FEASIBILITY STUDY

FOR THE

TREATMENT OF SHIPBOARD GENERATED

OILY WASTEWATERS

A Thesis

Presented to

the Faculty of the Department of Civil Engineering

The University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Master of Science, MS EGR/10

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by

John R. Piskura

July, 1975

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ABSTRACT

The operation of ocean-going vessels, particularly tankers, results in the generation of certain types of oily wastes. The three principal categories of such wastewaters are 1) ballast water, 2) tank cleaning slops and 3) bilge water. Due to ever increasingly stringent pollution control regulations, discharges from ships must be of a sufficiently high quality to comply with legal standards in regards to oil content. The vessel operator must equip his ship with a system capable of treating the oily wastewaters.

In this thesis, the author examines the feasibility of using various physical/chemical processes as oil/water separation techniques. The treatment system had to function as an emulsion breaker as well since the action of ship motion and cleaning devices and pumps produces mechanical oil and water emulsions.

A filtration technique was studied and proved satisfactory within the limits of research. Oil removal can be accomplished producing effluents with oil concentrations less than 15 parts per million. The use of deep bed dual media filtration as a polishing device following gravity settling appears to be a promising application.

Recommendations for further research are made to refine the technique.

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CHAPTER 1

INTRODUCTION

General

Oil pollution has for many years been acknowledged as a major problem endangering public health, safety and our natural resources. Since the first federal legislation addressing the problem in the early 1920's, oil production has been one of the most regulated industries in the world. Since the Torrey Canyon spill off England in 1967, oil transportation (especially shipping and watercraft) has been the focus of considerable attention. Spectacular spills, however, are not felt to be the major contributor to oil pollution. Deliberate oil discharges from vessels are due to tank cleaning, deballasting and bilge pumping. According to Porricelli (1) tank barges, tankers and other vessels such as freighters and passenger ships account for 47 percent of the total amount of oil entering the world's oceans. The National Academy of Science (2) reports that nearly 2 million metric tons of oil a year enters the marine environment due to ocean transportation.

The purpose of this thesis to to define the nature of the contribution of watercraft to oil pollution, to study the individual sources of shipboard generated oily waste and to propose and evaluate a method to treat these oily wastes to minimize damage to the marine environment.

Sources of Shipboard Oily Wastes

The sources of shipboard oily wastes can be classified in three major categories:

1) Ballast water which is primarily related to tanker and tank barge operations;

2) Tank cleaning water which is also primarily related to tanker and tank barge operations; and

3) Bilge water which is associated with all manner of watercraft.

Ballast Water

Ballast water refers to the water which is used to fill the cargo tanks of a vessel to give that vessel the necessary draft and trim for safe maneuvering. Once the tanks have been emptied of cargo, a vessel floats high in the water. Ballast water gives the ship added weight to allow the propeller and rudder to be submerged to provide maximum control while underway. The water used as ballast can either be salt water or fresh water depending on the location of the ship whenever she is taking on ballast. The amount of ballast at any instant is at the discretion of the ship's captain and will vary depending on weather and sea conditions.

When the ballast water enters the cargo tank it mixes with the oil which was left clinging to the tank walls after the bulk of the cargo was pumped out. A quantity of oil is usually left in a pool on the tank bottom since it is virtually impossible to pump a tank completely "dry". Clingage factors have been estimated to vary from 0.1% of the tanks capacity for ships with specially coated tank walls to 0.4% for uncoated tanks. Clingage factors also vary depending on tank configuration and the nature of the cargo. But what this means is that a vessel with a cargo capacity of 100,000 tons could leave up to 400 tons of oil clinging to the tank walls and bottoms after the cargo has been offloaded. All this oil could conceivably be mixed with the ballast water.

Normal practice is to fill approximately one-third of the vessel's capacity with ballast water. Thus in the example of the 100,000 ton vessel, nearly 33,000 tons of ballast water would be pumped aboard. All this volume of liquid must then be discharged prior to loading.the next cargo. Unless special equipment was on-board or special techniques were utilized, the 400 tons of oil would escape into the sea when the ballast was discharged. This was exactly the case a number of years ago but, even with the legal restrictions and control practices (to be discussed later in this thesis), oil pollution due to ballast water discharge is still a significant problem.

Tank Cleaning Water

In order to facilitate ballast discharge, cargo tanks are often washed prior to ballasting. In this way, the tank carries "clean" ballast as opposed to oil contaminated or "dirty" ballast. Of course due to time and operation constraints not all tanks can be washed prior to ballasting, so dirty ballast continues to be a problem.

Cargo tanks must also be cleaned to prepare them for the next cargo if it is a higher grade than the last one. Tanks must be cleaned and freed of gases to permit men to enter the tank for repair work. A specialized machine is in use in the American tanker fleet for tank cleaning which consists of a rotating nozzle device which is fixed to the end of a flexible hose. Water under pressure enters the machine through the hose and exits as a jet from the nozzles. The nozzles rotate slowly horizontally and vertically; and as the machine is lowered into a cargo tank, the jets of water cover the entire interior surface of the tank. The machines are commonly referred to by the name of the manufacturer such as Butterworth, Gamlen and Vicjet (to mention a few).

As discussed above, the tank walls are coated with oil and as the oil is washed off the walls by the water jets it becomes highly emulsified. This mechanical emulsion proves a problem for oil/water separation. In some cases, the emulsion may be formed by the use of detergent tank cleaners. Such chemicals may be injected in the suction side of the "butterworth" pump in small dosages to aid in the cleaning process.

As an indication of the complexity of tank cleaning operations, Table 1 presents a chart developed through interviews with tanker operators showing the cleaning methods involved for various commonly carried petroleum products.

TABLE 1
TANK CLEANING PROCEDURES

Previous Voyage: / Present Voyage:	Aviation Gasoline	Automotive Gasoline	Light Diesel	Benzene Toluene	Solvent	Kerosene	Heating Oil	Light Lube Oils	#6 Fuel Heavy Diesel	Crude Oil
Aviation Gasoline	---	Cld BW	Cld BW	Cld BW GF	Cld BW	BW	BW S Dry	BW Spec	X	X
Auto Gasoline	S Dry	---	S Dry	Cld BW GF	S Dry	Cld BW	Cld BW	BW	X	X
Light Diesel	Cld BW	Cld BW	---	Cld BW GF	S Dry	S Dry	S Dry	BW	X	X
Benzene-Toluene	BW GF	BW GF	BW GF	---	BW GF	BW Spec	BW Spec	X	X	X
Solvent	Cld BW GF	Cld BW GF	Cld BW GF	Cld BW GF	---	Cld BW	R BW	BW Spec	X	X
Kerosene	Cld BW GF	Cld BW GF	Cld BW BW	Cld BW GF	S Dry	---	BW R	BW Spec	X	X
Heating Oil	Cld BW	Cld BW	Cld BW	Cld BW GF	S Dry	S Dry	---	BW	BW Spec	BW Spec
Light Lube Oils	BW NM	BW NM	BW NM	BW NM	BW NM	NM	NM	---	X	X
#6 Fuel Heavy Diesel	S Dry	S Dry	S Dry	S Dry	S Dry	S Dry	S Dry	S Dry	---	S Dry
Crudes	S Dry	S Dry	S Dry	S Dry	S Dry	S Dry	S Dry	S Dry	S Dry	---

NOTE: Procedure may vary for coated tanks.

TANK CLEANING PROCEDURES (continued)

LEGEND

BW	Hot Butterworth--strip dry
Cld BW	Butterworth with cold water--strip dry
S Dry	Carefully strip tank dry of all previous cargo or water
NM	No moisture--muck tank and wipe dry
Special	BW and muck tank and consult special instructions of shore personnel
GF	Gas free--pipes must be free of product or water
R	Remove rust and scale and rinse tank bottoms
X	Extensive cleaning required--impractical

The result of all the tank cleaning is a large quantity of tank washings containing emulsified oil and in some cases suspended solids. These tank washings must be processed in some manner to reduce the total volume to be retained on-board the vessel. In other words, the oil must be separated from the water to allow the bulk of the liquid to be discharged into the sea without pumping harmful quantities of oil along with it.

Bilge Water

The bilge system on-board a ship is designed to collect water from machinery drains and leakage from pumps, piping and machinery. For this reason, the bilge is the lowest interior portion of a vessel.

Most of the water resulting from condensation, drains and leakage is relatively clean prior to entering the bilge spaces. The amount of water generated per day varies according to operating conditions, machinery conditions, and the age of the vessel in question.

Contamination of bilge water results primarily from the introduction of different chemicals and oils, usually as a result of various leaks throughout the machinery spaces. The characteristics of bilge water can vary considerably but may be summarized as reported by Bruderly and this author (3) as having an oil content of normally between zero and one percent. Oil types may include fuel oil, diesel oil, hydraulic oil and lubricating oil. Solid concentrations average 400 parts per million.

Generally, the bilges are pumped down once a watch (every four hours) to prevent a large accumulation of water. This is done primarily because a water level much in excess of one or two feet in depth is usually sufficient to submerge some equipment in the engine spaces. Also, a relatively dry bilge space provides a margin of safety should a serious leak occur.

In the past, the bilge water with all its contaminants was pumped directly overboard into the sea. Now regulations are requiring some methods of preventing the discharge of oil.

Legal Restrictions and Requirements

Regulations impacting on oil discharges have been controversial in their intent and application. Adding to the confusion is the fact that marine vessels must comply not only with state and federal statutes but must meet international standards as well.

Federal Laws

The first U. S. law prohibiting oil discharges from vessels (which is still in effect) was the Refuse Act of 1899. The act requires U.S. Army Corps of Engineers' permits for any discharges into United States waters.

The first federal law to specifically address oil pollution was the Oil Pollution Act of 1924 which prohibited the discharge of oil from any vessel within 3 miles of the coastline. Gross negligence or willfulness had to be proven to enforce an action against a vessel owner.

Following some dramatic incidents, such as the Torrey Canyon in the late sixties, the question of oil pollution was again addressed by the Federal Water Pollution Control Act as amended in 1972. The 1972 Act prohibits the discharge, in harmful quantities, of oil into navigable waters of the United States. The Environmental Protection Agency has defined the term "harmful quantities of oil" to include all discharges which violate applicable water quality standards or cause a visible sheen upon the water. The oil sheen criteria has drawn much criticism because it is qualitative rather than quantitative. The visibility of an oil sheen depends to a large degree on the concentration of oil present in the receiving waters. For example, an effluent containing 10 parts per million of oil concentration may cause a sheen in a harbor if the harbor waters already contain trace amounts of oil. This is usually the case since harbor complexes usually include industrial discharges. The same vessel unable to discharge its 10 ppm effluent, in another location may be able to discharge an effluent with 20 to 25 ppm oil concentration and not violate the "visible sheen" criteria if the receiving waters are initially free of oil.

Beynon (4) has developed a chart to indicate the film thicknesses at which visible sheens appear. As shown in Table 2 a very thin layer of oil can produce a sheen.

Theoretically, just dropping an oily bolt overboard would be a violation of the law. Normal discharges of oil from a properly

TABLE 2

Characteristics of Oil Films

Appearance of Film	Film Thickness (10^{-3} millimeters)
Barely visible under most light conditions	0.05
Visible as silvery sheen on water surface	0.10
First traces of color observable	0.15
Bright bands of color	0.30
Colors begin to turn dull	1.0
Much darker colors	2.0

functioning engine such as an outboard motor are exempt. Oily bilge water, however, is covered by the law. With this criterion, discharging "clean" ballast within U.S. waters carries a risk of violating the law. Penalties can be quite severe.

International Regulations

Outside U.S. waters, international regulations as implemented by Congress rule the operation of marine watercraft. The current law in effect is the International Convention for the Prevention of Pollution of the Sea by Oil of 1954. The U. S. Oil Pollution Act of 1961 implemented this Convention. The Convention prohibited discharge of oil and oily mixtures within 50 miles of the nearest land. Vessels built after 1961 and over 20,000 gross tons capacity are prohibited from discharging oil or oily mixtures in all sea areas. Normal bilge pumping operations are exempted from restrictions of the Convention. Oil discharges are defined as 100 parts per million of oil or greater. Oil is defined as "persistent oil", (i.e. crude oil, fuel oil, etc.) as opposed to gasolines or kerosene.

In 1969 and 1971 amendments were made to the International Convention for the Prevention of Pollution of the Sea by Oil of 1954. Congress adopted these revisions in 1973. The amendments permit the discharge of oil only (1) if the vessel is proceeding enroute to its next port of call; (2) the discharge is at an instantaneous rate not exceeding 60 liters per nautical mile; (3) the oil content is less than 100 parts per million; and (4) the discharge is as far from the nearest shoreline as practicable. Further restrictions are placed on tankers while on the ballast leg of a voyage. The total amount of oil discharged in this case may not exceed one 15,000th of the total carrying capacity. In the case of our previous example of the 100,000 ton vessel with the 400 tons of oil "clinging" to the interior walls, only about 7 tons could be discharged to sea. This discharge must take place at least 50 miles from the nearest land as well.

Future Restrictions

In late 1973 another International Convention on marine pollution was held and some significant requirements were signed by the attending nations. These requirements do not have the force of law for U.S. vessels unless ratified by Congress. Ratification and implementation proceedings may take several years. The main points of the 1973 Convention concerning oil pollution are (1) that no discharges of oil or oily mixtures are permitted except at a distance of greater than 50 nautical miles from the nearest land while enroute to the next port of call; (2) the instantaneous rate of discharge must not exceed 60 liters per mile; (3) the total amount of oil must not exceed one 15,000th of the total cargo capacity for existing tankers or one 30,000th of the cargo capacity for tankers built after the Convention comes into effect; and (4) the discharge must be equipped with a monitoring device to record oil concentrations. Clean ballast discharges may contain up to 15 parts per million of oil.

Vessels other than tankers may discharge if the oil content is less than 100 parts per million if equipped with a monitoring device and an acceptable oil/water separation system. The Convention failed to define what sort of oil/water separation system would be acceptable.

The trend obviously is to stricter regulations concerning oil pollution on an international scale. Some questions exist whether the technology is available to keep pace with the legislation. In any case, the public outcry is to prevent oil pollution seemingly no matter how high the cost. Serious study is then called for to allow vessel owners to operate their vessels in light of the current and future legislation and restrictions.

CHAPTER 2

STATE OF THE ART - SHIPBOARD TREATMENT

General

Faced with stringent legislative restrictions, what options are available to vessel operators in order to comply with such laws? The alternatives can be broken down into two categories:

1.) Shoreside Treatment

2.) Shipboard Treatment

Shoreside treatment would require that all oily wastes be retained onboard the vessel for discharge to a shoreside reception facility. This alternative enables the tanker to comply with the most stringent anti-pollution objectives. However, it inherently requires that reception facilities be available in most ports and shipyards around the world. This is unfortunately not the case. The number of ports with adequate reception facilities is surprisingly small. The capital investment required to install such facilities would be tremendous. Many ports actually require that vessels arrive with only clean ballast, therefore the vessel operator has no choice but to clean his cargo tanks at sea.

Even where oily waste reception facilities are available, their capacity is limited. The huge quantity of ballast water would overload the systems if there were not some way to reduce the total amount.

This alternative transfers the problem from the vessel to the shoreside facilities. However, all any shoreside system can do is treat the wastes and discharge the effluent back to sea, most probably in the local harbor area. Conventional waste treatment is considered effective if the oil concentrations can be reduced to approximately 20 parts per million. The 20 ppm concentration discharged into the harbor zone may actually be more harmful than 100 ppm discharged by a tanker miles offshore. Thus for all the above mentioned reasons the value of the shoreside treatment option is questionable.

Since the vessel owner and operator cannot rely on shoreside facilities, he must depend on some method of shipboard treatment. The following section examines in detail, the state-of-the-art of shipboard treatment.

Shipboard Treatment

Perhaps the most widely used method for reducing the amount of oil discharged to sea by tanker operations is the "Load-On-Top (LOT)" procedure. Gray (5) estimates 75 to 80 percent of the world's tanker tonnage practice "Load-On-Top".

LOT consists of the following operations:

a.) After discharging her cargo, a tanker fills a number of her cargo tanks with the water on which the vessel is floating.

b.) The unballasted tanks are then washed with high pressure nozzles to remove the oil clinging to the tank's walls.

c.) The wash waters are pumped to a designated "slop" tank, which is usually one of the cargo tanks at the after end of the vessel.

d.) The now "clean" tanks are filled with sea water ballast.

e.) The "dirty" ballast tanks have now been allowed to stand so that some gravity separation has been allowed to take place. Ideally the oil should form a layer over the ballast water. The underlying clear water can then be "decanted" retaining the oily wastes in the tank. The decanted water is discharged to sea.

f.) The oily wastewater mixture remaining in the "dirty" ballast tank is pumped to the slop tank. The ballast tank is then washed with high pressure nozzles and the tank washings in turn are pumped to the slop tank.

g.) Once all washing is completed, the slop tank is allowed to settle so that the oil will form a layer over the top of the clear water. The water is then pumped overboard at a slow rate until the oil/water interface is reached.

h.) When the tanker arrives in port, the clean ballast can be discharged directly overboard. Since the slop tank essentially contains only oil, the next cargo can be loaded on top of the slops.

There are a number of difficulties associated with the load-on-top procedure. Even under ideal condidtions, unaided gravity separation will not consistently provide a clear water layer with oil concentrations much less than 100 parts per million. This is insufficient to meet most of the present legal standards.

Shipboard conditions are anything but ideal. Rough weather and sea conditions can have adverse effects on the gravity separation since as the ship rolls and pitches the oil will be remixed with the water.

Short voyages also impact on the quality of the oil/water separation. Short voyages may force vessel operators to accelerate the washing and decanting operations thus providing insufficient time to assure a clear liquid before decanting.

Problems also exist in detecting the oil/water interface. Most methods are after-the-fact approaches. The decanting is permitted until an oil discharge is seen and then the operation is halted. Under rough seas, an oil discharge may go undetected for a considerable length of time before the decanting is stopped. Electronic devices have been utilized to detect the interface but with little widespread success.

