Chapter 5 Distribution of Crude Oil, Petroleum Products and Gas

Chapter 5 Distribution of Crude Oil, Petroleum Products and Gas

5-1 Hydrocarbon Reserves in Trinidad and Tobago

5-1-1 Crude Oil

The country's proven crude oil reserves recorded the highest level of 670 million barrels in 1978, the year of peak oil production. Since then, however, the proven reserves have declined significantly. The proven reserves as of January 1, 1992 are listed at 494 million barrels, representing about 0.05 percent of the world's total reserves. Table 5-1 shows the country's total crude oil reserves as of January 1, 1992.

Table 5-1 Crude Oil Reserves

(Unit: Million Barrels)

Area	Average API	Reserves as of January 1, 1992			
		Proven	Probable	Possible	Total
Onshore	22	170.2	178.0	100.0	448.2
Offshore					
East Coast	33	160.7			
West Coast	21	163.1			
Total Offshore		323.8	250.0	325.0	898.8
Total		494.0	428.0	425.0	1,347.0

Source: Draft Policy Paper on Energy, November 1992

As shown in Table 5-1, the proven oil reserves are evenly distributed among the three areas. It should be noted, however, that the probable and possible reserves are located mainly in the younger fields in the marine areas. Approximately 25 percent of the proven reserves in the west coast marine area are heavy oil which are not economically recoverable under current market conditions. In addition to the reserves shown in the above table, huge amounts of heavy oil accumulations are considered to exist.

The proven reserves of crude oil in the beginning of 1994 slightly exceeded 400 million barrels, calculated by deducting oil production in 1992 and 1993 from the proven reserve shown in the above table. At the production rate of 1993, the proven reserves can be expected to last approximately nine years. If the total reserve potential materializes, the reserve to production ratio increases to 28 years.

5-1-2 Natural Gas

The natural gas reserves of the country are located principally in the two areas. Approximately 62 percent of the proven reserves occur in the east coast marine area which is currently under development and production. The natural gas in this area contains about seven percent ethane and heavier hydrocarbons (C_2^+). The other significant deposits are located in the north coast marine area. The gas in this area is a dry gas, and the content of C_2^+ is about 0.3 percent. The proven reserve of natural gas in the country as of January 1, 1992 amounted to 8.4 billion cubic feet, representing about 0.2 percent of the world's proven reserves. At the production rate of 1991 (712 MMSCFD), the reserve to production ratio exceeds 30 years. If the reserve potential shown in the following table materializes, the reserve potential ratio increases to about 77 years. Table 5-2 summarizes the natural gas reserves as of January 1, 1992.

Table 5-2 Natural Gas Reserves

(Unit: BCF)

Area	Reserves as of January 1, 1992			
	Proven	Probable	Possible	Total
East Coast Offshore	5,233	3,217	3,883	12,333
North Coast Offshore	2,990	1,369	1,100	5,459
Others	182	57	2,200	2,439
Total	8,405	4,643	7,183	20,231

Source: Draft Policy Paper on Energy, November 1992

5-1-3 Condensate

This resource is located in the East Coast Marine area in association with natural gas. Until recently condensate did not play an important role in the country's industry. However, it is expected that condensate will play a more important role in development of the petrochemical industry. The proven reserves of condensate as of January 1, 1992 are about 79 million barrels. The total reserves including provable and possible reserves are estimated to be about 200 million barrels.

5-2 Production

5-2-1 Crude Oil

Crude oil has been produced in the central and southern parts of the Island of Trinidad, the east coast marine area of the island and the Gulf of Paria. As shown in Figure 5-1, the east coast, the Gulf of Paria and the onshore areas have shares of 48 percent, 26 percent and 26 percent, respectively. The onshore oil fields are concentrated in the southwestern part of the island, producing more than 80 percent of the total onshore production. The major producers on the east coast, and in the Gulf of Paria and onshore areas are AMOCO, TRINMAR and Petrotrin (formerly Trintoc and Trintopec), respectively. Table 5-3 summarizes annual oil production for 1992 and 1993 and the cumulative oil production through the end of 1993 by oil field in each area. Figure 5-2 indicates the locations of oil fields.

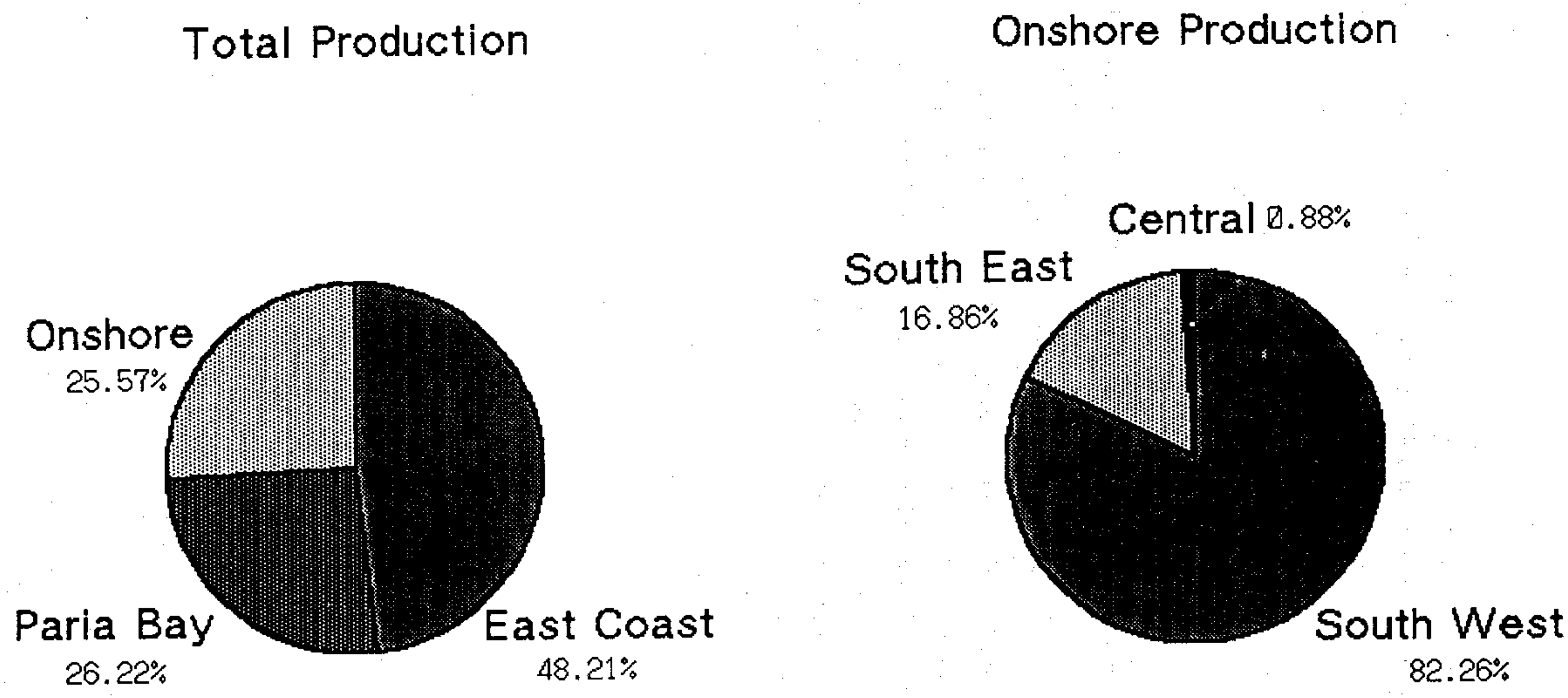


Figure 5-1 Crude Oil Production by Area

Table 5-3 Crude Oil Production by Fields (1/3)

(Unit: Barrels)

Operator	Field	Annual Production		Cum. Production (1'000 Barrels)
		1992	1993	
Offshore				
East Coast				
AMOCO				
	Teak	11,798,440	8,547,612	298,989
	Poui	6,697,380	6,488,880	191,616
	Samman	4,194,053	3,868,621	201,896
	Cassia	809,005	587,616	17,933
	Mora	53,665	21,089	945
	Flambouyant	0	599,937	600
AMOCO Total		23,552,543	20,113,755	711,978
Trintomar				
	Pelican	936,939	687,453	3,867
Trintomar Total		936,939	687,453	3,867
Trintopec				
	Galeota	670,566	611,978	19,600
Trintopec Total		670,566	611,978	19,600
ENRON				
	Kiskadee	0	35,870	36
ENRON Total		0	35,870	36
East-Coast Total		**25,160,048**	**21,449,056**	**735,481**
Gulf of Paria				
TRINMAR				
	Soldado	11,617,269	11,249,476	537,660
	Fortin Offshore	90,346	145,078	7,486
TRINMAR Total		11,707,615	11,394,554	545,146
Trintoc				
	Brighton	310,633	273,302	71,868
	Couva Marine	0	0	301
Trintoc Total		310,633	273,302	72,169
Gulf of Paria Total		**12,018,248**	**11,667,856**	**617,315**
Offshore Total		**37,178,296**	**33,116,912**	**1,352,796**

Source: Ministry of Energy and Energy Industries

Table 5-3 Crude Oil Production by Fields (2/3)

(Unit: Barrels)

Operator	Field	Annual Production		Cum. Production (1'000 Barrels)
		1992	1993	
Onshore				
Caroni/Central Range				
Trintoc				
	Oropouche	66,438	71,675	7,000
Trintoc Total		66,438	71,675	7,000
Trintopec				
	Oropouche	0	0	274
	Tabaquite	33,749	28,714	1,959
Trintopec Total		33,749	28,714	2,233
Caroni/Central Range Total		**100,187**	**100,389**	**9,233**
South-Eastern				
Trintoc				
	Barrackpore	825,018	708,941	37,017
	Guayaguayare	543,948	516,769	90,429
	Penal	271,487	240,228	64,119
	Catshill	136,300	173,113	23,831
	Trinity	89,431	79,749	15,763
	Balata East & West	78,006	70,974	3,872
	Inniss	12,081	10,265	6,321
	Balata Central	0	0	371
	Rock Dome	0	0	16
Trintoc Total		1,956,271	1,800,039	241,739
Trintopec				
	Moruga West	41,154	33,634	9,419
	Moruga East	19,684	38,384	2,806
	Goudron	11,351	10,763	49
	Moruga North	7,021	4,440	1,085
	Barrackpore	0	0	129
Trintopec Total		79,210	87,221	13,488
PREMIER				
	Barrackpore	31,479	30,292	514
PREMIER Total		31,479	30,292	514
South-eastern Total		**2,066,960**	**1,917,552**	**255,741**

Note: Cumulative production includes production by Lease Operators and Defunctioned Fields.

Source: Ministry of Energy and Energy Industries

Table 5-3 Crude Oil Production by Fields (3/3)

(Unit: Barrels)

Operator	Field	Annual Production		Cum. Production (1'000 Barrels)
		1992	1993	
South-Western				
Trintoc				
	Forest Reserve	1,429,958	1,324,223	267,116
	Pt. Fortin Central	545,260	492,104	23,219
	Area IV & Guapo	528,014	545,697	41,624
	Palo Seco	514,547	482,179	96,535
	Parrylands 1-5	353,883	367,240	42,796
	Grand Ravine	162,643	161,937	27,616
	Pt. Fortin West	145,552	143,961	21,350
	Pt. Ligoure	114,457	95,373	3,090
	Wilson	47,679	43,465	20,298
	Cruse	38,533	87,580	26,097
	Erin	10,612	0	2,380
	New Dome	6,156	7,068	3,163
	Siparia	3,461	3,638	7
	Morne Diablo	1,866	1,482	331
	San Francique	0	0	5,983
	Los Bajos	0	0	546
	Erin	0	11,050	710
Trintoc Total		3,902,621	3,766,997	582,861
Trintopec				
	Palo Seco/Erin/Mc Kenzie	2,628,150	2,433,940	133,600
	Guapo/Boodoosingh	854,638	805,748	51,244
	Fyzabad/Apex Quarry	765,334	840,738	176,475
	Central Los Bajos	762,460	712,151	13,479
	Coora/Quarry	540,266	523,828	94,808
	Morne Diablo/Quinam	16,886	17,881	7,490
Trintopec Total		5,567,734	5,334,286	477,096
PREMIER				
	San Francique	167,930	163,604	4,579
	Fyzabad/Roodal	79,989	80,093	13,847
	Icacos	4,924	5,172	521
	Palo Seco	4,895	3,892	1,680
	Siparia	3,462	3,636	916
PREMIER Total		261,200	256,397	21,543
South-Western Total		**9,731,555**	**9,357,680**	**1,081,500**
Onshore Total		**11,898,702**	**11,375,621**	**1,346,474**
Grand Total		**49,076,998**	**44,492,533**	**2,699,270**

Note: Cumulative production includes production by Lease Operators and Defunctioned Fields.

Source: Ministry of Energy and Energy Industries

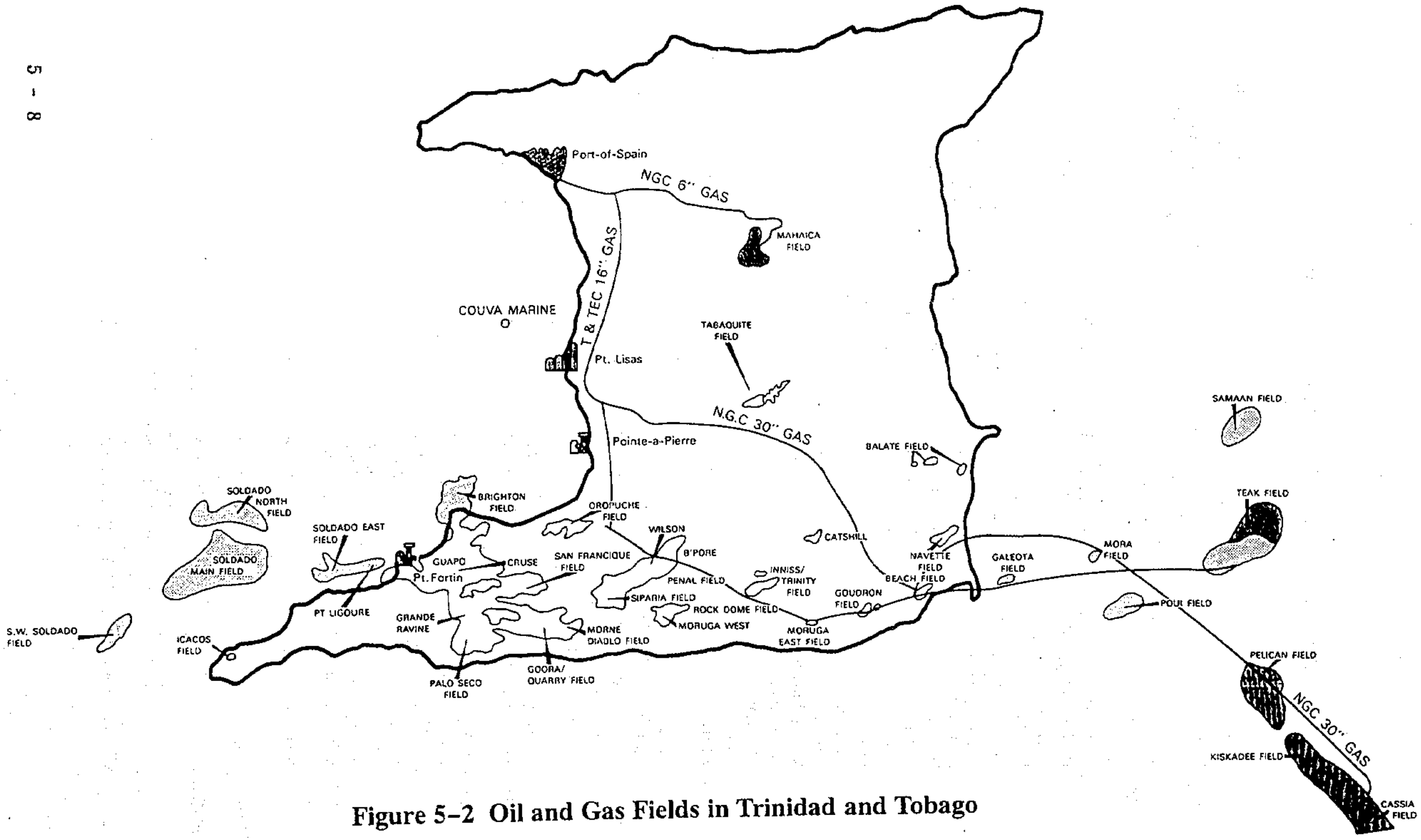


Figure 5–2 Oil and Gas Fields in Trinidad and Tobago

5-2-2 Natural Gas

At present, Trinidad and Tobago produces about 700 MMCFD of natural gas. The major gas fields are all located in the east coast marine area of the Island of Trinidad, and about 90 percent of gas is produced in this area. AMOCO, the biggest producer of natural gas in Trinidad and Tobago, produces gas at the Cassia, Teak, Poui and Flambouyant fields located in the east coast marine area. The share of this company in gas production is about 80 percent of the total production. AMOCO uses about 25 percent of its own production for gas lift for oil production, and sells the balance to NGC. Trintomar, a state-owned gas company, has been producing natural gas at Pelican Field located off the east coast since 1990; production has been rapidly decreasing due mainly to the reserves being lower than originally estimated. On land, Petrotrin, taking over the operation of Trintoc, is producing a small amount of gas at Mahaica Field located in the central part of the Island of Trinidad. Petrotrin is recovering and using the gas produced in association with crude oil at various oil fields. Petrotrin consumes all the associated gas for themselves. The gas produced at Mahaica Field and also the gas produced by Trintomar is sold to NGC. TRINMAR is producing gas in the Gulf of Paria. This gas is used for oil production and as fuel by the operating company. In addition, ENRON is producing oil and gas at Kiskadee Field located in the east coast marine area since 1993. Table 5-4 summarizes the natural gas sales to NGC by company.

5-2-3 Condensate

Condensate is produced in association with natural gas by three companies in the east coast marine area of the Island of Trinidad. The production of condensate is negligibly small in comparison with that of crude oil. Table 5-5 summarizes the condensate production.

Table 5-4 Natural Gas Sales to NGC

(Unit: MMCFD)

Operator	1989	1990	1991	1992	1993
AMOCO					
Production					
Cassia	373.61	303.96	284.97	305.14	276.61
Teak	164.38	106.46	173.08	182.74	131.69
Samaan	0.00	68.83	56.99	60.06	64.10
Poui	41.46	40.18	39.45	41.94	45.89
Flambouyant	0.00	0.00	0.00	0.00	78.29
Total	579.45	519.43	554.49	589.88	596.58
Own Use	138.80	115.16	127.71	132.90	132.38
Sale to NGC	440.65	404.27	426.78	456.98	464.20
Trintomar	0.00	51.00	60.47	39.61	16.86
Enron	0.00	0.00	0.00	0.00	2.53
Petrotrin (Mahaica Only)*	1.00	1.00	1.00	1.00	1.00
Total Sale to NGC	441.65	456.27	488.25	497.59	484.59

Note: * Rough estimation based on published data
Source: Ministry of Energy and Energy Industries

Table 5-5 Condensate Production

(Unit: BPD)

Operator	1987	1988	1989	1990	1991	1992	1993
AMOCO	6,960	6,161	3,898	3,728	3,477	2,796	3,930
Trintomar	0	0	0	2,494	3,667	2,568	1,885
Enron	0	0	0	0	0	0	98
Total	6,960	6,161	3,898	6,222	7,144	5,364	5,913

Source: Ministry of Energy and Energy Industries

5-3 Transportation

5-3-1 Crude Oil

Crude oil produced in Trinidad and Tobago has been transported mainly through pipeline; a small amount of oil is transported by truck to tank farms. This study summaries the crude oil transportation system by company, laying stress on the onshore fields in the scope of this study. The imported crude oil for processing is not transported over a long distance, because the crude oil is received through unloading facilities next to the refineries.

(1) AMOCO

AMOCO has been producing oil and gas in the east coast marine area of the Island of Trinidad. As shown in Table 5-3, their major oil fields are Teak, Samaan and Poui. The Cassia and Mora fields are gas fields where condensate is produced in association with gas. The condensate of Cassia is transported to Platform-A at Teak through an 8-inch pipeline. The condensate from Cassia and Teak-A is transported to the onshore terminal facility at Galeota Point. Mora's production is transported to Poui by a pipeline. Crude oil from Samaan is sent to the platform-B at Teak through a 16-inch pipeline, and sent to Poui together with the crude oil from Teak. The combined crude and condensate from Samaan, Teak-B, Mora and Poui is sent to the terminal facility through a 24-inch pipeline. All liquid products collected at the terminal facility are exported to the USA. Figure 5-3 depicts the AMOCO's transportation system.

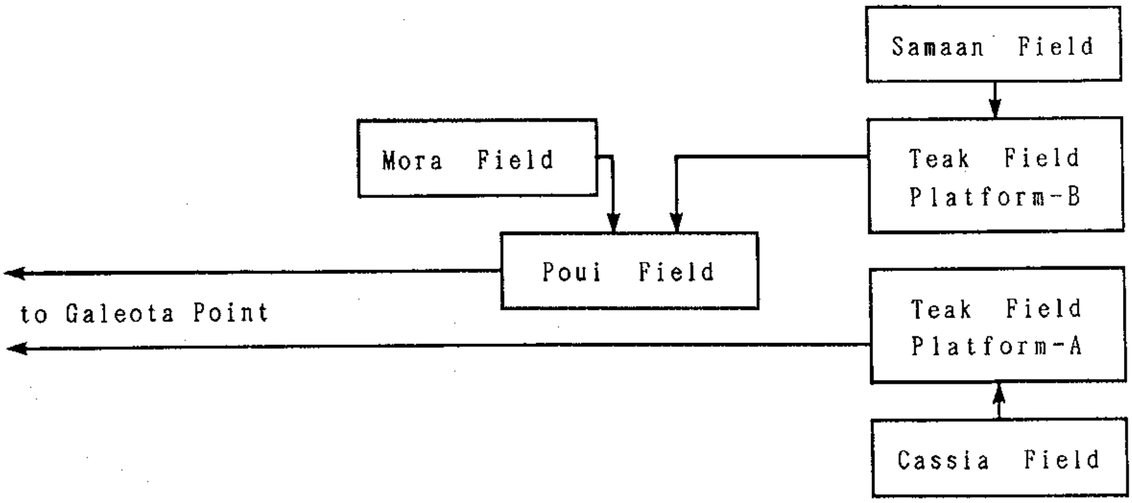


Figure 5-3 ATOC's Crude Oil Transportation System

(2) Petrotrin

In Trinidad and Tobago, Trintoc and Trintopec had independently constructed and operated their pipeline systems. After the establishment of Petrotrin by merger of the above two companies, a study was done for streamlining the pipeline systems including abolition and unification of the existing pipelines. However, at the time of the second field survey, the complicated pipeline system built by the two companies were still in use. The following is a summary of the companies' pipeline systems.

