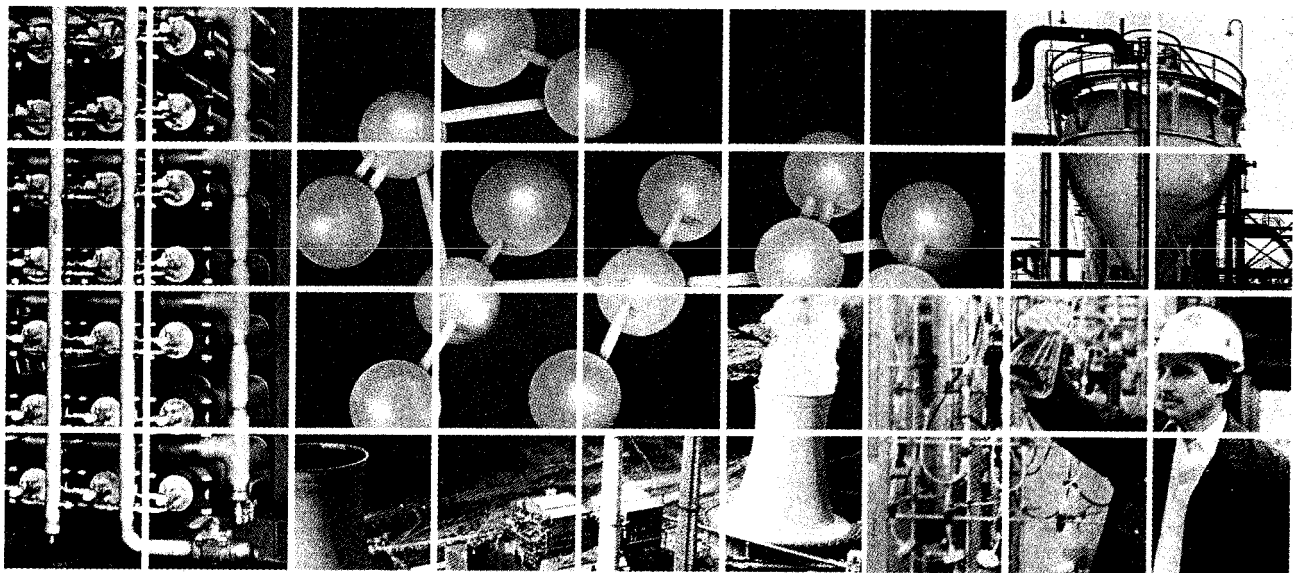


THE APPLICATION OF GRANULAR RESIN COALESCER TO PRODUCED WATER DEOILING



The Application of Granular Resin Coalescer to Produced Water Deoiling

By

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INTRODUCTION

During the last three years, Graver has been conducting laboratory and field studies on the unique TRISEP oil/water separation technology. This technology utilizes a novel coalescing medium which is a synthetic ion exchange resin with oleophilic groups attached to a portion of the available exchange sites. The oleophilic groups are strongly affixed and are not removed over a pH range of 2 to 12. Also, the bonds are stable in saturated brine solutions.

PROCESS DESCRIPTION

Produced waters are deoiled by being passed through a bed of the oleophilic resin (Figure No. 1). Dispersed oil droplets coalesce onto the resin beads, driven by the low interfacial surface tension between the oil and the resin. The efficiency of a coalescer can be described by:(1)

$$E = 1 - \exp ((K_D AZ)/V)$$

Where

E = efficiency of the coalescer

K_D = mass transfer coefficient of the dispersed phase

A = average specific interfacial surface per unit volume

Z = depth of packed bed

V = superficial velocity

K_D is a function of the interfacial tension between the dispersed phase (oil) and the coalescing medium.

To maximize efficiency, the resin bed presents an abundance of surface area to the dispersed oil droplets. Every cubic foot of resin contains more than 1500 ft² (139 m²) of bead surface area. Obviously, this amount of surface area will greatly enhance the efficiency of the coalescing process.

As the produced water flows downward through the resin bed, an oil film forms on the exposed surface of the beads. The oil film will continue to grow on the bead surfaces until the forces working on the oil film exceed those holding the film. In this case, the shear force of the continuous phase flowing through the interstitial spaces of the porous medium must be greater than the combination of the gravitation forces and the attraction of the oil for the resin surface. The free oil released from the bead surfaces will combine, forming drops upon exiting the bed through the resin retention strainers (Figure No.2). The drops leaving the bed are now at least an order of magnitude greater than those entering (typically 0.5 mm diameter). Once steady state conditions are reached (i.e., the entire bed is oil saturated), the mass of oil entering the bed is essentially equal to that exiting. The drop size distribution being the significant variant.

Upon entering the cavity under the bed, the drops are carried by the bulk fluid flow to the separation zone. The flow is directed upward from the cavity through an internal riser pipe. This riser pipe may be fitted with a porous secondary coalescing material to optimize droplet size. The flow velocity in the riser is controlled to avoid drop redispersion and to provide upward momentum to the drops. As the water