Another important factor detracting from the success of the load-on-top procedure is emulsification. The action of the vessel in the sea, the high pressure washing nozzles and the pumping operations tend to produce oil and water emulsions which do not necessarily respond to gravity separation. Centrifugal pumps (which are the most widely used type aboard tankers) possess the most serious emulsification characteristics compared to other pumps such as reciprocating pumps, screw pumps and diaphragm pumps.(6) Oil/Water emulsions also impact on many of the other shipboard treatment schemes.

It is appropriate to discuss some of the treatment technologies available in addition to the specialized gravity separation methods discussed above.

There are other types of gravity separation which depend primarily upon the difference between the specific gravity of the oil and water. This difference enables the free oil and oil globules to rise to the surface of the water. The rate of rise is the primary factor in designing gravity separators.

Gravity separation may be accelerated by the addition of heat. Heating influences the viscosity of the oily wastwater phases and increases the difference in the specific gravities of the oil and water components. Heat can also aid in breaking certain emulsions. The load-on-top technique discussed above is sometimes aided by steam heating coils in the bottoms of the cargo tanks.

Another approach to improving gravity separation is to reduce the distance the oil globule must travel to reach a collecting surface. This idea has been applied successfully to the treatment of refinery wastes. The accelerated gravity separation is accomplished by closely spaced inclined plates. At these multiple collection surfaces, the oil globules agglomerate, resulting in larger, faster rising globules. They then move up the underside of the plates and rise to the surface of the water. For shipboard use, a specially designed parallel plate separator could continuously process the flow of ballast water and tank washings.

Dissolved air flotation is actually a method of gravity separation. Minute air or gas bubbles are generated in the wastewater and as they float up through the liquid, the bubbles attach themselves to the oil globules. This causes a net reduction in the specific gravity of the oil globule and an increase in its rate of rise. The bubbles are produced by injecting air into the wastewater pressurized to 30 or 40 psig. Once the pressure is reduced to atmospheric, the supersaturated stream releases the excess dissolved air in the form of microscopic bubbles. A variation of this method is to aerate the wastewater at atmospheric pressure and then reduce the pressure by means of a vacuum to release the bubbles. Wybenga (7) has performed experiments with this method in the civil engineering laboratories at the University of Houston for barge cleaning operations.

Centrifugation is a form of oil/water separation which operates by imparting a rotational motion in the form of radial and axial energy to the fluid mixture. The centrifugal forces thus produced act on the density differential between the oil and water, causing the oil to centripetally migrate to the central portion of the rotating mass. Centrifuges are the most widely used in the marine industry to remove water from lube oil. Some attempts are being made to apply the principles of centrifugation on a larger scale for the treatment of bilge, ballast and tank washings.

There are three principal types of centrifuges. They are the tubular type, the basket type and the disc type. In the case of the tubular type, the oily mixture enters the bottom of a hollow barrel which rotates. Inside the barrel is a triple wing device that forces the liquid to rotate at the same speed as the bowl. The separated oil and water are discharged out the opposite end of the barrel from where the mixture enters.

In the basket type centrifuge, the oily mixture flows into an annulus between inner and outer baskets that rotate as a single assembly. In the annulus, the mixture is subjected to both radial and axial forces which separate the two liquids and direct them to a device at the opposite end of the concentric baskets which splits the flow into two separate streams. The separated fluids are then discharged through separate concentric pipes located along the centerline.

In the disc type, the oil/water mixture is directed through a stack of concentric discs. As the discs rotate, the oil and water are separated by the rotational forces acting on the thin oil/water films.

Vortex separation is a technique which takes advantage of the same rotational forces as centrifugation. Separation is accomplished by imparting rotational motion to an oil/water mixture contained in a non-rotating cylindrical container. A pump impeller imparts both axial and radial energy to the oily wastes contained in a length of pipe, causing the less dense oil to travel toward the center of the pipe and form a central core around which the water flows concentrically. The oil is removed via tubes in the center of the core.

Membrane separation is a technique which utilizes water repellent or water attractive membranes for oil/water separation. In the case of a hydrophobic or water repellent membrane, the media is preferentially wetted by the oil phases of the mixture. In the case of water attractive or hydrophilic membrane, the media is preferentially wetted by the water phase. The phase that is immiscible with that preferentially wetting or filling the capillaries of the membrane will be retained at the surface of the membrane.

Electric/Magnetic separation uses an oil soluble iron solution. This "ferrofluid" is insoluble in water and consists of stable dispersions of ferromagnetic particles. This ferrofluid is added to an oil and water mixture thus giving the oil phase magnetic properties. The mixture is then subjected to an electromagnetic field. The oil is attracted to the magnetic elements and the water passes through. When the magnetic elements are saturated with oil the current is shut off to the magnetic field and the oil can be washed out and collected.

Coalescers/Filters are devices that separate oil and water by lowering interfacial tension. Woven meshes, screens, mats and glass fibers have been used to physically break interfacial films. Primarily applications for such filters have been in the purification of fuel oils such as diesel oils and jet fuels by removing trace quantities of water.

Granular media can be used for oil and water separation. A number of different principles are at work in this case. Oil globules may be absorbed by the granular media allowing the water to pass through. If the oil is adsorbed until the media is saturated, coalesced oil globules may be formed through the media.

Some oil and water mixtures are actually emulsions which are stabilized by solids. A bed of granular media can filter the solids, rupture interfacial films and promote coalescense of the oil. The oil is removed from the bed by backwashing at a high rate.

CHAPTER 3

TREATMENT SYSTEM SELECTION AND EVALUATION

Selection of the Best Treatment System

Before selecting a treatment system for oily wastes, it is necessary to develop the characteristics on which the candidate systems are to be judged. A shipboard environment places strict requirements on the use of any pollution control device. The following are the criteria upon which the selection of an oil/water separation technique for shipboard use was based:

A. Safety

This factor is concerned with minimizing the risk to the crew and the vessel involved with the installation and operation of a system. Typical hazards might include the likelihood of fire or explosion or the hazards to personnel in handling chemicals and the like.

B. Space Constraints

Since a ship's purpose for the most part is to transport cargo, the space available for extra equipment is very limited, especially in the case of older vessels. The machinery spaces are designed to make maximum utilization of existing space for propulsion machinery and crew support equipment. Since oil pollution regulations have only recently come into effect, except in the case of the very newest ships, oil/water separation equipment must be added into whatever space is available to accomodate it.

C. Weight Constraints

As with space constraints, the weight of a system may have significant impact. The added weight may in fact necessitate a reduction in the cargo capacity of a vessel. This would be an important factor in the case of older vessels.

D. Stability

This factor is closely linked with weight and space constraints in that the placement of a system may affect the stability of the vessel. Stability refers to the characteristics of a vessel to right herself when acted upon by the forces of the sea. In other words, the tendency of a vessel to return to her original position after a force causes the vessel to roll. For the sake of stability, a system should not materially change the vessel's center of gravity.

E. Operability

This factor deals with how easily the system may be automated and what skill levels may be required for operating personnel.

F. Vessel Travel Characteristics

This factor refers to the requirements imposed on a treatment system based on the fact whether a vessel spends considerable time in port, in coastal waters or out in the open sea.

G. Effluent Characteristics

This is perhaps the most important factor. Some systems are incapable of producing an effluent of consistently high quality to meet the necessary legal requirements.

H. Reliability

This factor refers to the dependability of a system to operate with a minimum of down-time and maintenance requirements.

Before evaluating the candidate techniques against the various above mentioned factors, the criteria must be more closely defined by reference to a typical vessel. An ocean-going tanker was selected as being typical of the type of watercraft which would require an oil/water separation system. Based on discussions with vessel operators, the tanker S.S. Texaco Massachusetts was selected as a vessel representative of the domestic U.S. tanker fleet.

Table 3 lists the pertinent characteristics of the selected vessel. Space available for an oil/water separation device can be found in the engine room spaces with a surface area of about 50 square feet. Weight would not be a major consideration since the operating weight could be as much as 50 tons without any adverse effects. The crew aboard such a vessel carry U.S. Coast Guard certifications and should have skills necessary to operate most types of equipment. (However, automatic operation is a fairly important requirement for all shipboard equipment). The vessel spends a considerable amount of time in port and in U.S. coastal waters. A treatment system must therefore be able to consistently meet the requirement of producing an effluent which does not leave a visible sheen on the surface of the water.

TABLE 3

Pertinent Characteristics of a

Typical Ocean Going Tanker

Name	Texaco Massachusetts
Operator	Texaco Inc.
Date of Construction	1963
Length Overall	604 feet
Beam (i.e. width)	78 feet
Loaded Displacement	34,097 Tons
Cargo Capacity	26,500 Tons
Main Propulsion	Steam Turbine
Shaft Horsepower	15,000 H.P.
Percentage Time in Coastal Waters	30%
Crew Complement	40

Each of the available alternatives were then examined in light of the selection factors bearing in mind the typical conditions aboard the representative tanker. The purpose of this evaluation was to determine which technique should be selected for further research.

Gravity separation was eliminated from consideration due to the fact that the effluent characteristics of this technique are not acceptable. Most studies in the literature indicate that under good conditions an effluent quality of between 50 and 100 parts per million is the best that can be obtained.

Gravity separation is adversely affected by the roll and pitch of a ship and so even these concentrations cannot be guaranteed. In addition, gravity separation is a slow process requiring several days for acceptable results. A typical trip from an East Coast port to a Gulf Coast port is only five days. The primary use of gravity separation seems to be as a pretreatment step to remove the bulk of oil before polishing by means of one of the other techniques.

Dissolved air flotation is another technique that was eliminated from consideration for shipboard use because of the adverse effect of vessel motion. From a safety standpoint, the mixture of air and oil may produce hazardous vapors.

Centrifuges have been used to successfully remove water from oil, but the reverse process may prove much more difficult. The small density differences require large centrifugal force for separation, and the large amounts of oily wastes to be treated would result in heavy, high-power units. Centrifugation also becomes inefficient and uneconomical when the percentage of water in the mixture is large.

For this reason, centrifuges and vortex separators were eliminated from consideration.

Membrane separation meets nearly all criteria except reliability. If a breakdown of the system occurred at sea necessitating the replacement of a membrane, the repairs would probably be major. Membranes are susceptible to clogging and plugging; so, reliability may be a real problem.

Electro-magnetic separation presents an operational problem since it involves adding the correct dosage of ferrofluid to the wastewaters. The great quantity of liquid to be handled makes this method unattractive. Also the fact that additional material is added to the wastes in itself may present more problems when the oil is to be re-refined for reuse.

Coalescence/filtration appears to be the best candidate technique. Its major advantage is its relative insensitivity to the motion of the ship. Granular media adds the advantage of easy replacement of the filter media. Since bilge and ballast waters may contain suspended solids, granular media filtration is well suited to handle their removal. For these reasons, a granular media filter was selected as the technique to undergo study to see if the required effluent quality could be attained.

Evaluation of the Selected System

The objective of the research is to determine if passage through a bed of granular media can be effective in separating oil and water in waste typical of those found aboard ocean-going tankers.

To accomplish this, some pilot plant studies were undertaken. Prior to the studies, some of the theoretical aspects of the system were studied as discussed in the next chapter.

CHAPTER 4

THEORETICAL CONSIDERATIONS

General

To understand the functioning of the proposed method of oil/water separation, it is necessary to look at the theory of oil/water emulsions since emulsions are most likely to be encountered in shipboard generated oily wastes.

It is then also important to look at the mechanics of the filtration process itself.

Emulsion Theory

The type of emulsion most likely to be encountered with shipboard oily wastes is the oil-in-water emulsion. An emulsion is defined as " a stable dispersion of one liquid in a second immiscible liquid"(8). In the case of an oil-in-water emulsion, oil is the dispersed phase and water is the continuous phase. Emulsions are particulary troublesome in that they do not readily respond to gravity separation. Emulsions are formed by the mechanical agitation aboard ship by the action of pumps and high pressure tank cleaning nozzles. The hydraulic shearing stresses and impact stresses disperse the oil throughout the water phase.

To determine how to break an emulsion, it is necessary to learn what makes an emulsion stable. One of the most important elements in forming stable emulsions is surface tension. According to Berkman and Egloff (9), low surface tension at the interface between two liquids favors emulsification. In the case of two immiscible liquids such as oil and water, when agitation disperses fine globules of oil into the water, the surface of each liquid becomes greatly extended. The potential energy of the surface tension acts to reduce the surface area and undo the emulsion. If the surface tension is low then the chances the emulsion will be maintained is greater. Certain materials such as fine solids and chemical agents can lower surface tension and thus help to form stable emulsions. Solids are often found in crude oil which helps to explain why crude oil emulsions are generally stable.

Along with surface tension, the viscosity of the liquids has some effect on the stability of an emulsion. The viscosity of the liquid can decrease the rate of thinning of the film between the globules. Thus, coalescence can be retarded or prevented (10)

Another factor that is important to a discussion of oil-in-water emulsions is the size of the oil globules that are dispersed throughout the water. Berkman indicates that the maximum size of an oil globule found in a stable emulsion is one and a half microns in diameter, with the vast majority of the globules being much smaller. When globules are much larger than 1.5 microns, they tend to collide with each other and coalesce into still larger globules until soon the emulsion is broken as smaller globules are enveloped.

Some researchers claim electrical charges may influence the stability of an emulsion. Electrical charges on the surface of the globules would cause the globules to repel each other and thus prevent coalescence since the globules could not form larger globules. According to Becker (11) two electrically charged layers can be formed around a globule. The charged double layer constitutes a kind of spherical condenser with the radius being large in comparison to its thickness. Since each globule would carry a charge of the similar sign as they approach one another, they would be repelled and thus coalescence would effectively be prevented. Figure 1 is a visual interpretation of how the charged double layer might look.

Once a stable emulsion is formed, it may be broken either chemically or physically. Chemical methods are aimed at producing a change in the surface tension to promote coalescence. The most common means of chemically breaking an emulsion involves the addition of an acid or an acid salt such as alum, ferrous sulfate or ferric chloride (12).

Physical methods include heat treating and filtration. (13) Heat can be used to increase the difference in specific gravities of the liquids. The viscoscity of oil also changes according to temperature. At higher temperatures, the film surrounding the oil globule will thin, thus increasing the likelihood that globules will collide and coalesce as they rise in response to changes in specific gravity.

Filtration works to break an emulsion by forcing the liquids through the tiny passages in the filter media. By this action

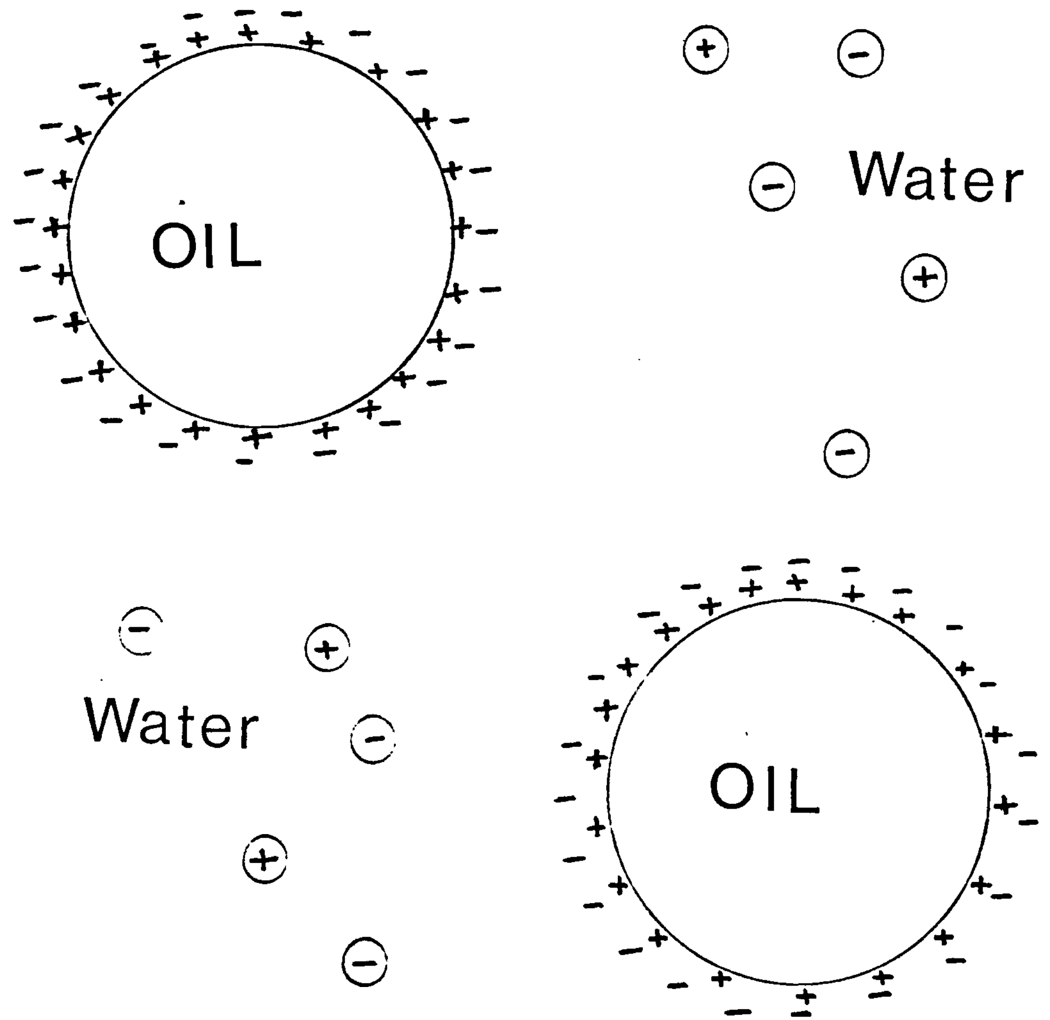

FIGURE 1

REPRESENTATION OF ELECTRICAL

DOUBLE LAYER

the particles are subject to the forces of direct impact and friction. Capillary action is also at work to some degree due to the small size of the openings through the media. The frictional resistance varies between oil and water due to their different viscosities. The thin film surrounding the oil globules can coalesce to form larger globules until finally the oil has been effectively separated from the water.