1) Former Trintoc

The former Trintoc produces oil in the east coast marine area, west coast marine area (the Gulf of Paria) and on the Island of Trinidad. The oil produced from the Galeota field on the east coast marine area is sent onshore (Galeota Point) through an 8-inch pipeline. All landed oil is exported, although there is a pipeline for sending oil to the refineries. The oil produced at the Brighton field on the Gulf of Paria is transported to Pointe-a-Pierre Refinery.

Oil from the southeastern onshore oilfields is gathered chiefly at Barrackpore Tank Farm, and oil from the southwestern fields is gathered at Bernstein Tank Farm. The oil from Barrackpore is transported by a pipeline to Philippine and connected to the line from Bernstein at this point. The combined oil is sent to Pointe-a-Pierre Refinery. The domestic crude oil is not sent to Point Fortin Refinery. This refinery processes imported crude oil only. Figure 5-4 shows the block flow diagram of the former Trintoc's crude oil transportation system.

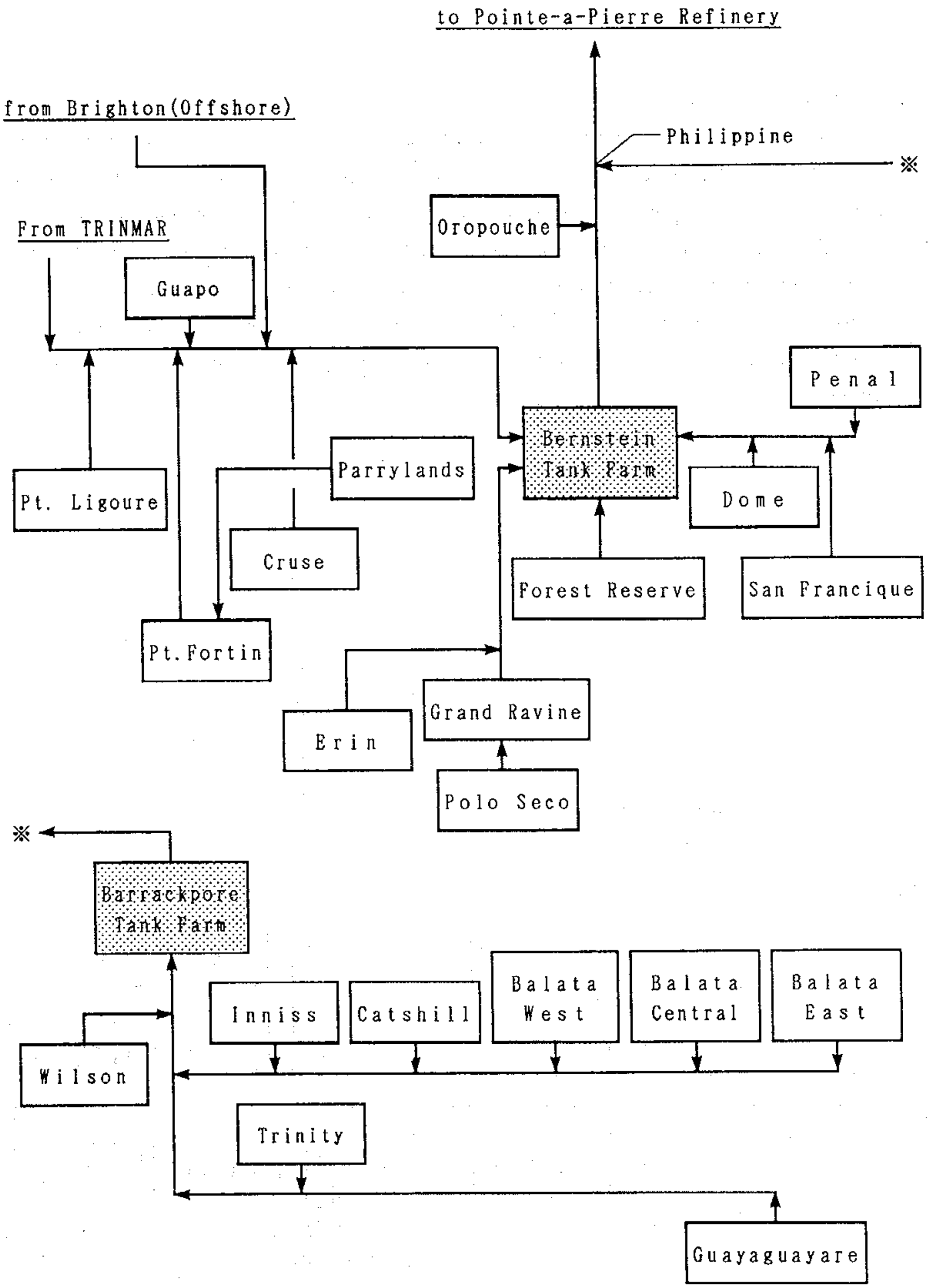


Figure 5-4 TRINTOC's Crude Oil Transportation System

2) Former Trintopec

The major oil fields of the former Trintopec are located along the southern coast of the Island of Trinidad. The oils produced at these fields are sent to Los Bajos Tank Farm. Formerly, the oil gathered at Los Bajos was sent to Point Fortin Refinery. However, since the suspension of domestic oil processing at this refinery, the oils have been sent to former Trintoc's Bernstein Tank Farm through its own Fyzabad Main Storage. Presently, oil is sent directly from Los Bajos to Bernstein without passing Fyzabad. Figure 5-5 shows the former Trintopec's crude oil transportation system. In this figure, the portions indicated by a broken line are former Trintoc's facilities.

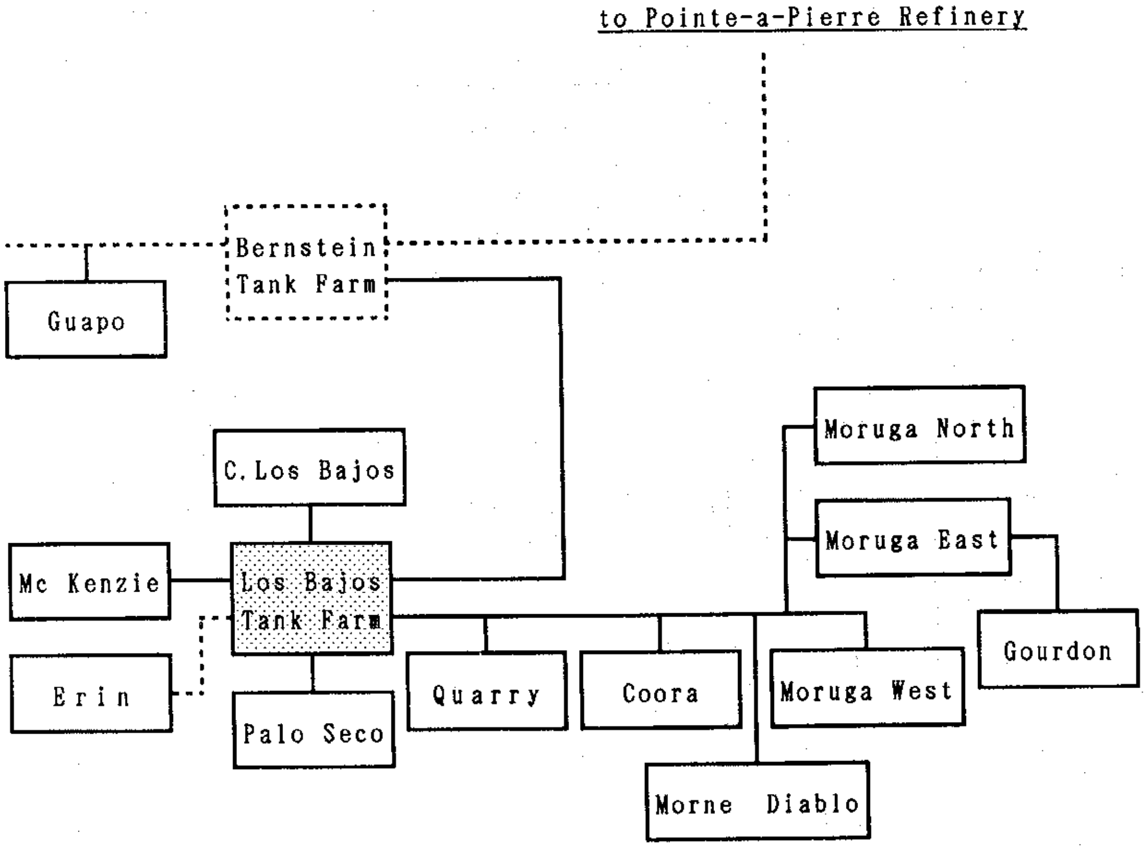


Figure 5-5 Trintopec's Crude Oil Transportation System

(3) TRINMAR

TRINMAR is producing at the Soldado and Fortin offshore fields, both located in the Gulf of Paria. The Soldado field consists of the Main, North, East and South-West fields. Oils produced from these fields are sent to the company's main storage at Point Ligoure through a 16-inch pipeline from the offshore platforms. The crude oil is degassed and dewatered at the main storage and is sent to Pointe-a-Pierre Refinery through the pipelines of Petrotrin.

(4) PECOL

PECOL's oil production comes from the fields of San Francique, Fyzabad/Roodal, Icacos, Palo Seco and Siparia. The oils from Icacos and Palo Seco are trucked to Fyzabad. The oils sent to Fyzabad and produced at other fields are pumped to Pointe-a-Pierre Refinery through the pipelines of Petrotrin.

5-3-2 Natural Gas

The gas pipeline system of Trinidad and Tobago was installed to send the gas produced in the east coast marine area to consuming areas such as the Point Lisas Industrial Estate and the Port of Spain metropolitan area. The gas pipeline system is widely divided into four lines. The first is NGC's 30-inch pipeline from AMOCO's Cassia gas field to the Point Lisas Industrial Estate, laid through the Pelican gas field of Trintomar, Mora gas field, passing the south of Navette oil field and the west of Beach oil field. The second is NGC's 24-inch pipeline from AMOCO's Teak oil field to the above pipeline through Galeota Point located at the southeast corner of the Island of Trinidad. The third is T&TEC's 16-inch pipeline from Point Lisas Industrial Estate to Port of Spain for supplying natural gas to the power station at Port of Spain. Further, NGC is sending gas by a 6-inch pipeline from Petrotrin's Mahaica gas field to the above T&TEC's pipeline. The location of the gas pipelines is shown in Figure 5-2.

5-3-3 Petroleum Products

The majority of the petroleum products produced at both Point-a-Pierre and Point Fortin Refineries are exported from the shipping facilities next to the refineries. In the local market, the National Petroleum Marketing Company (NPMC) exclusively distributes all petroleum products excluding lubricating oil. There is no pipeline for transporting petroleum products to dealers and/or consumers. All petroleum products are transported by truck. Gasoline, the most demanded petroleum product in the country, has been distributed to consumers through 212 service stations. The service stations are owned either by NPMC or dealers. The number of the service stations owned by NPMC is 86. Regionally, 203 stations are located in the Island of Trinidad and nine in the Island of Tobago. The number of service stations in this country is too large vis-a-vis the number of cars. It is planned therefore to streamline geographical distribution of the service stations.

Chapter 6 Emulsions

Chapter 6 Emulsions

6-1 Origins and Formation of Emulsions

6-1-1 Emulsions and Treatment of Emulsions

An emulsion is a system in which fine liquid droplets are dispersed in another insoluble liquid. Milk, cream and mayonnaise are typical examples. Two liquids which are insoluble in each other, such as water and oil, form an emulsion when they are shaken together. However, such an emulsion is normally unstable, and readily separates into the two liquid phases. In order to make a stable and rich emulsion, it is generally necessary to add a third substance. Such a substance is called emulsifying agent. Surfactants such as soap are typical emulsifying agents. Pulverized solid materials, soot or silts for example, also act as emulsifying agents.

With the system of water and oil, there are two kinds of emulsion. One is the oil-in-water type in which oil is dispersed in water, and the other is the water-in-oil type in which water is dispersed in oil.

Emulsions are frequently formed when crude oil is produced with water. Oil, gas and water are contained in the pores of the reservoir rocks. The water originates from sea water. In the case of onshore oil fields of Trinidad and Tobago, crude oils generally have high gravities and viscosities. The formation water is low in salt content as is typical of the Cenozoic formation. The mobility of the oil is low and the ratio of water to oil tends to be high. The difference in specific gravity between oil and water is low. These conditions combine to facilitate formation of emulsions. Moreover, the excessive production of oil increases the water/oil ratio by coning and channeling from the water zone. The water flooding or thermal secondary recovery, notably steam injection, done to maintain the reservoir pressure increases production of water by water breakthrough. All these contribute to formation of oil-containing emulsions.

The most serious problem in the petroleum pollution in Trinidad and Tobago is discharge of such emulsions to the environment without proper treatment to remove oil. The solution of this problem requires first and foremost breaking the emulsions into oil and clear water.

Chemical methods, heating and freezing, centrifugation and coagulation are commonly employed for this purpose. The selection of the proper method requires understanding of the character of the subject emulsions.

This chapter studies characteristics and methods of treating the emulsions which cause petroleum pollution in Trinidad and Tobago. The results of the experiments done on actual samples to achieve such objectives are presented.

6-1-2 Emulsions by Source

The emulsions causing the petroleum pollution in Trinidad and Tobago are formed mainly in association with crude oil production. Fluids produced from oil wells, actually mixtures of crude oil and water, referred to hereinafter as "crude oil/water mix", are gathered at gathering stations and then transferred to tank farms where they are supposed to be separated into water and crude oil. Crude oil, after its water content has been reduced to a certain standard, is transferred to the refinery through a trunk pipeline. The separated water is in the form of an oil-in-water emulsion. Such water is discharged to the public waters through API separators or pits that are intended to remove oil but are not actually effective.

Water flooding using abundant ground water and gas lift is extensively done. Steam injection is also used to increase oil production. The water content of the fluid produced by steam injection, hereinafter referred to as "thermal crude", contains as much as 70 to 85 percent water. The yields of crude oil at the Bernstein thermal wells are, for example, as low as 15 percent. In such thermal cases, the separated water forms tough and stable emulsions resembling normal muddy river water. Such an emulsion exhibits no sigh of separation even after quietly standing for months.

The intermediate emulsion of water-in-oil type is very stable. Such emulsions are contained at first in the oil floating on the API separators but migrate to various places, because they are neither easily broken nor processable as they are.

(1) Emulsions Generated from Oil Wells, Tank Farms and Refinery

The oil pollution arising in the area from the oil wells to the gathering stations and tank farms is caused either by mechanical troubles with the facilities, deterioration of pipelines for example, or by operational errors like undue draining of water at tank farms. The emulsions that may be discharged are crude oil/water mix in the former case and separated water containing oil, or oil-in-water emulsions, in the latter case.

One of the functions of the tank farms is to remove from the crude oil/water mix the impurities coming from underground and to make the oil meet the pipeline specifications. The separation between oil and water is the most important purpose; removal of mineral matter such as silt and clay, and organic matter like sludge, is another purpose. The oily effluent from tank farms that contains water, mineral matter, and sludge consists mainly of the following three components.

1) Water Separated in Washing Tanks

The problem here is the water separated after demulsifiers are added to the crude oil/water mix. The quantity and degree of oil contamination of water vary with the characteristics and water content of the crude oil/water mix. A sample of water separated from the Bernstein thermal crude shows the following quality.

Type of emulsion	O/W
Oil & Grease (mg/liter)	More than 10,000
pH	7 - 8

Fine oil droplets thoroughly dispersed in water to the extent of as high as one percent form a stable emulsion. Certain substances which breaks the surface tension and fine mineral particles can stabilize the emulsions. This question will be discussed later.

This emulsion resembles normal muddy brown river water. It flows naturally just like water because the continuous phase is water. This oil-in-water emulsion exhibits no sign of separation of oil by natural flotation even after quietly standing for months.

Large amounts of such an emulsion, containing oil in very high contents, are discharged to the public water. This emulsion is the greatest factor in the oil pollution in the study area.

2) Hydrous and Oily Sludge at the Bottom of Washing Tank

The hydrous and oily sludges settling down in earthen pits or at the bottoms of API separators have the following quality. Such sludges are very tough and stable complexes composed of mineral matter, insoluble organic materials, and crude oil/water mixes combined in complicated ways. Although the characteristics of the sludges differ from one well to another depending on the conditions of the wells, the following are their typical properties.

Appearance	Viscous paste
Water content	More than 40 percent

Type of emulsion	Mixtures of W/O type and O/W type

3) Skimmed Oil Recovered from API Separator

The separated water mentioned above 1) containing a large quantity of oil and oil spilled from operational causes and defective production facilities are introduced to API separators where floating oil is skimmed and gathered to pits for further separation. The skimmed oil typically has the following properties.

Appearance	Creamy
Water content	30 to 50 percent
Type of emulsion	W/O

(2) Floating oil on the API Separators in the Refinery

Oily effluent water from the production units is introduced to the four API separators. Floating oil is recovered as skimmed oil. Although characteristics of the oil vary according to oil composition, the oil characteristics are typically as follows.

Appearance	Creamy liquid
Water content	30 to 50 percent
Type of emulsion	W/O

Table 6-1 shows the appearance of representative samples collected during the first field survey.

Table 6-1 Appearance of Emulsion Samples

Sample Name	Appearance
BERNSTEIN TANK FARM Wash Tank Bleed Water (Secondary Production)	Brown, opaque, stable suspen.
Fisicalisation Tank Bleed Water (Secondary Production)	Brown, opaque, stable suspen.
Fisicalisation Tank Bleed Water (Primary Production)	Light brown, turbid
API Inlet Water	Brown, turbid
API Outlet Water	Brown, turbid
Earthen Pit Outlet Water	Brown, turbid
No. 5 tank Bleed Water (Primary Production)	Light Brown, turbid
POINT-A-PIERRE REFINERY No. 1 API Outlet Water	Light yellow, trans.
No. 2 API Outlet Water	Light yellow, trans.
No. 3 API Outlet Water	Light yellow, trans.
No. 4 API Outlet Water	Nearly colorless, trans.
PENAL EARTHEN CATCHMENT PIT Oily Water in the Pit	Light yellow, trans.

6-1-3 Characteristics of Emulsions

In order to find the proper means of treating the emulsions, tests were done to clarify the characteristics of these emulsions. Analysis of the components, observations under microscope, determination of particle sizes and their distribution were done on the oil-in-water emulsions collected in the study area. The following results were obtained.

(1) Analysis of Oil Content

Table 6-2 shows the results of oil content analysis of typical oil-in-water emulsion samples collected during the first field survey. The analytical method was based on the Japanese Industrial Standards (JIS) K0102 for extraction by the normal-hexane method or extraction by the carbon tetrachloride method. In Trinidad and Tobago, the ASTM D-4281 method for extraction by freon is officially applied to the analysis of oil content in effluent water. Therefore, it is required to consider the difference in the results obtained by different analytical methods in the evaluation of the results shown on Table 6-2. The details will be described in chapter 19.

Table 6-2 shows that the oil contents of the emulsions of separated water from the thermal oil wells are very high, at about 10,000 to 20,000 mg/liter. Considering the fact that cow's milk contains 3.0 to 3.5 percent fat, such oil content of the emulsion must be regarded as very high. Although there are fluctuations in data, the measured oil contents of the emulsion from the primary oil wells are from 100 to 300 mg/liter. These measured values are very low in comparison with those of the thermal oil wells. The measured oil content of water at inlets to the API separators in Bernstein Tank Farm shows values close to 1,000 mg/liter.

(2) Observation under Microscope

The emulsions are generated with the production of crude oil. Of these emulsions, the oil-in-water emulsions separated from the thermal oil contain oil in very high content. The emulsions are very stable. It was at first suspected that something contained in the emulsions stabilized these emulsions. At first, the suspended silt was considered to be the stabilizer because of the appearance resembling muddy water. The diameter of silt particles normally ranges from 1/16 to 1/265 millimeters, and can easily be visually distinguished from oil particles under an optical microscope. The samples were examined under a microscope to clarify the nature of the emulsion. The micro-photographs obtained are shown on Figures 6-1(1) to 6-1(3).

Table 6-2 Analysis of Oil & Grease in Emulsions

(milligrams/liter)

Sample Name	Oil & Grease CTC Method(*)	 N-Hexane	pH
BERNSTEIN TANK FARM Wash Tank Bleed Water (Secondary Production)	10,833	11,000	-
Fiscal. Tank Bleed Water (Secondary Production)	9,900	17,000	7.95
No. 5 tank Bleed Water (Primary Production)	49.2	150	8.01
Fiscal. Tank Bleed Water (Primary Production)	251	220	7.93
Earthen Pit Outlet Water	113	220	8.16
API Inlet Water	933	600	-
API Outlet Water(1)	269	140	8.11
API Outlet Water(2)	900	836	-
POINT-A-PIERRE REFINERY No. 1 API Outlet Water	132	120	7.10
No. 2 API Outlet Water	372	400	7.39
No. 3 API Outlet Water	4.25	13	7.02
No. 4 API Outlet Water	4.30	4.80	6.69
PENAL EARTHEN CATCHMENT PIT Oily Water in the Pit	4.75	12	7.04

(*): Carbon Tetrachloride Method

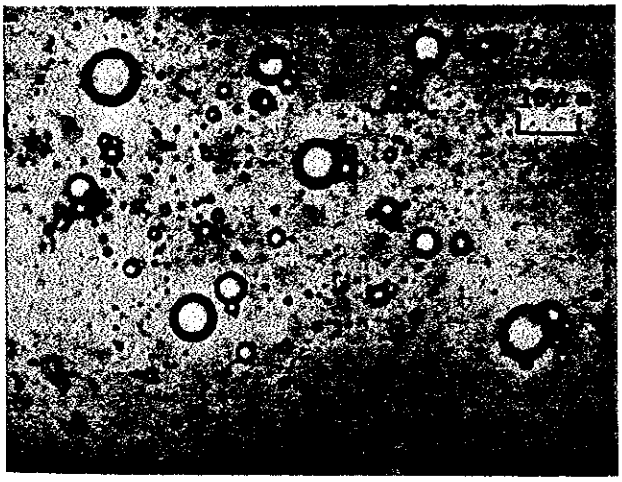
Spherical globules are seem dispersed throughout the samples of the water separated in the wash tanks for thermal oil and bled water from the fiscalization tanks of Bernstein Tank Farm, chosen as a typical example of stable emulsions of the highest oil content. Inorganic matter such as silt has irregular shapes while liquid droplets form spheres by their surface tension. It follows therefore that the observed spherical matter is fine droplets of crude oil dispersed in water, not suspended particles of silt. The droplets range in diameter from less than one micron to 10 microns. There are no signs of inorganic matter like suspended particles of silt adhering to the surfaces of the suspended oil particles to stabilize the emulsion, contrary to what was suspected at first.

