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Refinery wastewater characteristics vary with refinery size and process sophistication. The major sources of free or slop oil in refinery wastewaters are crude oil and product storage, crude oil desalting, and asphalt productions. Crude oil and product storage, and crude oil desalting also serve as major sources of emulsified oil along with crude oil distillation.[1] The amount of oil and grease in petroleum refinery effluents has been strictly regulated by recent federal acts.[2]

Typically the major portion of free and emulsified oil in refinery effluent is removed by using American Petroleum Institute (API) or baffle plate separators followed by chemical clarifiers, dissolved air flotation (DAF), or filters. Removal of emulsified oil by DAF is poorly understood, consequently a laboratory and pilot plant study was initiated for the following reasons:

1. To investigate relationships between surface chemical and colloidal properties of oil emulsions which influence oil droplet coagulation and air bubble contact in air flotation equipment.
2. To understand the predominant mechanisms of oil droplet-air bubble interaction which might permit the description of a model of the flotation process.
3. To evaluate the feasibility and economy of using organic surface active agents and polyelectrolytes as coagulants in the DAF process without contaminating the oil float with hydrolyzing metal salts (alum, ferric chloride).

This paper deals primarily with the last two objectives. A detailed discussion of the surface chemical properties of refinery wastewater oil droplets is presented elsewhere,[3] and summarized in the following section.

In DAF a portion of the influent, or recycled effluent, is saturated with air at a pressure of 275 to 410 kN/m^2 (40 to 60 psig). The wastewater or effluent recycle is released at atmospheric pressure in a flotation chamber with the air coming out of solution in the form of minute air bubbles. The air bubbles collect and carry the emulsified oil droplets to the water surface to form a froth which is removed by mechanical scrapers. Effluent recycle pressurization is more commonly used than influent pressurization for oil removal applications.[4]

Design criteria and performance data for the pilot DAF process used in this study and for processes reported by others [4-10] are shown in Table I. Usually the processes are designed with hydraulic surface loading (overflow) rates and recycle rates able to meet peak flow (storm flow) conditions. It was reported by the EPA [1] that DAF plants with exemplary operation should remove 70 to 85 percent of API separator effluent oil, with suspended effluent oil concentrations ranging from 5 to 20 mg/l.

THEORETICAL DEVELOPMENTS

Flocculation kinetics. Numerous operations data prove that coagulation prior to flotation improves the performance of the DAF process. Experiences described subsequently show that the rise rates of flocculated oil droplets increase greatly even without air, and contact with air bubbles hastens the rise rate appreciably.

TABLE I. Performance of DAF units with preliminary flocculation and DAF design criteria.

Ref.	Influent Oil mg/l	% Oil Removed (% SS Removed)	Overflow* Rate l/m²·s (gpm/ft²)	Detention Times (min): Flocculator, (Flotation Chamber) [Air Retention Tank]	Recycle Ratio % of Feed	Recycle Pressure kN/m² (psig)
4	—	—	1.4–1.7 (2.0–2.5)	5–20 (10–40) [1–2]	20–50	275 (40)
5	—	70–85 (30–50)	2.4 (3.5)	18 (19.5) —	25	345 (50)
6	70	92 (72)	2.0 (2.9)	— (27) [1–2]	33	275 (40)
7	112	65	1.6 (2.3)	— (20) —	(full stream)	275–345 (40–50)
8	—	75	2.7 (4.0)	— (10) —	50	275 (40)
9	—	85–95 (70–75)	2.0 (3)	— (15–20) [2]	50	240–380 (35–55)
10	—	—	1.4–2.0 (2–3)	15 (20) [2]	50	345 (50)
This study	747	98.6 (96.6)	1.3 (1.88)	15 (17) [2.5]	50	345 (50)

* Influent plus any recycle divided by flotation chamber surface area.

The classic theory of emulsion stabilization against flocculation is founded on the theory of the stability of colloids. The basis of the theory is that if the sum of the energies of London-Van der Waals attraction and electrostatic repulsion are such that there is a net attraction between oil droplets, the emulsion will aggregate. Orthokinetic flocculation is aggregation created primarily by collisions between particles as a result of different rates of movements in a gravitation field or in shear flow; this type of flocculation predominates in oil emulsions containing 1-μ or larger droplets.[11] The Smoluchowski equation for orthokinetic flocculation in idealized shear flow is [12]

$$J_{ij} = \tfrac{4}{3} n_i n_j R_{ij} \frac{\mathrm{d}u}{\mathrm{d}z} \tag{1}$$

where J_{ij} is the collision frequency due to fluid motion, n_i and n_j are number concentrations of particles with collision radii R_{ij} equal to the sum of particle radii $R_i + R_j$, and $\mathrm{d}u/\mathrm{d}z$ is the local mean velocity gradient.

Camp and Stein [13] proposed an expression relating the average velocity gradient with power input to a flocculator as follows:

$$G = \left[\frac{P}{V\mu}\right]^{\frac{1}{2}} \tag{2}$$

where G is the mean velocity gradient (s^{-1}), P the net power input to the flocculation chamber, V the water volume of the flocculator, and μ the absolute water viscosity. The power may be measured by torquemeters in the case of paddle type flocculation, or friction head loss in the case of hydraulic (pipe flow) flocculation.

A semi-empirical working equation based on Smoluchowski's theory including a term to account for floc breakup owing to excessive values of G is[14, 15]

$$\frac{dN}{dt} = -K_A N G + K_B G^2 \quad (3)$$

where K_A is an aggregation rate coefficient, K_B is a floc breakup coefficient, and N is the turbidity remaining in suspension after flocculation and a specified period of settling.

Equation 3 was transformed[14] to fit continuous flow stirred tank reactor (CSTR) operation of the type commonly used in paddle flocculators, or

$$N_o/N_m = \prod_{i=1}^{m} \left[\frac{1 + K_A N_o G_i T/m}{1 + K_B (N_o/N_{i-1}) G_i^2 T/m} \right] \quad (4)$$

where the subscript i stands for ith CSTR reactor in the chain and T the overall mean residence time (total reactor volume divided by the flow). If the configuration of the compartments are the same and if the paddles are turned at the same speeds, then the mean velocity gradient and residence time are the same in each compartment. In this case Equation 4 reduces to:

$$N_o/N_m = \frac{(1 + K_A GT/m)^m}{1 + K_B G^2 T/m \sum_{i=0}^{m-1} (1 + K_A GT/m)^i} \quad (5)$$

The rate coefficient K_A is dependent on the chemical conditioning employed and K_B is dependent on the resistance of the formed flocs to breakup in shear flow.

The Smoluchowski equation is completely valid but in truth very little has been done with it aside from the equations listed above because it requires the complete description of floc sizes, an extremely laborious and expensive procedure. In addition, the causes for and the kinetics of floc shear are virtually unknown.

