

# Oily Wastewater Cleanup By Gas Flotation

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*Produced wastewater from hydrocarbon reservoirs always contains some oil. The free oil is often in an emulsified form with the median droplet diameter usually in the range of 3-20  $\mu\text{m}$ . Gas flotation of oily wastewater is a process in which fine gas bubbles are injected into a water phase. Oil droplets and oil-coated solids, which are suspended in the water, become attached to these bubbles, rise to the surface, are trapped in the resulting foam and removed when the foam is skimmed from the surface. The effectiveness of flotation depends on the traditional gravity separation parameters of density difference, oil droplet size, and temperature but also critical are the gas bubble size distribution and an even dispersion of the bubbles. Gas flotation is particularly valuable for removing oil droplets when the oil density is close to that of water (i.e., heavy oil), such as in Trinidad. This paper discusses the operation of the gas flotation process for oily wastewater including the mechanisms behind the process, particularly the gas attachment to oil droplets. A clearer understanding of oil/bubble contact and the influence of surfactants in aiding this contact could make flotation applications more widely considered for Trinidad's oily wastewater treatment.*

## 1. Introduction

### 1.1 Oily Wastewater

Produced water is the water that comes with oil and gas during hydrocarbon production. It always contains some oil. The treatment of this produced oily water to an environmentally accepted level before disposal has become mandatory in most countries. In Trinidad and Tobago, government environmental pressure to improve the quality of oil-water separation in the oilfields is increasing, with 40 parts per million (40 mg per litre) being the quoted legislated standard. Elsewhere in environmentally sensitive countries, e.g., Norway, lower figures are mentioned, even zero. This implies that dissolved and non-dissolved components will have to be removed from wastewater before disposal.

The non-dissolved oil in wastewater is in three forms as:

1. Drops  $>150 \mu\text{m}$  in diameter, which can be separated by conventional methods, except for heavy oil discussed in 1.1 below;
2. As free droplets 15 - 150  $\mu\text{m}$  ;
3. As a stabilised (often with indigenous anionic surfactants) oil-in-water emulsion, with the median droplet diameter usually in the range of 3 - 20  $\mu\text{m}$  [3].

Such oil-in-water emulsions are generated by shearing in pumps and by turbulent flow in pipes as well as from steam injection EOR methods. These crude-in-water emulsions are often stabilised by the variety of surfactants indigenous to the crude oil.

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The formation of an emulsion involves the creation of enormous areas of interface, typically  $\sim 1\text{m}^2$  per cc of oil if the droplets are of  $10\ \mu\text{m}$  in diameter.

The dissolved form has to be removed through ion exchange or bioremediation [1, 2]; these processes will not be discussed further here.

The separated water must be de-oiled before disposal, otherwise it could become an (expensive) environmental embarrassment if oil pollutes potable water sources or rivers. Large volumes of oily wastewater are being produced. Additionally, the water is saline, with concentrations of salts as high as 25% by weight, but fortunately is usually less (remembering that seawater is  $\approx 3.5\%$ ) and itself could be an environmental hazard.

The oily wastewater treating facilities currently being used by many companies in Trinidad use only gravity-induced separators and guard basins, however, discharge effluent often have oil concentrations that exceed 50 parts per million. There are a wide variety of separator designs and configurations, some with rather exotic proprietary internal devices. The equipment chosen for any wastewater treatment facility must be according to the characteristics of the water to be treated and to its ultimate disposal. The standard oil water gravity separator is well discussed elsewhere [4-7].

### 1.2 The Problems of Heavy Oil

Heavy oil has a density close to that of water. Much of Trinidad's oil is heavy so that due to this small density differential, these oily wastewaters cannot be separated into oil and water by gravity separators. Additionally, these heavy crude oils tend to form stable emulsions because of the waxes, asphaltines particles and other impurities present, which, in combination with properties such as high viscosities and densities and foaming characteristics, make these wastewaters difficult to treat by traditional treatment systems. For heavy oil, the industry typically uses large separators, long retention times and heat plus dosing the system with quantities of demulsifier chemicals. Such facilities are expensive and increase the cost of a product whose value is currently lower than that of light crude. Additionally, the product may still not meet specifications.