Likewise, water separated from the primary crude oil has similar fine droplets thoroughly dispersed, the particle diameters are slightly larger than in the case of water from the thermal crude. Some oil particles cling together to form a cluster five to 50 microns across. The water from the thermal crude, although the oil content is tens of times higher than that of the water from the primary crude, is more stable and does not show signs of such clusterization. Considering the results obtained by the examination under microscope, it may be surmised that there exist one or more substances in the water phase that reduce the surface tension of oil droplets, thereby preventing them from coalescing. This will be discussed in more detail in (4) Analysis of Composition.

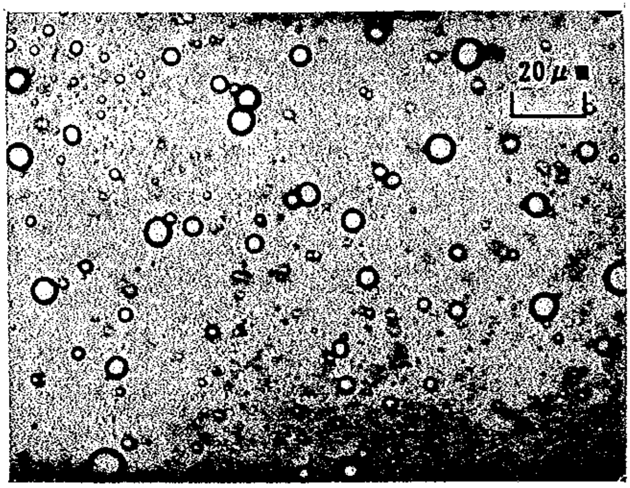
(3) Measurement of Particle Size Distribution

After having confirmed as a result of the microscopic examination that the water resembling muddy river water discharged from the tank farms is an emulsion in which fine oil particles, not silt particles, are dispersed in water, particle sizes and particle size distribution were measured. The Coulter counter method based on electric resistance was used. Tables 6-3(1) to 6-3(5) show the result of measurement. Figures 6-3(1) to 6-3(5) show size distribution curves developed from the data shown on these tables. These curves, frequency curves and oversize curves, indicate size distributions by number and volume. In this calculation, the particles were assumed to be perfect spheres. The frequency curves show the number of particles and their volumes corresponding to each diameter bracket. The oversize curves show the cumulative ratios of particle numbers to the total particle number and cumulative ratios of particle volumes to total particle volume in the order of increasing diameter bracket.

The median diameter* of the emulsions, or water separated from thermal crude, is approximately 2.5 microns. That of the emulsion, or water separated from primary crude, is from 8 to 10 microns, much larger than that from the thermal crude. These results agree well with the results of observations under the microscope. The minimum particle diameter amenable to treatment by gravity-induced separators like API separators or CPI is from 30 to 70 microns. The results of the measurements of particle size distributions indicate that gravity-induced oil separators are not applicable to this kind of emulsion. The total volume of oil droplets calculated from particle distribution agrees well with the measured oil content. Table 6-4 shows the median diameter of each sample. (Note: The median diameter is defined as the diameter corresponding to the 50 percent point on the oversize curve (D_{50}).)

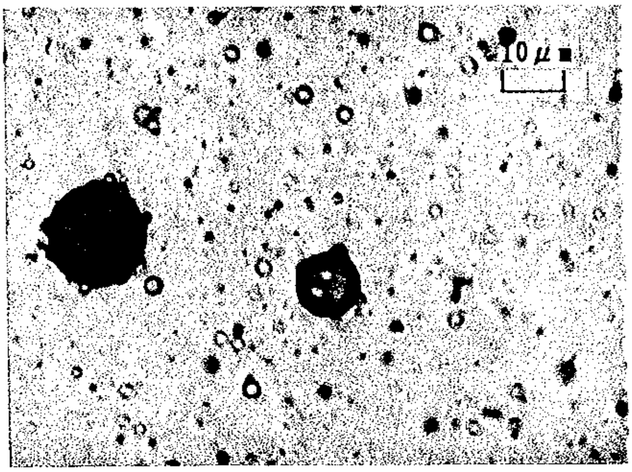


Wash Tank (Thermal) Bleed Water
(Bernstein Main Storage)

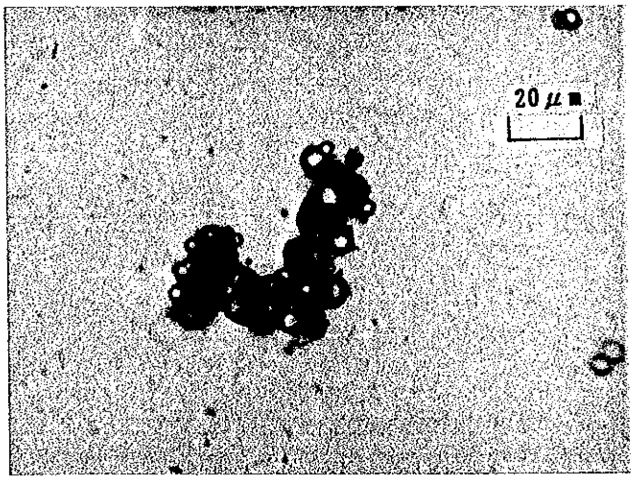


Wash Tank (Thermal) Bleed Water
(Bernstein Main Storage)

Figure 6-1(1) Microphotograph of O/W Type Emulsion

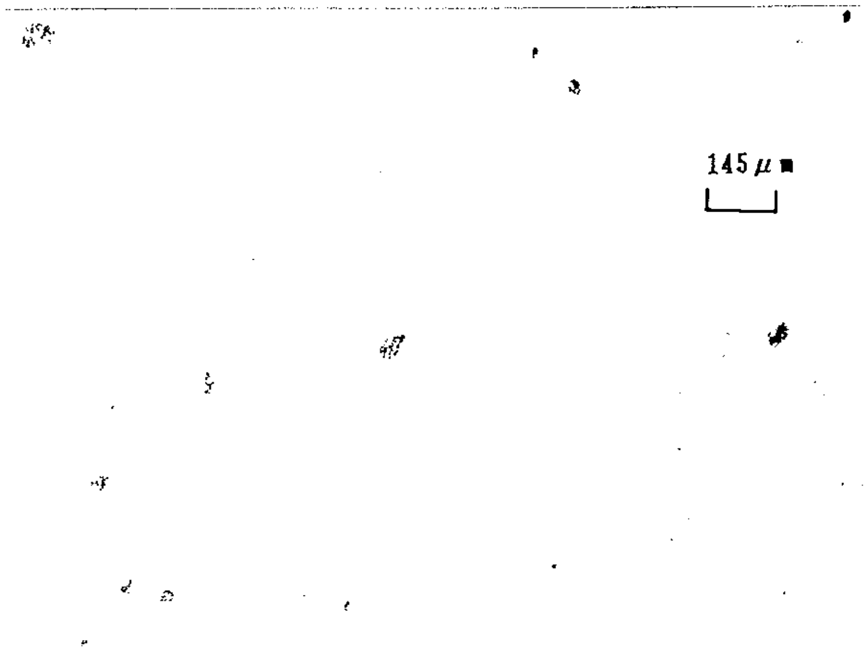


Fiscalisation Tank (Thermal) Bleed Water
(Bernstein Main Storage)

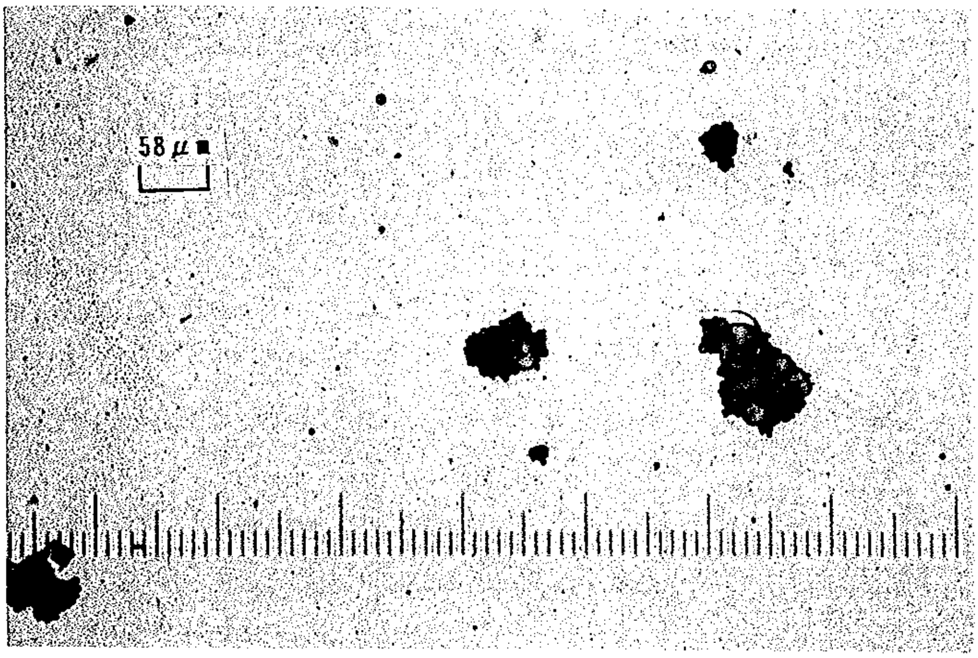


API Skimmer Outlet Water
(Bernstein Main Storage)

Figure 6-1(2) Microphotograph of O/W Type Emulsion



API Separator Outlet Water
(Bernstein Main Storage)



API Separator Outlet Water
(Bernstein Main Storage)

Figure 6-1(3) Microphotograph of O/W Type Emulsion

Table 6-3(1) Particle Size Distribution

SAMPLE NAME: BERNSTEIN MAIN STORAGE FISCALIZATION TANK BLEED WATER/THERMAL

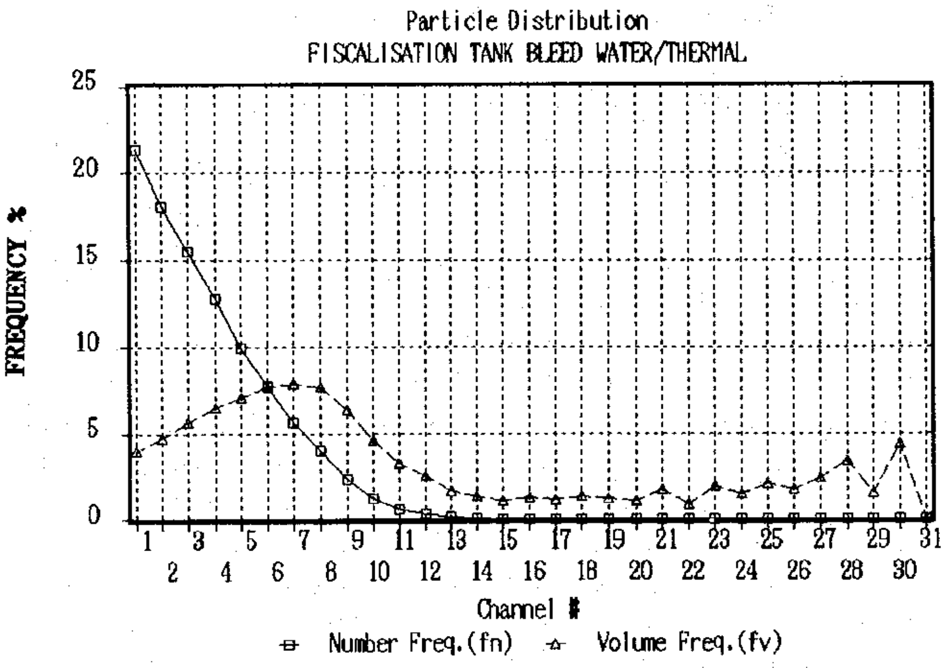
CHANNEL #	Diameter 〔μm〕	No. of Particle 〔 /ml〕	No. Accum. 〔 /ml〕	fn %	Rn %	Vol. of Particle 〔ml/ml〕	Vol.Accum. 〔ml/ml〕	fv %	Rv %
		(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)
1	1.03 - 1.15	5.713E+08	2.680E+09	21.31	100.00	3.873E-04	9.745E-03	3.97	100.00
2	1.15 - 1.29	4.848E+08	2.109E+09	18.09	78.69	4.610E-04	9.357E-03	4.73	96.03
3	1.29 - 1.44	4.147E+08	1.624E+09	15.47	60.60	5.522E-04	8.896E-03	5.67	91.29
4	1.44 - 1.61	3.421E+08	1.209E+09	12.76	45.12	6.352E-04	8.344E-03	6.52	85.63
5	1.61 - 1.80	2.668E+08	8.674E+08	9.96	32.36	6.925E-04	7.709E-03	7.11	79.11
6	1.80 - 2.01	2.077E+08	6.005E+08	7.75	22.41	7.520E-04	7.016E-03	7.72	72.00
7	2.01 - 2.25	1.523E+08	3.928E+08	5.68	14.66	7.704E-04	6.264E-03	7.91	64.29
8	2.25 - 2.51	1.066E+08	2.405E+08	3.98	8.97	7.526E-04	5.494E-03	7.72	56.38
9	2.51 - 2.81	6.286E+07	1.339E+08	2.35	5.00	6.194E-04	4.741E-03	6.36	48.66
10	2.81 - 3.14	3.266E+07	7.106E+07	1.22	2.65	4.503E-04	4.122E-03	4.62	42.30
11	3.14 - 3.51	1.644E+07	3.840E+07	0.61	1.43	3.164E-04	3.672E-03	3.25	37.68
12	3.51 - 3.92	9.240E+06	2.196E+07	0.34	0.82	2.480E-04	3.355E-03	2.55	34.43
13	3.92 - 4.38	4.340E+06	1.272E+07	0.16	0.47	1.624E-04	3.107E-03	1.67	31.89
14	4.38 - 4.90	2.460E+06	8.380E+06	0.09	0.31	1.287E-04	2.945E-03	1.32	30.22
15	4.90 - 5.47	1.460E+06	5.920E+06	0.05	0.22	1.066E-04	2.816E-03	1.09	28.90
16	5.47 - 6.11	1.240E+06	4.460E+06	0.05	0.17	1.260E-04	2.710E-03	1.29	27.81
17	6.11 - 6.83	7.800E+05	3.220E+06	0.03	0.12	1.106E-04	2.584E-03	1.14	26.51
18	6.83 - 7.63	6.800E+05	2.440E+06	0.03	0.09	1.346E-04	2.473E-03	1.38	25.38
19	7.63 - 8.53	4.200E+05	1.760E+06	0.02	0.07	1.160E-04	2.338E-03	1.19	24.00
20	8.53 - 9.53	2.800E+05	1.340E+06	0.01	0.05	1.079E-04	2.222E-03	1.11	22.81
21	9.53 - 10.6	3.200E+05	1.060E+06	0.01	0.04	1.708E-04	2.114E-03	1.75	21.70
22	10.6 - 11.9	1.200E+05	7.400E+05	0.00	0.03	8.946E-05	1.944E-03	0.92	19.95
23	11.9 - 13.3	1.800E+05	6.200E+05	0.01	0.02	1.885E-04	1.854E-03	1.93	19.03
24	13.3 - 14.8	1.000E+05	4.400E+05	0.00	0.02	1.452E-04	1.666E-03	1.49	17.09
25	14.8 - 16.6	1.000E+05	3.400E+05	0.00	0.01	2.026E-04	1.520E-03	2.08	15.60
26	16.6 - 18.5	6.000E+04	2.400E+05	0.00	0.01	1.698E-04	1.318E-03	1.74	13.52
27	18.5 - 20.7	6.000E+04	1.800E+05	0.00	0.01	2.365E-04	1.148E-03	2.43	11.78
28	20.7 - 23.1	6.000E+04	1.200E+05	0.00	0.00	3.300E-04	9.115E-04	3.39	9.35
29	23.1 - 25.8	2.000E+04	6.000E+04	0.00	0.00	1.531E-04	5.815E-04	1.57	5.97
30	25.8 - 28.9	4.000E+04	4.000E+04	0.00	0.00	4.285E-04	4.285E-04	4.40	4.40
31	28.9 - 32.2	0.000E+00	0.000E+00	0.00	0.00	0.000E+00	0.000E+00	0.00	0.00

fn: Rate of Particle Number=(A)/Total Number of Particles=(A)/2.680E+09.

Rn: Accumulation of fn.

fv: Rate of Particle Volume=(E)/Total Volume of Particles=(E)/9.74E-03.

Rv: Accumulation of fv.



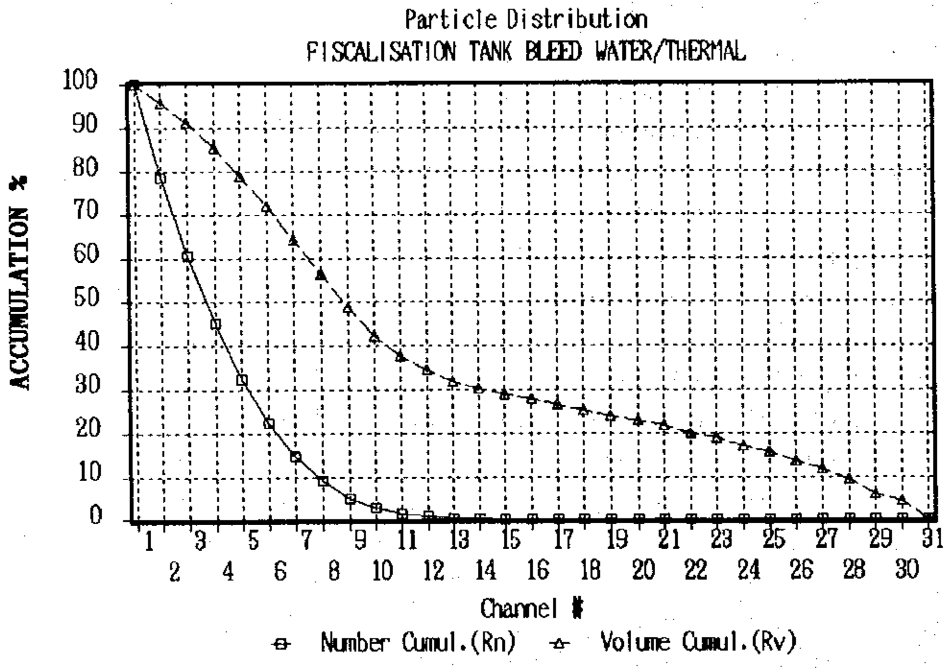


Figure 6-2(1) Particle Size Distribution

Table 6-3(2) Particle Size Distribution

SAMPLE NAME: BERNSTEIN MAIN STORAGE WASH TANK BLEED WATER/THERMAL

CHANNEL #	Diameter (μm)	No. of Particle (/ml)	No. Accum. (/ml)	fn %	Rn %	Vol. of Particle (ml/ml)	Vol. Accum. (ml/ml)	fv %	Rv %
		(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)
1	1.03 - 1.15	4.779E+08	2.195E+09	21.77	100.00	3.241E-04	8.982E-03	3.61	100.00
2	1.15 - 1.29	4.032E+08	1.717E+09	18.37	78.23	3.833E-04	8.658E-03	4.27	96.39
3	1.29 - 1.44	3.309E+08	1.314E+09	15.08	59.86	4.407E-04	8.275E-03	4.91	92.12
4	1.44 - 1.61	2.633E+08	9.831E+08	11.99	44.79	4.889E-04	7.834E-03	5.44	87.22
5	1.61 - 1.80	2.134E+08	7.198E+08	9.72	32.79	5.538E-04	7.345E-03	6.17	81.78
6	1.80 - 2.01	1.640E+08	5.064E+08	7.47	23.07	5.935E-04	6.792E-03	6.61	75.61
7	2.01 - 2.25	1.194E+08	3.425E+08	5.44	15.60	6.041E-04	6.198E-03	6.73	69.00
8	2.25 - 2.51	8.696E+07	2.231E+08	3.96	10.16	6.138E-04	5.594E-03	6.83	62.28
9	2.51 - 2.81	5.578E+07	1.361E+08	2.54	6.20	5.497E-04	4.980E-03	6.12	55.44
10	2.81 - 3.14	3.222E+07	8.034E+07	1.47	3.66	4.442E-04	4.430E-03	4.95	49.32
11	3.14 - 3.51	1.850E+07	4.812E+07	0.84	2.19	3.561E-04	3.986E-03	3.96	44.38
12	3.51 - 3.92	1.060E+07	2.962E+07	0.48	1.35	2.846E-04	3.630E-03	3.17	40.42
13	3.92 - 4.38	6.300E+06	1.902E+07	0.29	0.87	2.358E-04	3.346E-03	2.62	37.25
14	4.38 - 4.90	3.460E+06	1.272E+07	0.16	0.58	1.810E-04	3.110E-03	2.01	34.62
15	4.90 - 5.47	2.600E+06	9.260E+06	0.12	0.42	1.898E-04	2.929E-03	2.11	32.61
16	5.47 - 6.11	1.680E+06	6.660E+06	0.08	0.30	1.707E-04	2.739E-03	1.90	30.50
17	6.11 - 6.83	1.380E+06	4.980E+06	0.06	0.23	1.957E-04	2.568E-03	2.18	28.59
18	6.83 - 7.63	1.140E+06	3.600E+06	0.05	0.16	2.256E-04	2.373E-03	2.51	26.42
19	7.63 - 8.53	7.400E+05	2.460E+06	0.03	0.11	2.044E-04	2.147E-03	2.28	23.90
20	8.53 - 9.53	4.400E+05	1.720E+06	0.02	0.08	1.696E-04	1.943E-03	1.89	21.63
21	9.53 - 10.6	3.400E+05	1.280E+06	0.02	0.06	1.815E-04	1.773E-03	2.02	19.74
22	10.6 - 11.9	3.000E+05	9.400E+05	0.01	0.04	2.236E-04	1.592E-03	2.49	17.72
23	11.9 - 13.3	1.600E+05	6.400E+05	0.01	0.03	1.676E-04	1.368E-03	1.87	15.23
24	13.3 - 14.8	8.000E+04	4.800E+05	0.00	0.02	1.162E-04	1.200E-03	1.29	13.36
25	14.8 - 16.6	2.200E+05	4.000E+05	0.01	0.02	4.458E-04	1.084E-03	4.96	12.07
26	16.6 - 18.5	1.200E+05	1.800E+05	0.01	0.01	3.396E-04	6.384E-04	3.78	7.11
27	18.5 - 20.7	2.000E+04	6.000E+04	0.00	0.00	7.885E-05	2.988E-04	0.88	3.33
28	20.7 - 23.1	4.000E+04	4.000E+04	0.00	0.00	2.200E-04	2.200E-04	2.45	2.45
29	23.1 - 25.8	0.000E+00	0.000E+00	0.00	0.00	0.000E+00	0.000E+00	0.00	0.00
30	25.8 - 28.9	0.000E+00	0.000E+00	0.00	0.00	0.000E+00	0.000E+00	0.00	0.00
31	28.9 - 32.2	0.000E+00	0.000E+00	0.00	0.00	0.000E+00	0.000E+00	0.00	0.00

fn: Rate of Particle Number=(A)/Total Number of Particles=(A)/2.195E+09

Rn: Accumulation of fn.

fv: Rate of Particle Volume=(E)/Total Volume of Particles=(E)/8.982E-03

Rv: Accumulation of fv.