Process Description

The use of granular media for oil and water separation involves more processes than simple filtration. Besides filtration, adsorption and coalescence are at work to varying degrees to accomplish the separation.

The term filtration is generally used to refer to a solid-liquid separation process. In fact, deep bed filters were developed to remove solid contaminants from water back in the early 19th century. In the filtration of oily wastes, solid-liquid separation may be at work when the wastewater contains suspended solids (as is generally the case when crude oils are involved). However, in the filtering of oily wastes, the principal concern is with liquid-liquid separation. The process depends upon the difference in viscosities and specific gravities of the two liquids.

Filtration is not the major mechanism at work, however. The characteristics of granular media are such that there is a combination of physical, chemical, and molecular forces which attract the oil globules to the surface of the media. The adhering of the oil to the surface of the media is called adsorption. In some cases, the adsorption forces may be sufficiently strong in themselves to overcome the stabilizing forces of an oil-in-water emulsion and may lead to the breaking of the emulsion. However, the breaking of an emulsion is due to a combination of forces.

(As oil is adsorped by the media and the impact forces and friction rupture the envelope surrounding the oil globules, the globules are forced into intimate contact with each other and coalesce.)

The granular media selected for use in the filter affects the performance of the separator. Sand has most often been used by industry in the past. In a sand filter, the gradation of sand proceeds from the finest at the top to the coarsest at the bottom. This means that during operation with the flow moving downward through the sand, filtration occurs only in the upper portion. As the particles proceed down through the bed, they encounter coarser sand and the associated larger voids. To overcome this drawback several media may be used. A dual media filter consists of a layer of sand capped with a layer of anthracite coal. The coal has a lighter density than sand and thus remains on top of the sand except for some intermixing at the interface of the two materials. Figure 2 indicates such a filter (14). Anthracite coal is used because it is preferentially wetted by oil. When two liquids meet a solid, one liquid will displace the other from the surface of the solid due to its greater specific molecular attraction for the solid.

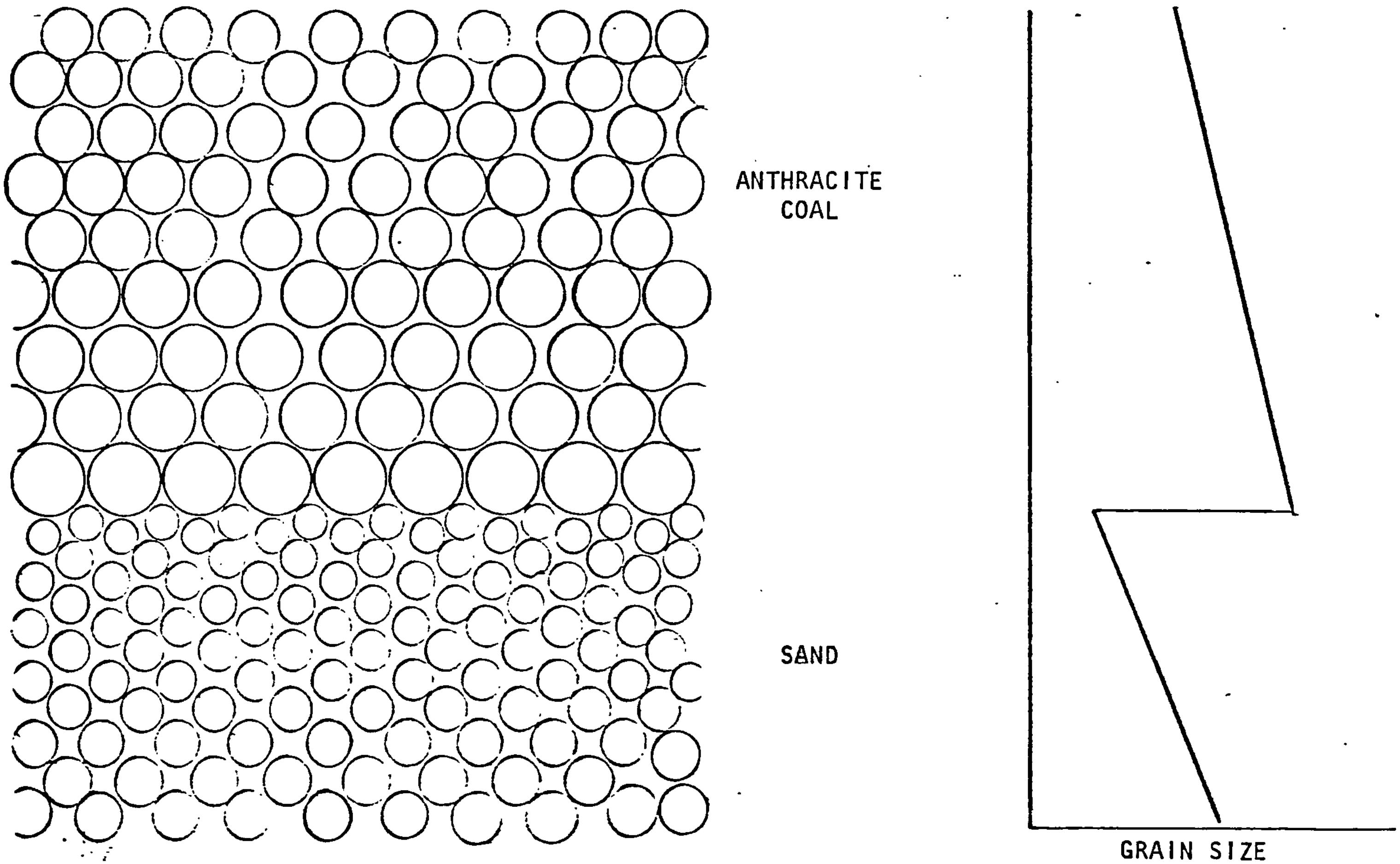

FIGURE 2

RELATIVE GRAIN SIZE DISTRIBUTION -

DUAL MEDIA GRANULAR FILTER

As an oil globule enters a bed of granular media, opposing forces are set up. One set of forces seeks to dislodge the globule from the granular bed and another set seeks to retain it. The retention force will be greater if the particular granular media is preferentially wetted by oil rather than by the water phase.

The dislodging force is a function of the volumetric flow through the bed or the pressure drop across the bed. So, an oil globule is more likely to be retained on a surface that is preferentially wetted by oil and thus more resistent to the dislodging forces.

Bed flux is the volumetric flow through a granular bed measured in gallons per minute per square feet. Typical rates for granular media filters range from 3 to 5 gallons per minute per square foot. Excessive hydraulic loading can result in oil being dislodged and carried through the bed.

In the operation of a deep bed granular filter oil globules accumulate in the bed until a certain pressure drop across the bed is reached which would make it ineffective to keep pumping due to the pressure build-up. When the pressure drop is reached or a specified time has elapsed, a backwash cycle is initiated. Backwashing involves pumping liquid in the opposite direction than that for filtering. The backwash cycle operates with a high flow rate which results in the expansion of the bed and produces a scrubbing action to remove the accumulated oil. Air may be used as well to provide additional scouring. The backwash wastes can then be collected and disposed of in an appropriate manner.

For experimental purposes, filtration runs are continued until breakthrough occurs, that is until the pressure drop is great enough or until the bed becomes so saturated that coalesced oil globules are carried through the bed and into the effluent stream. According to Hudson (15) breakthrough depends upon the flow rate, the depth of the granular media and the effective size of the media. He developed a formula for estimating the critical pressure drop at which breakthrough would occur.

$$H = CL/Vd^3$$

Where:

H = pressure drop at breakthrough in feet

C = constant representing resistance of filtered material to shear forces

L = bed depth in feet

V = bed flux in gallons per minute/square feet

d = effective size of media in millimeters

This formula was developed specifically for the filtration of solid particles and has not been refined to account for the filtering of liquids such as oil since this is a relatively new application.

Although by no means exhaustive, this discussion of the theoretical principles involved is meant to clarify what processes would be at work during the experimental studies. The experimental work is to test the feasibility of using the technique for one particular application. In-depth theoretical discussions can be found by referring to authors such as Purchas, Tchobanogolous and Tiller.

CHAPTER 5

TEST PROCEDURES AND RESULTS

Description of the Equipment

In order to evaluate the effectiveness of dual media deep bed filtration to separate emulsified oil and water, a test column had to be constructed. Two 30 inch long glass columns, two inches in diameter were connected. Twenty four inches of quartz sand with an effective particle size of 0.5 millimeters was topped with 18 inches of anthracite coal with an effective particle size of 1.8 millimeters. The column was equipped with copper tubing so that liquid could be pumped either to the top of the column or the bottom. Figure 3 shows the equipment layout. A more detailed description of the equipment can be found in the Appendix. The discharge from the column flowed into an observation basin to see if any oil in the effluent would form a visible sheen on the surface.

Studies Undertaken

Laboratory tests using the test column were undertaken. A sample of crude oil was obtained from a major oil company as being most representative of the type of oil transported by large ocean-going tankers. This oil was used to form oil in water emulsions mechanically in the laboratory for testing.

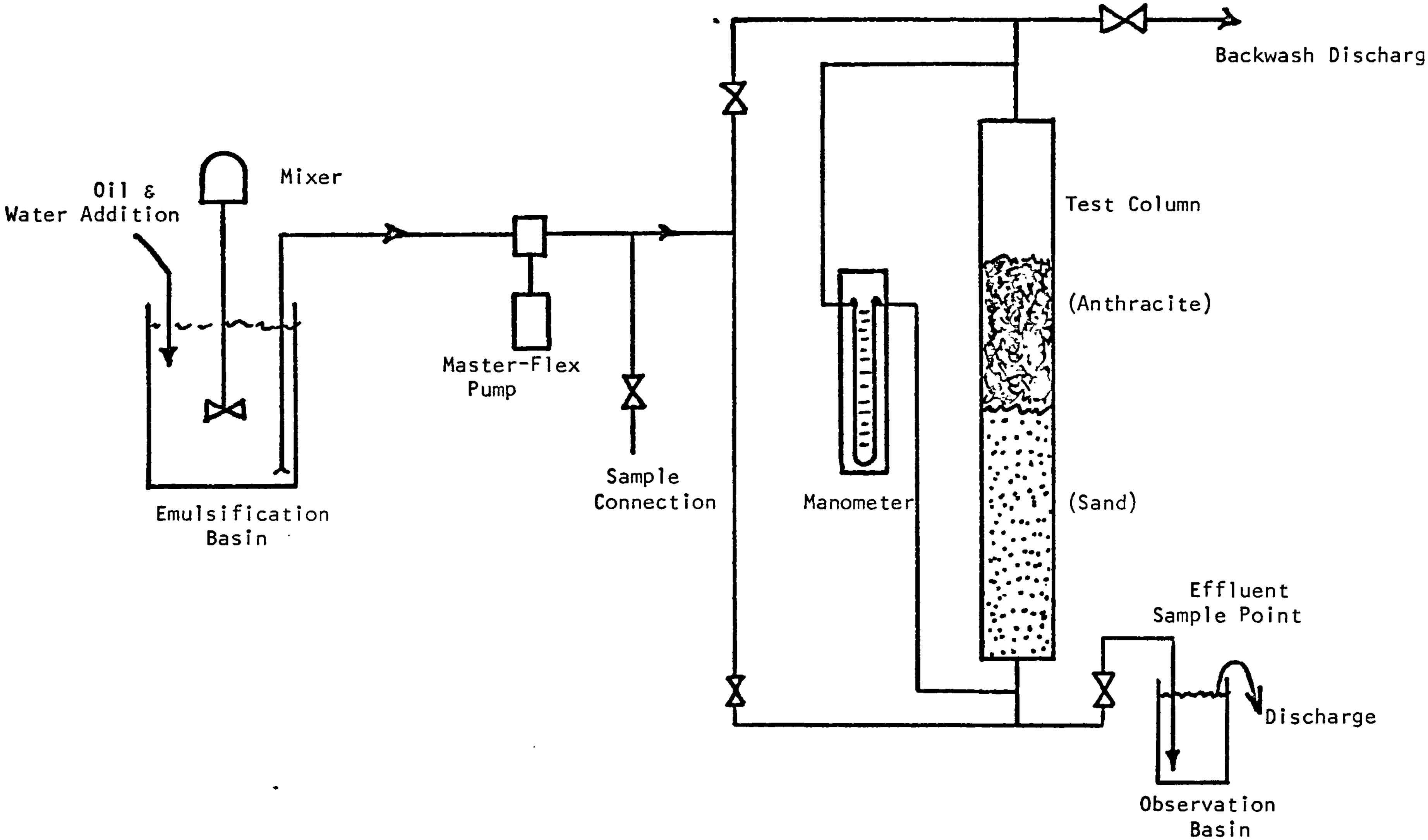

FIGURE 3

TEST EQUIPMENT CONFIGURATION

Since it was anticipated that a very large number of analyses of oil content would be required in this study, it was decided that the standard analysis for oil and grease would be too complicated and time consuming for the purposes of the experimental studies. Based on the success other researchers have had when faced with this problem, the test for chemical oxygen demand (COD) was selected to be the prime analytical method (16). To utilize the COD results an equivalency curve had to be established to convert the COD readings to oil concentrations. The development of the COD equivalency curve is discussed in the Appendix.

Laboratory studies involved numerous filter runs varying the flow rate and the influent oil concentrations. Several runs were conducted with the addition of fine solids to test the effectiveness of the column when solids had to be removed as well as the oil. All the above mentioned tests involved the use of solutions made in the laboratory.

To test the technique on an actual situation, a quantity of tank cleaning slops was obtained from an ocean-going tanker in the port of Houston. Two test runs were performed on this material. The results from these last runs are subject to some interpretation since the COD analysis could only give qualitative data due to the possibility that the slops contained other oxygen demanding materials besides oil.

Test Results

Run No. 1 was made at a flow rate of approximately 5 gallons per minute per square foot of bed cross sectional area (gpm/sq.ft.). This rate was chosen based on accepted rates in industry for a deep bed filter in other applications (17). Influent oil concentrations were maintained at approximately 100 parts per million (ppm) which as stated in a previous chapter was the best quality that could be expected after gravity settling. The liquid was pumped to the top of the column and then allowed to flow down through the media.

Samples of the effluent were taken initially every fifteen minutes. As the operation stablized, samples were taken at intervals of 30 minutes. The flow rate through the column was checked every half hour and the speed of the pump was adjusted accordingly to maintain the desired flow rate.

Figure 4 is a plot of oil concentrations in the effluent over the duration of the test run. Except for the first minutes of the run, the oil concentrations seemed to remain below 10 ppm. No traces of a visible sheen were seen in the observation basin. The average oil concentration for the run was 6.7 ppm vs. 100 ppm applied.

The test run was continued for a total period of eight hours. As the oil was adsorped in the bed the pressure drop increased slightly. Figure 5 indicates that by the end of the run the pressure difference across the media was approximately 4.5 inches of mercury or about 2.2 pounds per square inch. The pressure

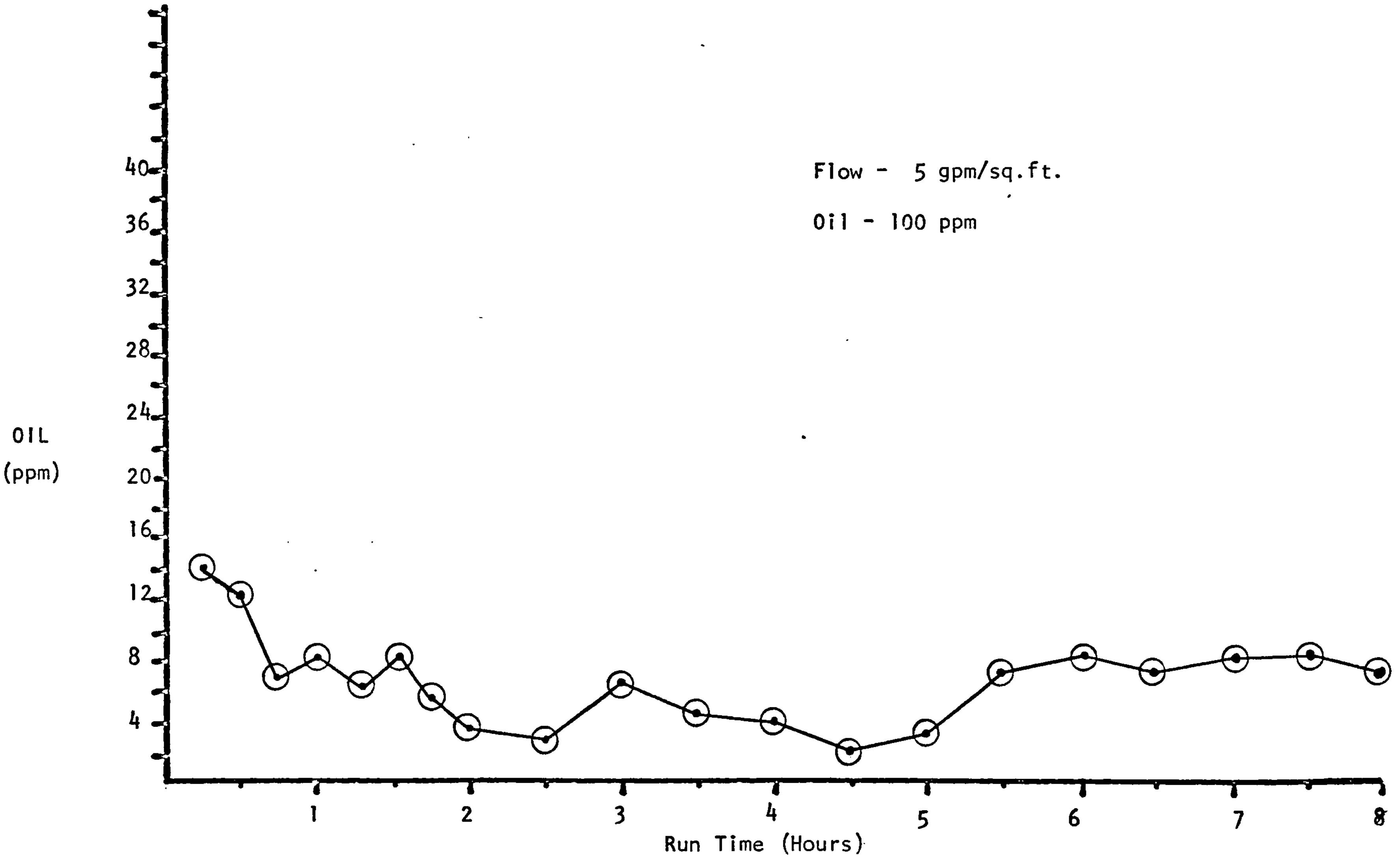

FIGURE 4

TEST RUN #1

OIL CONCENTRATION vs. RUN TIME

buildup required adjustments to the pump speed. With these adjustments the flow rate was maintained at an average of 5.04 gpm/ sq. ft.