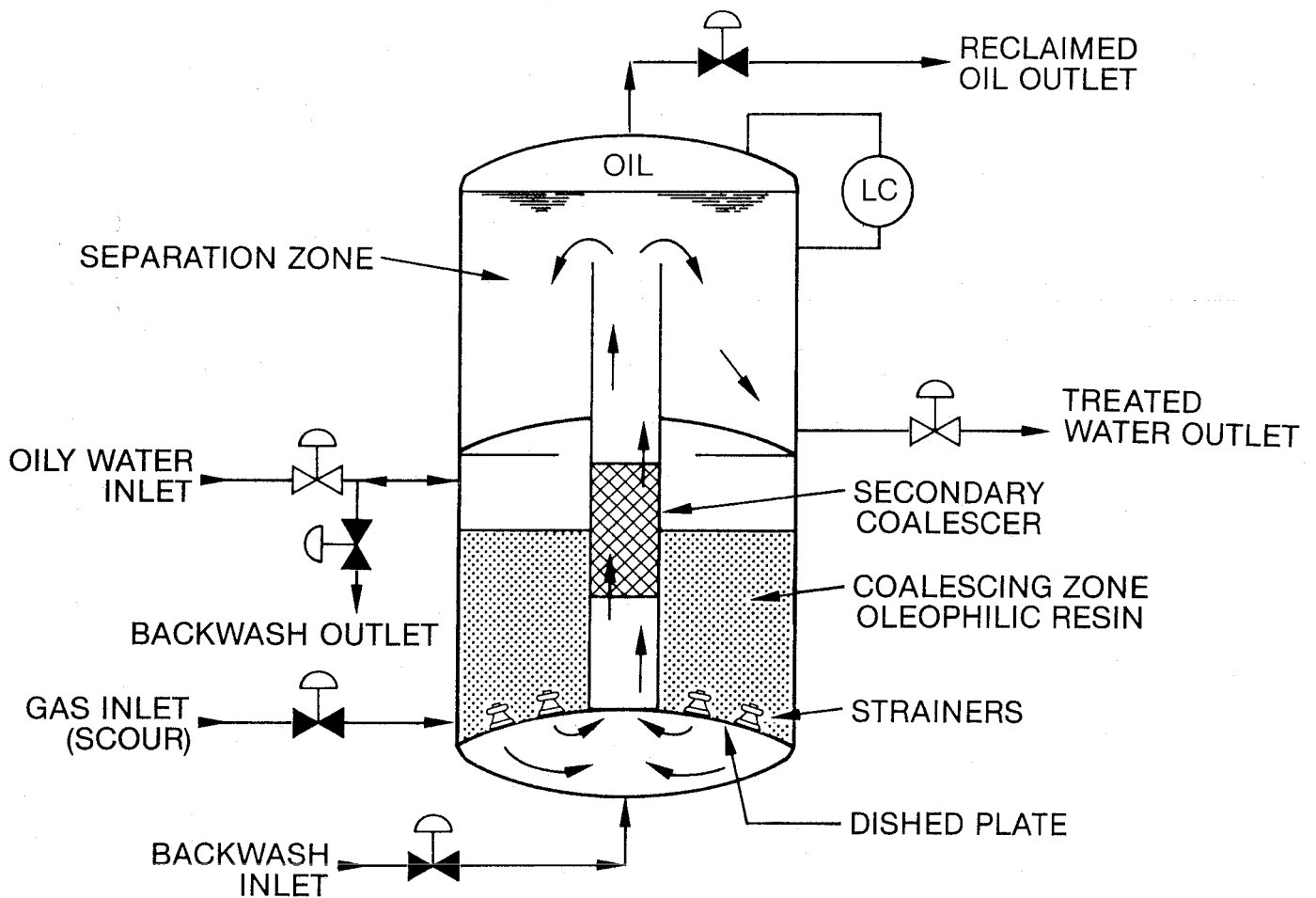


FIGURE No. 1

Photograph of coalesced oil droplets (10-12 mm) disengaging from a bed of oleophilic resin. Influent contained mechanically dispersed oil (less than 100 micron droplet size), which was introduced into the bottom of the 10 cm diameter column.

FIGURE No. 2

OIL/WATER COALESCER/SEPARATOR



departs from the riser, the flow is redirected downward to the effluent connection.

The oil droplets will separate from the water as the water flow is redirected. The momentum and bouyancy of the oil drops are sufficient to break them free of the water. The separation rise rate of the oil drops is described by:

$$V_o = \frac{1}{18} \frac{d^2 (P_w - P_o)}{\mu} g$$

Where

V_o = vertical velocity of the oil drop relative to the water

d = drop diameter

P_o = density of the oil

P_w = density of the water

g = acceleration due to gravity

μ = dynamic viscosity of the water

(Assuming Stoke's law region, i.e., $N_{Re} < 0.3$)(2)

Parameters affecting separation, such as oil gravity, water temperature and dissolved solids content, which affect differential density and viscosity, are independent of the process. Therefore, process design parameters are chosen to optimize drop size and consequently rise rate. As oil drops collect in the crown of the vessel, forming a layer that is typically greater than 90% oil.

The suspended solids removed from the produced waters during operation must be periodically cleaned from the bed. The cleaning procedure is critical, in that it must

be rigorous enough to efficiently remove suspended solids, yet leave the accreted oil layer intact. A water backwash with varying rates, occasionally with gas introduced simultaneously, has proven to achieve the desired constraints. The frequency of cleaning will be a function of the suspended solids' content of the produced water. The backwash water volumes, encountered during testing, were typically less than 2%. Waste volumes can be reduced further by diverting the flow to a cone-bottomed storage tank. The solids will settle to the bottom, and the water can be reprocessed through the coalescer/separator unit. In this manner, the only waste product from the process is the concentrated solids' blowdown from the cone-bottomed tank.