Chemical destabilization of oil emulsions. Coagulation may be promoted by reducing electrical charges of repulsion between oil droplets and by the addition of compounds which bridge and link the oil droplets. Hydrolyzing metal salts destabilize oil droplets by bridging between oil droplets as well as by charge neutralization of negatively charged oil droplets.

The theory of solids destabilization by polymeric coagulants is based on chemical bridging concepts.[16, 17] This theory suggests that a polymer may attach to a colloid at one or more sites. The rest of the polymer remains extended into solution where it can come into contact with vacant sites on other colloid particles, or the extended end of the polymer may bend around and absorb on the original particle. This implies that the rate of flocculation of oil droplets should first increase with the dosage of a polyelectrolyte and then decrease as a result of excessive coating of primary particles.

Experiences with kaolin clay[18] have shown that if the polyelectrolyte is not mixed rapidly throughout the suspension, some particles may receive an overdose, and others an insufficient dose. Flocculation performance then deteriorates with the amount of deterioration depending on the degree of initial segregation in the reacting streams. Another important property of polyelectrolyte flocculation is that once the flocs are sheared by excessive turbulence, they demonstrate little propensity for reformation even when the turbulence is reduced. This differs from hydroxo-metal coagulants which may begin to flocculate again upon rupture. It may be that the broken polyelectrolyte fragments are adsorbed tightly on the particles, making new floc formation impossible.

The results of the studies on the surface properties of oil emulsions[3] demonstrated clearly that the oil droplets possessed negative charges at all pH values in excess of two when immersed in the effluent of the API separator regardless of the source of the oil (various kinds of crude oil and waste oil obtained from the float of the API separator). These studies also indicated that the oil-water interfaces were probably saturated with anionic surfactants derived from the wastewater, and that only very modest concentrations of anionic surfactants were sufficient to affect oil-water interfacial properties. Indeed, the slight amounts of anionic surfactants contained in tap water were sufficient to impart some of the surface properties of wastewater emulsions. This indicated that the in-plant isolation of anionic surfactants from the waste oil streams would not be very practical.

The anionic surfactants were not readily displaced by cationic surfactants. This prevented the reversal of the negative droplet charges with reasonable doses of cationic surfactants. Long chain non-ionic and anionic polyelectrolytes were also ineffective wastewater oil droplet coagulants, probably because of interference from pre-sorbed anionic surfactants.

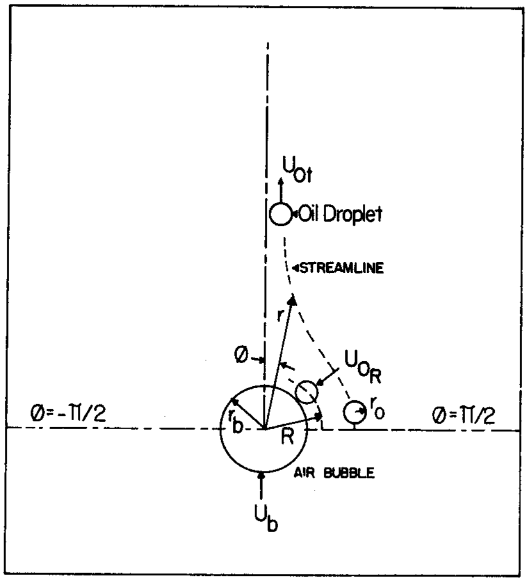

FIGURE 1. Trajectory of an oil droplet approaching an air bubble.

Interception of oil droplets with air bubbles. The removal of destabilized oil droplets from solution is enhanced by the interception and capture of the oil droplet flocs with air bubbles. At present little is known about the means by which air bubbles unite with oil droplets. Various researchers in the field of wastewater treatment have proposed possible mechanisms, but these are generally descriptive and lack experimental verification. One difficulty stems from the fact that upon release of pressure in a DAF process the air bubbles may form on the surfaces of the droplets, or in the bulk water with subsequent interception and capture of the droplets.

The mutual attraction of the water molecules must be overcome in order to form an air bubble in the bulk water or on a surface. This molecular attraction is greater on hydrophilic surfaces than in the bulk water,[20] and it was found that the surfaces of oil droplets suspended in refinery wastewater tended to be very much hydrophilic as a result of the sorption of surface active agents at the oil-water interfaces.[3] Nucleation might occur, however, on wastewater suspended solids if they contain crevice-like surface irregularities,[21] or on droplets possessing adhering gas which may act as pre-existing bubble nuclei.[22] It is assumed in the following developments that bubble nucleation on oil droplets surfaces is insignificant in comparison with the interception and capture of the oil droplets by the air bubbles.

Air bubbles in DAF may average 60 to 80 μ diameter,[19] and the fluid flow is laminar for such bubbles. The oil droplets tend to follow the fluid streamlines as shown in Figure 1 but they will deviate from the streamlines because of such forces as electrostatic attraction or repulsion between the droplet and bubble surfaces, droplet buoyancy, and the mass inertia of the droplets. Reay and Ratcliff[23] showed that the inertial forces should be insignificant for small particles, and ignoring electrostatic effects they derived an expression giving the rate of collision between suspended particles and a rising air bubble, allowing for the conditions of laminar flow around the bubble and buoyancy on the particles. Expressed in terms of the spherical coordinate system shown in Figure 1, the results of their work were

$$u_{oR} = -u_b \cos\phi\left[1 - u_{ot}^* - \frac{3r_b}{2R} + \frac{1}{2}\left(\frac{r_b}{R}\right)^3\right] \qquad (6)$$

where

u_{oR} = the velocity of collision between the oil droplets and the air bubble in a direction normal to the surface of the bubble.

u_b = rise velocity of the air bubble.

R = $r_o + r_b$ where r_o and r_b are the radii of the oil droplet and the air bubble, respectively.

u_{ot}^* = u_{ot}/u_b where u_{ot} is the terminal rise velocity of the oil droplet.

Letting n_o equal the number concentration of the oil droplets in the water phase, the number of oil droplet collisions with one air bubble per unit time I_o is

$$I_o = -n_o\int_0^{\pi/2} (2\pi R \sin\phi)u_{oR}(R d\phi)$$

Substituting Equation 6 into the above and integrating gives

$$I_o = \pi R^2 u_b \beta n_o \qquad (7)$$

where

$$\beta = 1 - u_{ot}^* - \frac{3}{2K} + \frac{1}{2K^3}$$

and

$$K = R/r_b = 1 + r_o/r_b$$

The collision rate between the oil droplets and the air bubbles per unit of reactor volume would then be

$$J_{ob} = \pi u_b R^2 \beta n_o n_b = \pi u_b r_b^2 K^2 \beta n_o n_b \qquad (8)$$

where $n_b =$ the number of bubbles per unit of reactor volume. This equation is not a working equation because the questions of droplet capture upon collision and the alteration of the air bubble properties with the capture of oil droplets have not been answered. It can be used to estimate qualitatively the effects of droplet and bubbles sizes on the DAF process, however, as shown below.