At the end of the run the filter was backwashed at 15 gpm/sq. ft. until it appeared that all the entrapped oil had been removed from the bed. During the run, the oil had penetrated about three-quarters of an inch into the anthracite layer. After backwashing there was no visual evidence of oil in the coal layer. The total volume of backwash water amounted to 26 liters or about 13% of the total volume of liquid filtered through the column.

During the backwash cycle, the bed expanded to approximately 130% of its original depth.

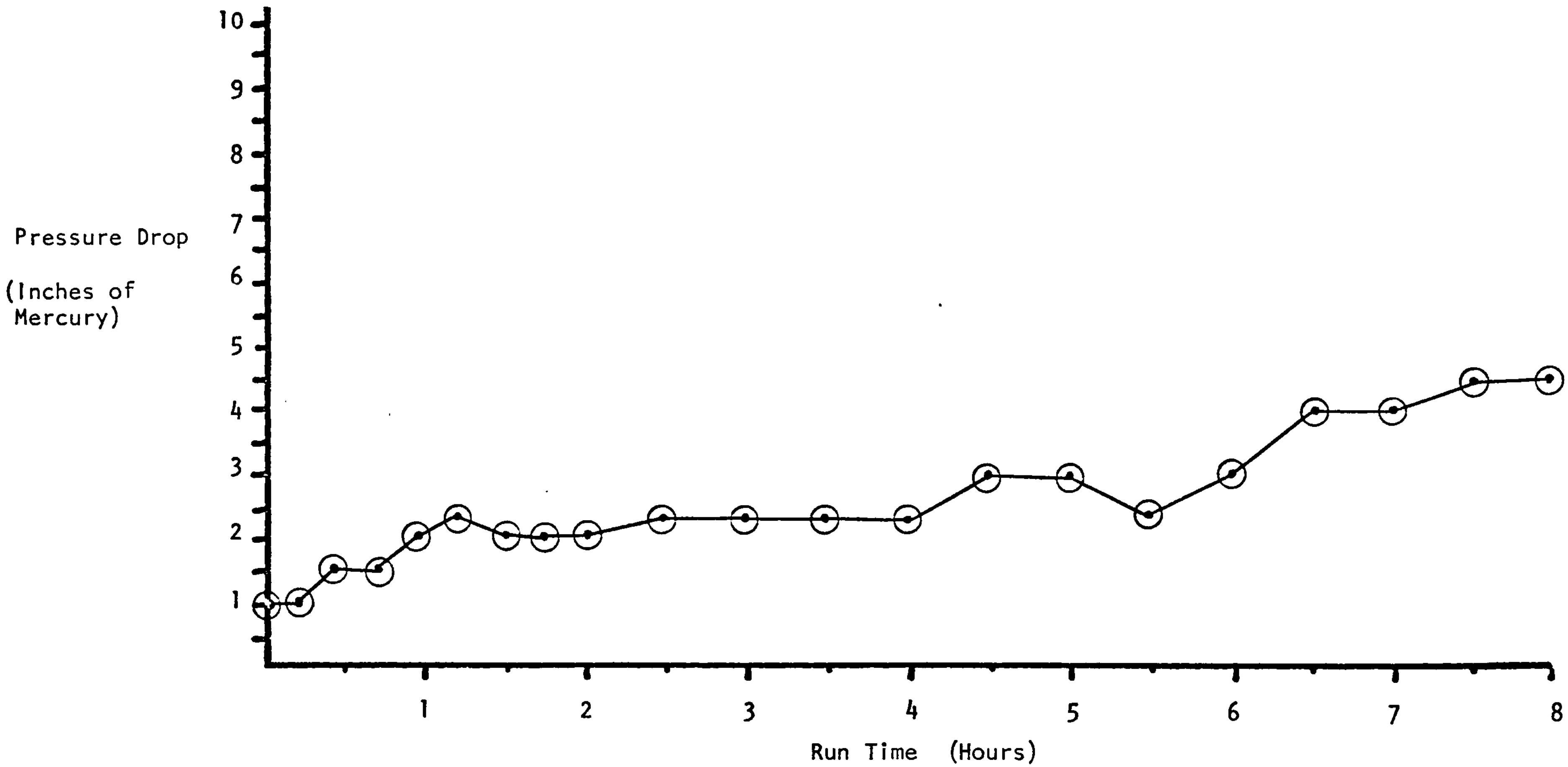

FIGURE 5

TEST RUN # 1
PRESSURE DROP VERSUS RUN TIME

Run No. 2 was made at the same flow rate as the previous run, however, the oil concentration of the wastewater to the column was increased to approximately 200 ppm.

As before, samples of the filtrate were at first taken every 15 minutes and then every 30 minutes. The flow rate was checked and adjusted at the same time that the samples were taken to maintain the desired flow rate.

Figure 6 indicates how the oil concentrations varied over the duration of the run. Although there appears to be some fluccuation, after a period of one hour, the concentrations remained between approximately 16 and 8. The average concentration for the entire run was 12.4 ppm. Visible traces of oil were seen in the observation basin immediately after start-up and then once again approximately one and one half hours later.

This test was continued for a period of 12 hours in an attempt to see if the buildup of oil would be great enough to break through the column with carryover into the effluent. No such breakthrough was observed.

Figure 7 shows the gradual pressure build-up in the bed over the duration of the test run. By the end of the 12 hours, the pressure drop across the filter bed had risen to approximately 8 inches of mercury or about 4 pounds per square inch. Even with this pressure drop by adjustment of the pump speed, the flow rate was maintained at an average rate of 4.99 gpm/sq.ft.

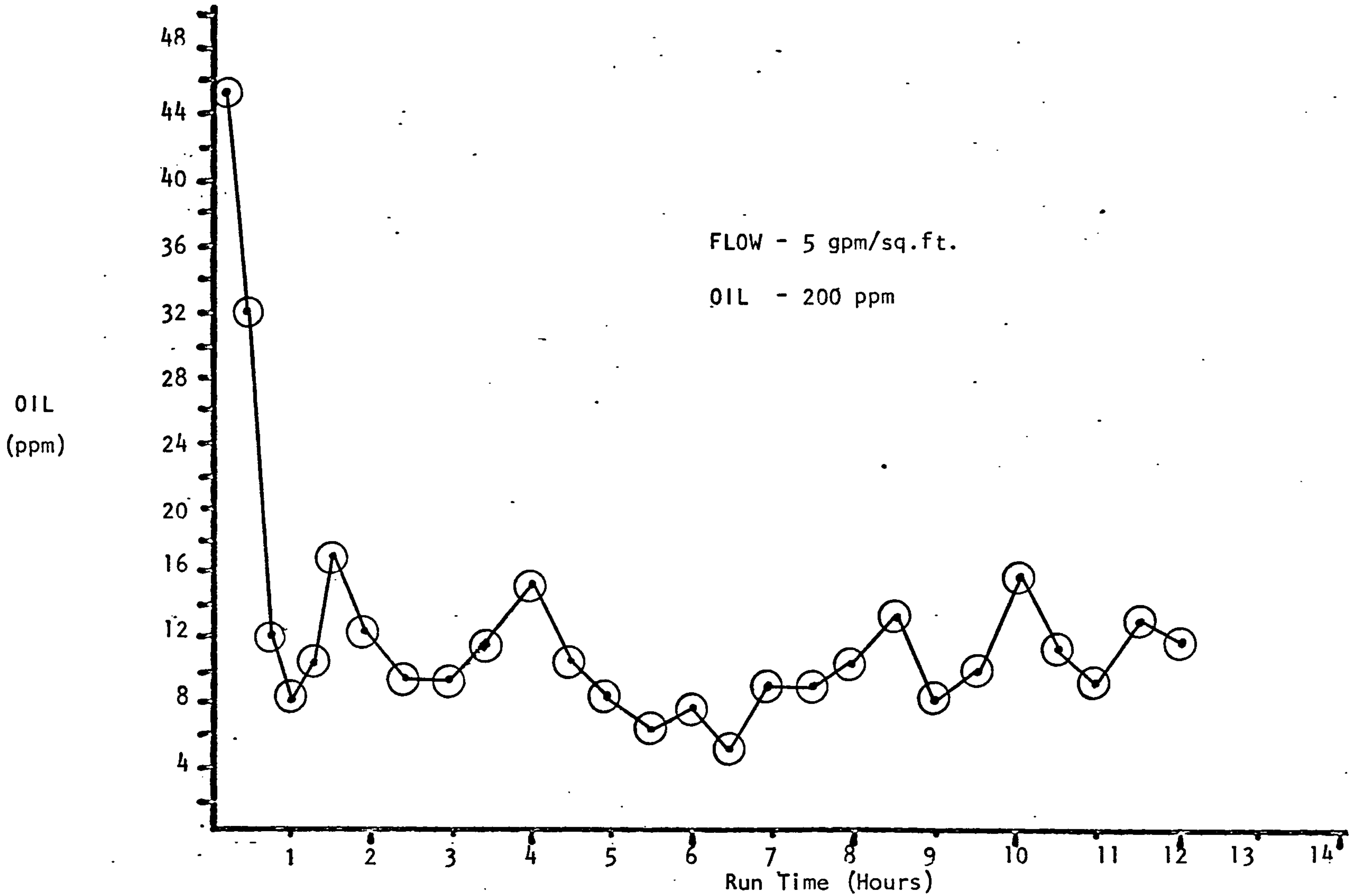

FIGURE 6
TEST RUN # 2
OIL CONCENTRATION VERSUS RUN TIME

At the end of the run the filter column was backwashed at a rate of 15 gpm/sq.ft. A backwash volume of 32 liters was required until all the oil was satisfactoryily removed from the bed. This amounted to about 11% of the total volume of liquid filtered through the column.

Bed expansion during backwash was similar to Run No. 1.

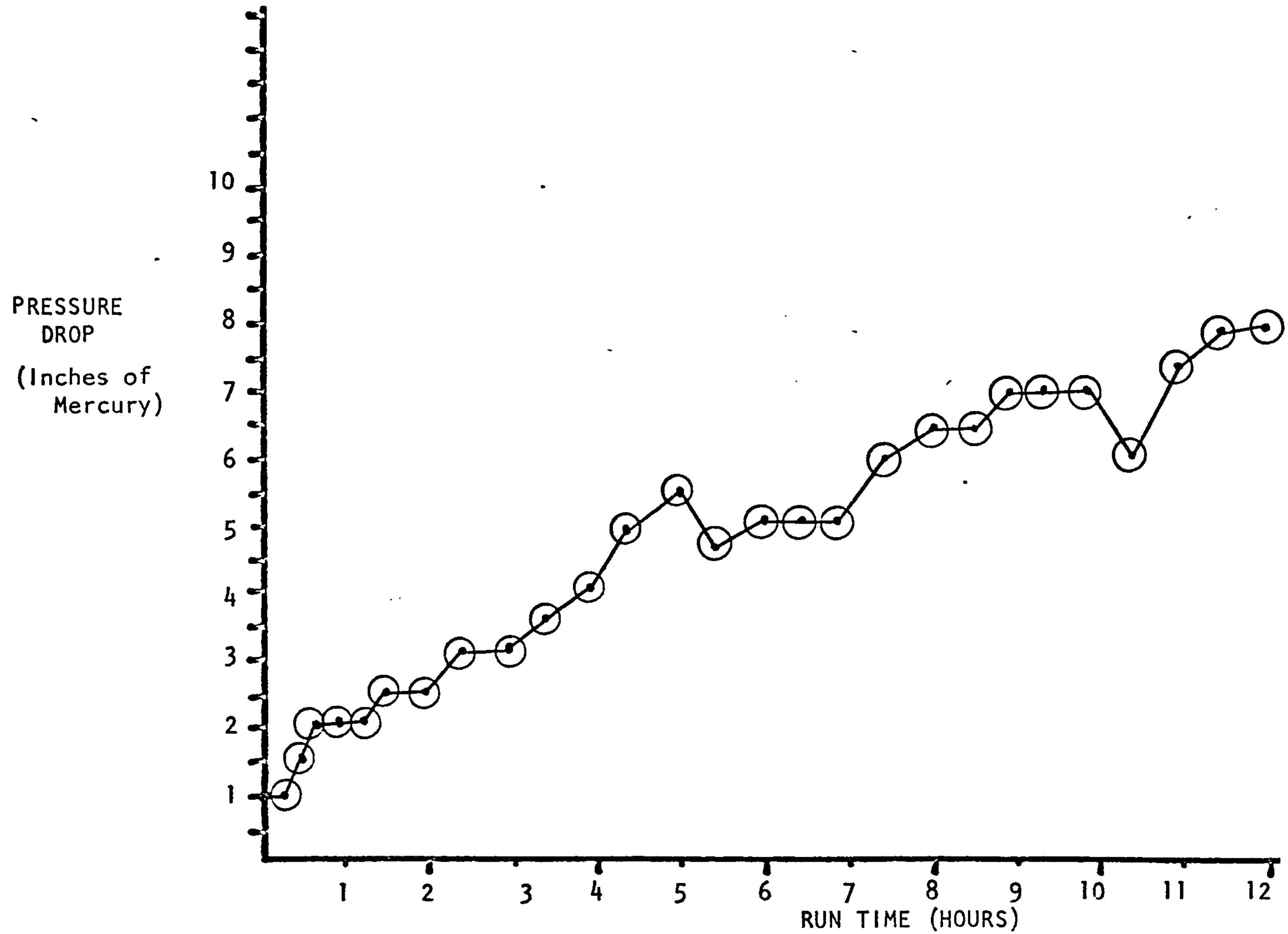

FIGURE 7
TEST RUN #2
PRESSURE DROP VERSUS RUN TIME

Run No. 3 was conducted to evaluate how the filter column would perform at an increased flow rate. The flow rate was maintained at 10 gpm/sq. ft. with an influent oil concentration of 100 ppm.

Samples of the treated effluent were taken every 30 minutes. The flow rate was adjusted periodically to maintain the desired flow as the pressure differential across the bed increased.

Figure 8 show the variations in effluent oil concentrations over the period of the test run. For the first hour and a half the oil concentrations appeared relatively high and traces of oil were visible in the observation basin. After 2 hours, the effluent concentrations dropped to lower levels and there was no visible sheen in the observation basin. The concentration of oil showed a gradual increase until it approached an approximate value of 16 ppm at the termination of the experiment. The average flow rate for the 8 hour test was 9.9 gpm/sq.ft. and the average oil concentration was 13.5 ppm.

Figure 9 indicates that during the test run the pressure drop across the filter media gradually increased. At the end of the experiment the pressure differential was approximately 15 psi.

The column was backwashed at a rate of 15 gpm/sq.ft. A total volume of 40 liters was required until the bed was judged to be clear of oil. This time the backwashing was supplemented by bubbling air through the column to aid in scouring the bed.

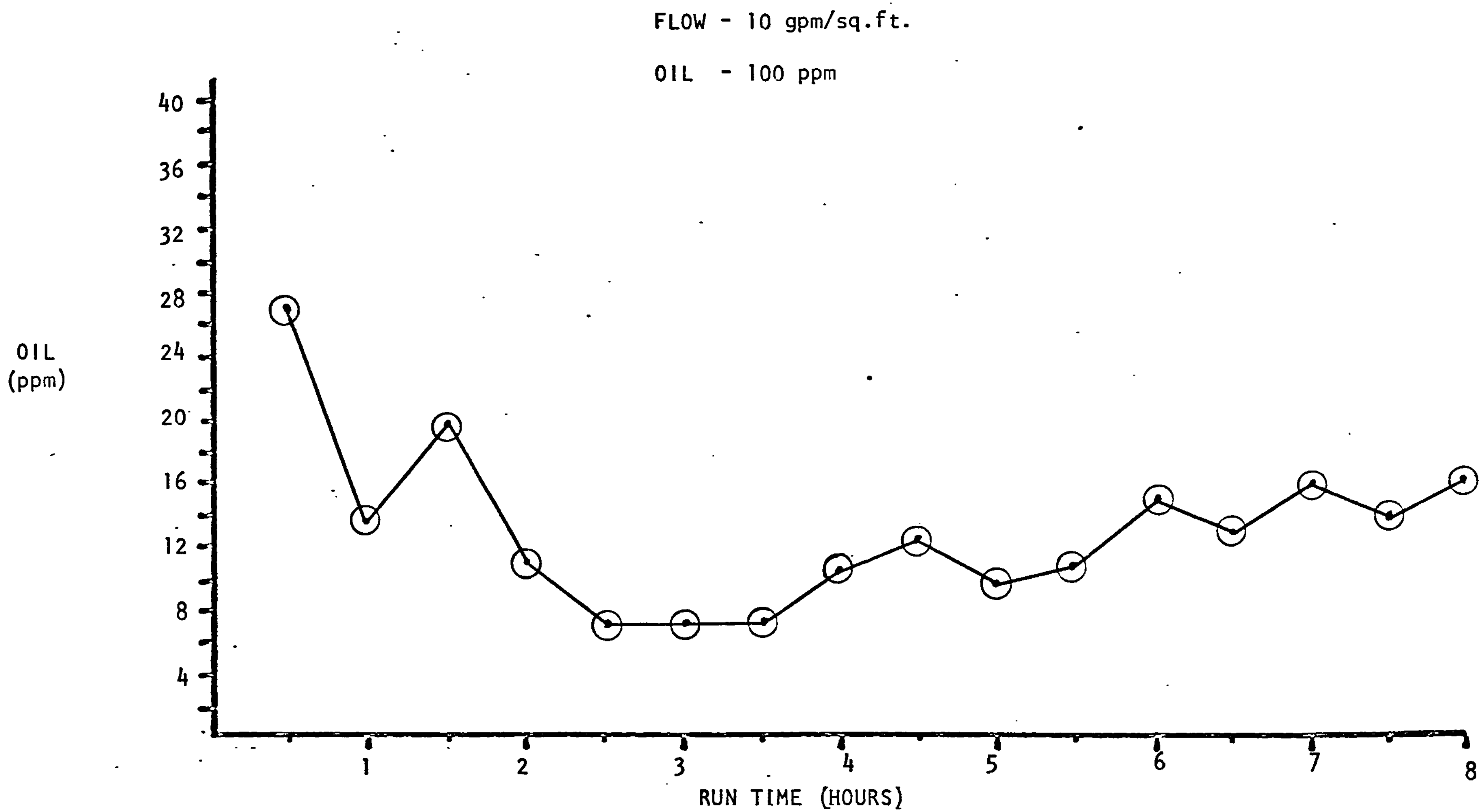

FIGURE 8
TEST RUN #3
OIL CONCENTRATION VERSUS RUN TIME

With the addition of this technique, it is believed that the amount of water needed was somewhat reduced. (A more thorough air volumetric study with rotameter measurements will establish this relationship). The backwash liquid amounted to 10% of the total volume of liquid filtered through the column.