The small density difference between the heavy oil and water make the separation by hydrocyclone or

centrifuge ineffective [8]. Further problems are created by the emulsions formed between the oil and the water being extremely strong. However, gas flotation is able to cope.

## 2. Gas Flotation

Gas flotation is a process in which numerous microscopic gas bubbles are injected into a water phase containing immiscible liquid (oil) or solid particles so that the bubbles attach themselves to the particles and decrease their density and enable separation. The oil droplets and oil-coated solids with attached gas rise to the water surface, are trapped in the resulting foam and are removed when the foam is skimmed from the surface. This foam is gently skimmed off while the clarified water flows out near the bottom of the tank (Figures 1 and 2).

In essence, the process of gas flotation is based on gravity separation. By attaching gas bubbles to droplets of oil, the density difference between itself and water is increased and the effective density of the oil is decreased and the oil appears lighter. Consequently, the oil rises faster, enabling faster and a more effective separation from the aqueous phase [9]. Clearly, as will be discussed later, the longer the residence time of the gas bubbles in the flotation tanks (smaller bubbles), the greater the contact efficiency (the number of gas bubble-oil droplet collisions), and thus the greater the oil removal. Gas flotation can achieve the required standards by reducing the emulsified oil droplet concentration in mg per litre to single figures.

Although gas flotation has been used in the treatment of oily wastewaters for many years [8], the processes happening within the gas flotation vessel have somewhat limited descriptions in texts on wastewater. Further clarification of the oil drop/bubble attachment process should enhance the selection and usage of types of chemicals, so as to optimise the entire process to achieve the desired environmental requirements at minimum cost. This clarification is what this paper attempts to do.

### 2.1 Stokes Law

The governing principle of fluid separation is given by Stokes Law. The velocity of bubble/drop rise in a large volume of water has been much studied [11, 12]. Solution of the Navier Stokes equation for the terminal rise velocity,  $V$ , for rigid spheres under the relevant