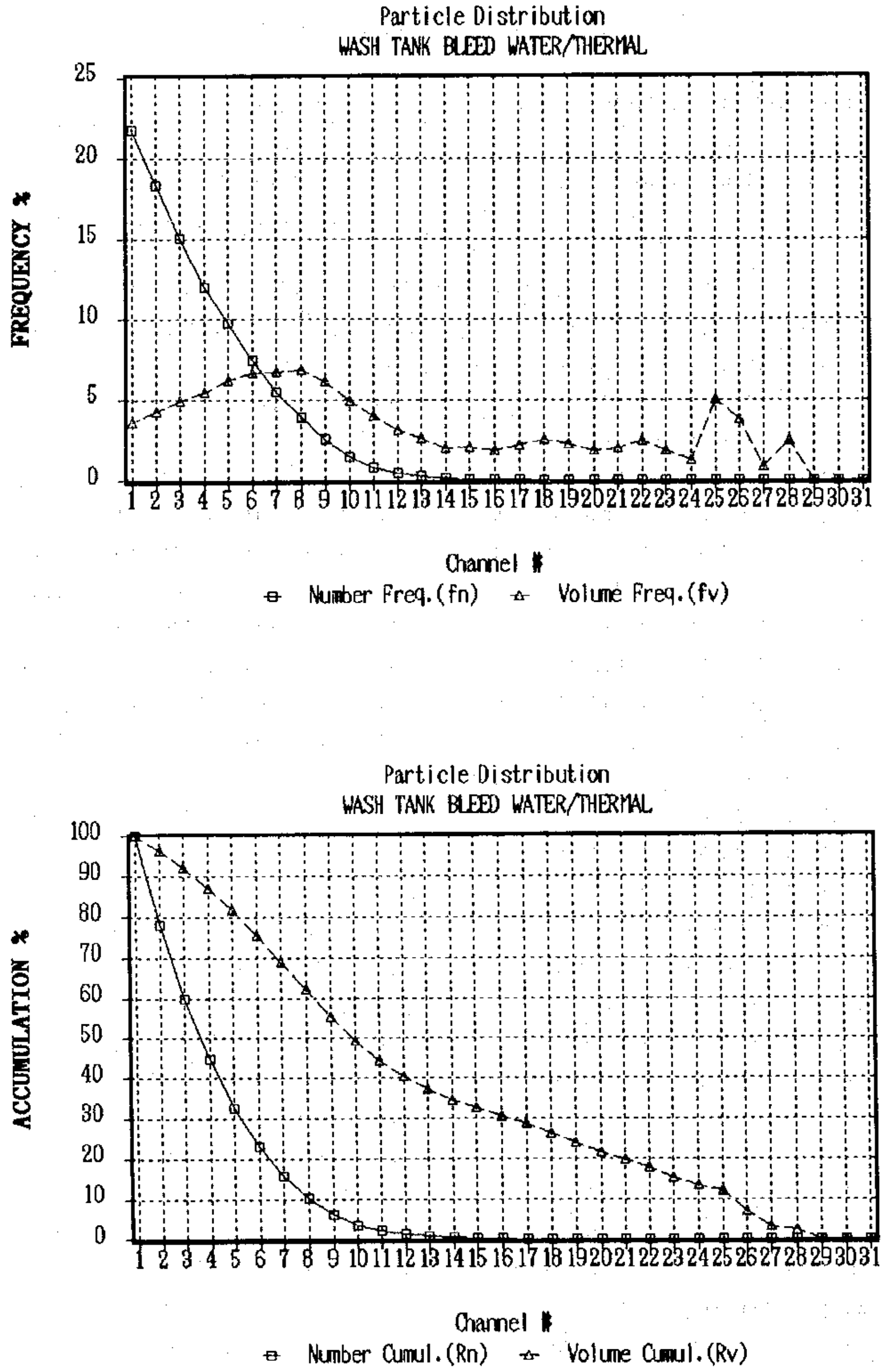


Figure 6-2(2) Particle Size Distribution

Table 6-3(3) Particle Size Distribution

SAMPLE NAME: BERNSTEIN MAIN STORAGE FISCALIZATION TANK BLEED WATER/NON-THERMAL

CHANNEL	Diameter	No. of		fn	Rn	Vol. of		fv	Rv
#		Particle	No. Accum.			Particle	Vol. Accum.		
	(μm)	(/ml)	(/ml)	%	%	(ml/ml)	(ml/ml)	%	%
		(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)
1	1.03 - 1.15	1.814E+07	3.891E+07	46.62	100.00	1.230E-05	2.531E-04	4.86	100.00
2	1.15 - 1.29	8.909E+06	2.077E+07	22.90	53.38	8.470E-06	2.408E-04	3.35	95.14
3	1.29 - 1.44	4.478E+06	1.186E+07	11.51	30.48	5.963E-06	2.323E-04	2.36	91.79
4	1.44 - 1.61	2.265E+06	7.383E+06	5.82	18.97	4.206E-06	2.264E-04	1.66	89.44
5	1.61 - 1.80	1.372E+06	5.118E+06	3.53	13.15	3.561E-06	2.221E-04	1.41	87.78
6	1.80 - 2.01	8.370E+05	3.746E+06	2.15	9.63	3.030E-06	2.186E-04	1.20	86.37
7	2.01 - 2.25	6.160E+05	2.909E+06	1.58	7.48	3.117E-06	2.156E-04	1.23	85.17
8	2.25 - 2.51	4.290E+05	2.293E+06	1.10	5.89	3.028E-06	2.124E-04	1.20	83.94
9	2.51 - 2.81	3.790E+05	1.864E+06	0.97	4.79	3.735E-06	2.094E-04	1.48	82.74
10	2.81 - 3.14	2.830E+05	1.485E+06	0.73	3.82	3.902E-06	2.057E-04	1.54	81.27
11	3.14 - 3.51	2.290E+05	1.202E+06	0.59	3.09	4.408E-06	2.018E-04	1.74	79.73
12	3.51 - 3.92	1.850E+05	9.730E+05	0.48	2.50	4.966E-06	1.974E-04	1.96	77.98
13	3.92 - 4.38	1.530E+05	7.880E+05	0.39	2.03	5.726E-06	1.924E-04	2.26	76.02
14	4.38 - 4.90	1.200E+05	6.350E+05	0.31	1.63	6.277E-06	1.867E-04	2.48	73.76
15	4.90 - 5.47	1.070E+05	5.150E+05	0.27	1.32	7.809E-06	1.804E-04	3.09	71.28
16	5.47 - 6.11	8.900E+04	4.080E+05	0.23	1.05	9.045E-06	1.726E-04	3.57	68.19
17	6.11 - 6.83	7.900E+04	3.190E+05	0.20	0.82	1.120E-05	1.635E-04	4.43	64.62
18	6.83 - 7.63	5.400E+04	2.400E+05	0.14	0.62	1.069E-05	1.523E-04	4.22	60.19
19	7.63 - 8.53	3.700E+04	1.860E+05	0.10	0.48	1.022E-05	1.417E-04	4.04	55.97
20	8.53 - 9.53	4.100E+04	1.490E+05	0.11	0.38	1.581E-05	1.314E-04	6.25	51.93
21	9.53 - 10.6	3.500E+04	1.080E+05	0.09	0.28	1.869E-05	1.156E-04	7.38	45.69
22	10.6 - 11.9	2.900E+04	7.300E+04	0.07	0.19	2.162E-05	9.695E-05	8.54	38.31
23	11.9 - 13.3	1.700E+04	4.400E+04	0.04	0.11	1.781E-05	7.533E-05	7.04	29.76
24	13.3 - 14.8	1.000E+04	2.700E+04	0.03	0.07	1.452E-05	5.752E-05	5.74	22.73
25	14.8 - 16.6	1.300E+04	1.700E+04	0.03	0.04	2.634E-05	4.300E-05	10.41	16.99
26	16.6 - 18.5	2.000E+03	4.000E+03	0.01	0.01	5.660E-06	1.666E-05	2.24	6.58
27	18.5 - 20.7	0.000E+00	2.000E+03	0.00	0.01	0.000E+00	1.100E-05	0.00	4.35
28	20.7 - 23.1	2.000E+03	2.000E+03	0.01	0.01	1.100E-05	1.100E-05	4.35	4.35
29	23.1 - 25.8	0.000E+00	0.000E+00	0.00	0.00	0.000E+00	0.000E+00	0.00	0.00
30	25.8 - 28.9	0.000E+00	0.000E+00	0.00	0.00	0.000E+00	0.000E+00	0.00	0.00
31	28.9 - 32.2	0.000E+00	0.000E+00	0.00	0.00	0.000E+00	0.000E+00	0.00	0.00

fn: Rate of Particle Number=(A)/Total Number of Particles=(A)/3.891E+07

Rn: Accumulation of fn.

fv: Rate of Particle Volume=(E)/Total Volume of Particles=(E)/2.531E-04

Rv: Accumulation of fv.

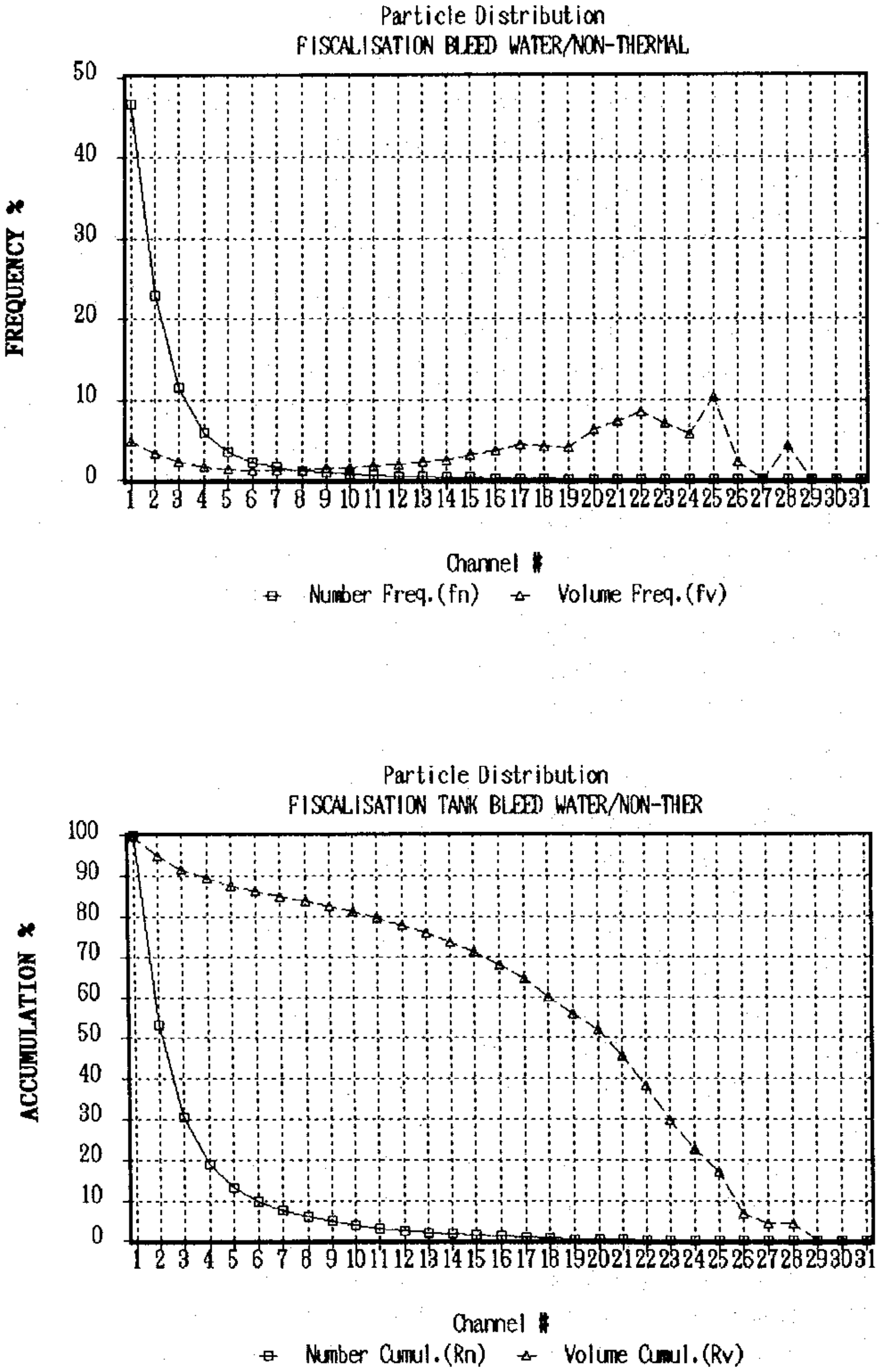


Figure 6-2(3) Particle Size Distribution

Table 6-3(4) Particle Size Distribution

SAMPLE NAME: BERNSTEIN MAIN STORAGE API SKIMMER INLET WATER

CHANNEL #	Diameter (μm)	No. of Particle (/ml) (A)	No. Accum. (/ml) (B)	fn % (C)	Rn % (D)	Vol. of Particle (ml/ml) (E)	Vol. Accum. (ml/ml) (F)	fv % (G)	Rv % (H)
1	1.03 - 1.15	2.905E+07	8.534E+07	34.05	100.00	1.970E-05	8.900E-04	2.21	100.00
2	1.15 - 1.29	1.829E+07	5.628E+07	21.44	65.95	1.739E-05	8.703E-04	1.95	97.79
3	1.29 - 1.44	1.175E+07	3.799E+07	13.77	44.52	1.564E-05	8.529E-04	1.76	95.83
4	1.44 - 1.61	7.820E+06	2.624E+07	9.16	30.75	1.452E-05	8.372E-04	1.63	94.07
5	1.61 - 1.80	5.326E+06	1.842E+07	6.24	21.59	1.382E-05	8.227E-04	1.55	92.44
6	1.80 - 2.01	3.400E+06	1.310E+07	3.98	15.35	1.231E-05	8.089E-04	1.38	90.89
7	2.01 - 2.25	2.134E+06	9.696E+06	2.50	11.36	1.080E-05	7.966E-04	1.21	89.51
8	2.25 - 2.51	1.608E+06	7.562E+06	1.88	8.86	1.135E-05	7.858E-04	1.28	88.29
9	2.51 - 2.81	1.166E+06	5.954E+06	1.37	6.98	1.149E-05	7.745E-04	1.29	87.02
10	2.81 - 3.14	8.840E+05	4.788E+06	1.04	5.61	1.219E-05	7.630E-04	1.37	85.73
11	3.14 - 3.51	6.820E+05	3.904E+06	0.80	4.57	1.313E-05	7.508E-04	1.47	84.36
12	3.51 - 3.92	6.680E+05	3.222E+06	0.78	3.78	1.793E-05	7.376E-04	2.01	82.88
13	3.92 - 4.38	5.060E+05	2.554E+06	0.59	2.99	1.894E-05	7.197E-04	2.13	80.87
14	4.38 - 4.90	4.480E+05	2.048E+06	0.52	2.40	2.343E-05	7.008E-04	2.63	78.74
15	4.90 - 5.47	3.840E+05	1.600E+06	0.45	1.87	2.803E-05	6.773E-04	3.15	76.11
16	5.47 - 6.11	2.940E+05	1.216E+06	0.34	1.42	2.988E-05	6.493E-04	3.36	72.96
17	6.11 - 6.83	2.220E+05	9.220E+05	0.26	1.08	3.148E-05	6.194E-04	3.54	69.60
18	6.83 - 7.63	1.220E+05	7.000E+05	0.14	0.82	2.414E-05	5.880E-04	2.71	66.06
19	7.63 - 8.53	1.480E+05	5.780E+05	0.17	0.68	4.088E-05	5.638E-04	4.59	63.35
20	8.53 - 9.53	1.180E+05	4.300E+05	0.14	0.50	4.549E-05	5.229E-04	5.11	58.76
21	9.53 - 10.6	9.400E+04	3.120E+05	0.11	0.37	5.018E-05	4.774E-04	5.64	53.65
22	10.6 - 11.9	5.800E+04	2.180E+05	0.07	0.26	4.324E-05	4.273E-04	4.86	48.01
23	11.9 - 13.3	4.400E+04	1.600E+05	0.05	0.19	4.608E-05	3.840E-04	5.18	43.15
24	13.3 - 14.8	4.000E+04	1.160E+05	0.05	0.14	5.809E-05	3.379E-04	6.53	37.97
25	14.8 - 16.6	4.000E+04	7.600E+04	0.05	0.09	8.105E-05	2.799E-04	9.11	31.45
26	16.6 - 18.5	1.200E+04	3.600E+04	0.01	0.04	3.396E-05	1.988E-04	3.82	22.34
27	18.5 - 20.7	6.000E+03	2.400E+04	0.01	0.03	2.365E-05	1.648E-04	2.66	18.52
28	20.7 - 23.1	8.000E+03	1.800E+04	0.01	0.02	4.400E-05	1.412E-04	4.94	15.86
29	23.1 - 25.8	6.000E+03	1.000E+04	0.01	0.01	4.592E-05	9.720E-05	5.16	10.92
30	25.8 - 28.9	2.000E+03	4.000E+03	0.00	0.00	2.142E-05	5.128E-05	2.41	5.76
31	28.9 - 32.2	2.000E+03	2.000E+03	0.00	0.00	2.986E-05	2.986E-05	3.35	3.35

fn: Rate of Particle Number=(A)/Total Number of Particles=(A)/8.534E+07

Rn: Accumulation of fn.

fv: Rate of Particle Volume=(E)/Total Volume of Particles=(E)/8.900E-04

Rv: Accumulation of fv.