Bed expansion due to the addition of air was slightly more than in previous runs amounting to about 140% of the original depth.

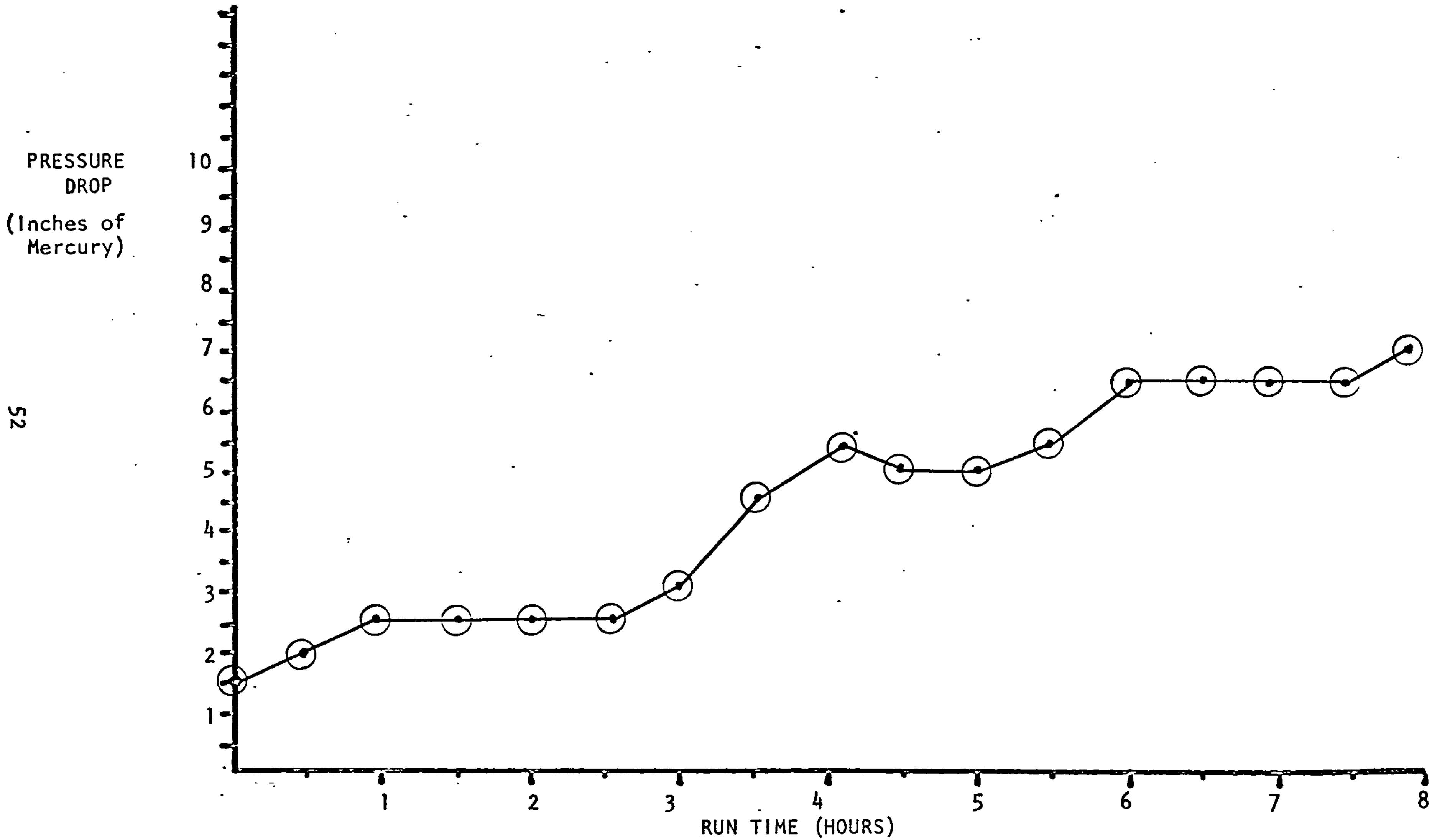

FIGURE 9
TEST RUN #3
PRESSURE DROP VERSUS RUN TIME

Run No. 4 was made at the same flow rate as that for the previous run since it seemed possible that the column would perform at the higher loading. The influent oil concentration was increased to 200 ppm.

Samples again were taken at intervals of 30 minutes with flow adjustments being made at the same time.

As shown in Figure 10, the initial oil concentration was quite high but quickly dropped to 10 ppm or less. After 3½ hours of operation, the effluent concentrations increased considerably and a sheen was observed on the surface of the water in the observation basin. After this point of break-through the oil concentration never dropped significantly and the test run was terminated after 6½ hours. The average oil concentration for the test was about 19.8 ppm.

Figure 11 indicates how the pressure drop across the bed varied for the run. The pressure increase necessitated adjustments to the pump speed to maintain an average flow rate of 10 gpm/sq. ft.

The column was backwashed at a rate of approximately 15 gpm/sq. ft. in combination with occasional intervals of air. The backwash volume required was 36 liters which represented 11% of the total filtered volume.

Bed expansion was similar to the previous run.

A comparison between Figure 8 (100 ppm oil, 10 gpm/sq. ft.) and Figure 10 (200 ppm oil, 10 gpm/sq.ft.) indicates the residual oil concentration increases considerably when the 100 ppm is applied vs the 200 ppm is applied. (In other words, after 7½ hours, the residual oil was 7 vs. 3 for the two initial concentrations).

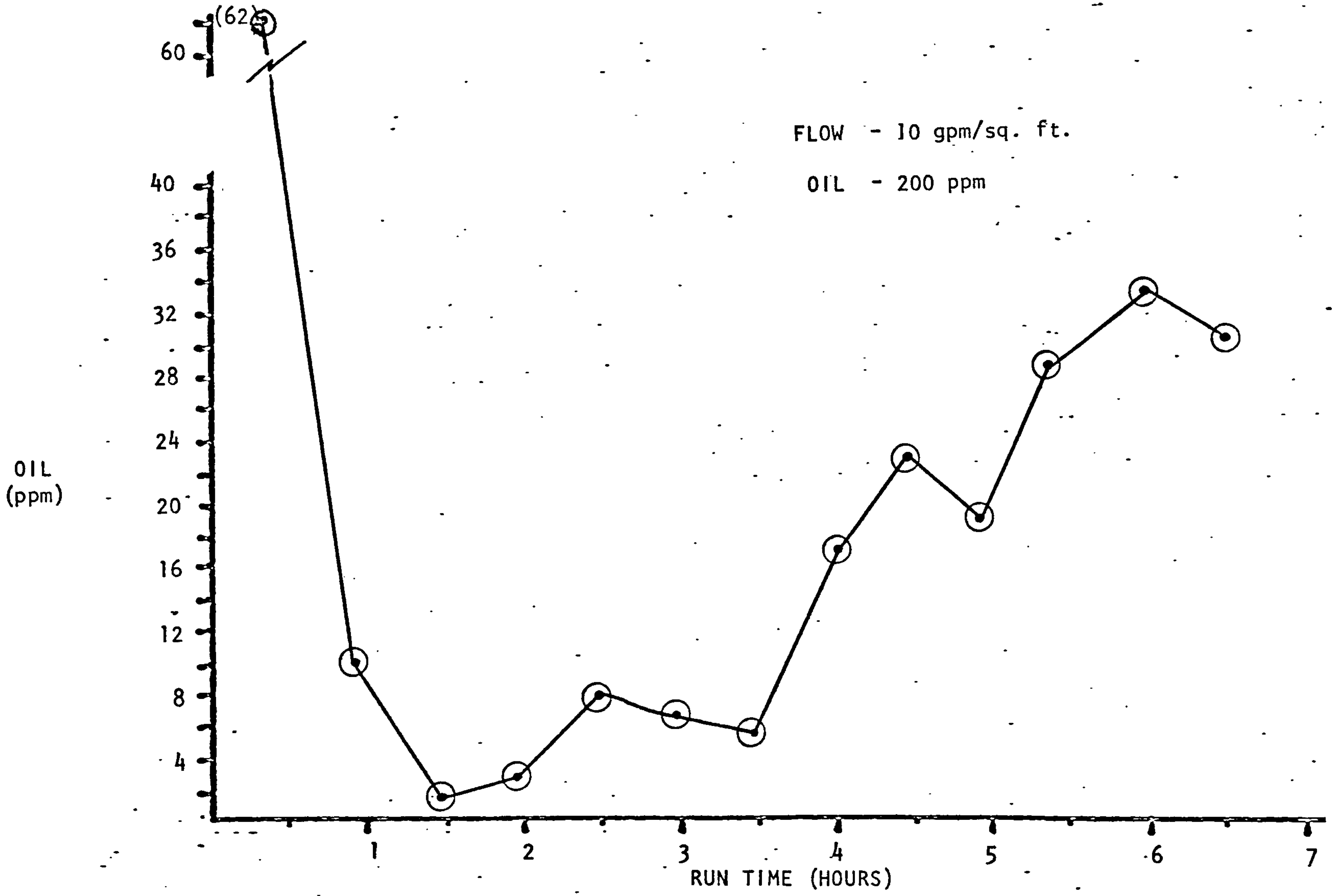

FIGURE 10
TEST RUN #4
OIL CONCENTRATION VERSUS RUN TIME

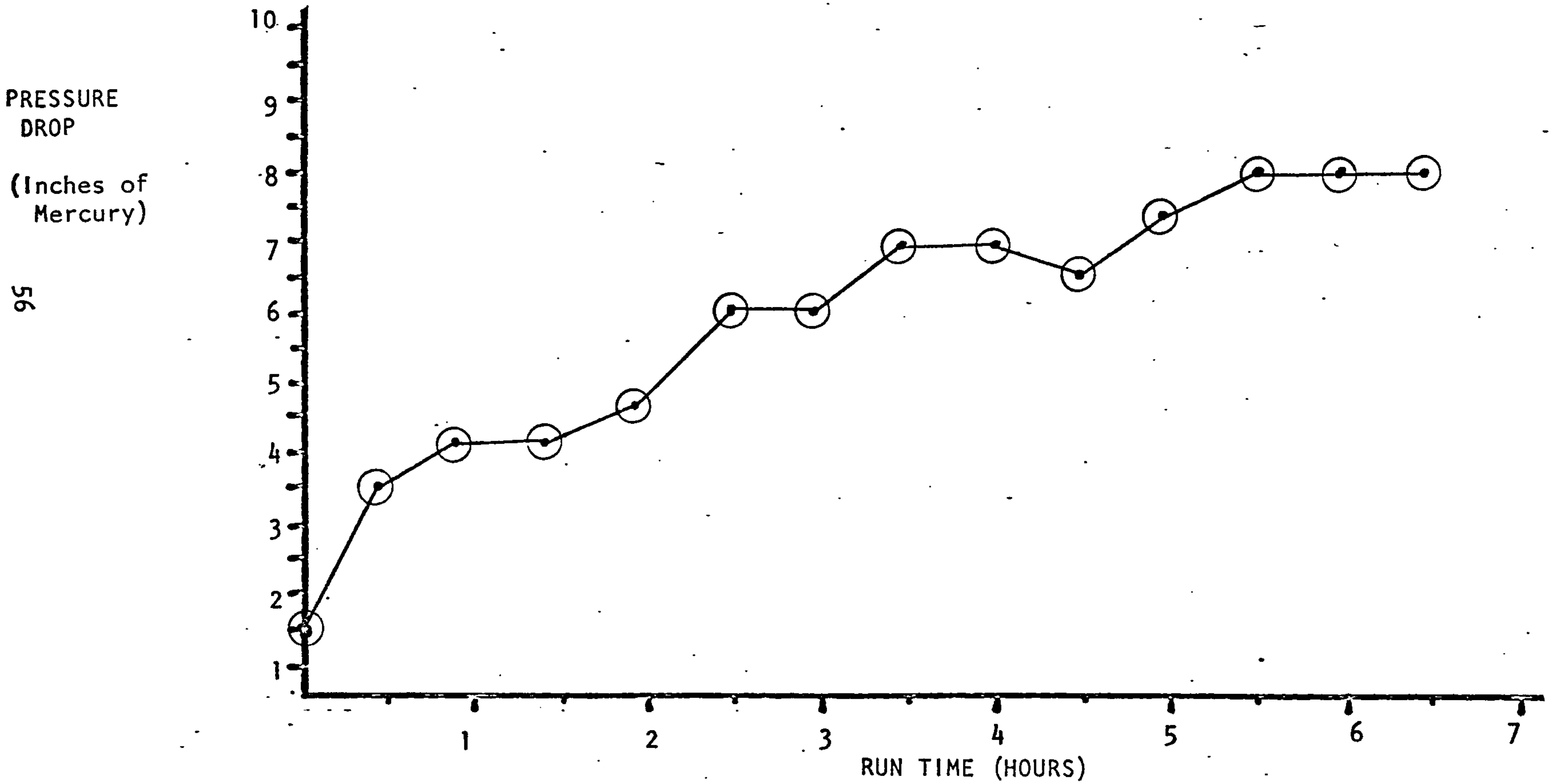

FIGURE 11
TEST RUN #4
PRESSURE DROP VERSUS RUN TIME

Run #5 was made at a flow rate of 5 gpm/sq. ft. with an oil concentration of 100 ppm. This time, however, solids were added. Fine solids can help stablize oil-in-water emulsions and are often found in crude oils. Fine bentonite clay solids were chosen for the experiment due to their dispersion characteristics and the fact that they were basically inert. A concentration of 50 ppm was maintained in the influent to the test column.

As shown in Figure 12 oil concentrations tended to remain low. At no time during the duration of the test was a sheen visible in the observation basin. The average oil concentration was approximately 6.1 ppm.

Figure 13 shows that the pressure drop across the bed increased significantly during the run. After 8 hours the pressure differential was approximately 14 psi. The average flow rate was 4.9 gpm/sq. ft.

The column was backwashed at a rate of 15 gpm/sq.ft. in combination with air. A total volume of 27 liters was generated during the backwash operation which represents 14% of the total filtered liquid.