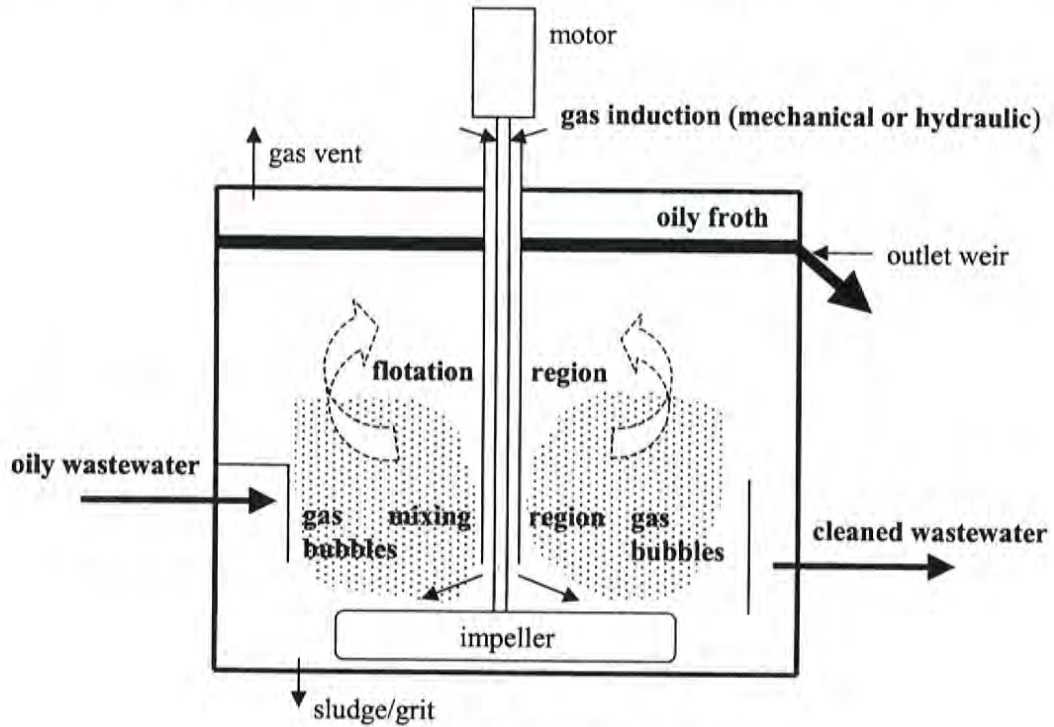


FIGURE 1: Schematic of Induced Gas Flotation

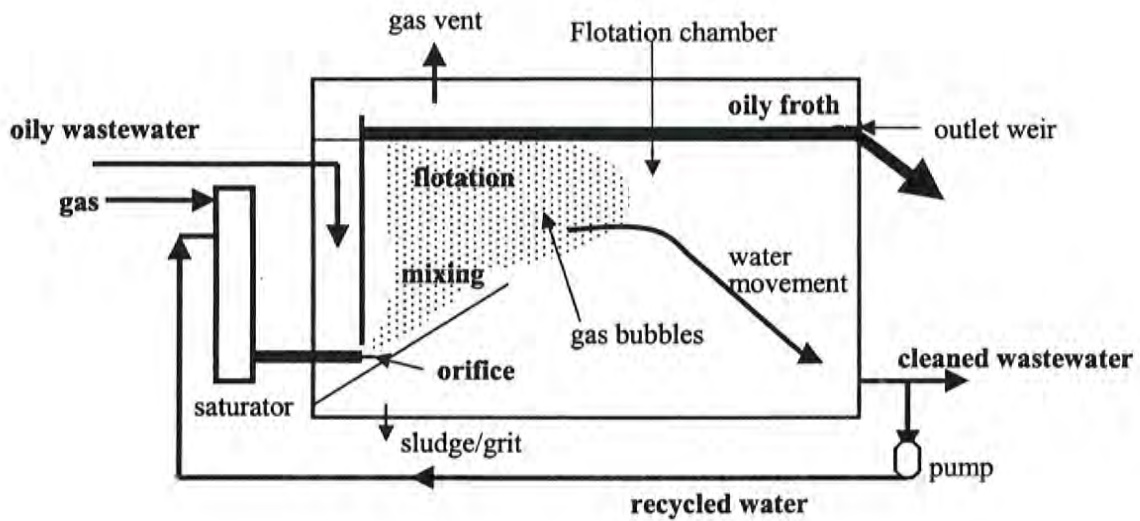


FIGURE 2: Schematic of Dissolved Gas Flotation



conditions for flotation (laminar flow) gives Stokes Law,

$$V = \frac{d^2 g (\rho_w - \rho_o)}{18 \mu_w}$$

where

- $V$  = droplet settling (rising or falling) velocity  
 $d$  = droplet diameter  
 $g$  = gravitational acceleration  
 $\rho_w - \rho_o$  = difference in density between continuous and droplet phase (oil or gas)  
 $\mu_w$  = dynamic viscosity of continuous phase

Stokes Law holds reasonably well for solids in the range  $10 < d < 200 \mu m$  [12]. Gas bubbles are deformable, however as surface active species are always present in the water and the effect of these surfactants is to rigidify the interface, Stokes Law is applicable for gas bubble rise. Clearly, to increase the droplet rise velocity (a major factor in separation efficiency), one may cause an increase in droplet size (comes into Stokes equation as a squared power, e.g., by promoting coalescence as needed in gas flotation and described later), an increase in the difference in fluid densities (e.g., gas flotation, as described in this paper), a decrease in the viscosity of the continuous phase (e.g., by increasing fluid temperature) or, in other applications, an increase in gravitational acceleration (e.g., by utilising centrifugal force).