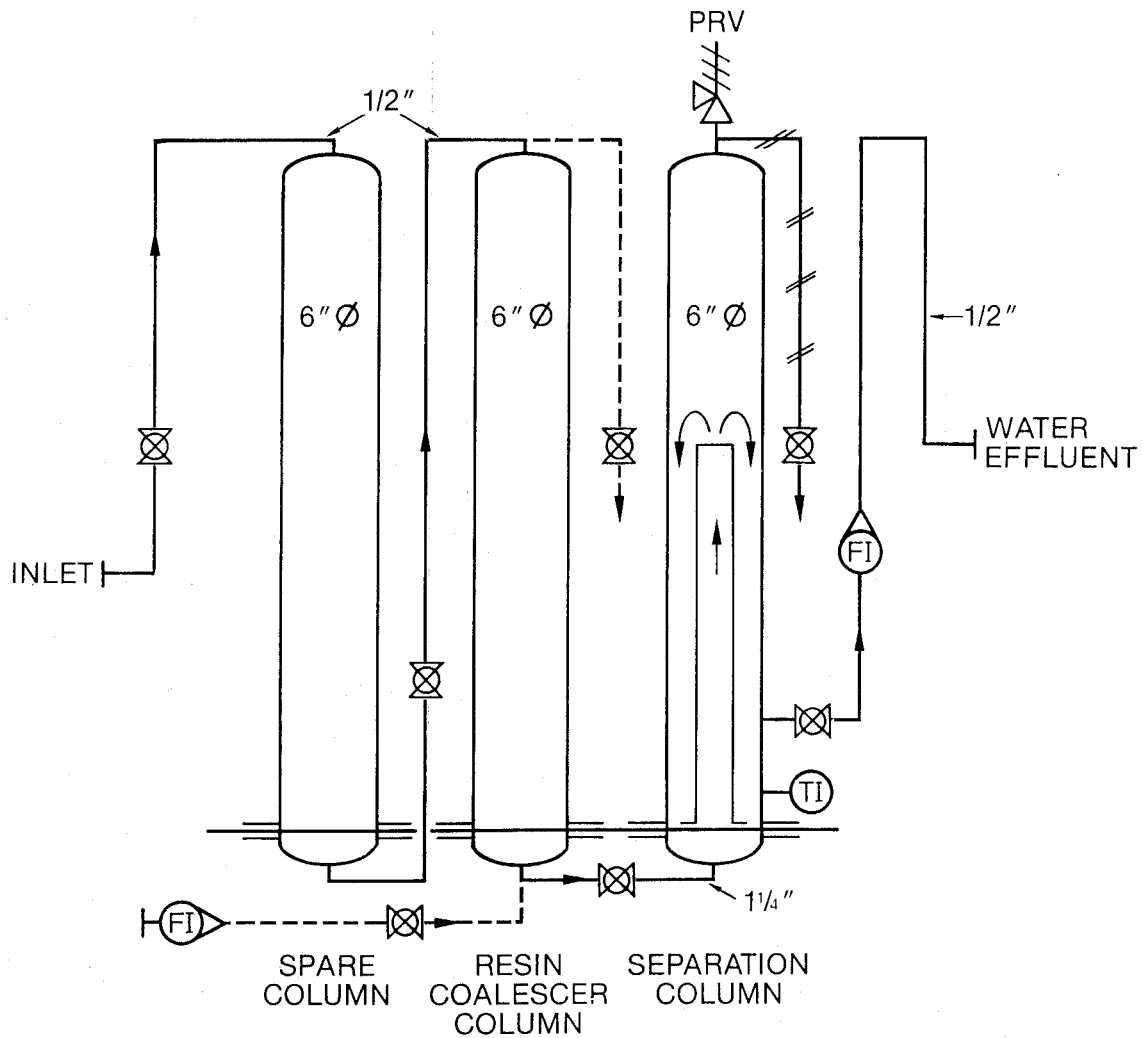
PILOT EQUIPMENT

The unit consisted of three stainless steel columns (6" diameter) as depicted in Figure Nos. 3 and 4. The right hand column was an empty spare which was never used. The center column was loaded with a 30-inch deep bed of oleophilic resin. Direction of the flow through this column was from the top to the bottom. Flow is then directed into the bottom of the separation column (left side). In order to observe the oil droplet sizing and flow pattern, the upper section was constructed of Pyrex® glass pipe. The effluent was routed from the side, up (to provide back pressure) and out. The collected oil is discharged through a connection at the top. The oil line was terminated at a level convenient for collection in a drum.

Figure No. 4 is a photograph of the pilot unit in operation on a produced water from heavy oil production. The rotometer on the left was

FIGURE No. 3

PILOT OIL/WATER COALESCER/SEPARATOR



SERVICE FLOW —————
 BACKWASH FLOW - - - - -
 RECLAIMED OIL — // — //

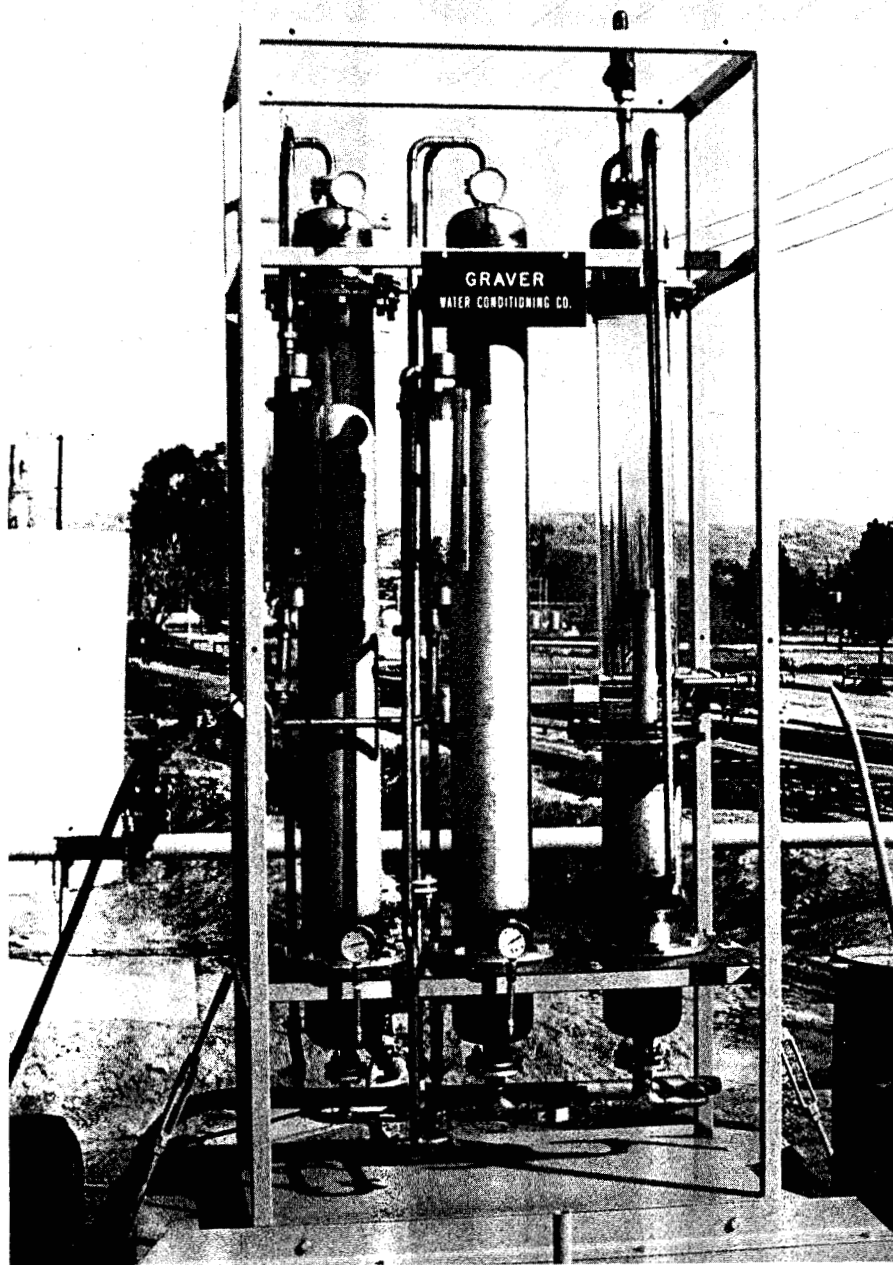


FIGURE No. 4
PILOT COALESCER/SEPARATOR

measuring the influent flow rate. Subsequently, the rotometer was moved to the effluent line to improve visibility. The glass column in the picture did have treated water flowing through at the time. The difference in the influent and effluent water qualities is more clearly illustrated in Figure No. 5. On the right hand side is a sample of the influent. In the center is an effluent sample from the pilot unit. On the left is an effluent sample from the conventional treatment unit operating parallel to the pilot unit.

Figure Nos. 6 and 7 are photographs of the coalesced oil droplets exiting the riser pipe. The approximate sizes of the oil droplets are 2 mm and 7.5 mm equivalent diameters. Reclaimed oil samples from the site had bottom sediment and water total cuts of 7, 6 and 9% with an API (60°F) gravity of 13 to 14.