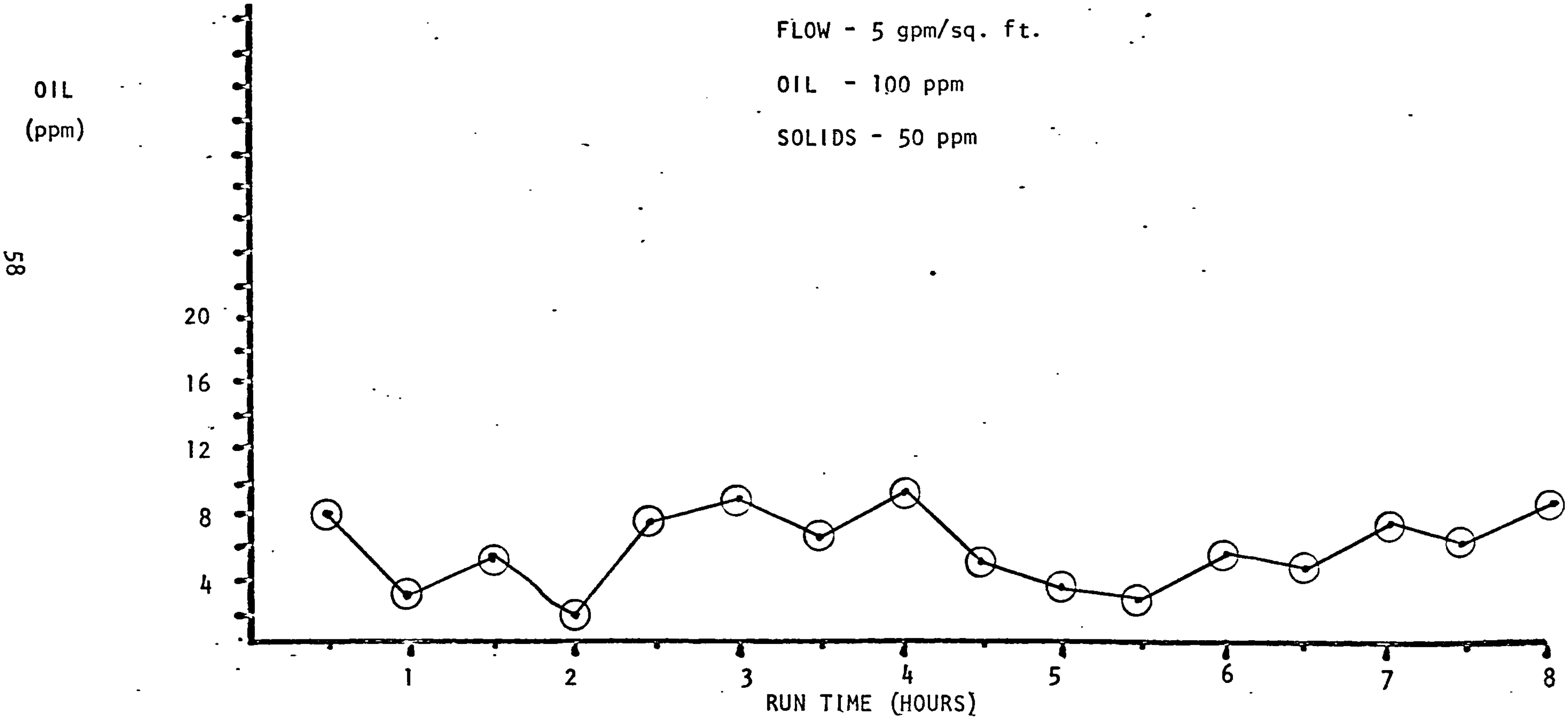

FIGURE 12
TEST RUN # 5
OIL CONCENTRATION VS. RUN TIME

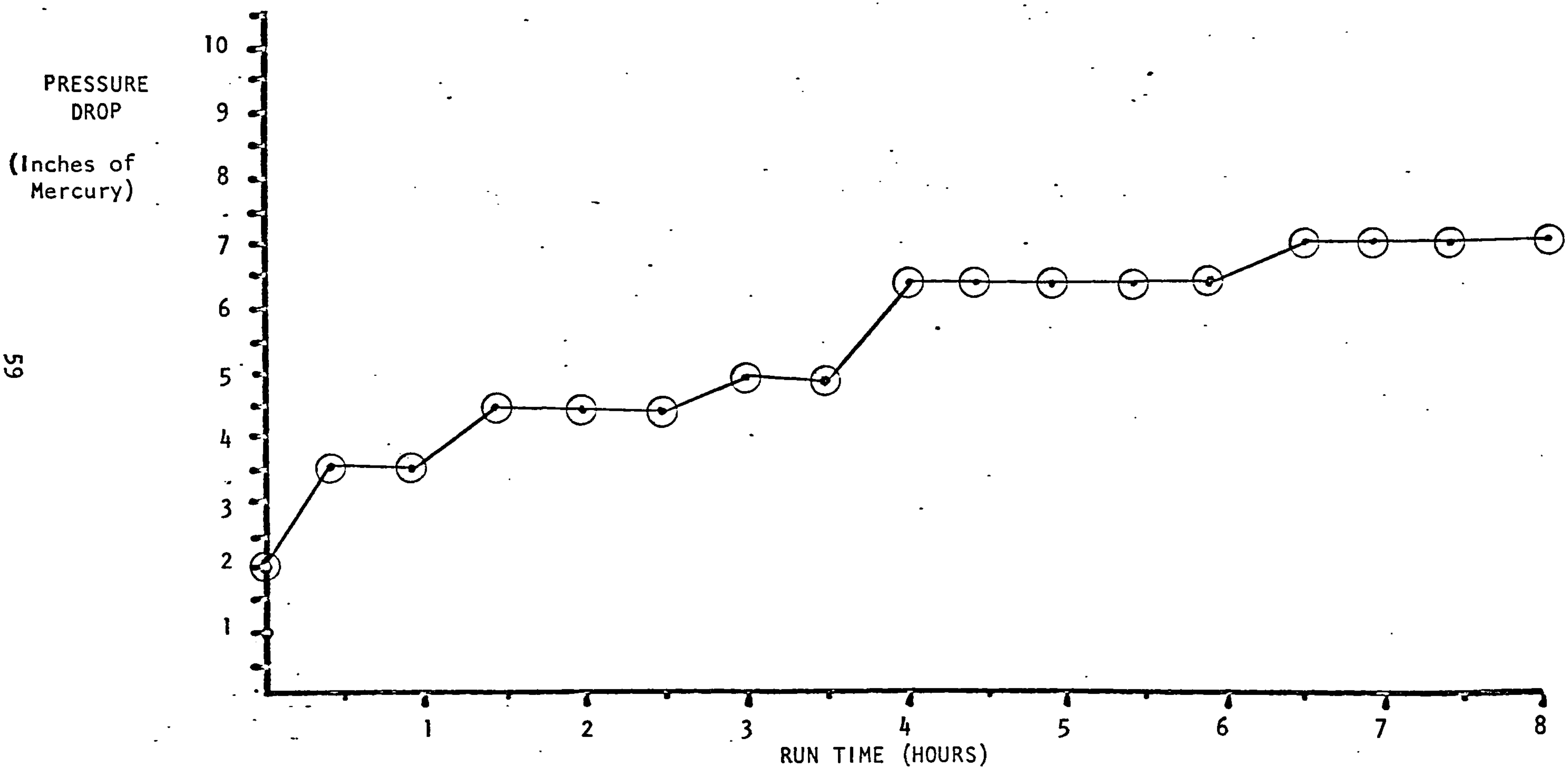

FIGURE 13
TEST RUN # 5
PRESSURE DROP VERSUS RUN TIME

Run No. 6 was made with the same oil and solids concentrations as the previous run, but this time the flow rate was increased to 10 gpm/sq. ft.

As shown in Figure 14, oil concentrations tended to remain fairly low for the entire duration of the run. Again at no time was oil visible in the observation basin. The average oil concentration for the entire run was 9.7 ppm.

The differential pressure across the bed increased sharply at first and then gradually rose through the test. Figure 15 shows the pressure buildup. The final pressure differential was recorded at approximately 16 psi. The average flow rate for the run was 9.9 gpm/sq. ft.

The column was backwashed with air and water at 15 gpm/sq. ft. Approximately 59 liters of backwash liquid was collected equalling about 15% of the forward flow.

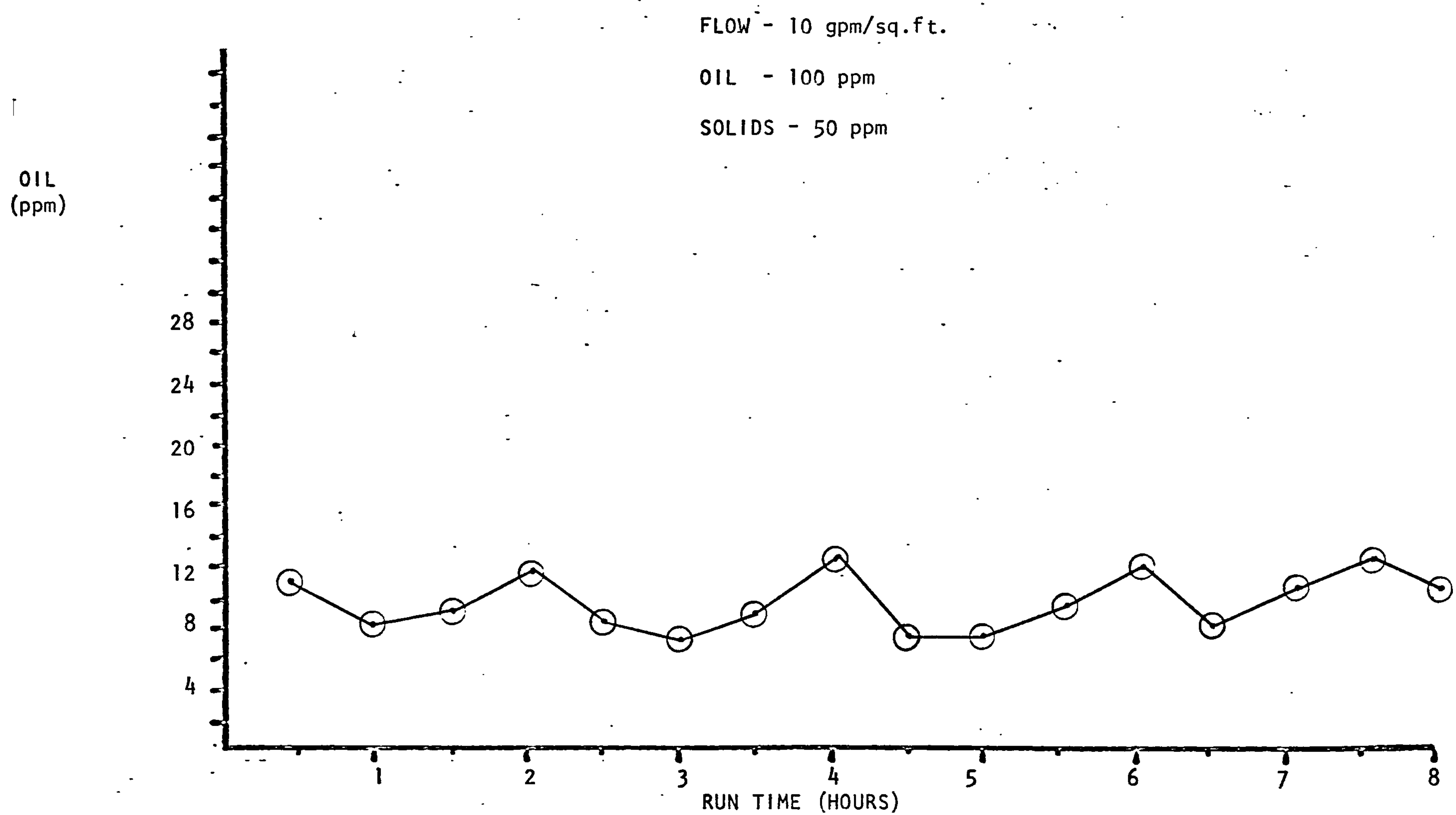

FIGURE 14
TEST RUN # 6
OIL CONCENTRATION VERSUS RUN TIME

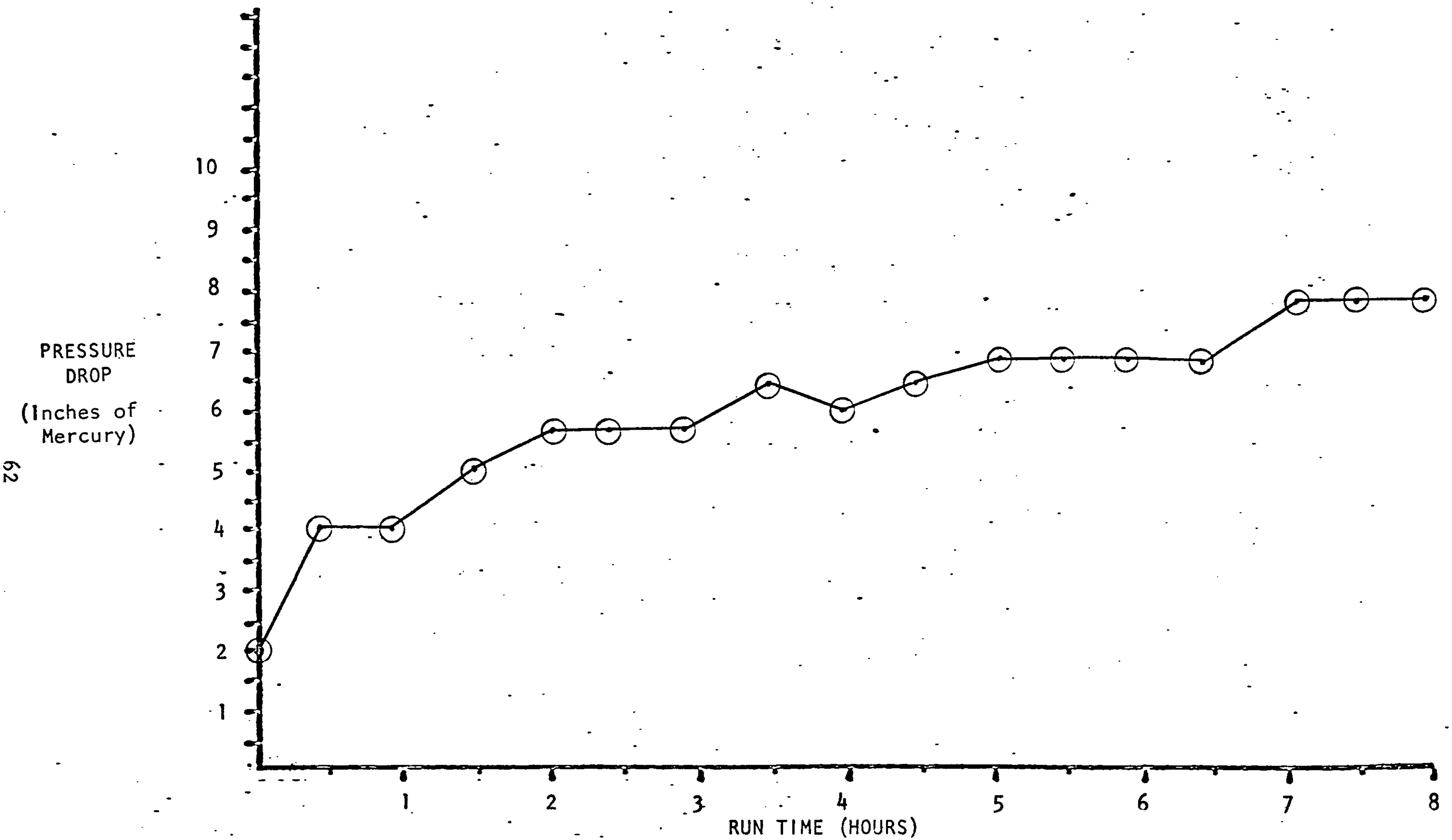

FIGURE 15
TEST RUN #6
PRESSURE DROP VERSUS RUN TIME

For Run No. 7, a sample of tank cleaning slops was obtained through a major oil company. The purpose of this run was to determine whether the filter system could perform well when an actual sample of wastewater was used. The general appearance of the wastewater was turbid with the appearance of dilute chocolate milk. Based on this observation it was assumed that most of the oil in the sample was emulsified. The results of the test run could not be quantitative since other oxygen demanding material most probably was present besides oil. However, the run should indicate generally how the system will perform.

The run was made at 5 gpm/sq. ft. Figure 16 shows that the oil concentrations dropped to a low value in the first minutes of operation and then gradually increased.

Figure 17 shows that the pressure differential increased quite significantly and after approximately 5 hours, the run had to be terminated because the high pressure was causing leaks at a number of fittings. At this point it was estimated that the pressure was 19 psi.

The flow rate for the shortened run averaged 4.8 gpm/sq. ft. and the oil concentrations averaged 15.6 ppm.

The filter was backwashed at a rate of 15 gpm/sq. ft. The column did not readily come clean; so a small quantity of detergent was added to the backwash water. A volume of 24