## 2.2 Gas Flotation - Generalities

The effectiveness of flotation depends not only on the traditional gravity separation parameters of liquid density difference, oil droplet size, type and temperature but also on gas bubble size and an even dispersion of the bubbles. This is because small bubbles distributed throughout the vessels are necessary to attach to, and float, the smallest oil droplets. When the oil concentration exceeds 1000 mg per litre, a primary separation must precede a flotation unit. The efficiency of gas flotation depends to a large extent on bubble size and number. When properly designed and

operated, oil concentrations of effluents from gas flotation units can generally be kept well below 20 mg per litre.

Flotation is dependent on the surface characteristics of the dispersed phase (oil) and on its interaction with the gas bubbles. Its overall efficiency is greatly increased when chemical agents are used. Any emulsion must first be broken and, preferably for reasons given later, the oil droplets grown before the flotation process takes place. Emulsion-breaking can be achieved by chemical, electrolytic or physical methods. Chemical treatment is normally used in oily wastewater treatment. The emulsion destabilisation is brought about by adding surface-active agents (surfactants, usually cationic discussed in 4.4) where the surfactant molecules orient themselves at the oil-water interface, causing the oil droplet to appear more positively charged than normal. This is now an opposite charge to the gas bubble (usually negatively charged [10]), which can then adhere to the oil and enable the flotation processes to occur.

## 2.3 Gases used for Flotation

Various gases have been used for the flotation process. Field gas is frequently used on oil production installations, but inert gas (sometimes air) may also be used. Air increases the oxygen content of the discharged water, but oxygen corrosion and particularly iron oxides and sulphides may be precipitated. These can attract oil and the oil floated on them. However, air often oxidises the oil as well as pose a safety risk due to the explosive possibilities when oil is combined with oxygen. Using natural gas, the iron can be kept in solution and scale formation can be minimised. Additionally, if the water is to be reinjected into the reservoir, the use of natural gas makes unnecessary further oxygen removal from the water to prevent rusting of tubulars. However, there are dangers of gas explosions.

## 3. Induced- and Dissolved-Gas Flotation

For effective oil - water separation, the following must be accomplished:

- ▶ Good flotation, followed by
- ▶ Efficient skimming of the oil that has floated to the surface with



- ▶ An effective chemical programme (minimum quantities and maximum oil removal)

Flotation units have developed over the years, initially for mineral processing. The water travels through the flotation chamber and by suitable placement of baffles and weirs moves downwards towards an exit, and the oily drops with attached gas tends to move upwards. Good flotation for oily wastewater is brought about by the introduction of a lot of fine bubbles. The smaller the bubbles, the better, since the small bubbles can capture the small oil droplets. However, once bubbles are released, they can collide and coalesce into larger bubbles but large bubbles are ineffective for flotation. They rise rapidly creating unfavourable turbulence and break-up of bubble-droplet agglomerates. How the bubbles are introduced into the water system is also important. Thus, critical design factors are the areas in the flotation chamber where the bubbles are created and where oil and gas attachment occurs.

Bubbles can be created in a number of ways, but in field practice, there are two common methods of introducing the gas bubbles - those of induced gas flotation (sometimes termed dispersed gas flotation), IGF, and dissolved gas flotation, DGF. The significant differences between the two flotation processes are the average bubble size, the mixing conditions and the hydraulic loading rating, with induced flotation having the higher value. There are other more sophisticated (and expensive) methods such as electrolytic gas bubble generation creating stable bubbles of  $\sim 10 \mu\text{m}$  diameter and gas sparging, where gas is pumped through porous tubes to create the gas bubbles but these are not discussed further here [11].