Using Stokes law for small bubbles and droplets

$$u_{ot}^* = u_{ot}/u_b = (1 - \rho_o/\rho)(r_o/r_b)^2 = (1 - \rho_o/\rho)(K - 1)^2$$

and

$$u_b = \frac{2}{9}\frac{g}{\mu}\rho r_b^2$$

where μ is the water viscosity, ρ the water density, and ρ_o the density of the oil droplets. The expression for β then becomes

$$\beta = 1 - (1 - \rho_o/\rho)(K - 1)^2 - \frac{3}{2K} + \frac{1}{2K^3}$$

The number concentration of air bubbles is approximately

$$n_b = \frac{3H}{(1 + H)4\pi r_b^3} \qquad (9)$$

if the air phase is homogeneously dispersed with r_b being the same for each air bubble. The symbol H stands for the gas hold-up (the volume of gas in the water divided by the volume of the water-air mixture). Likewise, the number concentration of the oil droplets n_o is directly proportional to the oil concentration if the oil phase is homogenously dispersed with r_o being the same for each droplet. Assuming the oil capture is directly proportional to the rate of bubble-droplet collision, Equation 8 then becomes

$$J_{ob} \propto -\frac{\partial n_o}{\partial t} \propto r_b(K^2\beta)\frac{H}{(1 + H)} n_o \qquad (10)$$

by making all of the substitutions indicated above and ignoring the many constants involved. The function $K^2\beta$ is very nearly proportional to $(r_o/r_b)^2$ when $0.90 < \rho_o/\rho < 1.0$ and $r_o/r_b \leq 1.0$; consequently

$$J_{ob} \propto -\frac{\partial n_o}{\partial t} \propto \frac{r_o^2}{r_b}\frac{H}{(1 + H)} n_o \qquad (11)$$

Equation 11 indicates that the rate of oil removal in the DAF process may be directly proportional to r_o^2 and inversely proportional to r_b for a given gas hold-up H and oil concentration. This equation implies that the oil droplets should be large and the air bubbles small for good process performance. It should be mentioned here that the above analysis ignores the effects, if any, of reactor turbulence and wastewater SS on DAF performance.

ANALYTICAL PROCEDURES

Oil determinations. The concentration of emulsified and free oil was determined as follows:

Total oil. Acidification of the sample to a pH of 5.0, addition of NaCl, extraction with carbon tetrachloride, and measurement of the solvent absorbancy with an infrared spectrophotometer. These procedures were conducted in accord with API Method No. 733-58.

Dissolved oil. Acidification of the sample to a pH of 5.0, addition of NaCl, filtration through a pre-coated (100 mg/l suspension of celite filter aid) Whatman No. 40 filter paper supported on a muslin disk, extraction of the filtrate with carbon tetrachloride and measurement of the solvent absorbancy with an infrared spectrophotometer. Aside from the filtration step these procedures were conducted in accord with the API Method No. 733-58.

Oil. Oil concentrations reported herein represent the difference between the total and dissolved oil concentrations unless specified otherwise.

The concentration of oil extracted was obtained by calibrating maximum absorbance with known concentrations of waste oil. The accuracy of this method of analysis was checked by extracting standards of 100 mg/l waste oil in clean water. Five samples were prepared, the average concentration obtained by this method was within 4 percent of the theoretical concentration and the coefficient of variation was about 5 percent.

API Method No. 733-58 for oil analysis has not been approved by the EPA.[25] One of the procedures approved by the EPA involved acidification of the sample to a pH of one to two followed by liquid-liquid extraction with trichlortrifluroethane and measurement of solvent absorbance in an infrared spectrophotometer. The differences between the carbon tetrachloride solvent used in this study and the one approved by the EPA cannot be significant for the purposes at hand; that is, the determination of waste petroleum oils at relatively high concentration. The difference in the degree of initial acidification employed prior to extraction might prove significant for such compounds as the salts of fatty acids (soaps) which do not dissociate fully at a pH of 5, but this difference should not prove significant in the case of emulsified and free refinery waste oil.

Tests were also conducted to determine if the surfactants and polyelectrolytes used in the pilot plant work were extracted in carbon tetrachloride by the oil determination procedure; experiments using known additions of these compounds showed that none of the surfactants or polyelectrolytes purposely dosed to the wastewater was detected at dosages up to 30 mg/l.

Suspended solids. The ss were determined by passing a wastewater sample through a Gooch filter crucible, washing the material with two 30-ml portions of chloroform, drying at 103° to 105°C, and weighing (API Method No. 709-53 [24]).

Oil droplet size distributions. Size distribution of oil droplets in wastewater were determined using the procedure of Brunsman *et al.*[26] The emulsion was stabilized, allowed to separate, combined with a gelatin setting mixture, and placed on a counting slide. The size distributions were computed in terms of

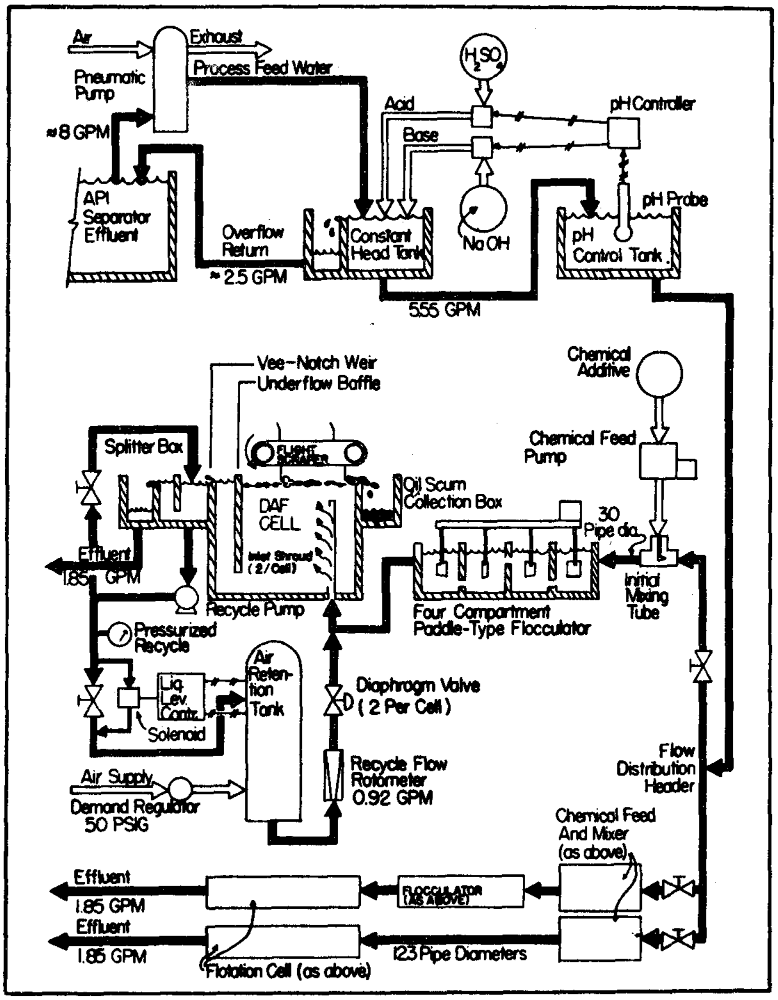

FIGURE 2. Schematic of flocculation—DAF pilot plant.

oil droplet volume, that is, one 20-μ droplet equaling eight 10-μ droplets, because the purpose of DAF processes is to remove as much weight of oil as possible from the separator effluent.