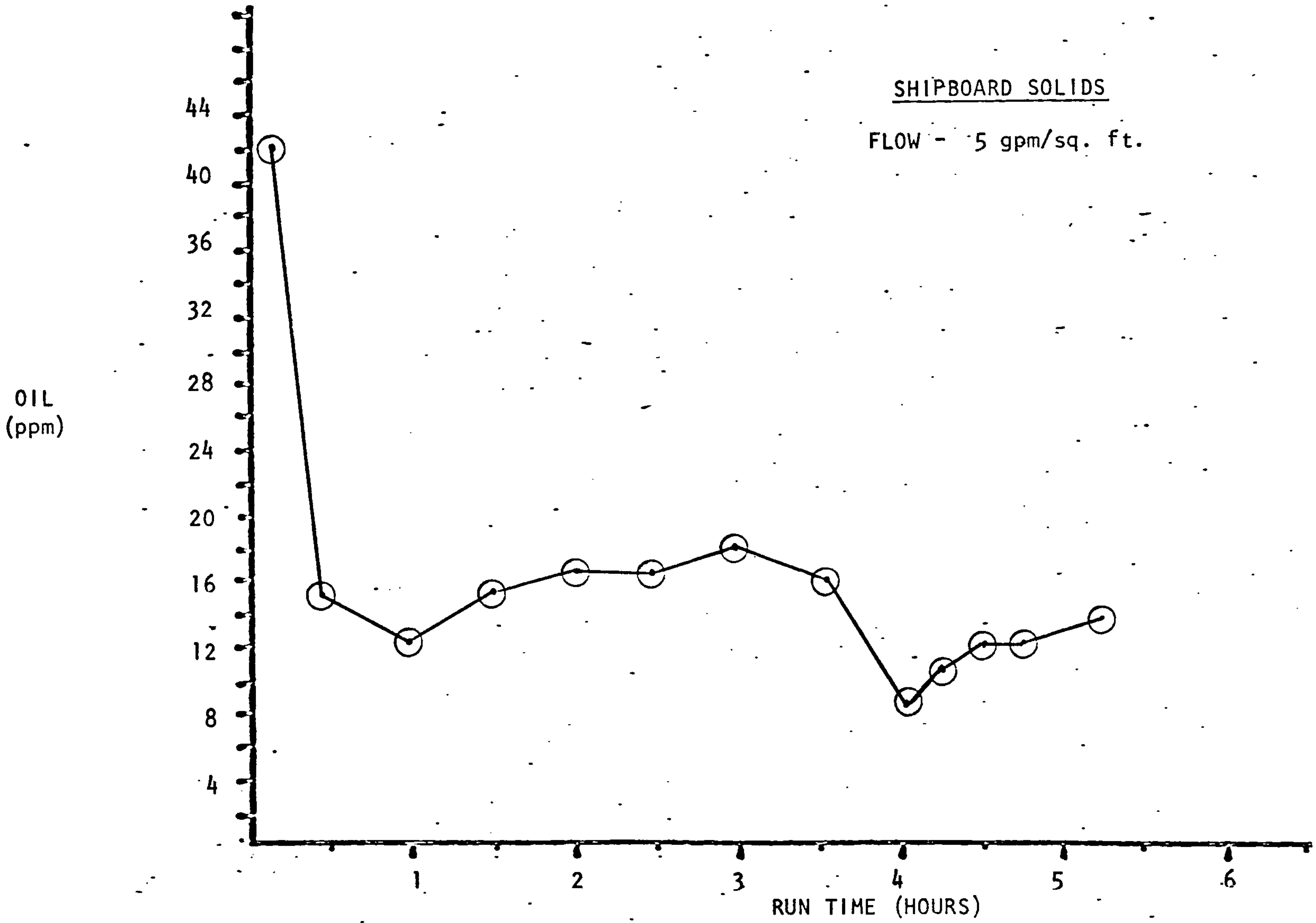

FIGURE 16
TEST RUN #7
OIL CONCENTRATION VERSUS RUN TIME

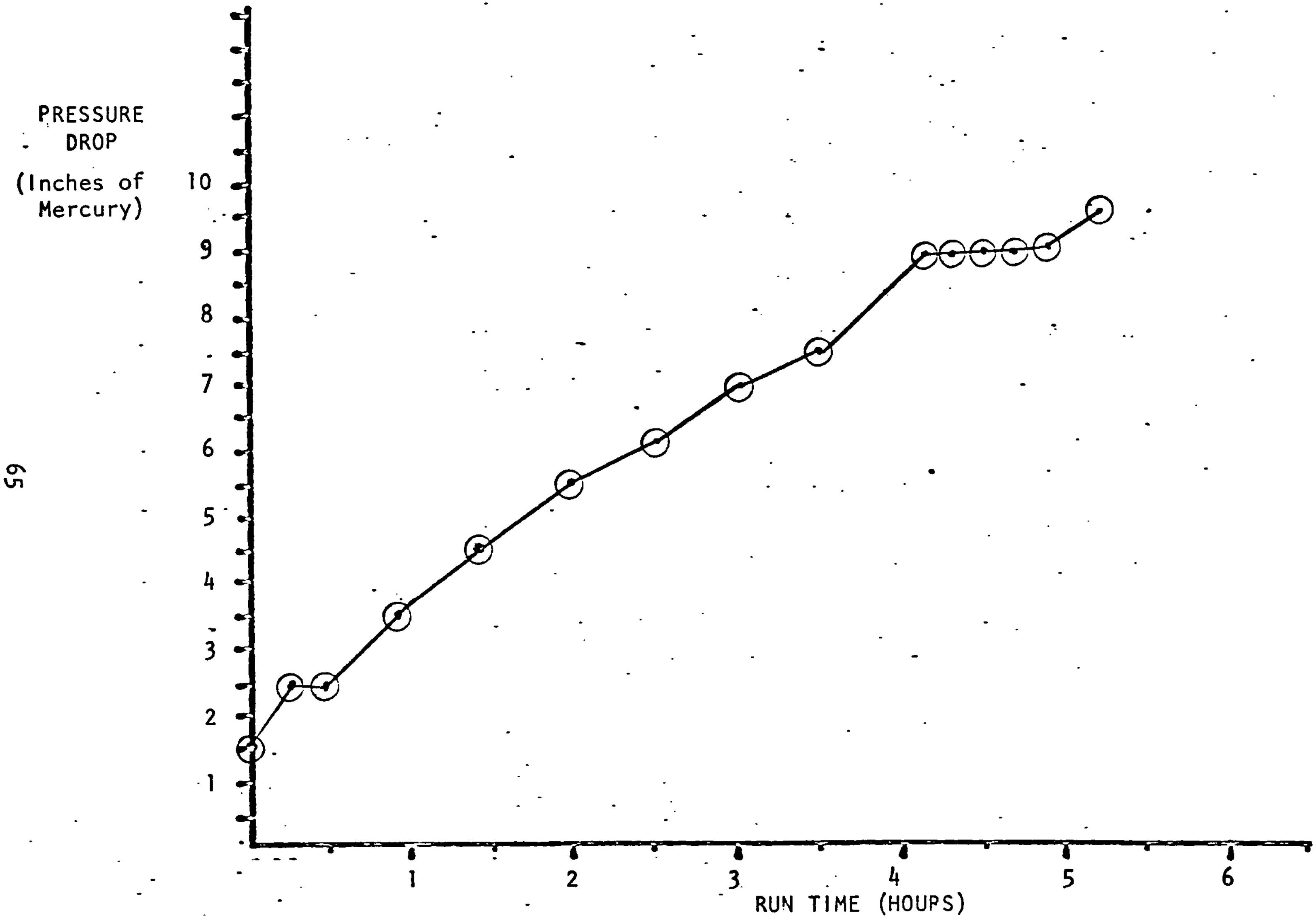

FIGURE 17
TEST RUN #7
PRESSURE DROP VERSUS RUN TIME

liters was required before the column was judged to be sufficiently clear of oil. This amounted to 19% of the total forward flow.

After tightening all the fittings, Run No. 8 was begun using the shipboard generated tank cleaning slops. This time the rate was maintained at approximately 10 gpm/sq. ft.

The run had to be terminated after 2½ hours because the entire quantity of slops had been used.

Figure 18 shows that the oil concentrations were relatively low at first but then gradually increased to a higher level. The average oil concentration for this abbreviated run was 37 ppm.

Figure 19 shows that the pressure drop across the bed increased sharply after one hour and then gradually built up until the run was terminated. The final pressure differential was about 12 psi. The average flow rate was 9.9 gpm/ sq. ft.

Approximately 12 liters were required during the backwash operation. This represented only 10% of the forward flow. Less backwashing was required because the oil had not had a chance to accumulate in the bed due to the shortness of the run.

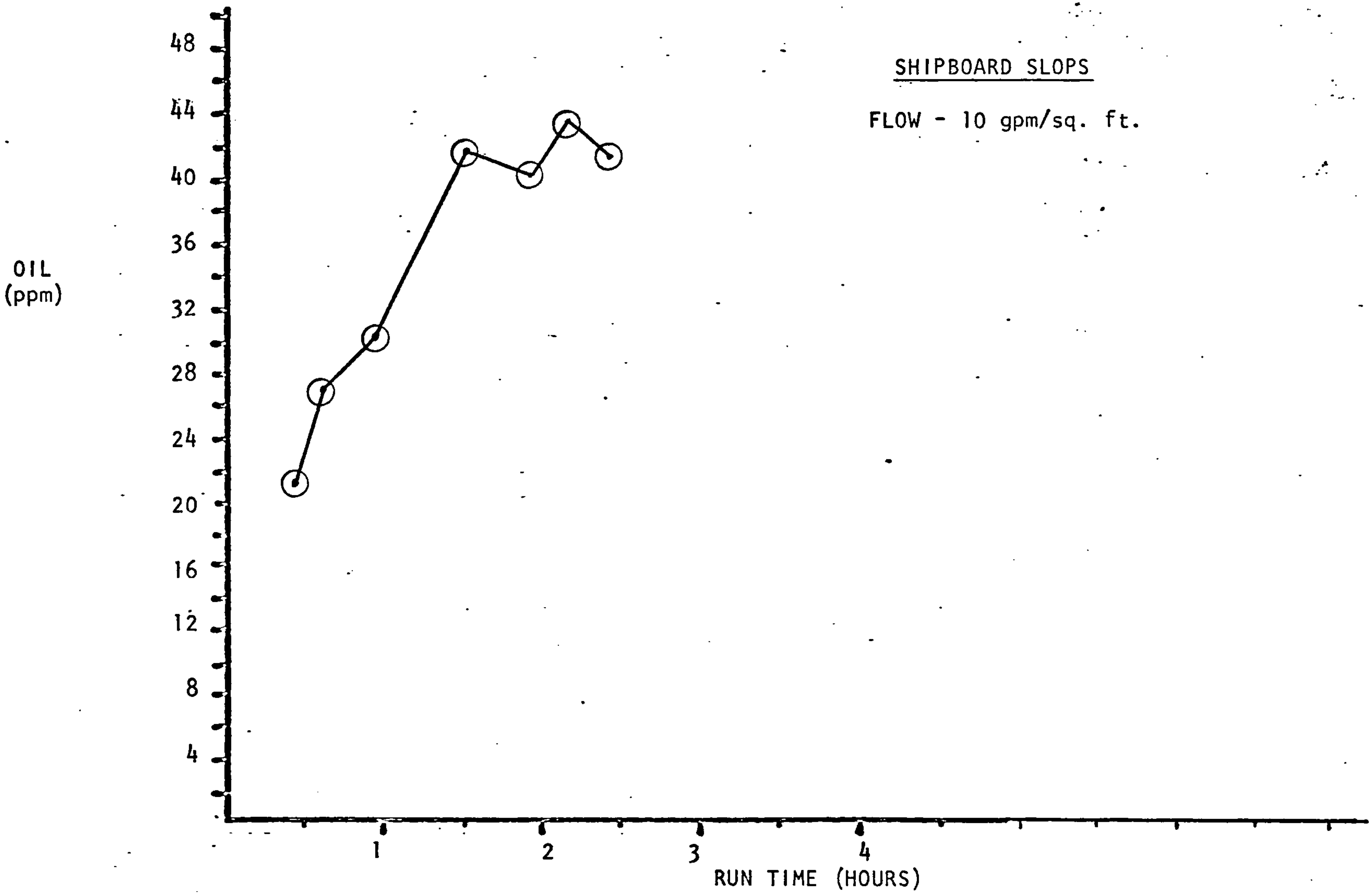

FIGURE 18
TEST RUN # 8
OIL CONCENTRATION VERSUS RUN TIME

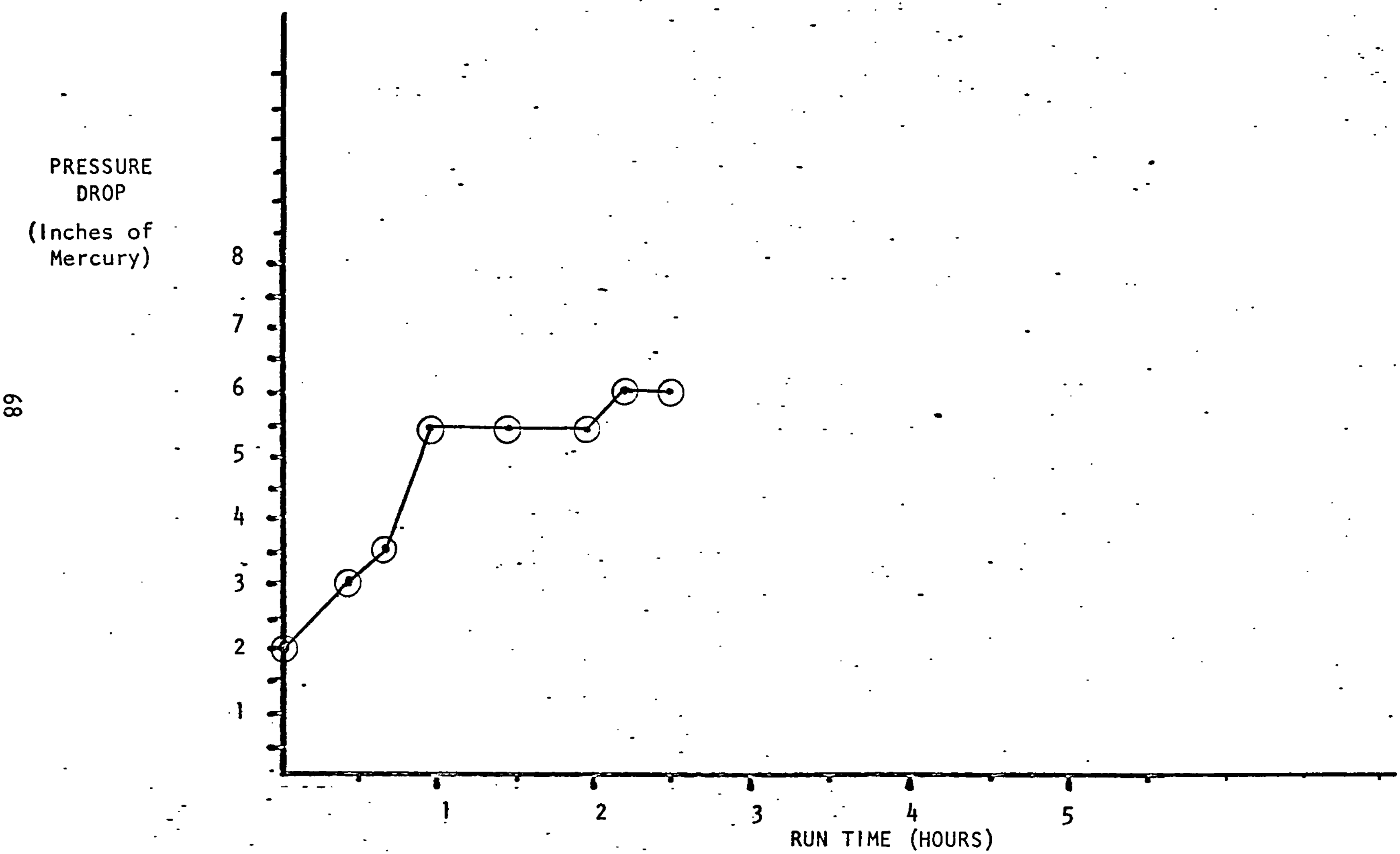

FIGURE 19
TEST RUN #8
PRESSURE DROP VERSUS RUN TIME

Discussion of Test Results

The performance of the filtration column was judged satisfactory. Use of a small diameter column has the potential for allowing a significant percentage of the liquid to "short circuit" the media and travel down the sides of the column. However, there was no evidence of channeling or sidewall effects during any of the runs.

In general, the column appeared efficient in reducing oil concentrations. Lower flow rates produced the better quality effluents. At higher flow rates, performance was also good. When solids were contained in the wastewater, the filter performed best of all. This may be attributable to the fine solids filling the voids between the media and increasing the contact surface for the oil.

Although both test runs with actual shipboard tank cleaning slops were abbreviated, they did indicate that deep bed dual media filtration would function under actual situations. The significant pressure buildup, however, may be a consideration. The concentration of solids may have been so great that the spaces between the media became too severely restricted, accounting for the increase in pressure. This may be alleviated by allowing the liquid and the heavier solids to settle so as not to block the filter.

The filter column appears to be most useful as a polishing filter. By allowing the shipboard generated oily wastes to gravity separate prior to filtering, a high quality effluent should be obtained. The gravity separation stage should allow bulk oil to float to the surface for recovery and allow solids to settle to the bottom. The filter column could then process the wastes without overloads and similar operating problems.

Another important feature is the fact the media is capable of readily releasing the entrained oil upon backwashing. In most cases a volume equal to approximately 10 percent of the forward flow was required to adequately backwash the column. The addition of an air scrub step can significantly reduce the volume of backwash liquid required.

Table 4 summarizes each test runs and the results obtained.

TABLE 4

Summary of Test Runs

Test No.	Hours of Run	Flow Rate (gpm/sq.ft.)	Initial Oil Concentration (ppm)	Average Effluent Oil Concentration (ppm)	Backwash to Remove Oil (% of Forward Flow)	Final Pressure Drop (Inches of Mercur
1	8	5	100	6.7	13	4.5
2	12	5	200	12.4	11	8
3	8	10	100	13.5	10	7.5
4	6.5	10	200	19.8	11	8
5	8	5	100 (50-Solids)	6.1	14	6.5
6	8	10	100 (50-Solids)	9.7	15	7.0
7	5	5	Shipboard Slops	15.6	19	9.5
8	2.5	10	Shipboard Slops	37	10	6.0

CHAPTER 6

CONCLUSIONS

General

The proper treatment of shipboard generated oily wastes is now being recognized as an important problem. Legislation addressing this issue is beginning to take effect. The consequences on not only tanker operators but all oil companies and ultimately the consumer will be widespread.

Three sources of shipboard generated oily wastes exist: ballast water, tank cleaning slops and bilge wastewaters. The characteristics of each source are slightly different but the basic problem remains the same, i.e. remove the oil from the water. The options available to accomplish this task are shoreside treatment and shipboard treatment. Handling the problem at the source - onboard the vessel - offers many advantages.

Effectiveness of the Selected System

Of a number of treatment techniques available, deep bed dual media filtration was selected for study due to its relatively uncomplicated design requirements and its potential for breaking oil-in-water emulsions.

The results of the laboratory testing indicate that the selected system performs satisfactorially under a variety of conditions. A good quality effluent can be obtained with oil concentrations of approximately 15 parts per million or less. With refinement such a system should enable vessel operators to comply even with "no visible sheen" regulations.

The addition of small concentrations of solid material do not interfere with the oil removal efficiency of the column. In fact, efficiency is somewhat improved as a result.

Although laboratory testing of actual shipboard oily wastes was not exhaustive, the results were encouraging and did indicate that effective oil removal could be attained by this method.

Problem Areas

Two areas desire special consideration. One item associated with the use of the filter column is a build-up of pressure across the bed. This will require a system designed to function under increasing pressure and adjustment of the pump speed if a constant flow rate is desired.

The filter requires backwashing after a certain period to avoid direct carryover of oil into the effluent. Consideration must be given to storing the backwash liquid for ultimate disposal. The studies indicate backwash volumes of at least 10% of the forward flow will be encountered. This material must either be reprocessed or disposed of in some manner.

System Considerations

During the initial stages of system selection candidate techniques were evaluated against a number of constraints. It is now appropriate to review these constraints in light of the findings of the laboratory studies.

In regards to safety, the deep bed dual media filtration concept has no significant hazards associated with its operation. The unit can be completely self contained. The only moving parts are associated with the pumps. No special chemicals are required.

To consider space and weight constraints, a typical shipboard system must be described. If,as in an earlier chapter,we consider a vessel of 100,000 tons cargo capacity, the maximum amount of oily waste may be approximately 33,000 tons or 7.9 million gallons. Assuming a typical voyage of one week and a processing rate of 10 gpm/sq. ft., the filtration system would require approximately 78 square feet of filter surface area. Three units would be required aboard the vessel, two for continuous operation with one unit being backwashed. Each unit would therefore need to be seven feet in diameter. A media depth of seven feet should be sufficient. Total space required therefore allowing some room for the pumping equipment would be approximately 810 cubic feet. Discussions with vessel operators had indicated that a space of 1000 cubic feet could be made available for pollution control equipment. It must be remembered that the size of the system is based upon an assumed maximum condition. In reality the actual volume of liquid to be treated by the system could be reduced by vessel operators by proper planning.

The weight of the system based on the specific gravities of coal (1.7) and sand (2.6) would be approximately 50 tons or 0.05 percent of the deadweight tonnage of the vessel. Although this weight may present some constraints, it should be able to be accomodated aboard such a vessel.