### 3.1 Induced, or Dispersed Gas Flotation (IGF)

IGF mechanically introduces the gas as bubbles. Initially, the gas is drawn into the mixing area, where (usually) a propeller mechanically agitates the oily water and shears the gas into  $\sim 100\text{-}1000 \mu\text{m}$  diameter bubbles (Figure 1). The gas is drawn into the water and mixed with it, unlike DGF (discussed below) where gas is dissolved in the water and comes out of solution by depressurisation. The retention time in the wastewater treatment unit may be as low as four minutes. Sludge is gradually formed from the input

water and if this is disturbed by the propellers and moved to the attachment zones, it can destroy the flotation process.

The IGF's units are usually multi-cell in design in order to improve their performance. The inlet gas nozzles, rotors or eductors (essentially vacuum pumps) and baffles are patented designs. IGF units can be operated at much higher hydraulic loading (higher flow throughput for equivalent surface areas) than DGF. Hence, the capital costs for treatment equipment are lower than DGF but because of the large gas bubble and small oil droplet sizes and the quiescent conditions needed for agglomerate formation, IGF is not now the preferred option for oily wastewater cleanup.

### 3.2 Dissolved Gas Flotation (DGF)

DGF introduces the gas bubbles in a different way. Water is saturated with gas under pressure (up to four atmospheres), so that gas is dissolved in the water and is released from solution by pressure drop to atmospheric pressure in the flotation chamber. The gas evolves from solution as small bubbles,  $10\text{-}100 \mu\text{m}$  diameter (Figure 2) often described as making the water go 'milky white' [11, 13]. DGF units are so designed that the gas bubbles form in the environment of the oil droplets. Retention time in the flotation chamber is usually about 15 - 30 mins. and is a fairly gentle process. Suspended solids and minor entrance turbulence act as nuclei for bubble formation. Clearly, the amount of gas available for flotation is dependent on the operating pressure for the gas-saturating system.

The loading rates are smaller than IGF but the bubbles are smaller hence have longer retention times in the flotation units, and slower particle rise rates. Multi-cell units are used in practice - often a set of five flotation cells. Turbulence is low in well-designed and properly operated systems. Chemicals, as discussed later in 4.4, are added to neutralise the negative charges on the bubbles and drops in order to flocculate the oil, break the emulsion drops to form large flocs, so that bubbles have even greater oil-floc area in which to attach. Gas bubbles are formed in and around the suspended solids and emulsified oil droplets. However, the flocs can become a continuous oily sludge.

There are a number of ways of designing the gas pressurisation systems, including [11]:



- *Total pressurisation of all the water feedwater.* Here, more gas/hr is needed which should lead to higher separation efficiency. Any solids in the influent must be pumped through the pressurisation chamber to the flotation chamber which can destroy floating agglomerates by collision. Additionally, the oil in the wastewater can be further emulsified within the pumps by shear. Higher power requirements are needed to run the pumping systems.
- *Pressurisation of only part of the inlet water.* Clearly, lower power is required compared to the full stream pressurisation and less gas/hr. Some influent solids and emulsification must be pumped.
- *Recycle pressurisation (Figure 2).* Here, some of the outlet water is pressurised with gas, up to about 60 psig and passed back into the flotation chambers. In the chamber, the pressure release generates the bubbles from the now supersaturated water, provided suitable nucleation sites are available. These are often cavitation turbulence. As the pressurised water is clean, no influent solids and emulsions are pumped through the gas solution chamber with this process. The recycle ratio of pressurised water can be varied from zero to 100%, but typically 10-50%. However, larger flotation cells than the other methods are needed (creating higher initial plant costs), but it is now the preferred method.