Jar tests. One-half liter samples were stirred rapidly for 30 seconds after pH adjustment and the addition of various doses of coagulants. This was followed by a flocculation period of 15 minutes with slower mixing. The samples were allowed to stand for 30 minutes, and aliquots were collected 4 cm from the surface for turbidity measurement.

Other measurements. MBAS and conductivity were determined by procedures given in "Standard Methods."[27] Electrokinetic mobility was measured with a Standard Zetameter;* eight to ten measurements were made and the average recorded as μ/s·v·cm.

DESCRIPTION OF PILOT PLANT

The pilot plant consisted of three identical DAF units employing independently pressurized effluent recycling. Four compartment, paddle type flocculators with overall residence times of 15 minutes preceded two of the flotation units. The third unit received pipe mixing but no other type of flocculation prior to flotation. The residence time in the DAF chambers was 17.5 minutes and the influent pH was controlled within the region of 7 to 8.5. A general schematic of the pilot plant is shown in Figure 2. The flow into each unit was 0.117 l/s (1.85 gpm); 50 percent effluent pressurization was employed at a pressure of 345 kN/m^2 (50 psig). Other characteristics of the pilot plant are compared to plant scale operations in Table I.

In order to avoid segregation in initial mixing, adequate mixing of chemical additives was insured by introducing the chemicals into the process feed via a Pitot-tube arrangement with the tube facing upstream. Straight flow-through diaphragm valves were used as the pressure reducing devices on the effluent recycle streams of the DAF units. These valves provided a means of controlling the recycle flow rate while achieving pressure reduction with a minimum of fluid shear; it being believed that fluid shear and turbulence in this portion of the apparatus enhances air bubble coalescence. The relationship between the flocculator paddle rotation speed and the flocculator mixing intensity G was determined with an in-line torquemeter mounted on the paddle shafts.

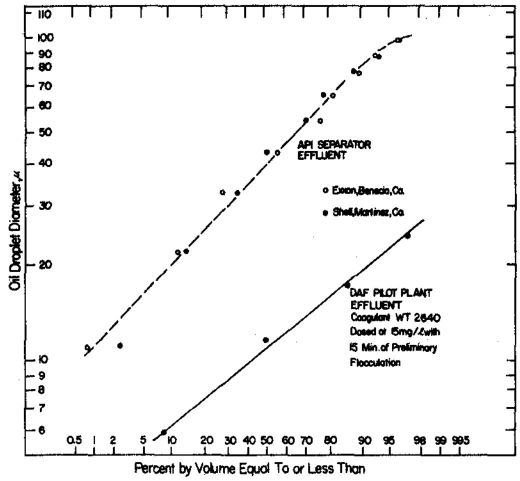

FIGURE 3. Distribution of oil droplet sizes in API separator effluents and in DAF pilot plant effluent (effluent oil concentration = 14.3 mg/l).

WASTEWATER INFLUENT CHARACTERISTICS

Laboratory and on-line DAF studies were conducted with the API separator effluent of a refinery which combined process wastewater, cooling water, septic tank overflow, and stormwater together in one main drain. No batch or pilot plant testing was performed at this refinery during storm flow conditions.

The concentration of oil in the API separator effluent which served as the influent to the pilot plant proved to be extremely variable, ranging from 200 to 1 800 mg/l when individual observations were averaged over 2-hour duration periods. The mean separator effluent concentration was approximately 570 mg/l.

The performance of the refinery separator can be compared approximately with industry-wide performance by taking an average plant flow of 15 000 m^3/d (4 mgd), an average effluent oil concentration of 570 mg/l, and a crude oil refinery throughput of 16 000 m^3/d (100 000 bbl/d). With these values the separator released about 540 kg oil/1 000 m^3 of crude oil throughput (190 lb/1 000 bbl). This was unusually high, even for lube subcategory refineries ($<$600 kg/1 000 m^3 90 percent of the time).[1]

The size of oil droplets in composite sam-

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* Zeta-Meter, Inc., N. Y.

TABLE II. Commercial polyelectrolytes investigated.

Type	Trade Name	Manufacturer	Description
Anionic	WT 3000	Calgon Corp.	A dry solid, high molecular weight, 5–10·10^6, highly anionic 30% hydrolyzed polyacrylamide
	WT 2900	Calgon Corp.	A dry solid, high molecular weight, 5–10·10^6, moderately anionic, 20% hydrolyzed polyacrylamide
	WT 2700	Calgon Corp.	A dry solid, high molecular weight, 5–10·10^6, weakly anionic, 11–12% hydrolyzed polyacrylamide
	WC-18	Tretolite Corporation	A dry solid, polystyrene sulfonate, approximate molecular weight 2·10^6
Nonionic	WT 2690	Calgon Corp.	A dry solid, high molecular weight, 5–10·10^6, completely nonionic polyacrylamide
Cationic	WT 2575	Calgon Corp.	A liquid copolymer, slightly cationic, 20% PDADMA,* molecular weight 2·10^6
	WT 2635	Calgon Corp.	A liquid copolymer, moderately cationic, 50% PDAMA, molecular weight 2·10^6
	WT 2640	Calgon Corp.	A liquid copolymer, strongly cationic, 75% PDADMA, molecular weight 1–2·10^6
	WT 2860	Calgon Corp.	A liquid copolymer, very strongly cationic, 95% PDADMA, molecular weight 1–2·10^6
	CAT FLOC	Calgon Corp.	A liquid copolymer, very strongly cationic, 100% PDADMA, molecular weight 3–4·10^5
	MAGNIFLOC 521-C	American Cyanamid	A liquid cationic polyamide, molecular weight 3–5·10^4
	WC-31	Tretolite Corp.	A liquid, polyacrylamine, molecular weight 2–3·10^4

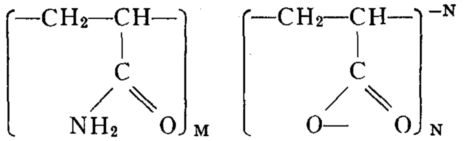
* PDADMA—Polydiallyldimethylammonium compound.

ples of the API separator effluent was measured and compared with the effluent of another refinery located in California with the results being shown in Figure 3. The distributions were log-normal with the largest droplets being in the order of 100-μ diameter, and the mean oil droplet volumes corresponding to a size of about 46 μ. The close correspondence between the sizes of the two API separator composite effluent samples may have been fortuitous.