PILOT UNIT RESULTS

Heavy Oil

Site A

The pilot unit was tested at two locations on the produced water line over a two-week period. The first location was on the outlet of a flat-bottomed separation tank. The second location was immediately after a second stream and was blended with the produced water. This site provided an interesting comparison of pilot unit performance at various temperatures. Table No. 1 is a summary representation of the temperature effect on effluent oil concentration. Effluent oil concentrations were grouped in accordance with temperature range (4°F increments). The mean effluent oil concentration was then computed for each range. The results were as shown on Table No. 1.

Location No. 1 was upstream of a flotation cell, location No. 2 was parallel to the flotation cell.

Overall performance was as follows:

Mean Influent Oil Concentration = 194 mg/l

Mean Pilot Unit Effluent Oil Concentration = 8.4 mg/l

Mean Flotation Cell Oil Concentration = 11.8 mg/l

The quality of reclaimed oil is shown in Table No. 2.

Site B

The pilot unit was again tested at two locations during a two-week period. This time the two locations had different sources of produced water. The two sites again had significantly different temperature ranges (82°F to 110°F at Location 1 vs. 132°F to 150°F at Location 2). However, the pilot unit performance was similar to each location (see Table No. 3). Both runs were made parallel to a flotation cell for comparison.

During the tests at both locations, a great variance in influent oil concentrations was encountered. These data compare the efficiency of the process as a function of influent concentration. Data were grouped in accordance with the influent oil concentration. Three ranges were considered: influent oil 200 mg/l, 200 mg/l 1000 mg/l and 1000 mg/l. Table No. 4 contains the mean percentage of oil removed and, in parenthesis, the actual mean effluent oil concentration.

Also, during these trials the effect of throughput rate on pilot unit performance was evaluated.

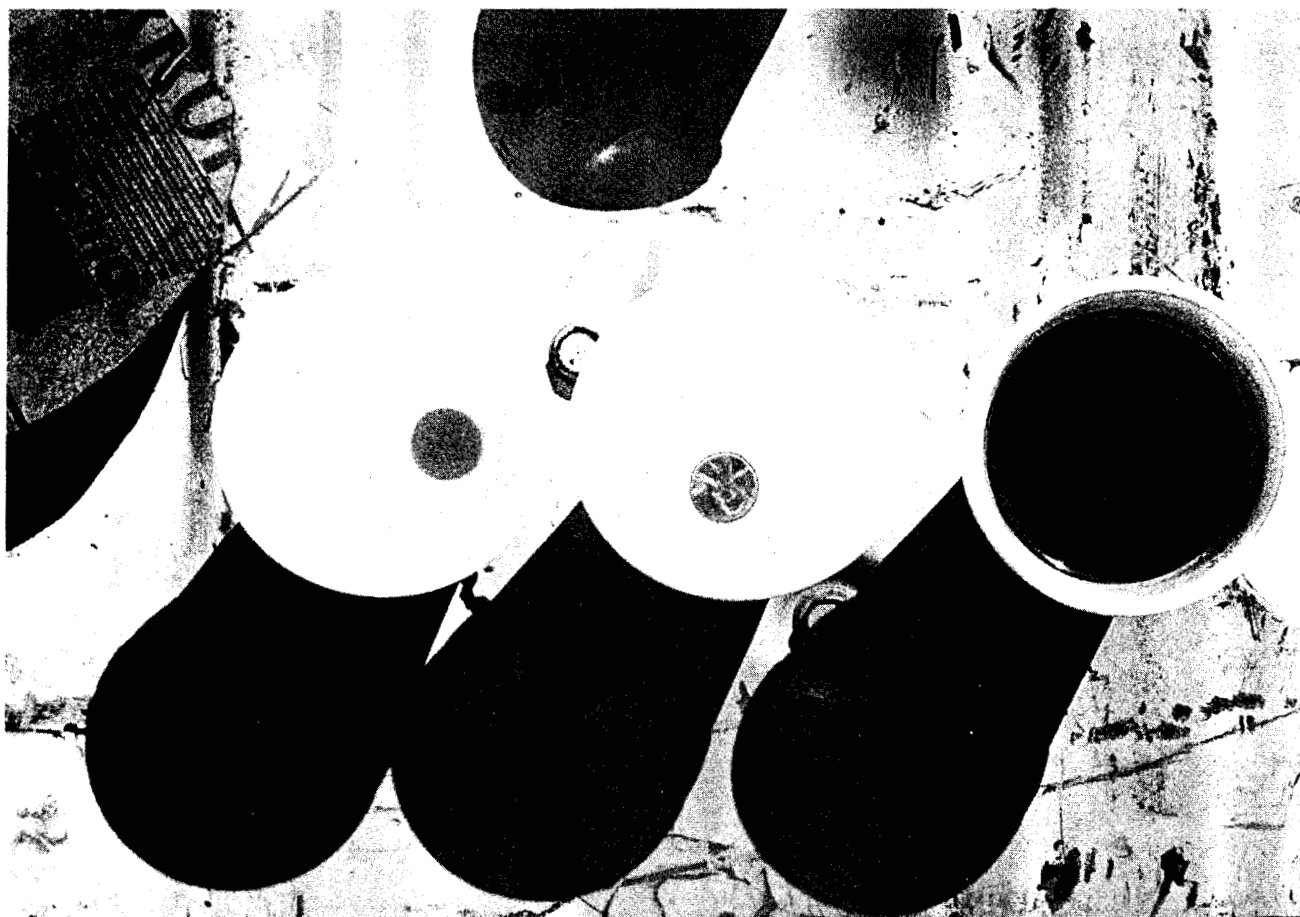


FIGURE No. 5

Left to right, conventional unit effluent
pilot unit effluent, and influent produced water.