### 3.3 DGF Designs

There are many different designs of flotation unit with design parameters specific to manufacturers' patents. The designs require a way to introduce the gas, a mixing region where the gas contacts the oil droplets, a flotation region where the oil-gas agglomerates separate which allows them to rise to surface and a means to skim off the froth. Clearly, proper mixing of water, chemicals and gas bubbles within the flotation

unit must occur to ensure maximum efficiency. This requires proper equipment design. Generally, gas inputs range from 0.2 to 0.5 scf/bbl of water to be treated with water flow rates of 2-6 bbls/hr per ft<sup>2</sup> of surface area of flotation cell. The cell depths are 6-9 ft of water. For the recycle pressurisation method, 10-50% of the treated water is normally recycled. Firstly, it is pumped into a saturation chamber - a column filled with open objects to give a large surface area where the gas is dissolved under pressure, usually 60 psig and then passed into the flotation cell through special orifices. Unfortunately, chemical scale can be formed at the orifices from the salts in the water. Natural gas can be a safety hazard if it is not vented or recycled carefully.

Generating small enough bubbles is critical but presents problems. One way is to add a small amount of a soluble surfactant (frother). The emerging stream of water, milky with micro-bubbles, passes into the flotation chamber (Figure 2). The exact process is not clearly understood but Kitchener has given a description [11]. In industrial practice, the super-saturated water is forced through needle-valves or special orifices, and clouds of microbubbles are produced just downstream of the constriction. The mechanism by which the microbubbles are formed is that a certain minimum velocity of flow through an orifice is needed to produce any bubbles at all (otherwise the water remains super-saturated). It seems that the microbubbles are formed by vapour pockets being torn off this cavity, and they grow from the water stream as they are carried along. The microbubbles formed at a cavitating orifice probably start as submicroscopic vacuoles torn off the ultrasonically oscillating vapour-cavity, for if the supply pressure is reduced just below that needed for visible cavitation, virtually no microbubbles are produced. A correctly operating orifice can be heard emitting a 'sizzling' sound, which is due to cavitation and high-frequency oscillation of a vapour cavity just below the neck. Nevertheless, the orifices used in DGF for the water injection also yield some gross gas bubbles, probably formed by growth of bubbles in corners or attached to the outlet pipes, for here the water is still partially super-saturated. These large bubbles can rise rapidly and destroy the quiescent conditions needed for flocculation. Additionally, it has been found that when supersaturated water is added to agglomerated oil drops, bubbles can grow within the agglomerates, suggesting that some suitable nuclei for



gas bubble generation are incorporated within the agglomerates.

Finally, the skimming device must remove the froth layer containing the oil at the surface and not create disturbances which send oil back into the flotation chamber.

### 3.4 Recent Developments in Gas Flotation Design

The designs of DGF units, types of flotation processes and chemical additives have undergone extensive modifications to improve effectiveness [13-23]. For instance, units include having multicell systems and incorporating coalescing media, creating microfine bubbles using a spinner design inside the vessel, having a hydrocyclone in the inlet piping which removes solids and larger drops of oil before they enter the flotation zone, adjustable weirs which remove free oil entering the flotation section of the vessel and diverter baffles to effect some coalescence of drops [20] and even incorporating a jet pump [21]. A recent flotation column suggestion [22] is a multi-stage loop. Here, concentric draft tubes establish a multi-stage operation within the single column which cause in each stage, the gas hold up difference between the inside (riser) of the draft tube and the outside (downcorner) and induces a fluid circulation which minimises back-mixing/entrainment. These are common problems affecting the effectiveness of conventional flotation machines. Other creative additions include using a spinner design inside the vessel or a hydrocyclone in the inlet piping [23] to aid the collision and attachment probability between gas bubbles and oil particles.