FLOCCULATION OF WASTEWATER WITH POLYELECTROLYTES

Oil droplet electrokinetic mobility and jar test flocculation experiments were conducted in the laboratory on composite samples of an API separator effluent using various doses of the polyelectrolytes listed in Table II. Most of these polyelectrolytes were contained in a series of polymers possessing similar molecular weight and variable charge density, the exceptions being CAT FLOC, MAGNIFLOC 521-C, and the WC-18 polymers.

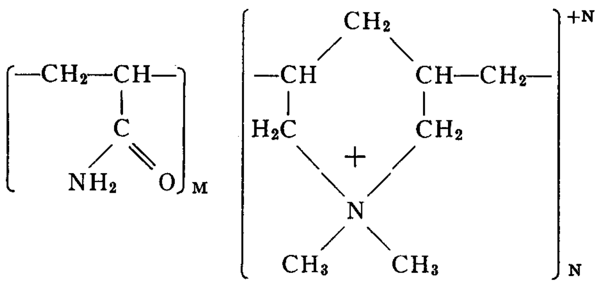
The anionic polyelectrolytes of the main series of polymers tested in this study were composed of polyacrylamides, with some of the acrylamide groups being hydrolyzed to acrylic acid to give the desired negative charge as shown below.



$$\left[-CH_2-CH-\right]_M\left(C(=O)NH_2\right)\quad\left[-CH_2-CH-\right]_N^{-N}\left(C(=O)O^-\right)$$

The anionic charge was expressed in percent of the ratio of the ionizable groups N to the total number of $N + M$ groups contained in the polymer chain. The non-ionic polymer WC 2690 contained no N groups.

The cationic polyelectrolytes were composed of acrylamide and polydiallyldimethylammonium (PDADMA) groups as shown below.



The polymer charge was expressed in a manner similar to the anionic polyelectrolytes; that is, the percent ratio of the N groups to the total number of $N + M$ groups. The CAT FLOC cationic polyelectrolyte was composed entirely of PDADMA groups and possessed a 100 percent charge concentration but the molecular weight of this particular polymer was about half that used in the main series of tests.

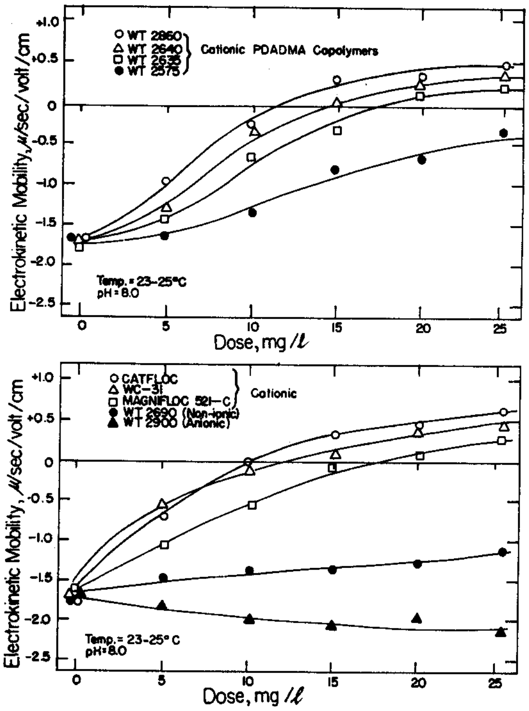


FIGURE 4. Electrokinetic mobility of *in situ* waste oil droplets in an API separator effluent dosed with polyelectrolytes.

Figure 4 shows the results of the electrokinetic mobility experiments conducted on the API separator effluent at a pH of 8.0. The upper half of the figure shows the results for the cationic PDADMA polyelectrolytes and it is apparent that the polymer dose required to reverse the charges on the waste oil droplets increased with decreasing polymer charge concentration. For example, the 95 percent charged WT 2860 polyelectrolyte required a dose of approximately 12 mg/l to reverse the oil droplet charge at a pH of 8.0, and the 50 percent charged WT 2635 polymer a dose of approximately 17 to 18 mg/l.

The lower portion of Figure 4 shows the results for the anionic polymers and some of those polyelectrolytes not fitting into the main test series. The 100 percent charged CAT FLOC cationic polymer required a dose of approximately 10 mg/l to reverse the charges on the waste oil droplets. The 20 percent charged anionic polyelectrolyte WT 2900 increased the negative charges on the oil droplets slightly.

Similar electrokinetic mobility data at a pH of 8.0 to 8.2 were obtained for alum. The results (data not shown) indicated a dose of approximately 25 mg/l was required to reverse the charge on the waste oil droplets.

Charge reversal alone does not necessarily mean good coagulation because tough interfacial films may prevent oil droplet coalescence.[3] The effects of polymer bridging between droplets may be ascertained with jar tests as shown in Figures 5 and 6.

Figure 5 shows that the best turbidity removals were achieved with doses of polyelectrolytes approximately equal to those required to reverse the electrokinetic mobilities of the oil droplets; that is, 10 to 15 mg/l for

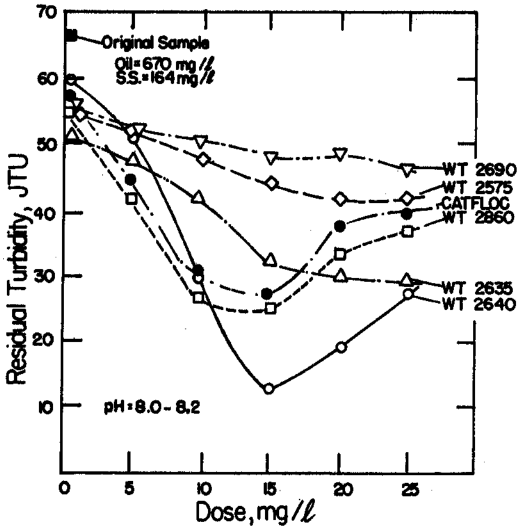


FIGURE 5. Results of jar tests using polyelectrolytes.

the 100 percent charged CAT FLOC and the 95 percent charged WT 2860, 15 mg/l for the 75 percent charged WT 2640, and so forth. At a pH of 8.0 the 75 percent charged WT 2640 outperformed all the other polyelectrolytes tested, however. The non-ionic polyelectrolyte WT 2690 and the anionic polyelectrolytes (data not shown) performed very poorly at doses ranging up to a maximum of 25 mg/l. The optimum dose for alum was in the region of 20 to 30 mg/l as shown in Figure 6, again at the dose required to reverse the electrokinetic mobilities of the oil droplets. It appears that both charge neutralization and polymer bridging have to occur simultaneously to coagulate oil droplets successfully, but too great or too low of a cationic polymer charge concentration interferes with the bridging mechanism. It also appears that the coagulant doses required to obtain charge neutralization are relatively independent of oil concentration or droplet size since essentially the same results were obtained in all the tests even though no attempt was made to control those parameters from one test to another.[3]