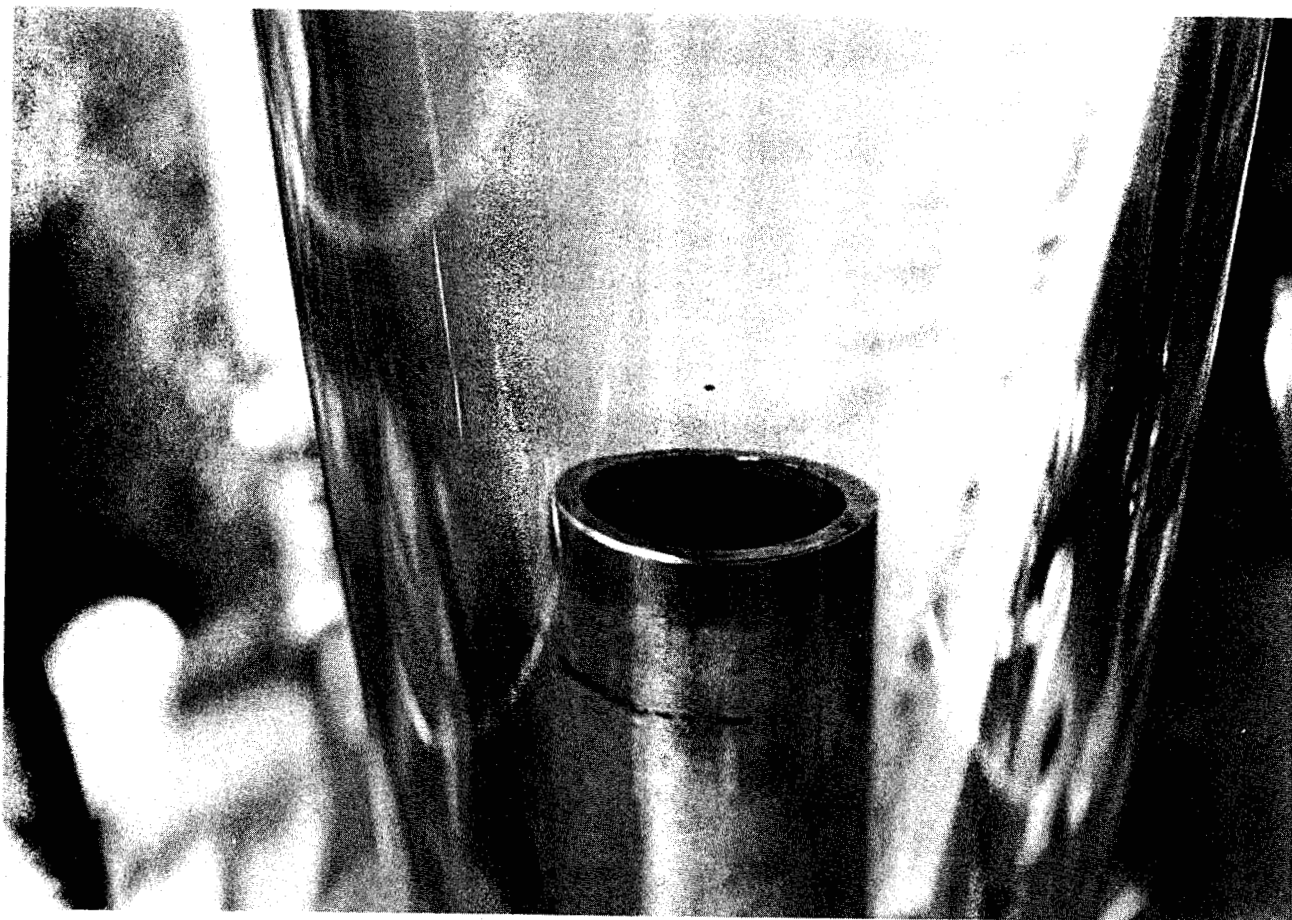


FIGURE No. 6

A 2mm coalesced oil drop,
entering the separation section.

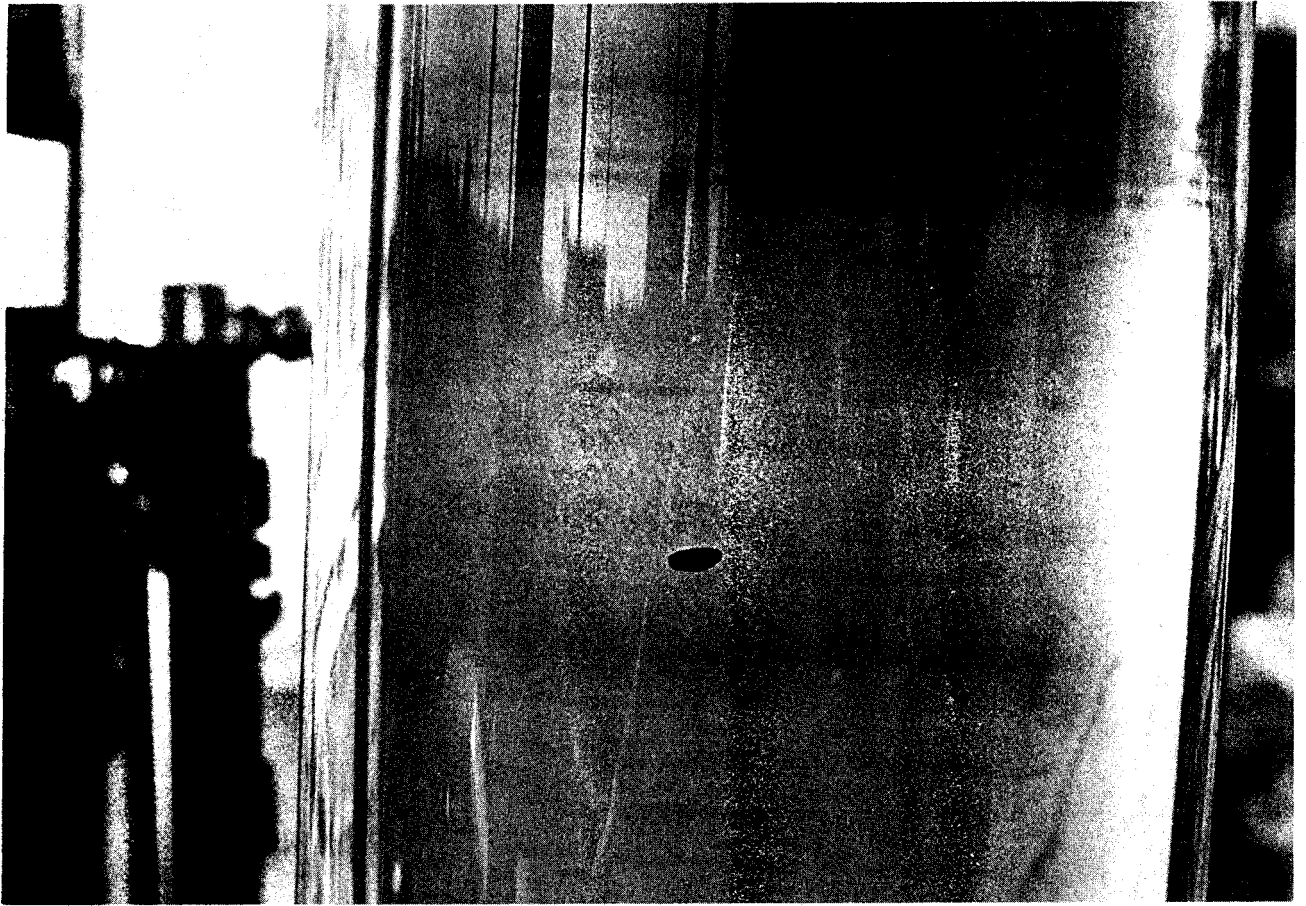


FIGURE No. 7

A 7.5mm coalesced oil drop
in the separation section.