## 4. Flotation Mechanisms

**4.1** Flotation is achieved by enabling oil drops to attach themselves to gas bubbles. This increase in density differential makes the oil rise to the surface of the wastewater. The efficiency of separation can be increased by coalescence of oil drops, which may be achieved by surfactants and/or chemical demulsifiers. The attachment of oil drops to gas bubbles and the formation of a stable bubble drop aggregate are the rate-controlling steps. The mechanisms involved in the attachment of the gas bubble to the oil drop are essentially the same as coalescence between two oil drops, except that the gas bubble possesses elasticity; hence the oil drop may 'bounce off' after the initial

approach of the bubble and drop. Fortunately, the drop does not always rebound, but may attach to the gas bubble and spread on its surface. The period during which the drop comes into contact with the bubble until it is ready to bounce off, is called the 'induction time'. During this period, thinning and rupture of the interstitial water film must occur as described later. Only after this has been achieved will attachment occur. The crux of gas flotation of oil is the adhesion of the gas bubble to the oil drop. This can only be optimised in practice if the surface science conditions are properly understood so that correct field conditions are created.

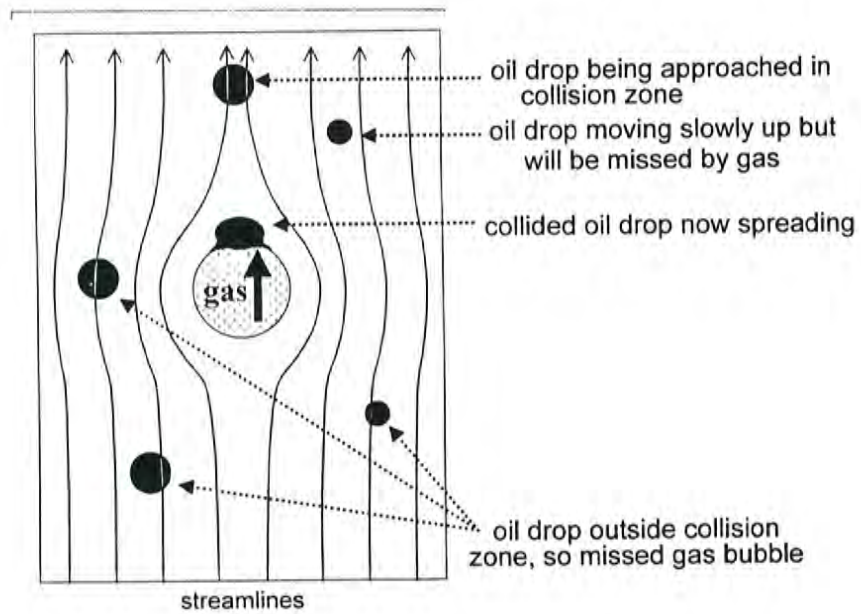
### 4.2 Collision

To begin with, the bubble and drop must first come into close proximity. To ensure that this happens, their mutual trajectories must lead to a collision stage (**Figure 3**). Hydrodynamic theories of the collision between particles and bubbles have been developed, with that by Reay and Ratcliff generally accepted as being elegant and satisfactory [24].

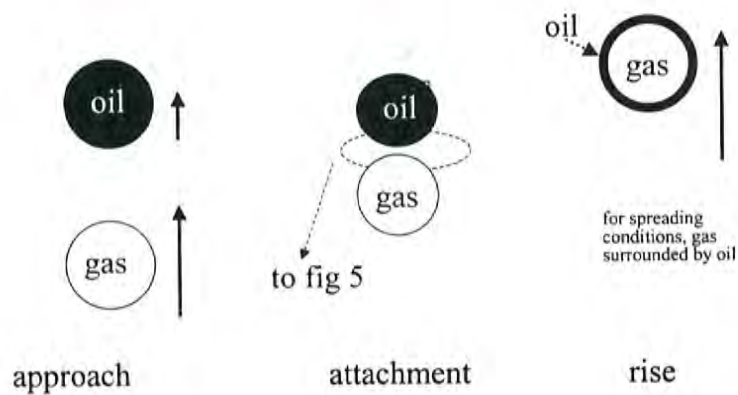
The collection efficiency,  $E$ , of a bubble and a drop is the product of the collision efficiency,  $E_c$  and the attachment efficiency,  $E_a$ , i.e.,  $E = E_c * E_a$ .