The coagulation and flocculation of the oil droplets contained in the API separator effluent were also checked with on-line operation of the pilot plant. In this case, 15 mg/l of the 75 percent charged polyelectrolyte WT 2640 was dosed to one of the parallel flocculation units and 25 mg/l of alum to the other. The flocculator paddle speeds were altered throughout the test run with 45 minutes of equilibrium time being permitted between each determination of flocculator performance. The flocculator performance was determined by comparing the oil concentration in the influent (N_0) with that in the effluent (N_4) after

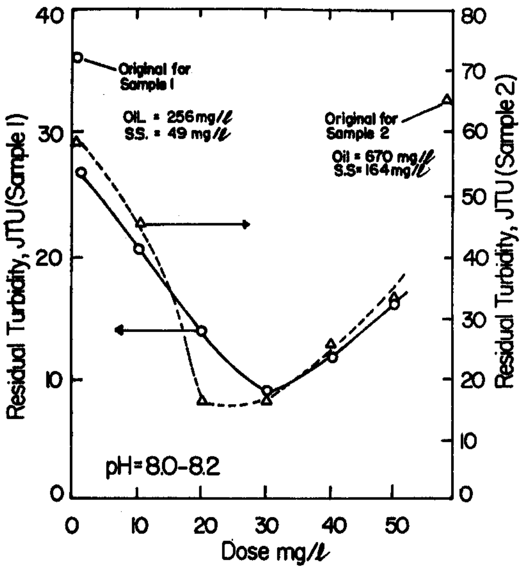


FIGURE 6. Results of jar tests using alum as the coagulant.

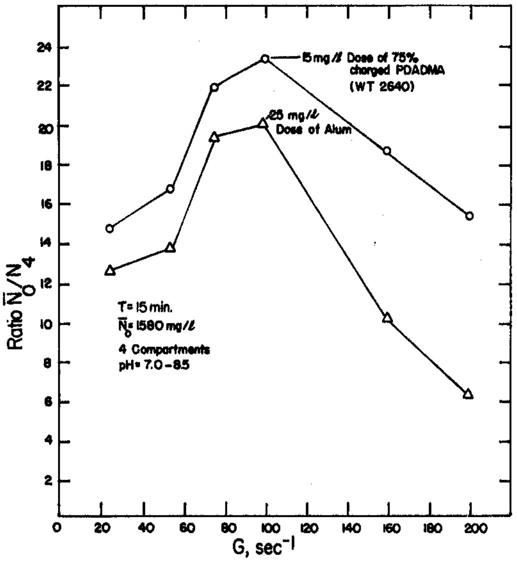


FIGURE 7. Performance of pilot plant flocculators with the influent being API separator effluent.

30 minutes of sample quiescent standing with the portions for the analytical determinations being collected 4 cm below the water surface. The ratio $N_0{:}N_4$ is shown plotted against the mean velocity gradient G in Figure 7 where N_0 stands for the average influent oil concentration encountered on that particular day (1 580 mg/l). The paddle speeds were the same in all the compartments of each flocculator during a particular run and the overall mean residence time was 15 minutes. The pH was controlled within a range of 7.0 to 8.5.

The figure shows that the 75 percent charged polyelectrolyte WT 2640 out-performed the alum at all paddle speeds. The best oil removals were achieved at paddle speeds equivalent to a mean velocity gradient G of 100/s for both coagulants. The data show that the oil concentration could be reduced from 1 580 mg/l to 68 mg/l for the polyelectrolyte, and to 80 mg/l for alum, with 15 minutes of flocculation followed by 30 minutes of quiescent standing.

An optimum G value of 100/s appears to be unusually high when compared with G values commonly used in the flocculation of colloidal clay suspensions (30 to 50/s). It should be recognized, however, that the determination of flocculation performance used in this series of tests was oil removal, not turbidity removal, and the largest oil droplets contain most of the oil. Apparently intense stirring was required to collect effectively the larger droplets in the alum or polyelectrolyte flocs at a mean detention time of 15 minutes.

Equation 5 might be used to evaluate the flocculation kinetics of the above experiments but the derivation of this equation was based on the assumption that turbidity results from the finest particles in the suspension (the primary particles), and the rate of coagulation and removal of the primary particles is proportional to the removal of turbidity.[14, 15] The rate of removal of the largest particles is of concern in oil removal, however, and the appropriate equation may differ considerably from Equation 5. The above does not negate the value of these observations; that is, that unusually high paddle speeds should be used to flocculate waste oil emulsions. Subsequent to these tests the flocculator paddle speeds were set constant at an equivalent G of 75/s for the pilot plant studies.

PILOT-PLANT STUDIES

The quality of the API separator effluent varied greatly from day to day. The best estimate of plant performance was obtained by allowing the pilot plant to attain pseudo-steady state (approximately 1.5 hours) and then averaging the influent analyses over a period of 3 or more hours. The effluent analyses were averaged over the same length of time but lagged about 30 minutes to allow for pilot plant hold-up. Considerable experience was gained with dose levels and types of coagulants added ahead of the flocculators or directly to the DAF chambers, but no attempt was made to vary the air bubble sizes during these experiments. Four separate runs demonstrated an average of 64 per-

TABLE III. Average oil removal in pilot plant dosed with various types of polyelectrolytes.

Influent	Unit 2 With Flocculation			Control Unit* With Flocculation	
	Additive				
Oil mg/l	Type†	Dose mg/l	Effl. Oil mg/l	Effl. Oil mg/l	% Rem.
775	CATFLOC	15	14.8	6.7	99
445	CATFLOC	10	19.7	9.7	98
558	WT 2860	15	20.7	14.3	97
1 740	WT 2860	10	32.0	$\sim$7	99.6
237	WT 2635	15	15.3	8.3	96
240	WT 2635	10	21.3	$\sim$6	98
257	WT 2575	15	31.3	11.4	96
375	WT 2690	15	54.7	14.3	96
488	WT 2900	15	33.0	11.1	98

* 15 mg/l dose of WT 2640.

† See Table II for complete description.

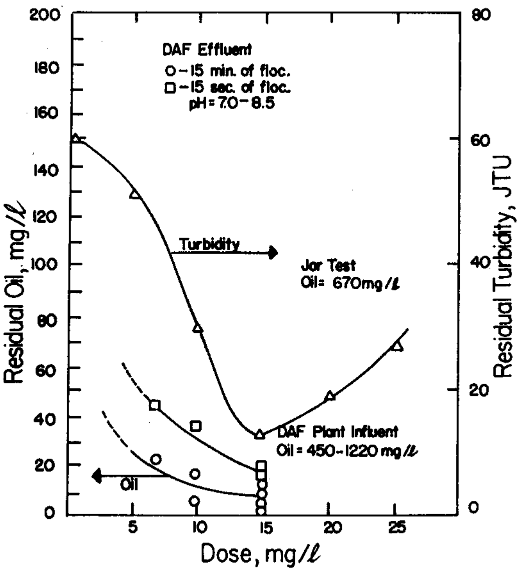


FIGURE 8. Comparison of DAF pilot plant performance with jar tests using the cationic polyelectrolyte WT 2640 as a coagulant.

cent removal of oil (270 to 97 mg/l) without the use of any coagulants whatsoever.