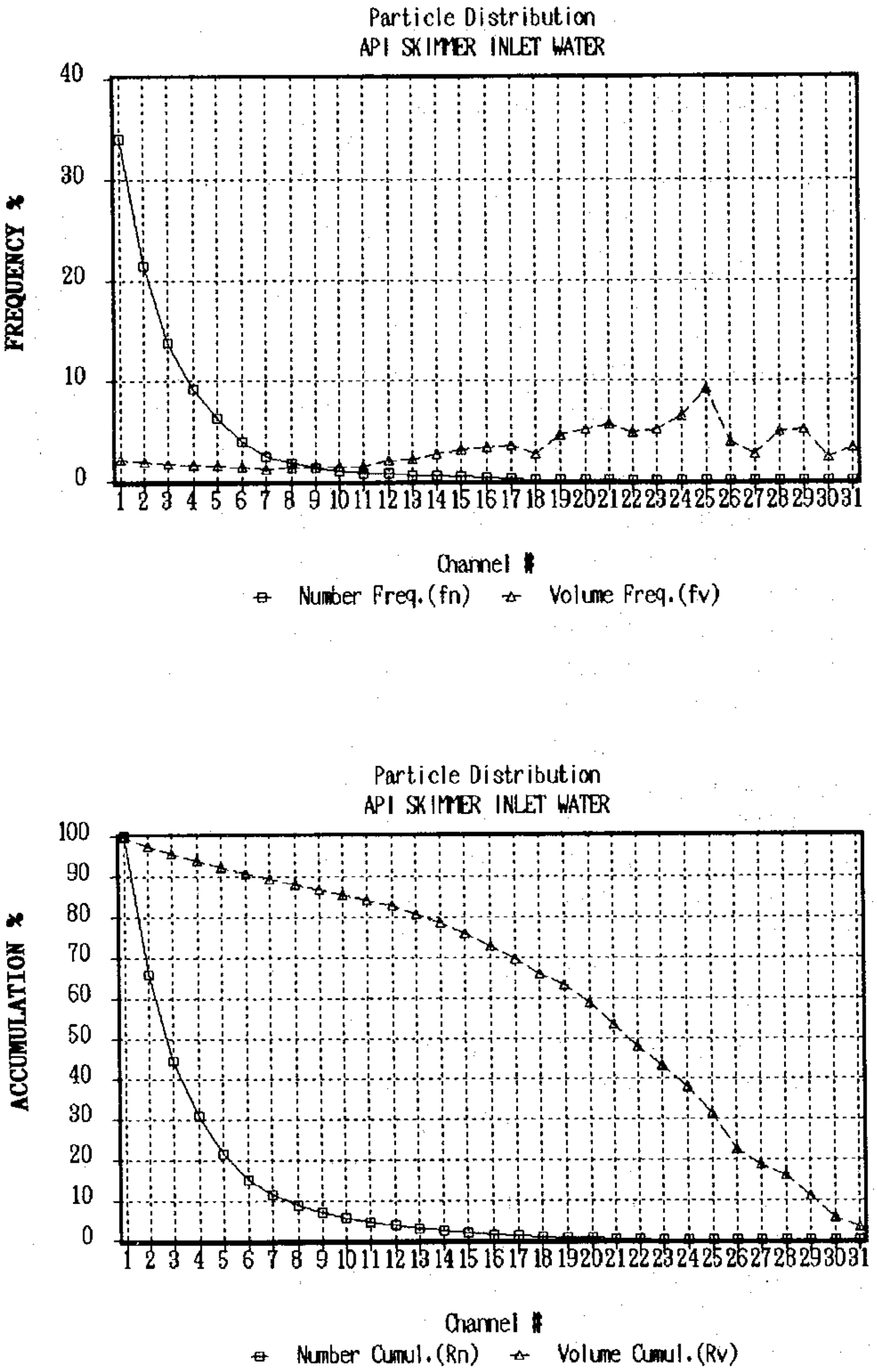


Figure 6-2(4) Particle Size Distribution

Table 6-3(5) Particle Size Distribution

SAMPLE NAME: BERNSTEIN MAIN STORAGE API SKIMMER OUTLET WATER/2ND SURVEY

CHANNEL #	Diameter (μm)	No. of Particle (/ml) (A)	No. Accum. (/ml) (B)	fn % (C)	Rn % (D)	Vol. of Particle (ml/ml) (E)	Vol. Accum. (ml/ml) (F)	fv % (G)	Rv % (H)
1	0.44 - 0.49	2.461E+08	1.121E+09	21.95	100.00	1.295E-05	4.627E-04	2.80	100.00
2	0.49 - 0.55	2.375E+08	8.750E+08	21.18	78.05	1.748E-05	4.498E-04	3.78	97.20
3	0.55 - 0.62	1.729E+08	6.375E+08	15.42	56.87	1.812E-05	4.323E-04	3.92	93.42
4	0.62 - 0.69	1.285E+08	4.646E+08	11.46	41.45	1.891E-05	4.142E-04	4.09	89.51
5	0.69 - 0.77	9.878E+07	3.361E+08	8.81	29.98	2.012E-05	3.952E-04	4.35	85.42
6	0.77 - 0.86	7.888E+07	2.373E+08	7.04	21.17	2.236E-05	3.751E-04	4.83	81.07
7	0.86 - 0.96	5.704E+07	1.585E+08	5.09	14.14	2.251E-05	3.528E-04	4.86	76.24
8	0.96 - 1.08	3.850E+07	1.014E+08	3.43	9.05	2.139E-05	3.303E-04	4.62	71.38
9	1.08 - 1.20	2.458E+07	6.292E+07	2.19	5.61	1.907E-05	3.089E-04	4.12	66.75
10	1.20 - 1.34	1.426E+07	3.834E+07	1.27	3.42	1.529E-05	2.898E-04	3.31	62.63
11	1.34 - 1.50	8.860E+06	2.408E+07	0.79	2.15	1.328E-05	2.745E-04	2.87	59.33
12	1.50 - 1.68	4.720E+06	1.522E+07	0.42	1.36	9.934E-06	2.612E-04	2.15	56.46
13	1.68 - 1.88	3.180E+06	1.050E+07	0.28	0.94	9.390E-06	2.513E-04	2.03	54.31
14	1.88 - 2.10	2.000E+06	7.320E+06	0.18	0.65	8.252E-06	2.419E-04	1.78	52.28
15	2.10 - 2.34	1.000E+06	5.320E+06	0.09	0.47	5.729E-06	2.336E-04	1.24	50.50
16	2.34 - 2.62	8.800E+05	4.320E+06	0.08	0.39	7.028E-06	2.279E-04	1.52	49.26
17	2.62 - 2.93	8.200E+05	3.440E+06	0.07	0.31	9.175E-06	2.209E-04	1.98	47.74
18	2.93 - 3.27	5.000E+05	2.620E+06	0.04	0.23	7.799E-06	2.117E-04	1.69	45.76
19	3.27 - 3.66	6.000E+05	2.120E+06	0.05	0.19	1.307E-05	2.039E-04	2.82	44.07
20	3.66 - 4.09	4.200E+05	1.520E+06	0.04	0.14	1.280E-05	1.908E-04	2.77	41.25
21	4.09 - 4.57	2.000E+05	1.100E+06	0.02	0.10	8.501E-06	1.781E-04	1.84	38.48
22	4.57 - 5.10	1.200E+05	9.000E+05	0.01	0.08	7.102E-06	1.696E-04	1.53	36.64
23	5.10 - 5.70	1.200E+05	7.800E+05	0.01	0.07	9.893E-06	1.625E-04	2.14	35.11
24	5.70 - 6.37	2.000E+05	6.600E+05	0.02	0.06	2.302E-05	1.526E-04	4.97	32.97
25	6.37 - 7.12	1.600E+05	4.600E+05	0.01	0.04	2.571E-05	1.295E-04	5.56	28.00
26	7.12 - 7.95	1.000E+05	3.000E+05	0.01	0.03	2.240E-05	1.038E-04	4.84	22.44
27	7.95 - 8.89	1.000E+05	2.000E+05	0.01	0.02	3.126E-05	8.143E-05	6.75	17.60
28	8.89 - 9.93	6.000E+04	1.000E+05	0.01	0.01	2.618E-05	5.018E-05	5.66	10.84
29	9.93 - 11.0	4.000E+04	4.000E+04	0.00	0.00	2.400E-05	2.400E-05	5.19	5.19

fn: Rate of Particle Number=(A)/Total Number of Particles=(A)/1.121E+09

Rn: Accumulation of fn.

fv: Rate of Particle Volume=(E)/Total Volume of Particles=(E)/4.627E-4

Rv: Accumulation of fv.

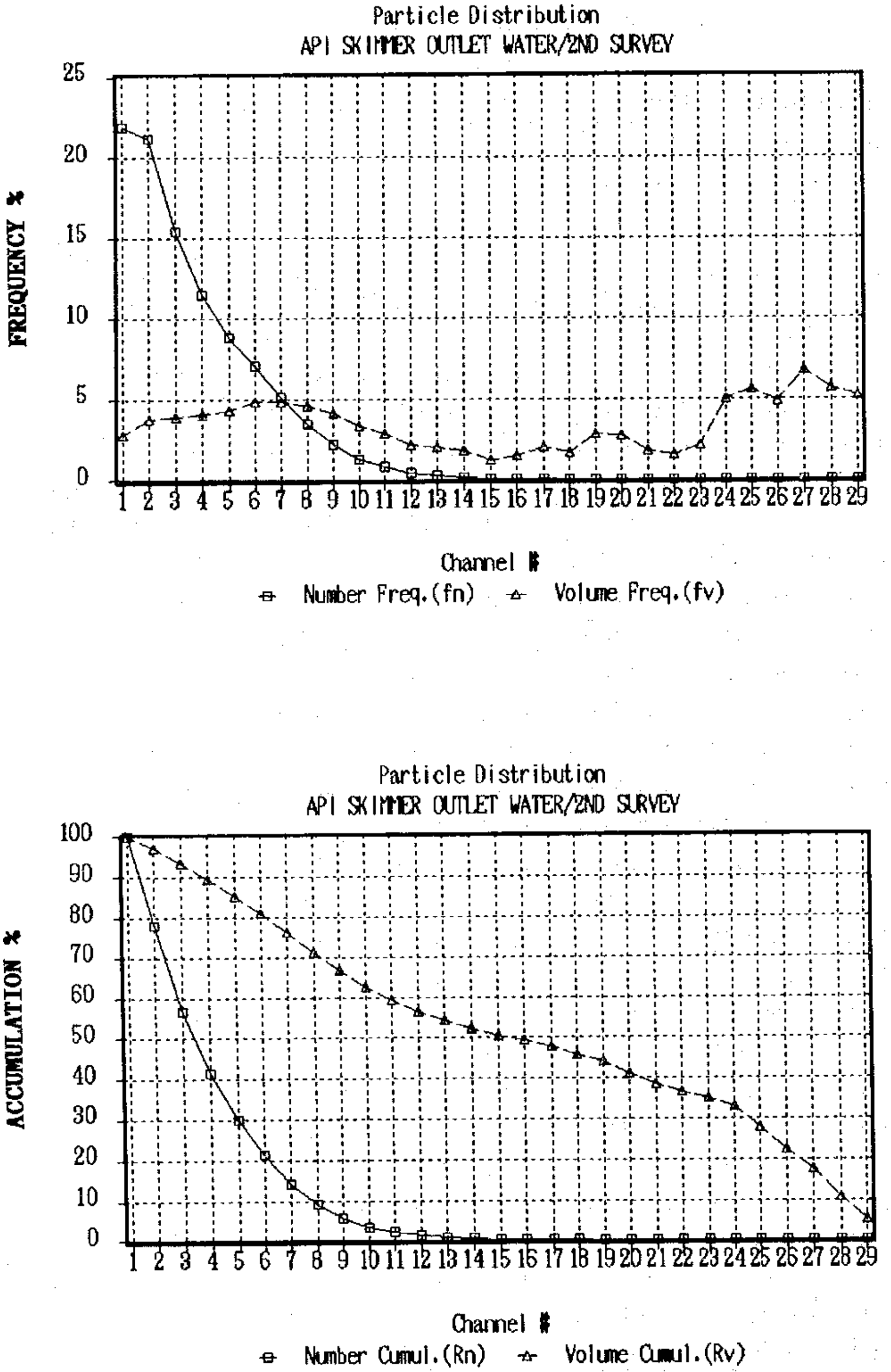


Figure 6-2(5) Particle Size Distribution

Table 6-4 Median Diameter of Oil Drops in Emulsion

(Unit: Micron)

Sample No.	1	2	3	4	5	6	7
Med. Dia.	2.7	2.3	8.1	11.0	5.2	9.1	2.7

Sample No.	
1	Wash tank bled water (Thermal)
2	Fisicalisation tank bled water (Thermal)
3	Fisicalisation tank bled water (Non-thermal)
4	API separator skimmer inlet water
5	API separator skimmer outlet water
6	Earthen pit outlet water
7	No. 5 Tank bled water (Non-thermal)

The samples tested were all collected from Bernstein Main Storage.

(4) Analysis of Composition

For effective treatment of waste water, it is necessary to understand its quality so that a proper combination of the treating methods that can achieve the objective may be employed. It was found through observation under microscope and measurement of particle size distribution that the average diameter of oil particles in the oil-in-water emulsions from the thermal oil was approximately 2.5 microns and that gravity-induced separators cannot separate such emulsions into water and oil. For this kind of emulsion, coagulation followed by flotation is generally considered necessary to separate oil and water and to purify the water. During the second field survey, flotation tests were carried out to confirm the effects of this method on the emulsions collected from the study areas.

Although clear water was obtained, some of the treated water samples exceeded the 50 mg/liter target. If oil droplets as small as one micron across are dispersed in water and their concentration is about 50 mg/liter, the water should be visually recognized to contain these particles by being slightly turbid. Therefore, the substance or substances measured as oil in excess of 50 mg/liter are considered to be substances dissolved in water. Substances dissolved in water are not amenable to treatment by flotation. Depending upon the concentration of the soluble substances left after treatment by air flotation, it is necessary to treat the water either by biological method or activated carbon adsorption. Existence of soluble substances seems also supported by stability of the emulsion and very high oil content.

Ordinarily, oil and grease in effluent water is analyzed by gravitational or infrared rays absorption methods. The gravitational methods extract oil and grease contained in water by such a solvent as normal hexane or freon and vaporize the solvent at fixed temperatures; the residual matter remaining after vaporization is measured as oil and grease. The infrared rays absorption method determines oil and grease by measuring absorption intensity at a particular wave length of infrared rays shown by the solvent after extracting oil and grease contained in the sample. Solvents such as carbon tetrachloride or chloroform are used. Accordingly, any substances extractable by the solvent used and remaining after vaporization in the case of the gravitational method or having absorption intensity in that particular wave length in the case of the infrared rays absorption method are measured as oil and grease.

The treatment of the emulsion to reduce oil content in water to the target level requires good understanding of the characteristics of the emulsion in question, and identities and concentrations of the substances dissolved in the sample if they really exist. Therefore the substances dissolved in the sample after flotation were studied.

Samples of oily water were taken at the outlets of the API separators at Bernstein Tank Farm during the second field survey and brought to Japan. These samples were treated with air flotation with an inorganic coagulant and/or a polymer coagulant, and clear water was obtained. For analysis of the dissolved substances, five samples of clear water were prepared; two of them were treated with activated carbon. A gas chromatograph mass spectrometer (GC/MS) was used for analysis. The model of GC/MS is JEOL DX-303HF (GC part: Hewlett Packard 589). The sample water conditions are shown in Table 6-5.

Table 6-5 Condition of Treated Water

Sample No.	Additive Chemicals						Treated Water		
	1		2		3		pH	Oil & Grease (mg/l)	
	Name	ppm	Name	ppm	Name	ppm		CTC(*)	N-hex(*)
1	Al_2SO_4	3,500	PA322 CP948	5 20	A.C.	500	7.4	75	127
2	Al_2SO_4	3,500	PA322 CP948	5 20	A.C.	2,000	7.4	36	-
3	Al_2SO_4	3,000	PA322	5	-	-	7.6	139	70

			CP948	20					
4	Al_2SO_4	10,000	PA322 CP948	10 40	-	-	5.9	60	-
5	PAC	10,000	A322 CP948	10 40	-	-	7.5	95	37

(*) CTC: Carbon Tetrachloride extraction-Infrared rays Method
N-HEX: Normal-Hexane extraction-Gravitational Method

1) Analysis by TIC

The subject emulsion originates from the crude oil/water mix produced from wells. The substances dissolved in the water obtained when the emulsion was broken came from the crude oil.

Hydrocarbons are the principal ingredients of the crude oil. Petroleum hydrocarbons are classified roughly into paraffinic, olefinic, naphthenic and aromatic hydrocarbons. Olefinic hydrocarbons do not normally exist in crude oil; therefore, analysis of paraffinic, naphthenic, and aromatic hydrocarbons was required.

Gas chromatograph mass spectrometers (GC/MS) are often used for the analysis of petroleum components. For qualitative analysis of unknown components, the Total Ion Current Chromatogram method (TIC) is used. This method checks each mass spectrum of separated peaks. Another method, the Selected Ion Monitoring method (SIM), has good selectivity and sensitivity for specified components and therefore is used for determination of each component. This time, identification of unknown components by TIC was first carried out.

Figure 6-3 shows the TIC chromatogram and mass spectrum of Sample No. 4. Paraffinic and aromatic hydrocarbons can be quantified based on particular mass spectra obtained after separation. The mass spectrum obtained for standard naphthenic acids procured in Japan is shown in Figure 6-4. "Naphthenic acids" is a generic term applied to all substances belonging to this group with varied carbon numbers. Therefore, the chromatogram does not have a sharp peak at a specific retention time but a gentle hilly peak over a wide range of retention times. In contrast to the spectrum of a single component substance which normally shows a few distinctive mass fragments, the mass spectrum of naphthenic acids is characterized by a large number of common mass fragments. Nevertheless, Figure 6-4 exhibits high intensity mass fragments at 81, 95 and 109 which are considered unique to naphthenic acids. This feature makes quantification of naphthenic acids possible. The naphthenic acids used for this analysis had a neutralization value of 220 Calcium equivalent.

The following results were obtained from the chromatograms and mass spectra of Sample Nos. 1 to 5.

1. There is no single constituent showing high concentration.
2. TIC chromatograms show gentle peaks; the retention times are nearly the same for all Samples Nos. 1 to 5.
3. Peak patterns of the samples are similar to those of standard naphthenic acids, but their retention times slightly differ from those shown by standard naphthenic acids.
4. The mass spectrum indicates no paraffinic or aromatic hydrocarbons within the sensitivity of this analysis.
5. The mass spectra show peaks unique to naphthenic acids.
6. Being composite homologues of varied carbon numbers, the retention time of the peaks shown by the standard naphthenic acids cannot serve as an absolute reference.
7. From the above it may be concluded that the peaks shown by Samples Nos. 1 to 5 correspond to naphthenic acids.

2) Analysis by SIM

Existence of the substances considered to be naphthenic acids is confirmed in Samples Nos. 1 to 5 by the TIC method. The TIC method is suited to qualitative analysis of multi-component substances. However, there is a drawback in that when a large peak exists, small peaks are overshadowed by it. Therefore, the GC/MS-SIM method was used for quantitative analysis of paraffinic, naphthenic, aromatic and aliphatic hydrocarbons because of its high sensitivity and selectivity to individual substances or groups. Paraffinic hydrocarbons with carbon numbers from 10 to 25 were quantified. Quantitative analysis was done on naphthenic acids using the Japanese standard naphthenic acids as explained above. For aromatic compounds, phenols (phenol, cresol and dimethylcresol) were quantitatively analyzed. The following mass numbers which characterize the each substance group are used for the monitoring.

	Paraffins	Naphthenic acid	Phenols	Aliphatics
Mass Number	99.0	95.0	94.0 108.0 22.0	60.0

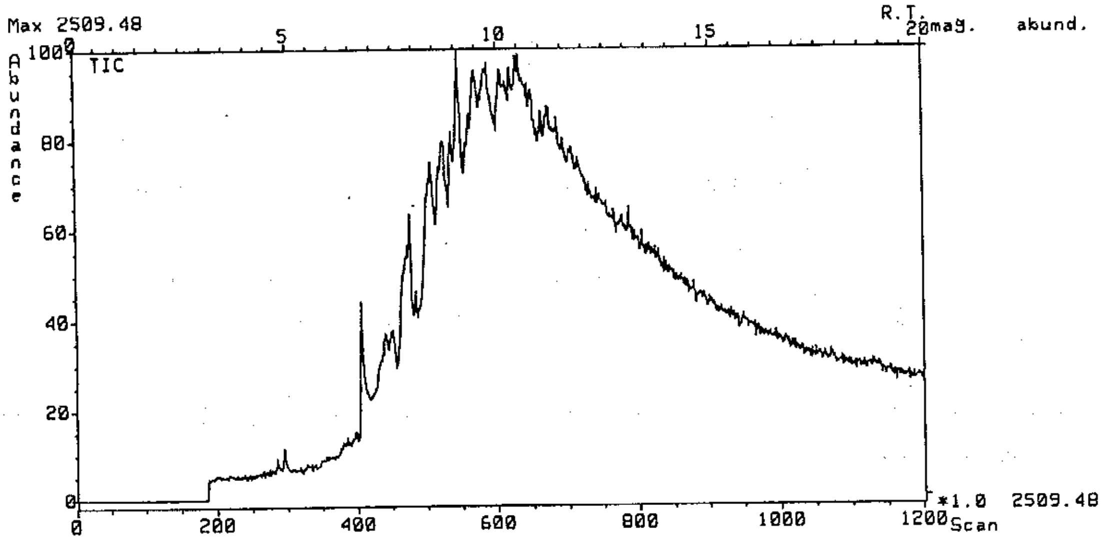
Figures 6-5(1) to 6-5(4) show SIM chromatograms. The results of the quantitative analysis are indicated in Table 6-6.

Table 6-6 Analysis of Water by GC/MS

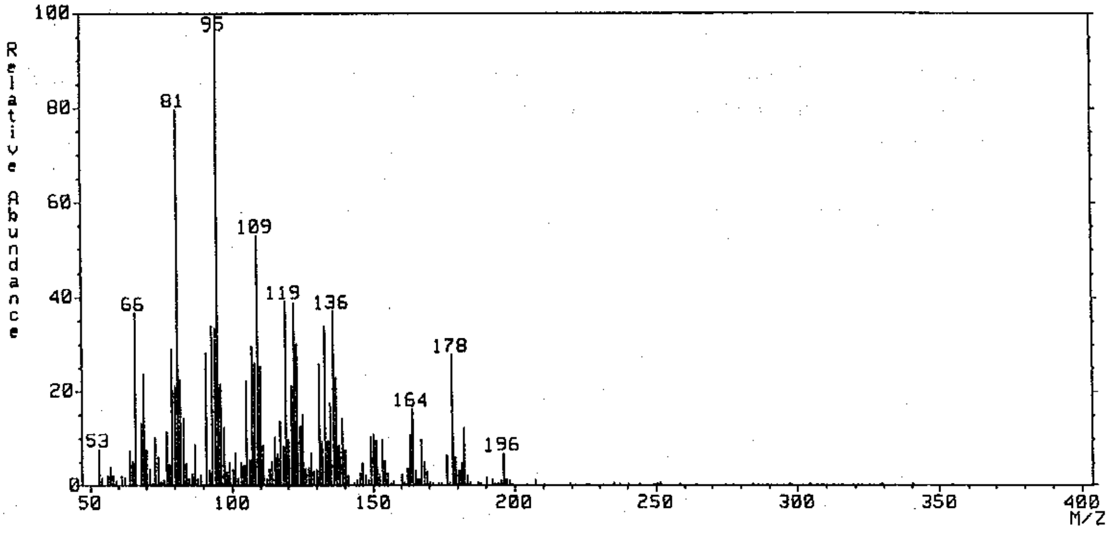
(Unit: mg/liter)

SAMPLE No.	Paraffinic Compounds	Naphthenic Compounds	Aromatic Compounds	Aliphatic Compounds	Total
1	1.9	31.3	0.56	-	33.8
2	1.3	12.8	0.07	-	14.2
3	1.6	55.7	1.27	-	58.6
4	1.9	14.5	1.93	-	18.3
5	1.9	42.7	2.71	-	47.3

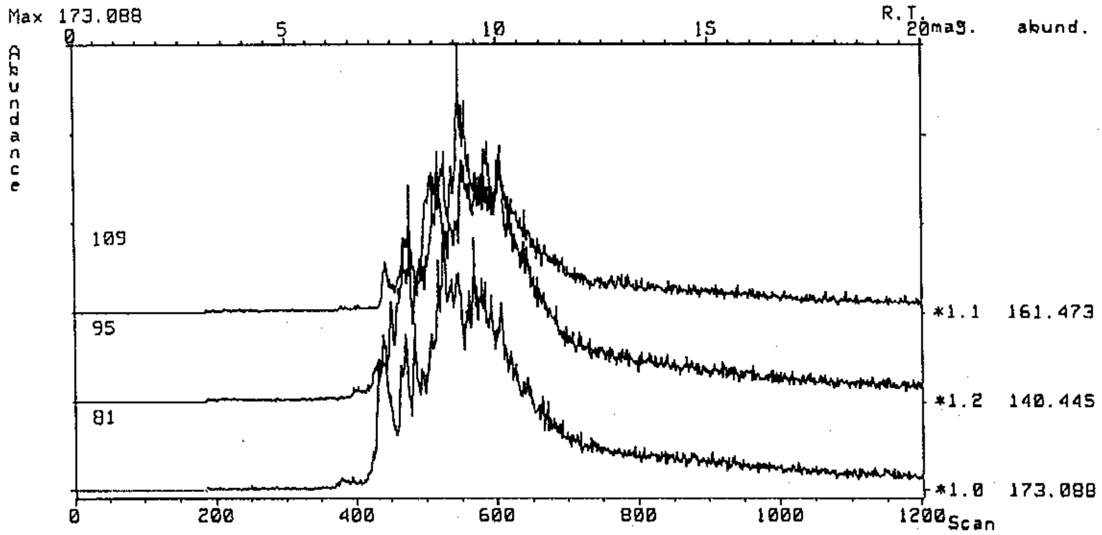
Source: Courtesy of Institute of Environmental Science and Technology, Yokohama National University