TABLE NO. 1

No. of Date Points	Temperature Range °F	Mean Effluent Oil Conc. mg/l	% Removal	
			Pilot Unit	Flotation Cell
2	86 - 89	14.0	92.2%	--
8	90 - 93	10.0	95.4	95.0
12	94 - 97	7.8	96.0	93.8
4	98 - 101	10.2	95.3	94.9
7	102 - 105	7.3	96.1	93.0
5	128 - 131	1.8	99.0	97.6

Overall performance was as follows:

Mean Influent Oil Concentration = 194 mg/l

Mean Pilot Unit Effluent Oil Concentration = 8.4 mg/l

Mean Flotation Cell Oil Concentration = 11.8 mg/l

TABLE NO. 2

Bottom Sediment & Water (Volume %)	Sample No.		
	1.	2.	3.
Total Cut	10.0	10.0	6.0
Emulsion	0	0	0
Water	10.0	9.5	5.3
Sediment	Trace	0.5	0.7
API Gravity (60°F)	13.2	13.9	12.5

TABLE NO. 3

Location	Temp. (°F)	Mean Oil Concentration		% Removal	
		Influent (mg/l)	Effluent (mg/l)	Pilot Unit	Flota- tion Cell
1	82-111	675	2.1 11.5	99.7	98.3
2	132-150	913	5.2 100.5	99.5	89.0

Table No. 5 contains the data on throughput rate (per unit bed surface area) versus mean effluent oil concentration and percentage oil removal.

From the standpoint of removal percentages, obviously the 137 to 171 bbl/d-ft² (4.0-4.9 gpm/ft²) rate was the most efficient. However, in all cases effluent quality was very good over the throughput ranges tested. Even at the minimum removal percentage (98.7%), mean influent oil concentration was 430 mg/l with a mean effluent concentration of 5.6 mg/l.

Backwash volumes during the test averaged 1.3% of the throughput volume. Reclaimed oil had bottom sediment and water contents as shown in Table No. 6.

Site C

The pilot unit was tried at three different locations on the same produced water line. The first location was prior to clarifiers (mean influent oil concentration of 1061 mg/l). The second location was immediately after the clarifiers (mean influent oil concentration of 354 mg/l). The third location was on the effluent of a conventional oil/water separation unit (mean influent oil concentration of 26.9 mg/l).

This trial afforded a direct comparison of unit performance over a variety of influent oil concentrations. The temperatures, water quality, and oil characteristics were sufficiently consistent for the sake of comparison. Table No. 7 and Figure No. 8 show the grouped mean influent and effluent oil concentrations. Coalescer effluent oil concentrations were consistent

throughout the entire inlet concentration range. The unit performance was obtained while holding the unit area flow rate between 206 and 257 bbl/d-ft² (6-7.5 gpm/ft²). Oil reclaimed during the test period had bottom sediment and water contents as shown in Table 8. As a comparison, operating data from flotation cells on this same water line are included in Table No. 7.

Light Oil Production

Site D

Site D was located on a platform in the Gulf of Mexico. Produced water from a low pressure separator was piped to the pilot unit. Oil produced on the platform is approximately 30° API. The results of the four-week trial are summarized in Table No. 9.

Throughput rates were varied between 210 and 300 bbl/d-ft² (6.1 and 8.7 gpm/ft²). Produced water temperature was consistently near 90°F.

Site E

Site E was located on the California coast. Produced water was taken from a central receiving tank and pumped through the pilot unit. Influent concentrations were consistently above 1%. Temperatures ranged between 116°F and 124°F. Oil reclaimed was 30° API (60°F) gravity. Table No. 10 contains the operating data from the pilot trial.

Unit was run on this source for a period of five days. Mean values are based upon 34 data points collected over the trial period. Throughput rates, per unit surface area, during the trial ranged between 120 and 240 bbl/d-ft² (3.5-

TABLE NO. 4

<u>Location</u>	<u>Influent Oil Concentration</u>		
	200		
	<u>200 mg/l</u>	<u>1000 mg/l</u>	<u>1000 mg/l</u>
1	97.4% (1.9 mg/l	99.6% (3.0 mg/l)	--
2	97.0% (3.5 mg/l)	99.0% (4.6 mg/l)	99.5% (6.5 mg/l)

TABLE NO. 5

<u>Throughput Rate</u> <u>bbl/d-ft² (gpm/ft²)</u>	<u>Mean Effluent</u> <u>Oil Concentration</u>	<u>Mean %</u> <u>Removal</u>
103-136 (3.0-3.9)	6.5	98.8
137-170 (4.0-4.9)	4.6	99.5
171-204 (5.0-5.9)	1.7	98.9
205-238 (6.0-6.9)	5.6	98.7

TABLE NO. 6

<u>Bottom Sediment and Water</u> <u>(Volume %)</u>	<u>Sample #1</u>	<u>Sample #2</u>
Total Cut	10.0%	12.0%
Emulsion	0.0	0.0
Water	8.6	10.6
Sediment	1.4	1.4

TABLE NO. 7

Influent Oil Concentration (mg/l)		No. of Data Points	Effluent Oil (mg/l)		% Removal	
Range	Group Mean		Mean Concentration Pilot	Flotation	Pilot Unit	Flotation Cell
0- 49	25.4	41	4.8	24.7	81.1	2.8
50- 99	68.1	40	3.1	26.7	95.4	60.8
100- 149	112.9	7	4.9	33.5	95.7	70.3
150- 199	-	-	-	-	-	-
200- 299	-	-	-	-	-	-
300- 399	360	2	2.5	28.1	99.3	92.2
400- 499	-	-	-	-	-	-
500- 599	-	-	-	-	-	-
600- 699	620	1	1.5	62.0	99.8	90.0
700- 799	-	-	-	-	-	-
800- 899	800	1	4.8	29.6	99.4	96.3
900- 999	-	-	-	-	-	-
1000-1499	1100	4	3.5	44.0	99.7	96.0
1500-1999	1800	1	3.0	-	99.8	-
2000-2999	2400	2	5.4	31.2	99.8	98.7
3000-3999	3267	3	3.5	-	99.9	-
4000-4999	4700	2	5.1	32.9	99.9	99.3
5000-5999	5300	1	2.3	-	99.9	-
6000	8000	1	3.0	-	99.9	-

TABLE NO. 8

<u>Bottom Sediment and Water</u> <u>(Volume %)</u>	<u>Sample #1</u>	<u>Sample #2</u>
Total Cut	20.0	20.0
Emulsion	0	0
Water	12.0	12.0
Sediment	8.0	8.0
API Gravity @ 60°F	11.1	10.3