The jar test experiments indicated that the best flocculation of the oil droplets was achieved with a dose of 15 mg/l of the 75 percent charged polyelectrolyte WT 2640. It was not certain that this would be the case for DAF operation and various doses of this polyelectrolyte as well as others were employed in these tests.

Table III compares the DAF oil removal performances of some of the polyelectrolytes listed in Table II with a constant dose of 15 mg/l of the WT 2640 polyelectrolyte. The experiments were conducted in parallel with all other factors being held constant. The results of this series of tests demonstrated clearly that the 75 percent charged-WT 2640 outperformed all the other polyelectrolytes tested when dosed within a range of 10 to 15 mg/l. Circumstances were such that the influent to the pilot plant during these runs contained concentrations of SS of <1 000 mg/l and the oil removals were relatively good with less than 15 mg/l of oil remaining in the DAF effluent for all of the WT 2640 polyelectrolyte runs.

Runs were then conducted on the WT 2640 polyelectrolyte to ascertain the effects of doses other than 15 mg/l and the need for flocculation prior to the DAF operation. The coagulant was added directly to the pipes leading to the DAF chambers when the flocculator units were bypassed and the detention time in the pipes was about 15 seconds and the *G* approximately 60/s. This gave a product *GT* of only 900 as compared to 67 500 when the flocculators were not bypassed. The results of these runs are shown in Figure 8.

The performance of the WT 2640 polyelectrolyte with 15 minutes of prior flocculation did not deteriorate grossly for doses of less than 15 mg/l, although DAF effluent oil concentrations of less than 20 mg/l could not be maintained for doses much less than 10 mg/l. Effluent oil concentrations of less than 20 mg/l were never achieved when the flocculators were bypassed but the performance under these operating conditions undoubtedly would have been improved by increasing the *G* and the detention time in the pipes leading to the DAF units. This consideration is significant because the capital costs of the process can be reduced appreciably if initial flocculation can be safely ignored.

Figure 9 shows the effect of varying alum dosage on the DAF process performance. The performance of the alum nearly paralleled that observed with the jar flocculation tests with the best performance being achieved at an alum dose of 25 mg/l. Comparison of the alum results at a dose of 25 mg/l with the plant scale data shown in Table I indicates that the DAF pilot plant was functioning very well, perhaps better than the average plant-

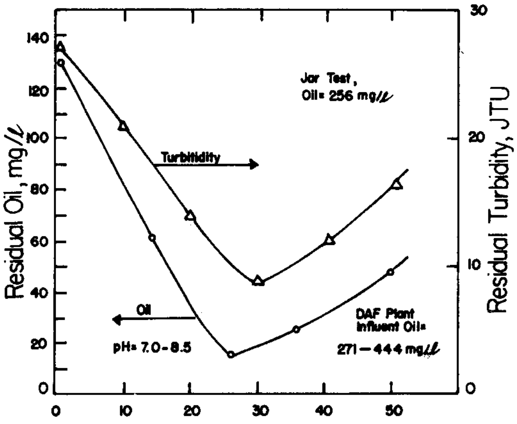


FIGURE 9. Comparison of DAF pilot plant performance with jar tests using alum as the coagulant.

scale DAF operation. The results presented in Figures 8 and 9 also support the hypothesis that good oil droplet coagulation and flocculation insures good oil removal in the DAF process, and that simple jar tests can be used to control the process.

Organic coagulants have sometimes been judged unreliable when used in conjunction with the DAF process. This was checked by conducting 21 separate runs with the WT 2640 polyelectrolyte dosed at a constant rate of 15 mg/l and flocculated for 15 minutes prior to the DAF process. The pH of the influent to the pilot plant was maintained within the region of 7.0 to 8.5. The mean results of these series of experiments are presented in Table IV.

The DAF pilot plant removed an average of 98.6 percent of the suspended oil and very little of the dissolved oil. The coefficient of variation (CV) of the suspended oil in the process effluent was much less than that observed in the influent for the same periods of time. The effluent suspended oil concentration never exceeded 19 mg/l and the average was 10 mg/l.

Additional data analyses and pilot plant experiments not described in detail herein indicated the following:

1. The effluent oil concentration was not directly dependent on the influent oil concentration. Indeed, some of the highest influent oil concentrations (~ 1 800 mg/l) yielded some of the lowest effluent oil concentrations (~ 5 mg/l).
2. Effluent oil concentrations did increase when the influent contained relatively high concentrations of nonextractable SS (> 1 000 mg/l), or when the DAF process was used to concentrate waste solids from secondary biological treatment processes in addition to oil removal.
3. The effluent oil concentrations did not increase significantly when the average influent water conductivity was increased from 4 000 μmhos/cm to 9 000 μmhos/cm with the addition of sodium chloride.

TABLE IV. Average DAF pilot plant performance with 15 mg/l of WT 2640 (21 separate runs).

Analyses	Influent Mean, mg/l	Influent C.V. (%)	Effluent Mean, mg/l	Effluent C.V. (%)
Suspended Oil	729	73	10.4	37
Dissolved Oil	18.2	18	18.0	17
Total Oil	747		28.4	

4. The effluent oil concentration did increase significantly when anionic surfactant was added to the influent in amounts sufficient to increase the MBAS concentration from an average of 4 to 14 mg/l. In this case the anionic surfactant may have reacted with the WT 2640 polyelectrolyte to form a salt.[28] The effluent oil concentration also tended to increase when 5 mg/l of a cationic surfactant was added to the influent. The decrease in the DAF process performance in this case was not very dramatic, however.

Solids balances. A solids balance was conducted on one run when 15 mg/l of the WT 2640 polyelectrolyte was being added to the influent of the pilot plant. This balance was made during a portion of the control experiment for the second run listed in Table III. The details are summarized in Table V.

The experiment was conducted for a period of 140 minutes at a flow rate of 7.0 l/min. The DAF chamber water surface was scraped clean at time zero and the scum collected at the end of the experiment. The average influent and effluent oil and nonextractable SS

TABLE V. Mass balances on oil and solids in DAF pilot plant (15 mg/l of WT 2640 and 15 min of initial flocculation).

Component	Wastewater Influent mg/l	Wastewater Effluent mg/l	Wastewater g* Removed	Weight† in Scum, g
Suspended Oil	1 218	~4	1 193	1 384
Dissolved Oil	16.8	16.8	0	—
Nonextractable Solids	183	6.3	174	199

* Based on a flow of 0.117 l/sec and 140 min of plant operation.

† Total weight of scum including water = 2 890 g.

concentrations indicated that 1 200 g of oil and 170 g of ss were removed from the water during the experiment. The scum collected from the DAF chamber contained 1 400 g of oil and 200 g of ss, indicating a relatively good mass balance between materials removed and recovered in the scum. A better ss mass balance could have been obtained by including the 15 mg/l of added polyelectrolyte in the weight of solids removed from the wastewater.

