265-3151

C. W. Curry, General Manager
SAN JACINTO RIVER AUTHORITY
201 Darden Building
Conroe, Texas 77301
(713) 756-3723

Jack Davis, General Manager
GULF COAST WASTE DISPOSAL AUTHORITY
16915 El Camino Real
Houston, Texas 77058
(713) 488-4115

Col. Walter J. Wells, General Manager
BRAZOS RIVER AUTHORITY
P.O. Box 755
Waco, Texas 76710
(817) 776-1441

Charles F. Herring, General Manager
LOWER COLORADO RIVER AUTHORITY
3700 Lake Austin Blvd.
Austin, Texas
(512) 478-6401

R. G. Hallingsworth
CENTRAL COLORADO RIVER AUTHORITY
Box 964
Coleman, Texas 76834
(915) 625-2838

Gerald C. Allen
UPPER COLORADO RIVER AUTHORITY
Box 7
Robert Lee, Texas
(915) 453-2843

Owen H. Ivie, General Manager
COLORADO RIVER MUNICIPAL WATER DISTRICT
Box 869
Big Spring, Texas 79721
(915) 276-6341

W. R. Farquhar, Jr.
LAVACA-NAVIDAD RIVER AUTHORITY
P. O. Box 788
Edna, Texas 77957
(512) 657-2382

John H. Specht, General Manager
GUADALUPE-BLANCO RIVER AUTHORITY
P. O. Box 271
Seguin, Texas 78155
(512) 379-5822

E. C. Parker, Jr.
UPPER GUADALUPE RIVER AUTHORITY
P. O. Box 790
Kerrville, Texas 78028
(512) 283-4611

Fred N. Pfeiffer, General Manager
SAN ANTONIO RIVER AUTHORITY
430 Three A Life Building
118 Broadway
San Antonio, Texas 78205
(512) 227-1373

John White
NUECES RIVER AUTHORITY
114 East North Street
Uvalde, Texas 78801
(512) 278-6810