TIC

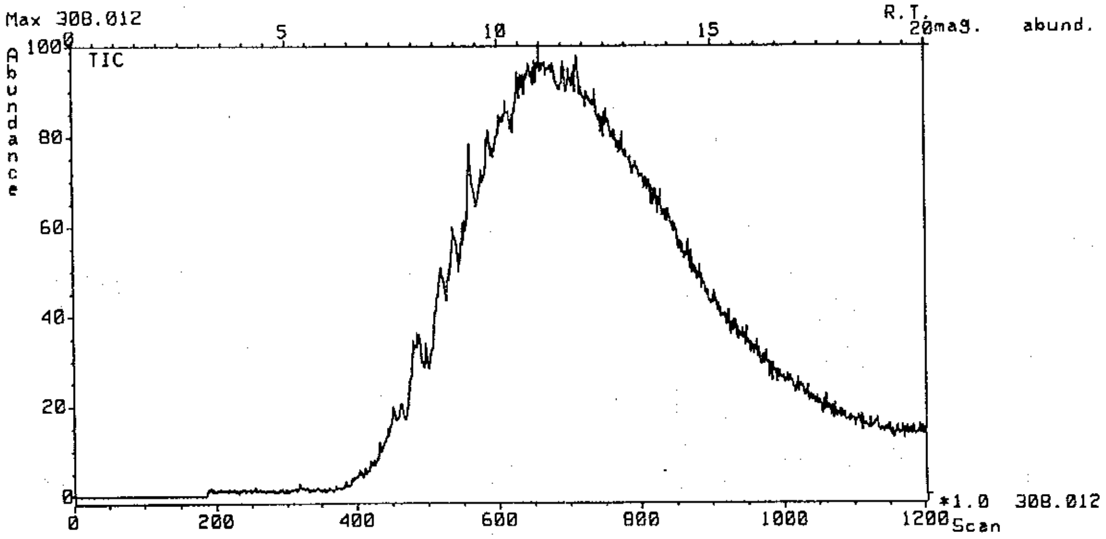


Mass Spectrum

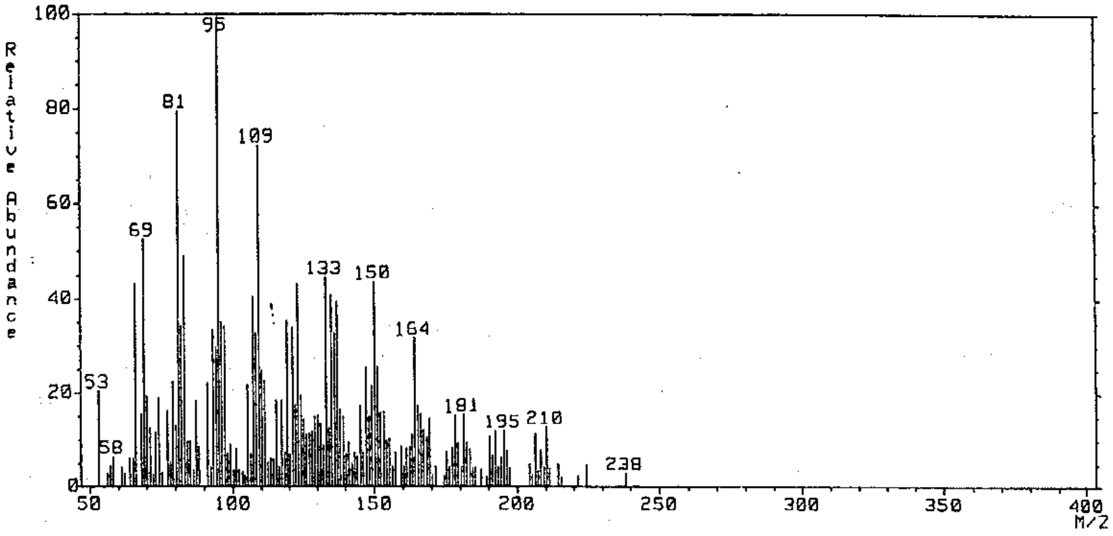


Mass Chromatogram

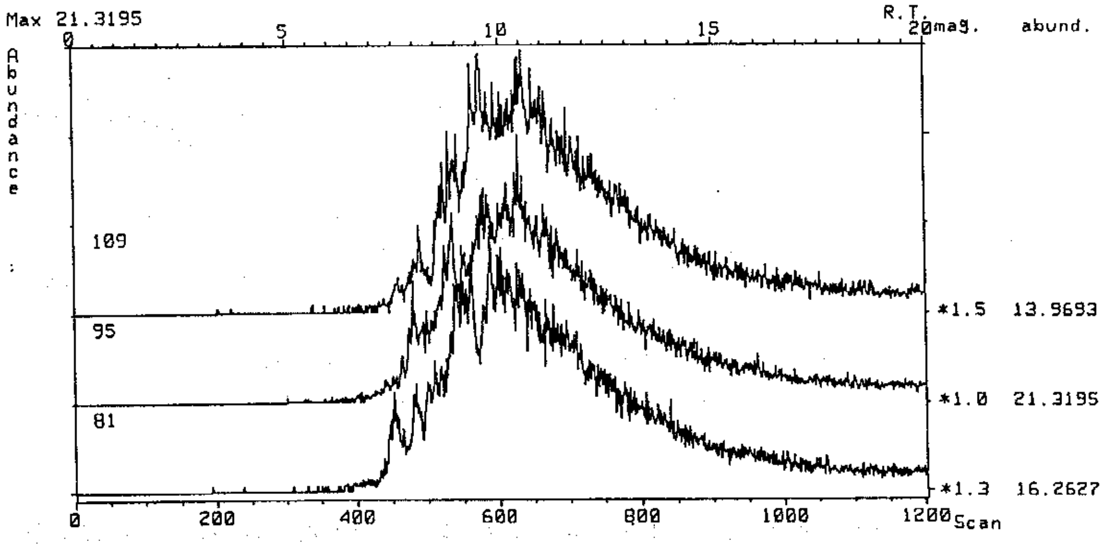
Figure 6-3 Chromatograms of Sample No. 4 by GC/MS



TIC

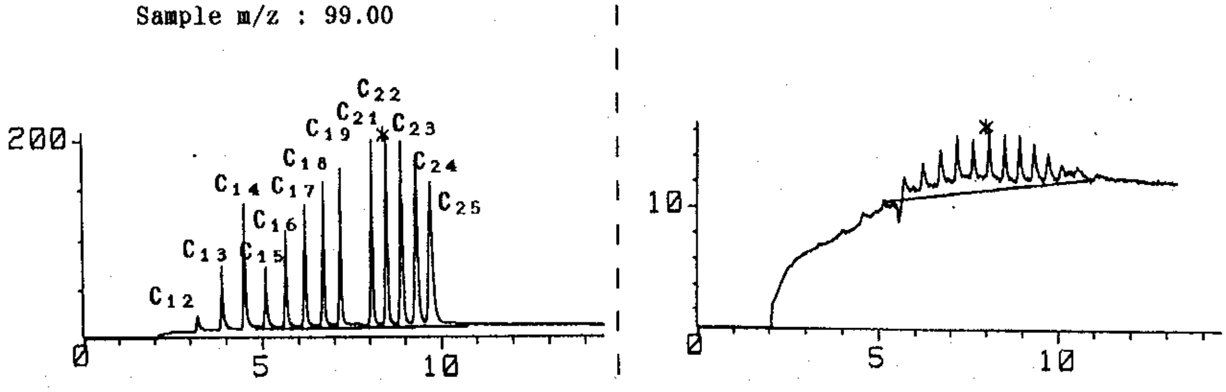


Mass Spectrum



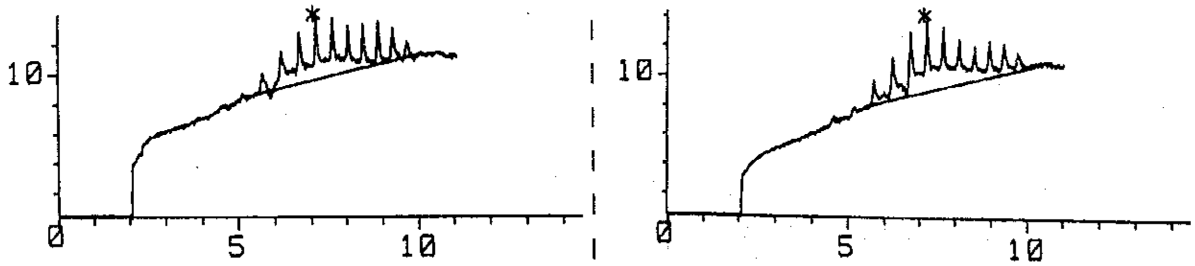
Mass Chromatogram

Figure 6-4 Chromatograms of Standard Sample by GC/MS



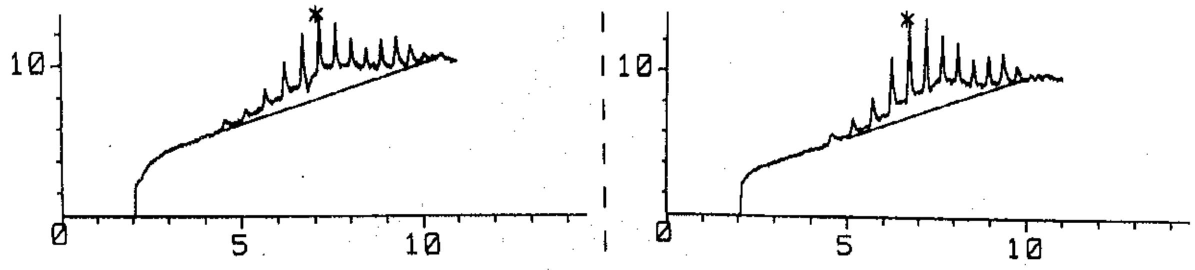
Standard : 40 ppm

Sample #1 : 1.9 ppm



Sample #2 : 1.3 ppm

Sample #3 : 1.6 ppm

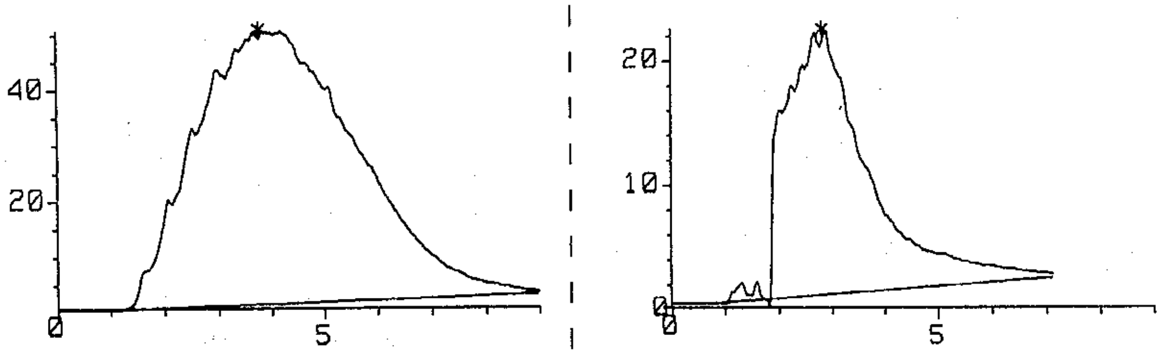


Sample #4 : 1.9 ppm

Sample #5 : 1.9 ppm

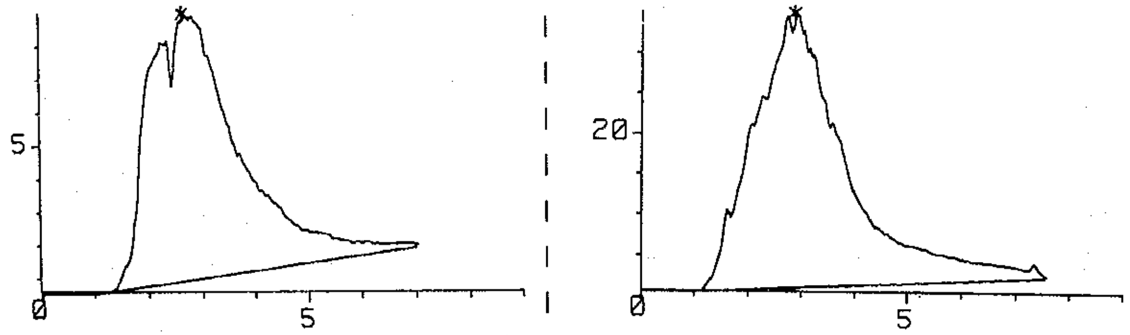
Figure 6-5(1) Quantitation of Paraffin Hydrocarbon by SIM

Sample m/z : 95.0



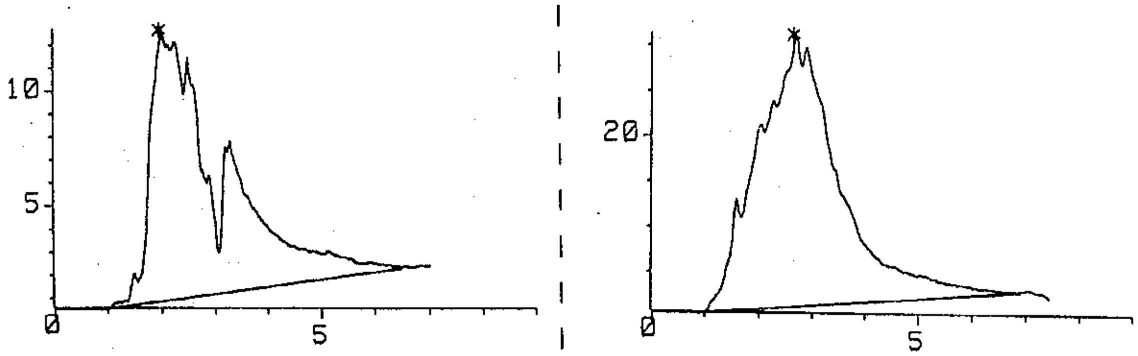
Standard : 140.0 ppm

Sample #1 : 31.3 ppm



Sample #2 12.8 ppm

sample #3 : 55.7 ppm

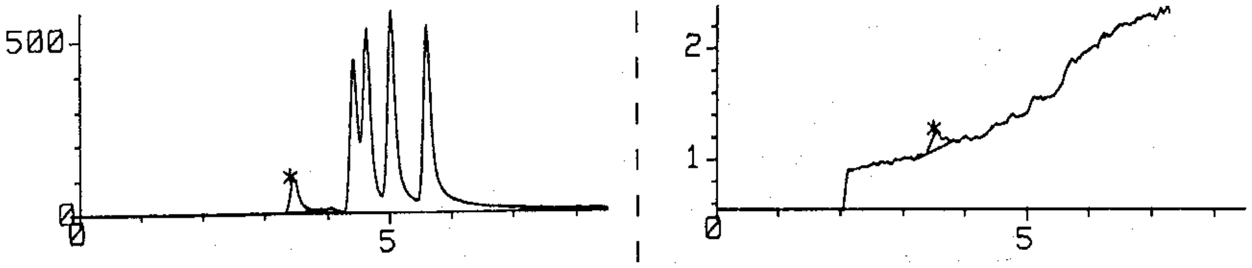


Sample #4 : 14.5 ppm

Sample #5 : 42.7 ppm

Figure 6-5(2) Quantitation of Naphthenic Acid by SIM

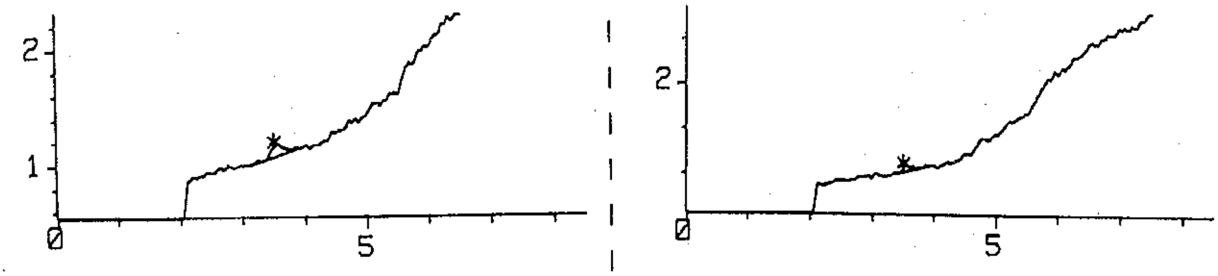
Sample m/z : 60.00



Standard : 102.9 ppm

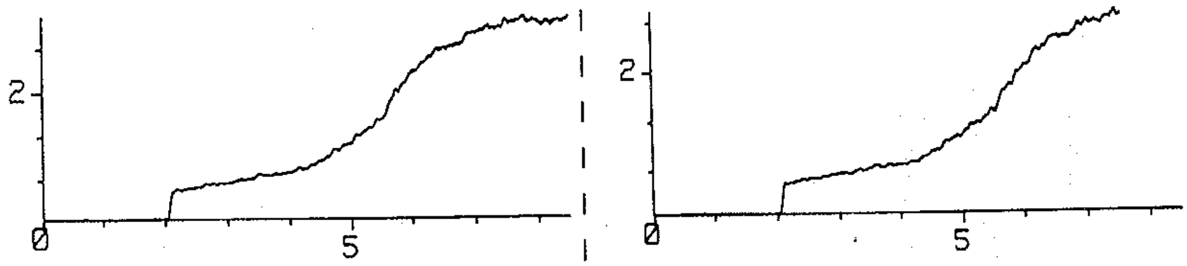
Sample #1 : ND

(ND : Less than 0.01 ppm)



Sample #2 : ND

Sample #3 : ND



Sample #4 : ND

Sample #5 : ND

Figure 6-5(3) Quantitation of Aliphatic hydrocarbon by SIM

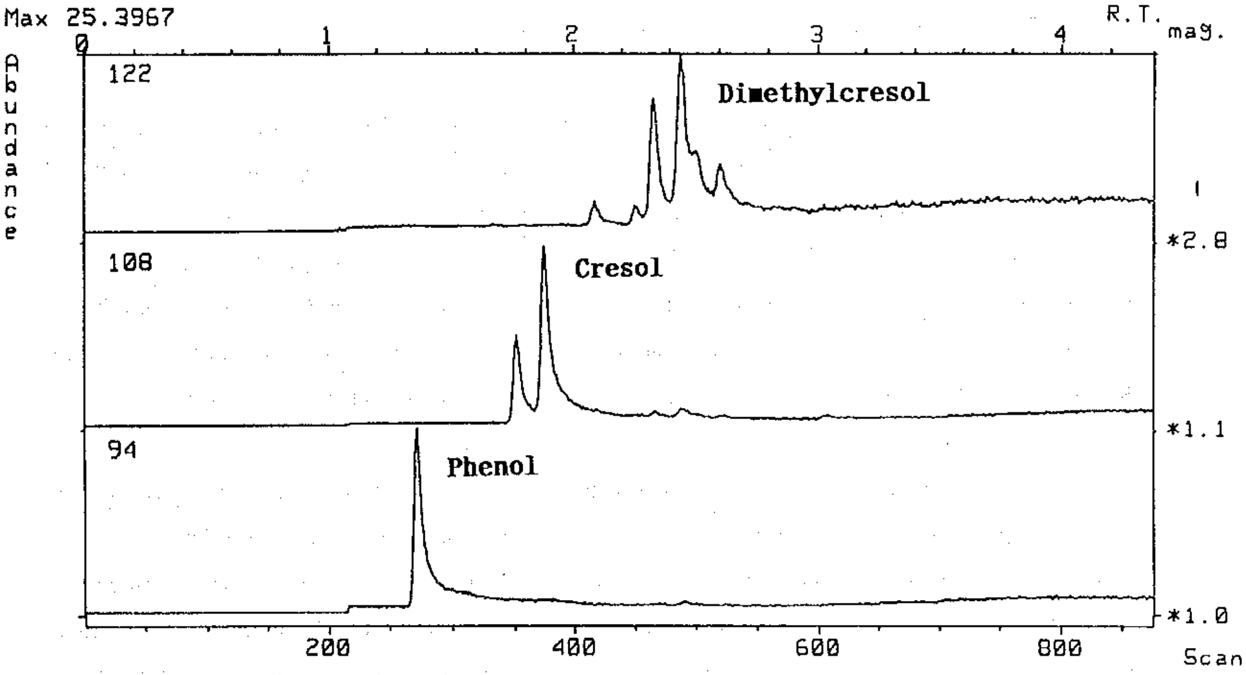


Figure 6-5(4) SIM Chromatogram of Phenols

6-2 Effects of Emulsions on the Petroleum Pollution

The two types of emulsions, oil-in-water and water-in-oil types, cause chronic petroleum pollution of various forms. The former behaves like water, passing through gravity-induced separators to the rivers without separating oil, and flows down the rivers as far as the sea, polluting all the way along the route and the Gulf of Paria. The latter, water-in-oil emulsion, though separable from the bulk of water, persistently resists all available measures for separation into oil and water. The sticky emulsions are seen floating at the dams and catches, along the shoreline near the Main Storage at Point Ligoure. They must have escaped from upstream petroleum facilities.

The oil-in-water emulsions are miscible with water. The complete miscibility of the emulsions, or water separated from the produced crude oil, is the very nature that makes petroleum pollution in the study area all the more serious and difficult to cope with. Once discharged to public waters like rivers or sea, it is almost impossible to collect the oil. Unlike floating oil, the damage is not limited to areas where the surface layer spreads but the entirety of the water body including the bed of the rivers and sea. It is also worth mentioning that the petroleum pollution caused by this type of emulsion is not very discernible, despite its serious nature. The emulsion resembles muddy river water and can deceive an observer of the rivers and sea in which it flows. Since this emulsion flows out of every tank farm in the study area, this emulsion is ubiquitous in this area and inflicts damage on the aquatic environment. Because of its miscibility with water, this type of emulsion could conceivably permeate soil as far down as the water table, contaminating underground water reservoirs.

The water-in-oil emulsion is by no means a less serious problem. The fact that such an emulsion is seen on the dams and catches, and on the rivers and sea suggests that the emulsion has escaped from petroleum facilities. Unlike the oil-in-water emulsion, this type of emulsion persistently stays, smearing everything that comes in contact with it. Because of the difficulty of breaking it into water and oil, it tends to accumulate in the separators and eventually escapes to the environment. The river banks and sea shores are particularly affected.

Table 6-7 shows the production of crude oil and accompanying water in the typical oil wells.

Table 6-7 Production of Emulsions

(Unit: barrels per day)

Oilfield	Oil	Water	Oil/Water Ratio
Forest Reserve (Thermal)	920	8,000	23/200
Forest Reserve (Non Thermal)	3,000	2,000	3/2
Forest Reserve (T & NT)	3,920	10,000	39.2/100
Point Fortin (Non Thermal)	3,300	800	33/8
Guapo (Thermal)	1,400	7,400	7/37
Guapo (Non Thermal)	700	50	70/5
Guapo (T & NT)	2,100	7,450	21/74.5
Central Los Bajos (Thermal)	1,600	6,400	1/8
Central Los Bajos (Non Thermal)	350	200	7/4
Central Los Bajos (T & NT)	1,950	6,600	13/44
Fyzabad (Thermal)	400	3,000	2/15
Fyzabad (Non Thermal)	1,600	1,100	16/11
Fyzabad	2,000	4,100	20/41

Note: *Thermal Fields are those fields where enhanced oil recovery by steam injection is practiced.
*T- refers to Thermal Fields.
*NT- refers to Non Thermal Fields.