Operability is a major advantage of the system since it is uncomplicated and would lend itself to automation.

The system has another advantage since it would be relatively insensitive to the motions of the vessel. This assures stability of operation even in adverse weather conditions. As far as the stability of the vessel is concerned, the weight of the unit would require that it be carefully positioned in the vessel so as not to have a detrimental effect of the ship's center of gravity.

Due to the fact that a high quality effluent can be obtained, a ship equipped with such a system could sail in practically any regulated waters without fear of violating oil pollution laws. The unit would require little shoreside support and should prove quite reliable.

The capital costs of a deep bed dual media filter system including the column filters, pumps and backwash system is estimated to cost approximately $200,000. The capital cost of a 100,000 deadweight ton tanker is estimated to be $50 million, so the cost of the oil pollution control system equals 0.4% of the total initial investment for the vessel.

Operating costs would be basically only the costs of pumping. Assuming the vessel must use the system 50% of the time, the electrical costs to operate 2 - 350 gpm pumps with an assumed 40 foot total dynamic head would equal approximately 16 cents per hour at 1.2 cents per kilowatt hour. Annual operating costs would therefore amount to about $700. This is a considerably small amount when compared to the total operating costs of a vessel.

In summary, it is concluded that deep bed media filtration is a viable method of treating shipboard generated oily wastes following some possible pretreatment.

CHAPTER 7

RECOMMENDATIONS

Areas for Further Research

Although the laboratory studies seem to indicate that deep bed dual media filtration is a feasible treatment method for oil and water separation, further study is warranted.

More complete studies are recommended on different flow rates through the filter bed to determine the optimum value for oil water separation. Studies should be undertaken to determine the best ratios of coal to sand to obtain the highest quality effluent and the longest filter runs. Experimentation with varying particle size should also prove useful.

Further studies are required to determine the optimum method of backwashing the filter column to minimize the total volume of backwash.

In addition other topics for consideration might include varying the temperature of the influent wastewater to improve emulsion breaking. Variations in pH might be studied to determine the effect on oil separation. Chemically stabilized emulsions would probably prove to be an even more difficult treatment problem.

Before an actual unit could be designed for shipboard use, more pilot plant studies are recommended on actual samples of tank cleaning slops, ballast water and bilge water. In particular, the settling period for actual shipboard wastes prior to dual media filtration should be investigated to prevent clogging the filter with excessive solids. Extensive research is required to assure a proper and efficient design.

Pilot plant studies should be performed with larger diameter columns. Tiller and others (18) suggest that sidewall friction can have an effect in interpreting data from experimental apparatus. His studies with compression permeability cells suggest that diameters larger than 4 to 6 inches would overcome this problem. Future oil/water separation studies with dual media filters should consider a minimum diameter cylinder to minimize sidewall effects.

CHAPTER 8

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APPENDIX A

RESEARCH EQUIPMENT

Emulsification Chamber

A twenty (20) liter glass container was used as a feed tank for the filter column. The container was filled with a known volume of water to which a known quality of oil was added. At first, the oil and water mixture was emulsified by violent bubbling through an air line into the container. This method resulted in a thick layer of oil floating on the surface of the water, although the underlying layer appeared to be adequately emulsified.with finely dispersed oil globules.

To help alleviate the problem of the thick oil layer, the bubbling system was replaced with a variable speed mixer. The mixer gave better emulsification characteristics.

Suction for the feed pump was taken at a point near the bottom of the glass container below the immediate vicinity of the mixer.

Known amounts of oil and water were added to the container periodically to maintain a sufficient volume through the duration of the test runs. The amount of oil or water was adjusted to maintain the desired influent oil concentration to the column.

Feed Pump

A Cole-Palmer variable speed master-flex pump was used to feed the column. The speed of the pump was controlled by a rheostat. The speed of the pump was adjusted throughout the duration of a test run to maintain as closely as possible a constant flow rate through the test column. A sample connection in the line permitted monitoring of the influent oil concentrations to the filter column.

Test Column

The column containing the filter media consisted of two thirty inch sections of pipe, connected by a bolt and flange arrangement with a teflon gasket. The lower portion of the pipe was bolted to an aluminum plate with a quarter inch copper tubing connection. A small piece of window screen covered the opening. The two inch diameter glass pipes were then filled with 24 inches of sand and topped with anthracite coal, to a depth of 18 inches. The sand particles were prescreened for an effective size of 0.5 mm. The anthracite had an effective size of 1.8 mm. Sufficient room was left at the top of the column to allow for expansion of the bed during backwashing operations.

The column was fitted with copper tubing in such a manner so that liquid could enter at the top,exit at the bottom for filtration runs or enter at the bottom and exit at the top for backwashing of the filter media.

Prior to the actual test runs, the column was backwashed and the finer anthracite particles were removed from the bed in this manner.

Manometer

A mercury manometer was connected by plastic (Tygon) tubing to both ends on the filter column. The manometer was used to monitor the pressure drop across the filter bed during the test runs.

APPENDIX B

OIL - COD EQUIVALENCY CURVE

Since the standard method for determining oil concentration is a complicated procedure requiring special equipment, it was decided to use the test for chemical oxygen demand (COD) as an indication of oil concentration.

Standard solutions were prepared in the laboratory by placing a known weight of oil in a reflux flask and adding a known volume of water. The standard procedure for COD was then performed on the solution. In this manner, a COD value could be obtained for a known concentration of oil. A total of seventeen standard solutions were analyzed in this manner with a number of replicates. The range of examination was limited approximately to 100 mg/L of oil or less for two reasons:

1.) the effluent concentrations from the filter column would be unacceptable above 100 mg/L and

2.) for levels much above 100 mg/L, all the oil was not oxidized. (During actual testing if a sample was expected to contain a concentration of 100 mg/L or more a dilute sample was taken).

The above procedure gave a number of scattered points. The relationship between COD concentration and oil concentration is linear since there are no other parameters involved. A least squares analysis was performed to obtain the straight line relationship using seventeen data points as determined by experimentation.

The least squares analysis involves making the sum of the squares of the differences between observed and calculated values a minimum.

The equation for a straight line is of the form y=a+bx. If we assume that D_k equals the difference between the kth pair of observed values y_k and x_k, then $D_k = (a+bx_k) - y_k$, where $(a+bx_k)$ is the calculated value of y, and y_k is the observed value. The constants a and b must therefore be determined so that the sum of the squares of the differences will be a minimum. In other words:

$$\sum D^2 = \sum \left[(a+bx)-y\right]^2 = \text{minimum.}$$

To solve such a problem, the first derivatives of $\sum D^2$ with respect to a and b can be set equal to zero.

$$\frac{\partial(\sum D^2)}{\partial a} = 2\sum D \left(\frac{\partial D}{\partial a}\right) = 2\sum (a+bx-y)=0$$

$$\frac{\partial(\sum D^2)}{\partial b} = 2\sum D \left(\frac{\partial D}{\partial b}\right) = 2\sum (a+bx-y)x = 0$$

For n pairs of observations, we can solve two simultaneous equations with two unknowns:

1. $\sum(a+bx-y) = na+b\sum x-\sum y=0$
2. $\sum(a+bx-y)x = a\sum x+b\sum x^2 -\sum xy=0$

Figure B-1 is a plot of the observed values in determining the COD equivalency with the straight line relationship determined by least squares analysis. The parameters a and b were found by using 17 observed values. The following equation was derived and used as a model of the oil-COD relationship:

$$\text{COD, mg/L} = 11.6 + 9.6\ (\text{Oil, mg/L})$$

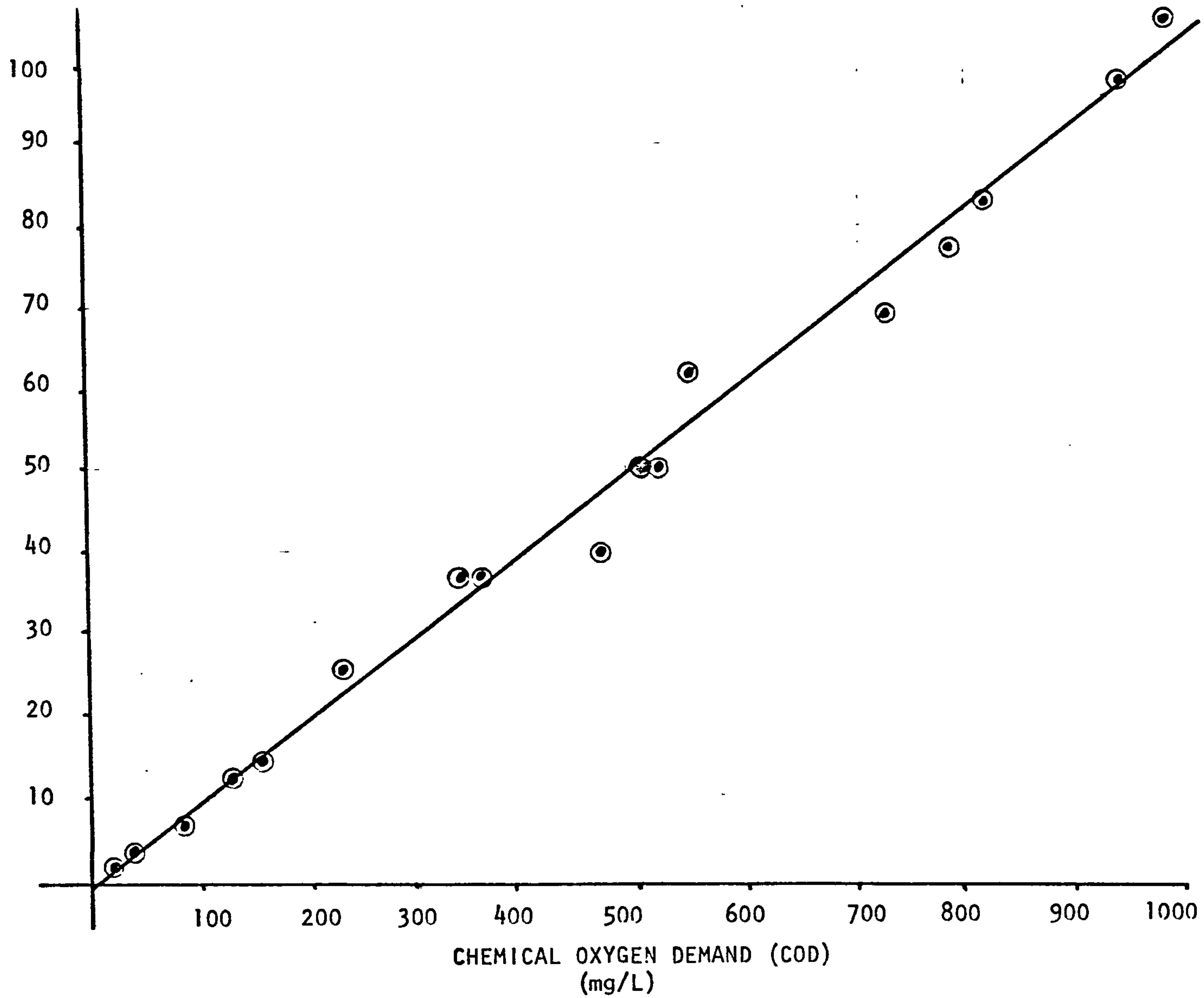

FIGURE B-1
OIL-COD EQUIVALENCY CURVE

APPENDIX C

EXPERIMENTAL DATA

TEST RUN #1

Influent Conditions: 100 ppm Oil, Flow 5 gpm/sq. ft.

TIME (hrs.)	PRESSURE (inches Hg)	FLOW (gpm/sq.ft.)	OIL (mg/L)
0	1.0	5.0	--
0.25	1.0	5.2	14
0.50	1.5	5.1	12
0.75	1.5	4.8	7
1.00	2.0	5.0	8
1.25	2.5	4.9	6
1.50	2.0	4.9	8
1.75	2.0	5.2	5
2.00	2.0	5.0	4
2.50	2.5	5.0	3
3.00	2.5	5.3	7
3.50	2.5	5.0	5
4.00	2.5	4.9	5
4.50	3.0	4.8	2
5.00	3.0	5.1	3
5.50	2.5	5.0	7
6.00	3.0	5.2	8

Test Run #1

TIME (hrs.)	PRESSURE (inches Hg)	FLOW (gpm/sq.ft.)	OIL (mg/L)
6.50	4.0	5.0	7
7.00	4.0	5.0	8
7.50	4.5	5.0	8
8.00	4.5	4.9	7

TEST RUN #2

Influent Conditions: 200 ppm Oil, Flow 5 gpm/sq. ft.

TIME (hrs.)	PRESSURE (inches Hg)	FLOW (gpm/sq.ft.)	OIL (mg/L)
0	1.0	5.0	--
0.25	1.0	5.1	45
0.50	1.5	5.0	32
0.75	2.0	4.9	12
1.00	2.0	5.0	8
1.25	2.0	5.0	10
1.50	2.5	4.8	17
2.00	2.5	5.0	12
2.50	3.0	4.9	9
3.00	3.0	5.0	9
3.50	3.5	5.1	11
4.00	4.0	5.1	15
4.50	5.0	4.7	10
5.00	5.5	4.9	8
5.50	4.5	5.0	6
6.00	5.0	4.8	7
6.50	5.0	5.0	5
7.00	5.0	4.9	9
7.50	6.0	5.2	9
8.00	6.5	4.9	10

Test Run #2

TIME (hrs.)	PRESSURE (inches Hg)	FLOW (gpm/sq.ft.)	OIL (mg/L)
8.50	6.5	5.0	13
9.00	7.0	5.1	8
9.50	7.0	5.2	10
10.00	7.0	4.9	16
10.50	6.5	5.1	11
11.00	7.5	5.0	9
11.50	8.0	5.1	13
12.00	8.0	5.2	12

TEST RUN #3

Influent Conditions: 100 ppm Oil, Flow 10 gpm/sq. ft.

TIME (hrs.)	PRESSURE (inches/Hg)	FLOW (gpm/sq.ft.)	OIL (mg/L)
0	1.5	10.0	--
.5	2.0	9.7	27
1.0	3.0	9.8	14
1.5	3.0	10.0	20
2.0	3.0	10.1	12
2.5	3.0	10.0	8
3.0	3.5	9.7	8
3.5	5.0	9.4	8
4.0	6.0	9.8	11
4.5	5.5	10.3	13
5.0	5.5	10.2	10
5.5	6.0	10.0	11
6.0	7.0	9.9	15
6.5	7.0	10.1	13
7.0	7.0	10.3	16
7.5	7.0	10.1	14
8.0	7.5	9.9	16

TEST RUN #4

Influent Conditions: 200 ppm Oil, Flow 10 gpm/sq. ft.

TIME (hrs.)	PRESSURE (inches Mercury)	FLOW (gpm/sq.ft.)	OIL (mg/L)
0	1.5	10	--
0.5	3.5	10.2	62
1.0	4.0	9.9	10
1.5	4.0	10.0	2
2.0	4.5	10.0	3
2.5	6.0	10.1	8
3.0	6.0	9.8	7
3.5	7.0	10.0	6
4.0	7.0	9.8	18
4.5	6.5	10.2	24
5.0	7.5	10.1	20
5.5	8.0	10.0	30
6.0	8.0	9.9	35
6.5	8.0	10.0	32

TEST RUN #5

Influent Conditions: 100 ppm Oil, 50 ppm Solids, Flow 5 gpm/sq.ft.

TIME (hrs.)	PRESSURE (inches Hg)	FLOW (gpm/sq.ft.)	OIL (mg/L)
0	2.0	5.0	--
0.5	3.5	4.8	8
1.0	3.5	4.9	3
1.5	4.5	5.1	5
2.0	4.5	4.7	2
2.5	4.5	4.8	7
3.0	5.0	4.0	9
3.5	5.0	5.2	6
4.0	6.5	4.9	10
4.5	6.5	4.8	5
5.0	6.5	5.1	4
5.5	6.5	5.0	3
6.0	6.5	4.9	6
6.5	7.0	5.0	5
7.0	7.0	5.1	8
7.5	7.0	4.8	7
8.0	7.0	4.9	9

TEST RUN #6

Influent Conditions: 100 ppm Oil, 50 gpm Solids, Flow 10 gpm/sq.ft.

TIME (hrs)	PRESSURE (inches Hg)	FLOW (gpm/sq.ft.)	OIL (mg/L)
0	2.0	10.0	--
0.5	4.0	10.1	11
1.0	4.0	9.8	8
1.5	5.0	9.9	9
2.0	5.5	9.8	12
2.5	5.5	10.0	8
3.0	5.5	10.0	7
3.5	6.5	9.8	9
4.0	6.0	9.7	13
4.5	6.5	10.1	7
5.0	7.0	9.9	7
5.5	7.0	9.9	10
6.0	7.0	9.9	12
6.5	7.0	10.0	8
7.0	8.0	9.8	11
7.5	8.0	10.1	13
8.0	8.0	9.9	11

TEST RUN #7

Influent Conditions: Shipboard Sample, Flow 5 gpm/sq. ft.

TIME (hrs)	PRESSURE (inches Hg)	FLOW (gpm/sq.ft.)	OIL (mg/L)
0	1.5	5.0	--
0.25	2.5	4.9	42
0.50	2.5	4.7	15
1.00	3.5	4.9	12
1.50	4.5	5.1	15
2.00	5.5	4.7	16
2.50	6.5	5.0	16
3.00	7.0	4.8	17
3.50	7.5	4.9	15
4.00	9.0	4.6	8
4.25	9.0	5.0	10
4.50	9.0	4.7	12
4.75	9.0	4.7	12
5.25	9.5	4.9	14

TEST RUN #8

Influent Conditions: Shipboard Sample, Flow 10 gpm/sq. ft.

TIME (hrs)	PRESSURE (inches Hg)	FLOW (gpm/sq.ft.)	OIL (mg/L)
0	2.0	10.0	--
0.50	3.0	9.7	21
0.75	3.5	9.9	29
1.00	5.5	9.6	32
1.50	5.5	10.1	44
2.00	5.5	10.2	42
2.25	6.0	9.8	45
2.50	6.0	10.0	43