The concentration of oil in the DAF tank scum was 48 percent by weight. This was relatively concentrated in comparison with the scums usually obtained when alum or ferric chloride is used as the coagulant.

Size of oil droplets in effluent. The distribution of the sizes of the oil droplets contained in the effluent of the DAF pilot plant during one run when 15 mg/l of the WT 2640 polyelectrolyte was being used as the coagulant is shown in Figure 3. When examined under a microscope these droplets gave no evidence of being in contact with any partially formed polyelectrolyte floc.

Approximately 95 percent of the residual oil (14.3 mg/l) was contained in droplet sizes of 25 μ or less. This may be compared with the other data shown in Figure 3 for the API separator effluent where 95 percent of the oil was contained in droplet sizes of 100 μ or less. Droplet sizes greater than 25 μ were apparently removed readily in the pilot plant during this particular run. Equation 11 and Figure 3 show that the very small oil droplets are not easily removed with DAF treatment.

Economics of oil recovery with polyelectrolyte coagulation. Approximate calculations indicate that polyelectrolyte treatment with oil recovery might be economically attractive. According to the plant studies, a plant scale process might remove 9.1 m^3 (57 bbl) of oil per day at a chemical cost of \$12.10/m^3 (\$1.93 bbl) of oil removed, based on a removal of 560 mg/l of oil with 15 mg/l of polyelectrolyte costing \$0.48/kg (\$0.22/lb). If the oil present in the DAF scum can be recovered and reprocessed, and the experiences gained by one refinery indicates that this is feasible when employing polyelectrolyte as a coagulant,[29] then the recovered oil might be worth \$50/m^3 (\$8/bbl). This would more than pay for the cost of the coagulant plus any additional facility required to dewater the scum.

The analysis of the scum produced in the pilot plant during the run in which this factor was studied indicated that it may contain 50 percent oil by weight. The volume of scum collected on an average day may thus be in the order of 0.12 percent of the total DAF process flow. The unit price for hauling the scum away for disposal may be about \$0.013/l (\$0.05/gal)[30]; hence scum disposal by trucking would cost \$25/m^3 of oil removed (\$4/bbl). Adding in the cost of the polyelectrolyte gives approximately \$38/m^3 of oil removed (\$6/bbl).

A net savings of \$63/m^3 (\$10/bbl) would be realized if the oil can be recovered and recycled through the refinery (the value of the recovered oil plus the cost of trucking for disposal minus the cost of the polyelectrolyte). This would amount to a net savings of \$500 to \$600/d for a wastewater flow of 15 000 m^3/d (4 mgd).

SUMMARY AND CONCLUSIONS

It was concluded from these studies and those presented elsewhere[3] that little can be done to enhance the removal of emulsified oil with the DAF process in terms of chemical additives other than using the appropriate coagulant and controlling pH. The waste oils, regardless of source, tend to assume very similar surface characteristics which may be imparted by the surfactants present in the wastewater, but it takes only minute concentrations of such surfactants to give detrimental oil-water interfacial characteristics. Even so, efforts should be made to reduce as much as possible the release of surface active chemicals to a wastewater destined for DAF treatment. Excessive releases of nonextractable ss should also be avoided because it was noted in this study that the DAF oil removals tended to decrease when the ss concentration attained a level of approximately 1 000 mg/l.

The appropriate polyelectrolyte or coagulant has to be able to neutralize the negatively charged oil droplets and simultaneously construct inter-droplet polymer bridges. The best polyelectrolyte for this purpose was found to be the 75 percent charged PDADMA cationic polyelectrolyte WT 2640 but this may not hold for pH values falling outside the range tested (7.0 to 8.5). The optimum dose of this polyelectrolyte was found to be equal to 15 mg/l, the dose necessary to neutralize the charge on the oil droplets at a pH of 8.0. This relatively large dose requirement appeared to be independent of the emulsified oil concentration or composition for concentrations ranging from a minimum of 200 mg/l to a maximum of nearly 2 000 mg/l. This concentration independence implies that the charge neutralization with the polyelectrolyte represents some type of electrical double layer compression and/or adsorption isotherm; that is, the bulk water concentration has to be 15 mg/l to neutralize fully the charge on the oil droplets. Considerable polyelectrolyte bridging can occur at doses less than 15 mg/l, however, because relatively good oil removals were obtained in the DAF process with doses as low as 10 mg/l.

The ability of an air bubble to collect the oil droplets may depend on the interfacial characteristics of the oil and the air. Some preliminary observations made during this study (data not shown) indicated that this was so, but the quickest capture appeared to occur when the rate of oil droplet coagulation was the most rapid; that is, the point of zero net charge in the oil droplets. It appears, therefore, that good coagulation also means good removal of oil in the DAF process and the problem of achieving the most efficient operation reduces to one of physical considerations represented by the Smoluchowski equation (Equation 1) for oil droplet flocculation, and the equation based on the work of Reay and Ratcliff (Equation 8) for the DAF process. The Smoluchowski equation is known to be valid and Equation 8 probably is reasonably valid but neither is a working equation of the type illustrated by Equation 3. The derivation of Equation 3 was based on simplifying assumptions which probably are not valid when oil concentration is the measure of concern. No attempt was made in this study to derive working equations which might be reasonably valid for estimating DAF performance because comprehensive measurements of the distribution of oil droplet sizes before and after coagulation, and after air flotation, were not obtained. Such work is both tedious and expensive but absolutely necessary to advance the theory of this process.

Enough is known about the DAF process to improve its performance without knowing the theoretical reaction kinetics. The polyelectrolyte should be mixed as quickly as possible with the wastewater and some preliminary flocculation time is necessary to achieve best results. The intensity of mixing should be much higher than normally used in water treatment. It is possible that a properly designed pipe mixer with a modest detention time might suffice for the preliminary flocculation and this would reduce the initial costs of the process.

The 75 per cent charged polyelectrolyte WT 2640 performed reliably under a wide variety of input conditions with DAF effluent oil concentration averaging 10 mg/l when the pH was controlled within a range of 7.0 to 8.5. Precise dosage levels did not appear critical for good coagulation. Limited data indicated that the concentration of the oil in DAF scum was high, in the order of 50 percent by weight, and that the removed oil is easily scraped from the surface of the air flotation chamber. The use of polyelectrolytes appears to be economically promising if the oil recovered for the DAF units can be reprocessed in the refinery.

RECOMMENDATIONS

The feasibility of reprocessing waste oil with polyelectrolyte coagulation has to be tested and verified under long term operating conditions. Additional studies are needed to evaluate the proper balance between gravity separation and the dissolved air flotation of waste oil. The results of this study indicated that high concentrations of coarse oil suspensions may not be detrimental to the DAF process and may not deplete the coagulant to such a degree as to impair initial coagulation of the oil droplets. It may be possible to decrease the detention time in the API separators greatly, or even to convert a portion of a gravity separation stage to flocculators with the wastewater then being lead directly to the dissolved air flotation units.

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