6-3 Breaking Emulsions

There are a number of methods to break emulsions into two phases: chemical methods that break the emulsifier stabilizing the emulsion; heating; or other methods which coalesce the dispersed materials in one way or another. The most suitable methods differ according to the type of emulsion; water-in-oil or oil-in-water. The water-in-oil emulsions, the crude oil/water mix from the oil wells in the case of this study, are separated into oil and water at tank farms. The water content is reduced to less than two percent and sent to the refinery. This type of emulsions is stable when the diameters of water particles are between 0.01 and several tens of microns. When the particle sizes become larger than this range the emulsions become unstable. The maximum water content that can be held in emulsion is between 30 and 40 percent. Water exceeding this maximum separates from the emulsion. The crude oil/water mix produced at primary wells in the Forest Reserve Area is in a state of water-in-oil emulsion, containing 30 percent or more water. The crude oil/water mix from the Bernstein thermal wells is separated in the tanks into crude oil containing some water in a water-in-oil emulsion and a water phase that is actually an oil-in-water emulsion.

The water phase that separates from the crude oil/water mix forms an oil-in-water emulsion. This type of emulsion is stable when the diameters of the dispersed particles range from less than 0.1 to several tens of microns. The oil content is from several hundred ppm to several percent. The most serious of the petroleum pollution problems lies in discharging this emulsion to the environment without effective treatment.

There are two elements of emulsion treatment important to this study. One is to find an effective way to treat the water-in-oil emulsions; the other concerns treatment of the separated water, oil-in-water emulsion, or removal of oil to obtain clear water.

(1) Breaking of Water-in-oil Emulsion

The methods of separation now in use in the study area are three-phase separation, tank separation, heating, and electric dehydration. Efforts are made to maintain the optimum operation conditions depending on the conditions of each oil field. In most cases, (an) emulsion breaker(s) supposed to be effective for water-in-oil emulsions is/are used. In the study area, considering the small scales of the oil fields and the characteristics of crude oil, tank separation and application of heat appear reasonable.

1) Three-phase Separation

In this method gas, oil and water simultaneously separate. Generally two or three two-phase separators are used in series. The first separator separates the fluid into gas and liquid. The second stage separates oil and water.

2) Tank Separation

The crude oil/water mix already rid of gas is sent to the storage tanks where water is separated by allowing the crude oil to stand for some time. This method tends to consume a relatively large amount of demulsifier, although the consumption varies depending on the characteristics of the crude oil/water mix. The upper layer becomes marketable crude oil after draining the bottom layer water.

3) Heating

This method is often applied to treating crude oils at offshore oil wells or crude oils of high pour points. The crude oil/water mix can either be heated and transported simultaneously, or heated while staying in tanks to separate water.

4) Electric Dehydration

This method is used chiefly for the crude oils produced in large quantities and containing high concentrations of salt and mud. Electric dehydration is frequently used at the very first stage of crude oil refining to protect the equipment from corrosion. Electric potential is applied to force the salt and mud to move to the added fresh water, breaking the emulsion.

Crude oils contain substances, natural emulsifiers, that can stabilize emulsions. Natural emulsifiers coat the surfaces of water particles in the crude oil/water mix and help maintain physico-chemical equilibrium between the two phases. The function of emulsion breakers for water-in-oil emulsions is to act on the dispersed water particles and break the conditions stabilized by the natural emulsifiers or by fine mineral particulate matter. The emulsion breakers unite water particles and finally separate the emulsion into water and oil layers. The emulsion breakers tend to be first absorbed in oil and then move to the surfaces of water particles.

(2) Breaking of Oil-in-water Emulsion

Reverse emulsion breakers are those chemicals effective in breaking oil-in-water emulsions. Oil particles dispersed in water are negatively charged and repel each other, thereby stabilizing the emulsion. When positively charged acids, inorganic or organic coagulants are added, the surfaces of these particles are neutralized. If conditions permit, the particles are bridged to form flocs. Polymer coagulants are particularly effective in bridging the particles and thus enlarging the flocs, making it easier for oil to separate from water. If anionic surfactants exist to stabilize the emulsions, acids effectively break emulsions by dislocating the surfactants from the surfaces of the oil particles.

1) Treatment of Oily Water

Water separated from crude oil/water mix contains crude oil and other suspended matter. The following facilities are used; the selection of any particular one depends upon the degree of separation required and difficulty associated with achieving the separation. They are introduced normally in the order given below with increasing required degree of separation.

(a) Pit, Oil Skimmer

These are the simplest of all types. These can only skim the top layer that should normally be the oil layer. Chemicals are normally not used with them.

(b) API, PPI, CPI

These are designed to separate oil and suspended matter by flotation and sedimentation. The separated oil is recovered.

(c) Coagulator

The coagulator uses inorganic and/or organic high-molecule coagulants. The coagulants separate oil by forming floc out of dispersed oil to obtain clear water. The floc becomes a waste. Generation of a large amount of floc could give rise to a waste treatment problem.

(d) Flotation Facility

Air is dissolved in a portion of the waste water under pressure. Air is released in an infinite number of fine bubbles when the pressure is released. The particles of oil come floating to the surface with the bubbles.

(e) Sand Filtration

A sand filter is used to supplement the effects of the above facilities when they are not effective enough.

(f) Adsorption by Activated Carbon

(g) Biological Treatment

These two methods are employed when the above methods are not effective enough.

2) Breaking of Oil-in-water Emulsions by Coagulants

(a) Effects

Coagulants separate oil particles in oil-in-water emulsions or other suspended matter from water by flotation or sedimentation. Conceptually, the coagulants destroy the equilibrium by neutralizing the electrically charged crude oil particles and suspended matter and coagulate these particles into flocs which either float to the surface or precipitate to the bottom.

(b) Use

Organic high molecular electrolytes are used in dilute solutions ranging in concentration from 0.1 to 0.5 percent, because of their high viscosities. The dosage of active ingredients is generally less than 10 ppm of the water to be treated. Too high a dosage could even stabilize the emulsion. The selection of the reverse emulsion breaker as well as emulsion breaker to be used should be done on the basis of the results of a jar test by confirming the effects and right dosage. The floc should be treated adequately as a waste.

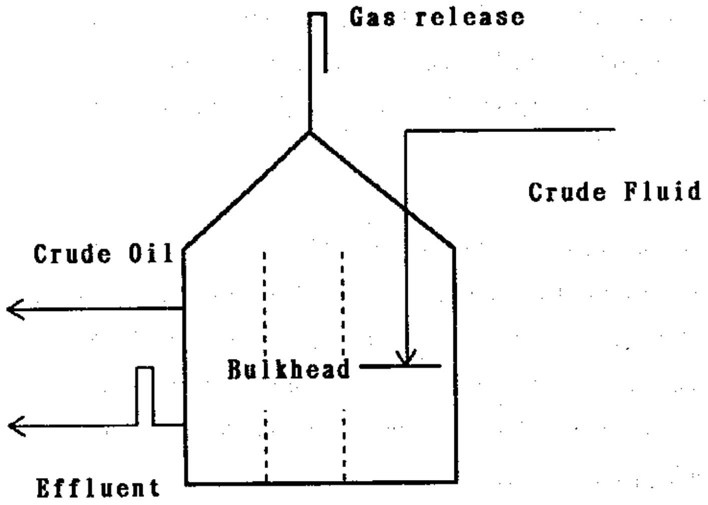
(3) Oil-water Separation Done in Trinidad and Tobago

1) Facilities and Process of Oil-water Separation

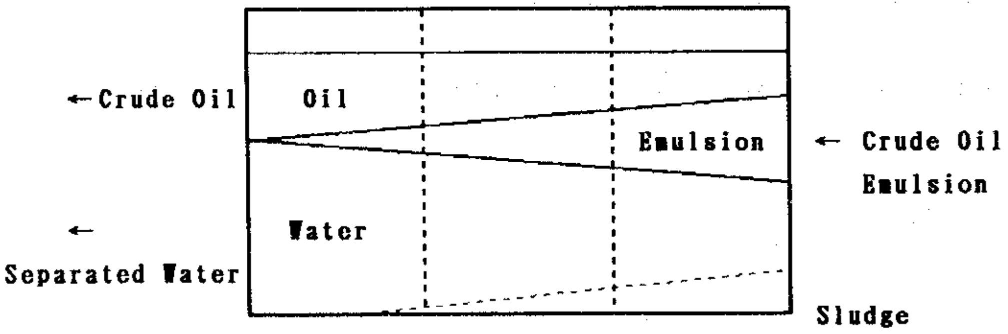
Separation of oil and water and recovery of oil done in oil fields in the study area are as follows.

Although there are some exceptions, the crude oil/water mixes are introduced from gathering stations to the wash tanks in the tank farms. There, the crude oil/water mix is heated for some time at controlled temperatures to separate oil from water.

The following figures show typical structures of wash tanks and process of separation in the wash tanks.



Structure of Wash Tank



Process of Separation in Wash Tank

A certain residence time is allowed for separation of the crude oil/water mix into oil and water. This operation is called tank separation. The crude oil is heavy for all the tank farms in the study area, and the method of tank separation employed is nearly the same for all the tank farms. The effect of tank separation is rather limited as explained below.

1. The water separated by tank separation from the crude oil/water mix could contain oil in very high content, as much as 10,000 ppm or even more in some cases.

2. The water separated is in a very stable oil-in-water emulsion which will not separate by just allowing it to stand still for months. A demulsifier with the ability to break reverse emulsions is added in certain cases to the water and the water is introduced to the API separators. The effect of adding demulsifier is virtually none. Oil floating to the surface is skimmed and stored in a pit. The top oil in the pit is returned intermittently to the wash tank for separation of oil. The separated oil is sent to the refinery.

3. The crude oil stored in the fiscalization tank is rid of water by allowing it to stand still. The oil is sent to the refinery after meeting the pipeline specifications. The bottom water is drained and returned to the API separators.

2) Use of Chemicals for Oil and Water Separation

Every oil well uses an emulsion breaker for water-in-oil emulsions and a reverse emulsion breaker for the separated water, or the oil-in-water emulsion. Appendices 6-1 and 6-2 show the emulsion breakers and reverse emulsion breakers mentioned in this chapter.

(a) Oil and Water Separation of Crude Oil/water Mix

The primary purpose of oil and water separation of the crude oil/ water mix is to reduce its water content to the pipeline specifications. For this purpose, emulsion breakers are injected at tank batteries located upstream of the tank farms. In Los Bajos, emulsion breakers are injected at four to six highest producing tank batteries among the total of 40. The crude oils containing emulsion breakers and those not containing them are mixed in pipe to effect the intended separation before reaching the tank farm.

Such a practice is normally done everywhere and is considered to be the right way of using emulsion breakers as long as the right ones are used. Table 6-8 shows the kinds of emulsion breakers and their consumption in the oil wells in the study area.

As Table 6-8 indicates, the kind of chemicals varies from one oil well to another. The emulsion breakers used exhibit expected performance.

Table 6-8 Emulsion Breakers Used in the Study Area

Oil Field	Production Method	Emulsion Breaker	Dosage (Gallons/day)
Bernstein	Primary	Petrolite V-3	5
		PCD 101B	2
	Thermal	So-Chem D-503	4
		Witco JM-29	4
Pt. Fortin	Prim. & Therm.	So-Chem D-503	-
Central Los Bajos	Prim. & Therm.	Petrolite RP-881	46
Pt. Fortin	Primary	PCD 110	85

(b) Clarification of Oily Separated Water

Although the residence time in the wash tanks is 10 to 20 hours, the water separated from the thermal crude oil/water mix contains oil in the form of an oil-in-water emulsion at the highest rates. The samples taken from Bernstein Main Storage, for example, contain more than 10,000 ppm oil.

Polymer-type reverse emulsion breakers are added to the separated water at the outlets of the wash tanks to coagulate oil particles to promote separation in the API separators. Obviously, recovery of oil at the API separators is far from being satisfactory as evidenced by very high measured oil contents, normally 600 or 1,000 ppm. Water of high content oil causes serious oil pollution along public rivers.

Table 6-9 shows the reverse emulsion breakers used in the study area.

Inexpensive and easy-to-use low molecular weight cationic coagulants are selected. The water separated from the Bernstein thermal crude oil/water mix does not separate even at a very high dosage of 15 ppm.

Table 6-9 Reverse Emulsion Breakers Used in the Study Area

Oil Field	Prod. Method	R-Emulsion Breaker	Dosage (Gallons/day)
Bernstein	Thermal	Witco C-5553 Amer: floc 42	4
Pt. Fortin	Prim. & Therm.	WE-93	4
Central Los Bajos	Prim. & Therm.	Drew 425-EP	17
Pt.Fortin	Primary	Breaxit 8072	24

(c) Treatment of Skimmed Oil from the API Separators

The water separated from the Bernstein thermal crude oil/water mix, to which a reverse emulsion breaker has been added, is introduced to the API separator. The oil floats to the surface, recovered by three-stage skimmers and gathered to the oil pit.

The top oil in the oil pit is pumped back to the wash tanks intermittently when oil accumulates in the oil pit. The returned top oil is expected to be further separated into oil and water there. This top oil contains about 35 percent water and a variety of impurities; some argue that oil and water separation of crude oil/water mix in the wash tanks may be adversely affected by these impurities.

6-4 Test on Breaking Emulsions

6-4-1 Test on the Effect of Emulsion Breakers in Use

A sample of crude oil/water mix collected at a gathering station before injection of an emulsion breaker was found to consist of 22 percent crude oil, actually a crude oil phase still containing 34 percent water, and 78 percent oily water. The oily water resembles muddy river water. The oily water contains about 1.5 percent crude oil.

The amount of crude oil obtainable after separation of water from such samples is too small to permit measurement of BS/W on the laboratory-scale bottle test that is normally used to evaluate the performance of emulsion breakers. Therefore, it is appropriate to use the quantity of separated water, speed of separation, and clarity of separated water as criteria to measure the performance of emulsion breakers. The emulsion breakers now in use in the Bernstein area were compared with other emulsion breakers with demonstrated performance for heavy crude oils by an internationally accepted bottle test method using 100 milliliter bottles.

The following are the results of tests using samples of Bernstein thermal and Forest Reserve primary crude oil/water mixes.

(1) Bernstein Thermal

Table 6-10 gives the emulsion breakers tested and test conditions. The test results may be summarized as follows.

1. D-503 now in use is the most effective and is considered to be the right choice for this oil field.

2. Oil content of the separated water is nearly the same as that before emulsion breakers are added. A variety of emulsion breakers were tested in vain with a view to reducing oil content in the separated water.

3. The measured oil content ranged from 10,000 to 15,000 ppm, although the measured values are subject to error due to adsorption of oil on the container surface and existence of floating oil which is not measured, and possibility of imperfect extraction by the solvent for testing.

Table 6-10 Performance of Emulsion Breakers (1)

(Sample: Bernstein/Thermal)

Run No.	1	2	3
Emulsion Breaker	D-503 RP-881 E-1 F-924	D-503 M-228D D-154 254 F-771 F-661	D-503 P-50 F-919 G-1 M-114
Temp. degree C	60	50	60
Dosage (ppm)	20, 50	50	100

(2) Forest Reserve Primary Crude Oil

Table 6-11 indicates conditions and emulsion breakers tested. Test results are summarized as follows.

1. Oil and water separate as quickly as in the thermal crude. D-503 and PCD-101D are both high performance emulsion breakers, internationally accepted. With its ability to rapidly effect separation, PCD-101D is effective at a low dosage and therefore is economical. However, the separated water tends to be turbid. This needs confirmation by testing before commercial application.

2. Appearance of separated water differs from that of thermal crude. It is faintly translucent; oil droplets and dispersed mineral matter are not observed. The interface between oil and water is rather clear; however, the floc is formed in the separated water immediately under the interface and then precipitates to the bottom. The measured oil content was about 400 ppm.

3. The measured BS/W of the separated crude oil was 2.6 percent, which is rather high considering that the measurement was done after the sample was allowed to stand still for 90 minutes. This drawback may be tolerated in view of the fact that in the field 14.5 hours are allowed for separation.

Table 6-11 Performance of Emulsion Breakers (2)

(Sample: Forest Reserve/Primary)

Run No.	4	5	6	7
Emulsion Breaker	D-503	D-503 M-109 F-154 M-228D	PCD-101D D-154	PCD-101D D-503 RP-881 V-3 2W-116 R-443 NO.254
Temp. degree C	45	45	45	45
Dosage (ppm)	20-110	20	20	100

6-4-2 Performance of Organic Coagulant

A variety of organic coagulants were tested on the samples of oil-in-water emulsions collected from the Bernstein Main Storage. The coagulants tested fall into anionic, cationic, nonionic, and amphoteric high-molecule coagulants, and polyamine-type and oligomer-type coagulants. Experiments were done by the bottle test method. Coagulants are administered to a maximum of 100 ppm. The coagulation effect, conditions of the floc formed and clarity of the liquid, etc. were observed as criteria for evaluation.

(1) Evaluation of Coagulant by Type

Table 6-12 shows the coagulants tested and test conditions.

Trial A, Trial S-0.1 and KP-1200 have been found most effective. In this condition, coagulation and flotation of oil in the separated water were very fast. Good flotation and clarification of water were achieved in several tens of minutes. The measured oil content of the water phase after 10 hours, arbitrarily set to be equal to the residence time at the tank farm, was 408 ppm in the case of Trial A.

Table 6-12 Evaluation of Coagulant by Type

1.	Polyacrylamides	Nonions: Cations:	NP-800 KP-108(*1), KA-005(*2), KP-1200B(*3)
2.	Special Cations:		K-405, HC-100
3.	Polyamines:		Trial A, Trial S-0.1
	Condition of Treatment	Dosage: 100ppm,	Temp.: 50 deg. C

Note: (*1): Weak, (*2): Medium, (*3): Strong

(2) Evaluation of Coagulant by Grade

Table 6-13 shows the coagulants tested and the test conditions.

Table 6-13 Evaluation of Coagulant by Grade

Polyacrylamides	Strong Cations:	KP-201 G, KP-1200 B, KP1200 S
	Medium Cation:	KP-204 B, KP-206, BH
	Neutral:	KP-1127 B, KA-003 , KA-205
	Weak	Cation: KP-1207
Polyamines:	Trial A, B(1), (2), (3) S-0.1, S-0.3, S-0.6	
Condition of Treatment	Dosage: 100ppm,	Temp.: a50 deg. C

The test results show that all coagulants were effective and there is little difference in the effect among these coagulants. Among high-molecule coagulants, KP-1200B, KP-1200S, KP-204B and KP-1227B show the same degrees of effectiveness. It was noted during the experiment that the oil separated by the high-molecule coagulants tended to be less fluid than that separated by the polyamide coagulants.

(3) Evaluation of Minimum Effective Dosage

Minimum effective dosages were searched for these polyamide coagulants, Trial A, S-0.1 and (1), with KP-1227B, a high molecular coagulant which showed relatively good performance as reference, used in dosages from 100 ppm to 20 ppm.

The results show that every polyamide coagulant exhibited a definite effect with the dosage range of from 35 to 100 ppm. Especially, Trial (1) was able to clarify the sample at 20 ppm dosage, with the separated water containing oil at 306 ppm.

6-4-3 Performance of Inorganic Coagulants and Acids

Several tests on inorganic coagulants and acids were done together with tests explained in 6-4-2, "Performance of Organic Coagulant", to investigate their performance. The following tests were done on samples of water bled from Tank No. 16 in the Bernstein Main Storage.

1. Extraction by kerosene of oil in emulsion,
2. Breaking of emulsion by inorganic salts, coagulation and separation of oil, and
3. Breaking of emulsion by acids

Results of the tests are as follows.

(1) Extraction by Kerosene of Oil in Emulsion

This test was done for the purpose of determining whether the dispersed particles could be extracted by kerosene, and if so, the degree of extraction and the conditions that would affect extraction. Tests were done over the kerosene to sample emulsion ratio (kerosene/sample emulsion) of zero to one. Every sample was carefully observed from the moment kerosene was added so that any change that could occur would not be overlooked. After kerosene was added the mixture was shaken very vigorously by hand. Some of the emulsion samples were tested for oil content after this experiment.

Table 6-14 shows the test results. As almost all components of crude oil are miscible with kerosene at any ratio, how much oil will be extracted by kerosene depends upon the efficiency of physical contacts between kerosene and the oil particles in the emulsion. Although in some of the tests discoloration of kerosene occurred to confirm that the intended extraction took place, the emulsion part scarcely showed any change from its original appearance, indicating that virtually no significant extraction took place. The droplet diameters, ranging from less than one micron to a maximum of ten microns, are too small to be able to contact the oil phase no matter how vigorously shaken by hand.

Table 6-14 Extraction of Dispersed Oil Particles by Kerosene

Kerosene/Sample (mg/l)	Oil & Grease in Water Phase	Appearance/ Effect
0	8,910	(Original Sample)
0.2	-	No effect Brown colored(*)
0.3	-	No effect Brown colored(*)
0.4	7,500	No effect Brown colored(*)
0.5	9,040	No effect Brown colored(*)

0.5	7,500	No effect Brown colored(*)
0.7	-	No effect Brown colored(*)
0.8	-	No effect Brown colored(*)
1.0	-	No effect Pale brown colored

(*): Color of kerosene phase

(2) Breaking of Emulsion by Inorganic Salts

Sodium chloride (NaCl), calcium chloride ($CaCl_2$) and ferric chloride (Fe_2Cl_3) were tested. The process of emulsion breaking and change in clarity of water were carefully observed. The salts were added to the samples; the samples were shaken and allowed to stand. The salts were added at rates ranging from 0.1 to 5 weight percent on the samples.

Table 6-15 shows the results of experiment. It was confirmed that these three salts are effective in emulsion breaking. The effectiveness differs among them. Ferric chloride is most effective on the basis of the added amount. The next is calcium chloride. Sodium chloride is least effective. The minimum dosage at which emulsion begins to break varies with oil content, particle diameter, pH and temperature. The following minimum requirements were obtained.

	NaCl	$CaCl_2$	$FeCl_3$
Dosage (wt%)	3.0	0.6	0.05

This result could be acceptable in view of the fact that the coagulation of particles occurs by neutralization of charged particle surfaces. Salts with higher valency are more effective in breaking emulsion. A small amount of ferric chloride could break the emulsion; however, it generates a floc difficult to separate from water. There are other drawbacks in that ferric chloride is corrosive and that the water becomes acidic. A large amount of sodium chloride would be needed to break an emulsion. The cost and high concentration of sodium chloride in the treated water would be problems in considering actual application. Calcium chloride is not very effective in terms of the amount that needs to be added. The floc generated is easier to separate from water. It is not very corrosive. Overall, calcium chloride is the best among these three salts. It is probably that other salts such as aluminum sulfate and iron sulfates are also effective in emulsion breaking.