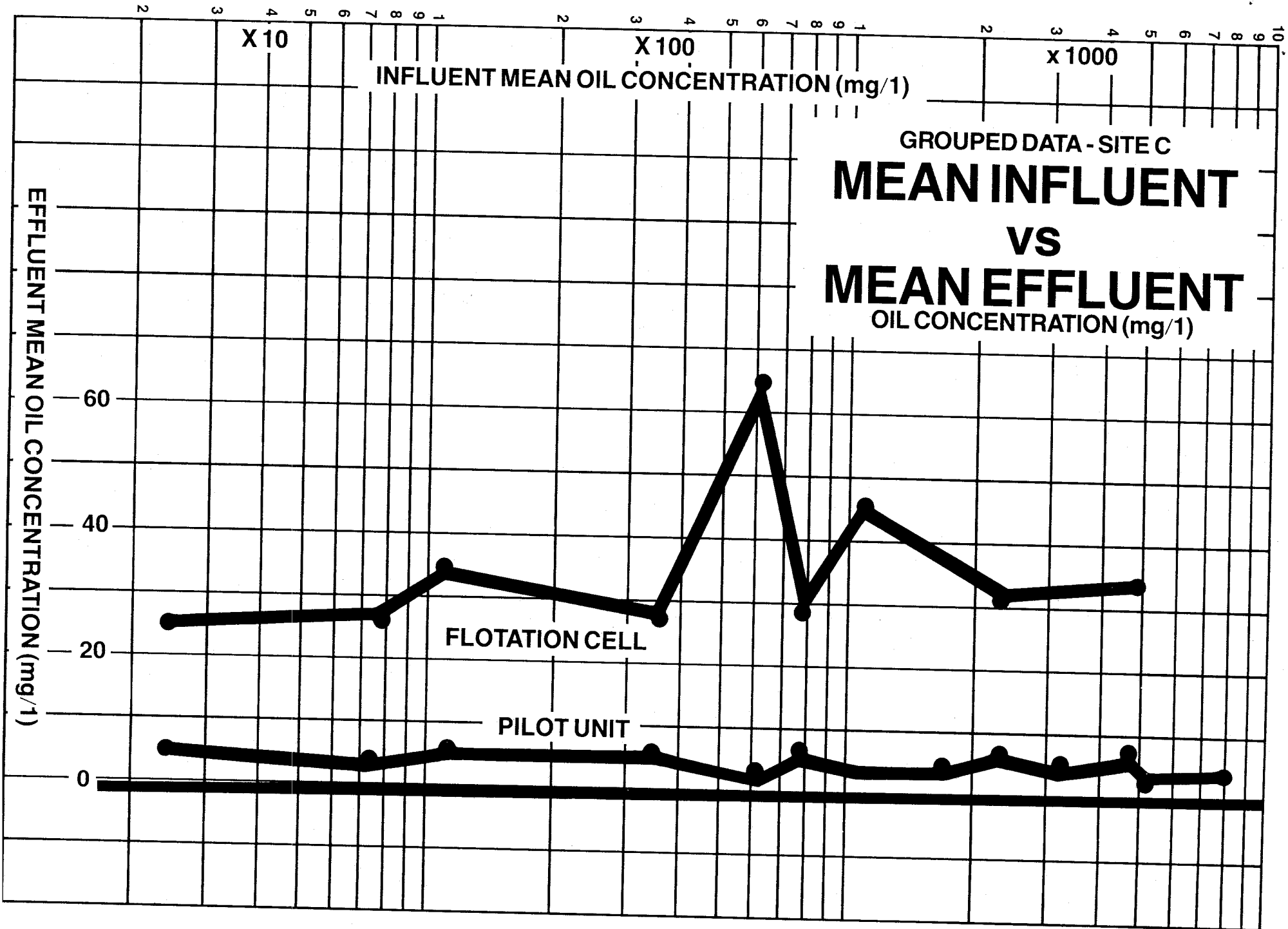


FIGURE No. 8

TABLE NO. 9

Mean Influent Oil Concentration	232 mg/l
Mean Effluent Oil Concentration	9 mg/l
Removal Percentage	95.25
Bottom Sediment and Water	Vol. %
Total Cut	3.0
Water	1.1
Emulsion	1.4
Solids	0.5

TABLE NO. 10

Mean Influent Oil Concentration	3.5%
Mean Effluent Oil Concentration	454 mg/l
% Removal	98.7%

TABLE NO. 11

<u>Location</u>	<u>Mean Oil Concentration (mg/l)</u>		<u>% Removal</u>
	<u>Influent</u>	<u>Effluent</u>	
Wastewater	5157	15.7	99.7
Sour Water	123	0.76	99.4
Desalting Water	5317	11.4	99.8

TABLE NO. 12

<u>Influent Oil</u> (mg/l)	<u>Mean Effluent Oil</u> (mg/l)	<u>% Removal</u>
< 1000 mg/l	1.9	99.0
> 1000 mg/l	20.8	99.7

7.0 gpm/ft²). Despite the relatively high mean effluent oil concentration, removal percentage was still in line with previous trials.

Refinery Wastewater Treatment

Site F

The pilot unit was tried at three different locations within this refinery. The first location was general plant wastewater for a period of five days. The second location was on sour water for a period of four days. The third location was on a crude oil desalting water for a period of three days. The pilot unit results at the three locations are given in Table No. 11.

The data collected for all three locations show an almost equal distribution of data points below (19) and above (17) 1000 mg/l influent oil concentration. These data mirror the removal percentages given in Table No. 11. Table No. 12 contains this information. The effect of operating rate on performance is given in Table No. 13.

Site G

At this location the unit was operated for a period of seven days on the refinery wastewater. This test had an interesting influent oil concentration distribution. Forty percent of the influent oil concentrations encountered were above 1000 mg/l. Fifty-three percent of the data points were below 100 mg/l. However, the mean effluent oil concentrations were almost identical. (see Table No. 14). This trial run was parallel to a CPI-flotation cell combination, comparative operating data are contained in Table 14.

The performance achieved with the influent oil concentration above 1000 mg/l oil was with a higher mean throughput rate. The mean throughput rate for influent oil concentrations above 1000 mg/l was 250 bbl/d-ft² (7.3 gpm/ft² versus 223 bbl/d-ft² (6.5 gpm/ft²) for influent oil concentration below 100 mg/l. The mean temperatures were identical (133°F) in both cases. It is difficult to say precisely where an operating break point will occur in terms of throughput rate and influent oil concentration. More test work is scheduled for this location.

DISCUSSION OF RESULTS

Befitting the divergency of the influent source, this discussion will deal separately with the heavy oil-produced waters, light oil-produced waters and refinery wastewaters.

Heavy Oil Produced Waters

The mean performance of the coalescer pilot at the three locations tested was typically greater than 95% removal of oil. The only exceptions were when the temperature was low (86°F to 89°F at Site A) or the influent oil concentration was very low (50 mg/l grouped mean influent at Site C). However, even under these conditions the effluent oil concentrations were excellent:

Site A

Low temperature operation -
180 mg/l mean influent oil
14 mg/l mean effluent oil
92.2% removal

TABLE NO. 13

Throughput Rate bbl/d-ft ² (gpm/ft ²)	Mean Oil Concentration (mg/l)		% Removal
	Influent	Effluent	
≤103 (≤ 3.0)	8210	8.6	99.9
>103 ≤171 (> 3.0 ≤5.0)	3122	20.5	99.3

TABLE NO. 14

	Mean Influent Oil Cond. (mg/l)	Mean Influent Oil Concentration (mg/l)		% Removal	
		Pilot Unit	CPI/Flota- tion Cell	Pilot Unit	CPI/Flota- tion Cell
For complete test	720	1.3	175	99.8	75.7
For Influent Oil <100 mg/l	50	1.3	64	97.4	-28.0
For Influent Oil >1000 mg/l	1653	1.4	125	99.9	92.4

greater than 99%. The unit performance at Site G was significantly better than the combination of a Corrugated Plate Interceptor followed by a flotation unit (99.8% mean removal vs. 75.7% mean removal). This was true even with high influent oil concentrations; for influents with more than 1000 mg/l, the coalescer removed 99.9% of the oil vs. 92.4% for the CPI/flotation unit combination. The performance of the flotation cell is similar to that reported by Ford and Manning⁽⁵⁾, i.e., 83.6% mean removal of oil from a refinery wastewater.

CONCLUSION

The pilot unit was operated at numerous sites with varying degrees of oil/water treatment difficulty. The unit performed extremely well in all cases without the plugging problems that typically plague coalescers⁽⁶⁾. The cleaning system is quite efficient in removing captured solids from the coalescing medium bed. Also, the pilot unit was able to handle severe influent oil concentration swings (from 100 mg/l to 1000 mg/l) without upset.

Oil recovered during the test runs typically were 80% to 95% oil for the heavy oil production sites and 95% to 97% oil for the light oil production sites. The absence of chemical conditioners should make oil reclaimed by the coalescer very easy to treat.

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- (5) Oil Removal From Wastewater by D. L. Ford and F. S. Manning, University of Tulsa, Environmental Protection Projects (no date)
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Site C

Low influent oil concentration -
25.4 mg/l mean influent oil
4.8 mg/l mean effluent oil
81.1% removal

The tests served to confirm that for a given influent-produced water operating efficiency was a function of temperature (see Table No. 1).

Interestingly enough, the assumption that increasing influent oil concentrations would result in increasing effluent oil concentrations was confirmed in one case (Site B - Table No. 4), but not in the other (Site C - Figure No. 8, Table No. 7). At Site B, pilot unit performance was as would be predicted. The mean effluent value with influent oil concentrations above 1000 mg/l was roughly twice that for influent oil concentrations below 200 mg/l (6.5 mg/l vs. 3.5 mg/l). At Site C the mean effluent oil concentrations at the lower influent oil concentrations were essentially equal to those at the higher influent oil concentrations. In retrospect, identifying the makeup of the influent oil concentrations (i.e., free, dispersed, emulsified oils, or oil-coated suspended solids) would have been helpful in explaining these differences in performance.

During all three tests the pilot unit was operated parallel to an induced gas flotation unit. In some cases the flotation unit performance lagged the coalescer performance slightly (Site A and Site B, Location No. 1). At Site A the flotation unit had a mean removal percentage of 93.9 (vs. 95.7% for the coalescer). At Site B, Location No. 1, the flotation unit had a mean removal percentage of 98.3 (vs. 99.7% for the coalescer). However, at Site B, Location No. 2, and Site

C there were significant differences in comparative performance (refer to Table Nos. 3 and 7, respectively). At Site B, Location No. 2, the flotation unit had a mean removal percentage of 89 (vs. 99.5% for the coalescer). At Site C the flotation unit operated relatively poorly when the influent oil concentration was less than 150 mg/l (49.2% removal vs. 92.3% removal for the coalescer). At high influent oil loadings (300 mg/l), the flotation unit performance was similar to that obtained at Site A and Site B, Location No. 1 (96% removal). In comparison, over the same range of influent oil loadings (300 mg/l), the coalescer had a removal percentage of 99.86%.

Leech, et al.⁽³⁾ reported flotation unit performance of 95.8% to 96.8% oil removal from similar heavy oil produced water, with an influent oil concentration of 187 to 239 mg/l.

Light Oil Produced Waters

Table No. 9 gives the performance of the pilot coalescer on a Gulf Coast platform. This performance (96.25% removal) compares very favorably with the reported performance of flotation units on Gulf Coast platforms⁽⁴⁾. The Crest study reported a removal percentage range of 71.3 to 99.3%, with a mean of 87.6% removal.

The recovered oil had a total cut (BS&W) of only 3%. Normally, this quality oil is considered pipeline quality.

Refinery Wastewater

The coalescer performed especially well at the refineries tested. Removal percentages were consistently

PARTIAL LIST OF OIL/WATER SEPARATOR INSTALLATIONS

Customer and Location	Quantity/Size	Total Capacity
Getty-Mohawk Refining Bakersfield, CA	(1) 6' - 0" dia.	5,000 bbl/day
Getty Production Kern River Field, CA	(1) 6' - 0" dia.	8,000 bbl/day
Rio Bravo Refining Bakersfield, CA	(1) 6' - 0" dia	7,200 bbl/day
Yacimientos Peroliferos Fiscales, ARGENTINA Douges Refinery, FRANCE	(2) 11' - 0" dia.	30,170 bbl/day
Elf Aquitaine Douges Refinery, FRANCE	(2) units	16,600 bbl/day
Elf Aquitain Ambes Refinery, FRANCE	(2) units	4,525 bbl/day
Elf Aquitaine Dunkerque Refinery, FRANCE	(1) unit	10,560 bbl/day
Santa Fe Energy Corporation Bakersfield, CA	(3) 8' - 0" dia.	23,000 bbl/day
Brest Harbour Authority FRANCE	(2) 9' - 10" dia.	42,170 bbl/day
Bayonne Harbour Authority Bayonne, FRANCE	(1) 8' - 2" dia.	15,000 bbl/day

*Although this paper was presented in November of 1983,
it accurately reflects the State-of-the-Art today.*