Table 6-15 Breaking of Emulsion by Inorganic Salts

Salts (wt %)	Content of Salts (*)	Appearance/Effect	Oil & Grease in Water Phase (mg/l)
NaCl	0.309	No effect	-
NaCl	0.686	No effect	-
NaCl	1.046	No effect	-
NaCl	2.994	Small effect Slightly light brown	-
NaCl	5.130	Effective Light brown	-
NaCl	7.010	Effective Yellow, Opaque	-
-	0	(Original Sample)	6,466
$CaCl_2$	1.103	Small effect Pale brown	1,006
$CaCl_2$	2.030	Small effect Pale brown	1,148
$CaCl_2$	3.088	Small effect Pale brown	958
$CaCl_2$	4.996	Effective Pale brown	209
$CaCl_2$	10.041	Effective Pale yellow	215
$FeCl_3$	0.0234	No effect	-
$FeCl_3$	0.0380	Small effect Brown	-
$FeCl_3$	0.0497	Effective Yellow	-
$FeCl_3$	0.0730 Pale yellow	Effective	-
$FeCl_3$	0.0964	Effective Pale yellow	-

Note: (*) Color of the water phase

(3) Breaking of Emulsion by Acid

Emulsion breaking and coagulation were observed at various pH values by adding hydrochloric acid to emulsion samples.

Table 6-16 shows the results of the experiments. Emulsions generally contain one or more emulsifiers. In case that the emulsifiers are anionic surfactants, acids can suppress the effects of dissociation of particles exerted by the surfactants; thus emulsions can break. In these tests, decomposition of the emulsions was observed at pH values lower than about 4.5. This could be interpreted to suggest that anionic substances participate in stabilizing the emulsions.

Table 6-16 Breaking of Emulsion by Acid

Acid	pH	Appearance/Effect
HCl	7.0	No effect
HCl	6.0	Color unchanged, Scum upper layer
HCl	5.5	Brown, Scum upper layer
HCl	5.0	Light brown, Scum upper layer
HCl	4.5	Light brown, Scum upper layer
HCl	4.0	Pale yellow, Scum upper layer
HCl	3.5	Clear yellow, Scum upper layer

6-4-4 Treatment of Slop, Persistent Water-in-oil Emulsion

The slop oil recovered from the API separators forms a very persistent emulsion; those produced at Bernstein Main Storage, for example, consist of about 40 to 50 percent water. These emulsions are collected at a pit and returned to the wash tanks. Tests were conducted during the first field survey to break such emulsions taken from Bernstein Main Storage into oil and water phases. Table 6-17 gives properties of the skimmed oil sample.

Table 6-17 Properties of Skimmed Oil

Specific gravity	0.972	Pycnometer
Water content, wt%	34.6	Xylene method
BS&W, wt%	36.0	Centrifuge method

Source: study team

The tests were done in two stages. Various emulsion breakers were first added to the sample to separate the upper layers; then other emulsion breakers were added to the upper layers. Table 6-18 gives the emulsion breakers used for the experiments and their dosages. The tests were done at 80 degrees centigrade. The samples were allowed to stand for two hours.

Table 6-18 Test on Skimmed Oil.

	One-Stage Treatment	Two-Stage Treatment
Demulsifiers	D-503 M-12M M-198 M-228D RP-881	M-198/M-12M M-198/DBSN M-228D/M-12M
Dosage, ppm	1,000 1,500 2,000	500 - 1,000 500 - 2,000

Source: Study team

Emulsion breakers of demonstrated performance were used for the first and second stage tests. In spite of the large dosages far exceeding the common dosages, none of them proved effective. Although a slight increase of separated water was observed in the second stage test, the maximum separation of water obtained reached only 30 percent of the original water content. To conclude, emulsion breakers are ineffective to the skimmed oil, or to this type of emulsion. The only practical way to deal with such an emulsion is incineration.

6-5 Conclusions on Emulsion Problems

Emulsions, a major cause of petroleum pollution in the southwest oilfield area of Trinidad and Tobago, were observed and tested from various viewpoints. The following conclusions have been drawn.

1. The liquids generated from oil wells form a crude oil/water mix, actually an emulsion of crude oil and water. Normally, the maximum water content of this emulsion is less than 30 to 40 percent. That from the Forest Reserve primary crude oil, for example, is about 30 percent and forms a homogeneous water-in-oil emulsion. The crude oil/water mix from the thermal wells contains water at

higher contents and separates into a water-in-oil and an oil-in-water emulsions before reaching ground level. In the case of the Bernstein thermal oil, the fluid contains about 85 percent water.

2. The water phase separated from crude oil/water mix forms an oil-in-water emulsion. In such emulsions, fine particles of oil ranging in diameter from less than one micron to several tens microns are dispersed. The oil content ranges from several hundred to several ten thousands mg/liter. Emulsions of this type from thermal oil wells are very stable and resemble ordinary brown muddy river water. The emulsions can contain more than 10,000 milligrams of oil per liter.

3. One of the major sources of oil pollution in Trinidad and Tobago is such oil-in-water emulsions. They are discharged to public waters without effective treatment.

4. The diameters of oil particles in such oil-in-water emulsions are distributed from less than 0.1 microns to 10 microns, with the average diameter at about 2.5 microns. Under a microscope it may be observed that the perfectly spherical oil droplets are dispersed uniformly in the water. There is no indication that the oil droplets are being stabilized by fine inorganic matter adsorbed on the surfaces of the droplets. The emulsions are conceivably stabilized by some non-solid natural stabilizers.

5. The diameters are therefore considered too small to be treated by gravity-induced oil separators such as API separators or CPI. In order to separate the contained oil from the water, breaking of the emulsion and association and coagulation of oil droplets are required.

6. One method of treating oil-in-water emulsions lies in adding (a) suitable reverse emulsion breaker(s) to separate the emulsions into oil and clear water.

7. Several reverse emulsion breakers are found to be effective. Cationic high molecular and polyamide coagulants are especially effective. Among the inorganic coagulants tested, calcium chloride is effective.

8. It may be considered from the above that reverse emulsion breakers are effective

in breaking the oil-in-water emulsions into oil and water.

9. Generally, coagulation is considered effective in treating oil-in-water emulsions. A combination of reverse emulsion breakers and dissolved air flotation can remove nearly all dispersed oil particles. Normally, water thus treated contains less than 10 milligrams of oil per liter.

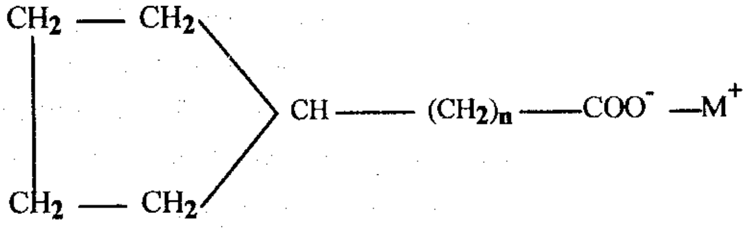
The water experimentally obtained after treatment by a combination of reverse emulsion breakers and dissolved air flotation is visually clear, indicating that dispersed oil particles have been completely removed. However this water is found to contain oil in concentration between 60 and 139 mg/liter in terms of normal hexane solubles, or carbon tetrachloride extraction plus infrared rays absorption. This indicates that the apparently clear water contains substances soluble in these solvents and measured as oil. To achieve the target oil content of 50 ppm, information on such substances is necessary. The GC/MS tests were done to examine these substances.

10. Prior to the GC/MS tests, organic substances were qualitatively analyzed by the TIC method. The TIC method is sensitive to all organic substances with a molecular weight smaller than about 1,000 and is therefore capable of qualitatively analyzing organic substances present in a few 10 ppm range. By this method no single substance was found to be present in high concentration; however, the presence of organic substances which increase the measured oil content was confirmed. These are compared with a standard sample of naphthenic acid obtained in Japan; the substances in question and the Japanese naphthenic acids show similar mass spectra although retention time differs somewhat between them. There is also similarity in the pattern of chromatograms between them. Further, quantitative analyses were done on paraffins, naphthenic acids, phenols and aliphatics by the SIM method. Paraffins, phenols and aliphatics are found to be present at only one mg/liter or less. In contrast, naphthenic acids show concentrations from 15 to 60 mg/liter.

11. The analytical results obtained on the same samples by the GC/MS method, normal hexane solubles, and carbon tetrachloride extraction plus infrared rays absorption method were compared. The latter two methods tend to yield higher values than the former but all are of the same order. In consideration of the

difference in method, use of the Japanese standard naphthenic acids that are not exactly the same as those in question, and exhibition of one large hilly peak by the GC/MS method that may be regarded as one single peak, the difference shown by these three methods is not decisive. The organic substances measured as oil by normal hexane solubles and carbon tetrachloride extraction plus infrared rays absorption presumably consist mainly of naphthenic acids and their derivatives.

12. The naphthenic acids in the oil-in-water emulsion may be considered to form salts with sodium and potassium. Naphthenic acids react with sodium or potassium compounds under the influence of the high temperature of the steam injected into the formation. The structure of salts formed between sodium or potassium and cyclopentane-based naphthenic acid, for example, is shown below.



(M^+ : Na^+, K^+ ,etc)

13. The salts of naphthenic acids are surfactants and soluble in water. Therefore, the presence of such salts in the oil-in-water emulsion separated from the crude oil/water mix helps stabilize the emulsion. The naphthenic acid salts may be contributing greatly to stabilizing the oil-in-water emulsion from the thermal crude oil even at such a high content of oil. The breakage of such oil-in-water emulsions by addition of acids may be attributed to suppression of the ability of the naphthenic acid salts to dissociate oil particles. Naphthenic acid salts are soluble in water and therefore not removable by dissolved air flotation. Treatments of a higher grade, like adsorption by activated carbon, are needed to remove naphthenic acids.

14. Overall, the results of the study in this chapter may be summarized as follows:

(1) Various inorganic and organic reverse emulsion breakers, coagulants, were tested on oil-in-water separated from the crude oil/water mixes. Normally, these coagulants are used for dissolved air flotation. In the case of this study, use of aluminum sulfate as inorganic coagulant and polymer coagulants as organic coagulants is proposed.

(2) Salts of naphthenic acids are considered to be formed underground by reactions with sodium and potassium existing there under the influence of the injected steam. These naphthenic acid salts act as surfactants and help stabilize the emulsions. The naphthenic acids exist in solution in the emulsions and are therefore not removable by dissolved air flotation. They are measured as oil by the tests using normal hexane or freon. Accordingly, the dissolved air flotation alone is not enough to reduce oil content to 50 mg/liter and adsorption by activated carbon is required.

(3) The thick water-in-oil emulsions, both components being in the range of 30 to 70 percent, are not broken into oil and water by any chemicals under ambient conditions. They are called slop, intermediate emulsion, middle layer emulsion; whatever their naming, they are difficult to deal with and not properly dispose of. Among them, those not properly treated into oil and water eventually end up being discharged to the environment. There seems no alternative but to incinerate them.

Appendix 6-1 Types and Components of Emulsion Breakers

Component(*1)	POAG	POAGE	POANAPE	LMS
Type(*2)	N or C	Weak A	N	Weak A
Name(*3)				
D-503	MA	SU		
RP-881	MA		SU	
PCD-101D		SU	MA	MI
E-1		MA		MI
F-924	MA			
M-228D	SU	SU	SU	MI
D-154		MA	SU	MI
NO254			MA	MI
F-771		SU	MA	MI
F-661		SU	MA	MI
P-50	MA			
P-51	MA			
F-919			MA	MI
G-1			MA	MI
M-114			MA	MI
M-109			MA	MI
2W-116			MA	MI
R-443	MA	SU	SU	MI

(*1): POAG: Polyoxalkyleneglycol, POAGE; Polyoxyalkylene glycol ester, POANAPE; Polyoxyalkylenenovolak type alkylephenol ether, LMS; Low molecular surfactant
(*2): N: Nonionic, C; Cationic, A; Anionic
(*3): MA: Major component, SU; Sub component, MI; Minor component

Appendix 6-2 Type of Reverse Emulsion Breakers

Type(*)		**Molecular Weight**	**Name**
	N	1,300	NP-800
Polyacrylamide	Strong C	300	KP-201 G, KP-1200 B, KP-1200 S
High Molecular	Medium C	400 - 600	KP-204 B, KP-206 BH, KA-005
	Medium AM	400	KP-1227 B, KA-003, KA-205
	Weak C	600 - 700	KP-1207, KP-108
Polyamine	Medium C		Trial A, B Trial (1), (2), (3) Trial S-0.1, S-0.3, S-0.6
Special Cation			K-405, HC-100

(*): A; Anionic, C; Cationic, N; Nonionic, AM; Amphoteric

Chapter 7 Overview of Petroleum Pollution

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7-1 General

Petroleum pollution is generally classified into three categories: air pollution, water pollution, and soil contamination. In Trinidad and Tobago, water pollution is the most serious among these three, especially in the rivers in southwestern Trinidad, where oil is produced from onshore oil fields. Black oil can sometimes be observed floating on the rivers, and dry oil is seen sticking alongside these river banks. The main cause of water pollution is the effluent water discharged from the tank farms and refineries in this area. A significant amount of water flows from the tank farms that receive crude oil produced by steam injection (Thermal Crude). This effluent water is actually a brown-colored, tough, oil-in-water emulsion which is the direct source of water pollution in this area. Although oil catches and dams are installed at certain locations on the rivers, these facilities are effective for the recovery of floating oil only but not for the oil-in-water emulsion.

Table 7-1 shows results of an analysis of oil content of water taken from the study area. Figure 7-1 shows photographs exhibiting the representative conditions of the polluted rivers in this area.

Table 7-1 Oil Pollution of Rivers in the Study Area

(Unit: mg/liter)

	Location	Oil & Grease (ASTM D-4281)
(1)	Techier River Catch	81
(2)	Guapo Main River (Intersection of Southern Main Road)	83
(3)	Outlet of Pollution Pit, McKenzie Oil Field	108
(4)	Outlet of TB33 Catch	204
(5)	Outlet of F20 Catch	18,676
(6)	Downstream of Vance River Catch	148
(7)	Silver Stream River Outlet of Bernstein Main Storage Pit	401
(8)	Outlet of Cocoa Catch	117
(9)	Outlet of Molai Catch	58
(10)	Outlet of John River Catch	18
(11)	Downstream of Arrowhead Dam	129

Source: Study Team

Upstream of Guapo River at TB-33 Oil Catch

Stream near Point Ligoure Tank Farm

Figure 7-1 Oil Polluted River in Study Area

All these rivers flow to the Gulf of Paria, and carry the pollution to the sea. The sea water looks brown as far as several hundred meters from the south coast of the Gulf of Paria. One reason for such a bad condition is that the Gulf is a semi-closed water system similar to the Persian Gulf. The degree of pollution seems much worse in this area than in the Persian Gulf. The most polluted marine area is reportedly offshore of Point Fortin, where the oil content sometimes exceeds 500 ppm.

Air pollution is not as serious a problem as water pollution. This is because natural gas is the main fuel used in this country. The major air pollution problem is the emission of SO_X at Pointe-a-Pierre Refinery; however, this problem will shortly be solved on completion of the "Upgrading Project" Petrotrin is implementing.

The major soil contamination issue is the practice of dumping oil sludge and/or slop oil directly into open earthen pits without pre-treatment or incineration. Such a disposal practice does not seem to arouse serious concerns about pollution among people, because the refineries and tank farms have sufficient spaces for digging such pits. Undoubtedly, however, the oil contained in such pits frequently leaks to public streams with rain water. The oil could also pollute the underground water. Leaks from pipelines are considered to be another source of localized soil contamination.

7-2 Characteristics of Oil Pollution in this Area

The Following is a summary of oil pollution in this area.

7-2-1 Oil Production Facilities

The main sources of pollution from oil production are gathering stations, where crude oil and associated water are collected from the production wells. Water is not supposed to be drained at the gathering stations in principle, but it is sometimes done at small stations. The oil content of such effluent water often exceeds 1,000 ppm.

Leakage from producing wells is another source of environmental oil pollution. Oil leaking from wells is led to small earthen pits, where floating oil is recovered. A considerable amount of oil is spilled out to public waters, especially in the rainy season, although the leak at each individual well is small.

The other source of pollution is leaks from the two-inch pipelines. Although crude oil is not one of corrosive nature, leakage sometimes occurs in the pipelines.

7-2-2 Tank Farms

Crude oil is transported from the gathering stations to the tank farms, where water is separated. The problem here is the character of water separated from thermal crude. The water contains oil at high contents. The water is really a tough oil-in-water emulsion, of which the oil content sometimes reaches 10,000 ppm. Presently, water is treated with earthen pits and/or API separators. Even though these facilities are effective for the recovery of floating oil, they are unable to recover oil from the emulsions. As a result, effluent water containing oil at over 1,000 ppm enters the public domain. In addition to the high oil content, the volume of such water is quite large; these combined inflict serious harm upon the environment. Typical of such tank farms in this category are those at Bernstein and Los Bajos.

The quantity of water produced with primary oil is fairly small and the degree of emulsification is also small. Water from thermal crude is treated similarly.

7-2-3 Trunk lines

Trunk lines are pipelines running between the tank farms and the refinery for transporting crude oil, of which 90 percent is buried in this district. No serious accident has been reported to date.

7-2-4 Pointe-a-Pierre Refinery

In this refinery, oil is separated and recovered from effluent water streams by four parallel API separators, guard basins, an oil boom, and several oil catches; however, these facilities do not necessarily function properly. The oil content in the effluent water from the API separators varies from 10 to several thousand ppm. Such a large fluctuation of oil content can be attributed partly to the greatly varying load on the API separators caused by uncontrolled inflows of rain water, the stream of which is not segregated from the process effluent water. As is experienced in the rainy season, the API separators cannot properly function when an enormous amount of water flows in.

Black oil is floating against the oil boom installed in the Guaracara River where the effluent water is finally discharged.

7-2-5 Retail and Marketing Stage

Disposal of spent lubricants also causes oil pollution in the study area. Around 80,000 barrels of lubricants are consumed per annum in Trinidad and Tobago. Some of the spent lubricating oil replaced at service stations and car repair shops flows to the rivers through sewers. Petrotrin has initiated a program to recover spent lubricating oil and plans to expand nationwide.

7-3 Role of Emulsion in Petroleum Pollution

The discharge to the rivers of the oil-in-water emulsion is the most serious cause of oil pollution from onshore oilfields. The emulsion is generated as a result of steam injection.

The production of thermal crude oil in the study area is about 10,000 bbls/day, and that of associated water could occasionally be as high as 100,000 bbls/day. Since the oil content of the separated water could be as high as 10,000 ppm, the amount of oil discharged to the environment could be as high as 1,000 bbls/day. On the other hand, the production of primary oil in this area is about 20,000 bbls/day, and about 40,000 bbls/day of water is produced. Assuming the oil content of the separated water to be 200 ppm, the quantity of oil discharged to the environment is eight bbls/day.

About 99 percent of the oil fed to water treatment facilities comes from the thermal operation. The oil content in the separated water varies depending on bleeding operations of tanks. It is difficult to break down the measured oil content into floating oil, dissolved oil, and suspended oil in the emulsion. However it is certain that a large amount of emulsion is produced as a result of steam injection activities. The emulsion is quite stable, with suspended oil particles less than 10 microns across. It is impossible to separate the emulsion into oil and water by means of conventional API separators, which are normally for removal of particles more than 150 microns in diameter.

Therefore, it is evident that the oil-in-water emulsion is the major cause of petroleum pollution in Trinidad and Tobago.

7-4 Oil Pollution in Public Waters

Here the amount of oil discharged to the public waters is estimated based upon the information on river flow rates and oil contents of their water. The estimation is based on the limited information collected during the field survey; therefore, the estimated values must be accepted with reserve.

7-4-1 Oil Contents of Major Rivers in the Study Area

The Vance, Guapo, Pt. Ligoure, Silver Stream, Rio Negro, and Guaracara Rivers were selected as subjects of study. Oil contents of water from these rivers were measured eight times from November 1993 to February 1994, and their averages were calculated as their representative values. As data representing the Guaracara River, the outlet points of Nos. 2 and 4 API separators were selected because of their greater flow rates. The results of the measurements are shown in Table 7-2.

Table 7-2 Oil Contents in Major Rivers

(Unit: ppm)

	2/11	16/11	26/11	14/12	24/12	11/1	25/1	17/2
Vance River	23	37	31	78	38	94	31	26
Guapo River	52	59	946	177	114	58	113	38
Pt. Ligoure	648	64	845	546	518	556	693	457
Silver Stream	149	117	37	86	159	191	142	99
Rio Negro	122	116	29	70	268	203	160	280
Guaracara River								
No. 2 API Outlet	1,015	603	--	230	234	519	49	186
No. 4 API Outlet	267	91	145	376	58	1,000	157	60

Source: Study Team

7-4-2 River Flow Rate Estimation

Based on the annual rainfall and runoff coefficient for each river basin, the study team has calculated the average flow rate for each river. For the Guaracara River next to Pointe-a-Pierre Refinery, the volumes of effluent water from Nos. 2 and 4 API separators are taken as the basis of calculation.

7-4-3 Estimation of Volume of Oil Flowing in Each River

The volume of oil flowing in each river is calculated by multiplying the average flow rate by the average oil content, of which the results are shown in Table 7-3. In this area a total of 284 bbls/day, or 100,000 bbls a year, is discharged to the rivers.

Table 7-3 Calculated Oil Discharge

(Unit: barrels/day)

	Av. Flow Rate	Av. Oil Content (ppm)	Oil Discharge
Vance River	67,400	45	3.0
Guapo River	370,600	200	74.1
Pt. Ligoure	17,000	540	9.2
Silver Stream	242,400	122	29.1
Rio Negro	195,100	156	30.4
Guaracara River			
No. 2 API Outlet	73,900	405	29.9
No. 4 API Outlet	403,200	269	108.5
Total	1,369,600	--	284.2

Source: Study Team

7-4-4 Volume of Oil Flowing in Each River

The total volume of oil discharged to the rivers was thus calculated by multiplying the estimated flow rate by the average measured oil content of water. The quantity of discharged oil varies depending on the operating conditions of the wells and associated facilities, so the oil content of the river water fluctuates considerably with the location, flow rate, and sampling method. In order to develop a more accurate estimate, periodic measurements over a long enough period are necessary to allow collection of a sufficient number of samples. The estimates shown on Table 7-3 cannot be taken to accurately represent the present situation, since the number of samples is too limited for them to be representative.

The calculated result shows that more than 50 percent of oil comes from the refinery; however, the study team believes that the tank farms are discharging far more oil than the refinery for the following reasons.

1. The emulsion is the worst source of oil pollution in Trinidad and Tobago. It comes from the tank farms and cannot be separated by the conventional gravity-induced separators such as API separator.

2. The tank farms dealing with thermal crude oil continuously discharge a significant amount of water which contains oil in suspension at very high concentrations possibly exceeding 10,000 ppm.

3. The water content of crude oil sent to the refinery is specified to be less than 2 percent; therefore, the volume of emulsion separated and discharged at the refinery is rather small.