$E_c$  is the fraction of oil drops in the bubble's path which collide with the gas bubble in the collision region (**Figure 3**). For particles  $>3$  and  $<100 \mu\text{m}$ ,  $E_c$  is shown to be proportional to the diameter of the oil drop squared (the trajectory of the drop must be within its diameter of the bubble surface - the collision region), and is not greatly affected by bubble size but significantly by bubble number density. This is because, as Reay and Ratcliff found,  $E_c$  is larger for more (i.e., smaller) bubbles for a given gas flow rate. Thus, they found it is better to have oil drops as large as possible and gas bubble size as small as possible (longer residence times). Reay and Ratcliff also examined  $E_c$  for particles  $<1 \mu\text{m}$ , when the motion is Brownian diffusion. They showed that collection was still possible but the mass of oil collected would be small, and their advice is to grow the drops by coalescence to about  $20 \mu\text{m}$  [24].

$E_a$  is the fraction of particles that collides with the bubbles that actually 'stick' and this clearly depends on the surface interfacial forces to attain film-thinning and spreading. The interfacial science controlling gas flotation of oil droplets by gas in oily wastewater is a combination of a number of processes as discussed later.

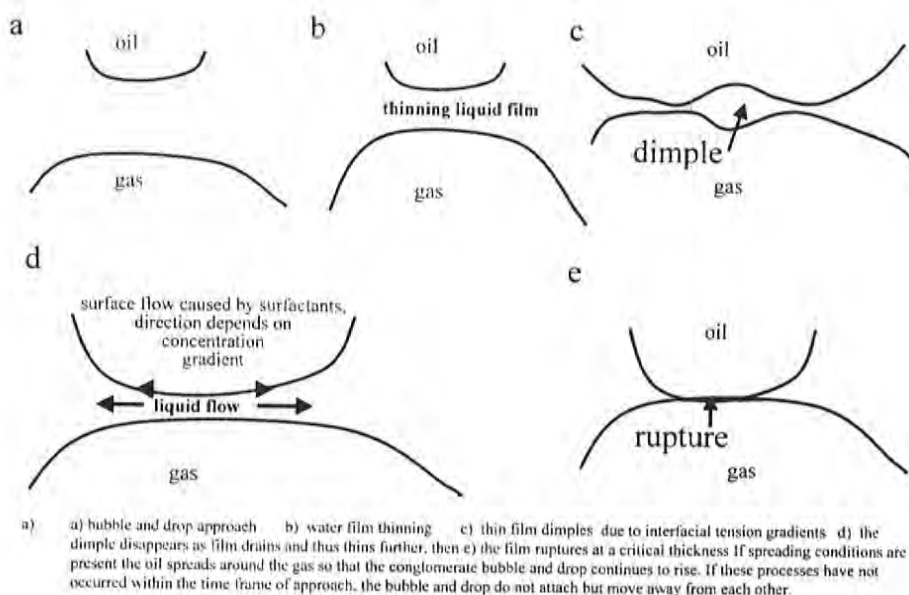


**FIGURE 3:** *The Collision Zone*



**FIGURE 4:** *The Gas Flotation Process*





**FIGURE 5: The Attachment Process**

### 4.3 Coalescence

Coalescence of oil drops and attachment of oil drop/gas bubble usually occur simultaneously, however the oil drop/gas bubble attachment is essential for flotation.

The flotation process between gas bubbles and oil droplets can be broadly classified into the following steps (Figures 4 and 5):

- ▶ Demulsification via coalescence of oil drops;
- ▶ Approach of gas bubble and oil droplet;
- ▶ Collision between the oil drop surface and the bubble;
- ▶ Oil/bubble attachment via film drainage and rupture;
- ▶ Spreading of oil on the gas;
- ▶ Rise to surface

These processes are affected by:

- ▶ Flowrate;
- ▶ Gas-input rate and volume of gas released per unit volume of liquid;
- ▶ Bubble size distribution and degree of dispersion;
- ▶ Temperature;
- ▶ pH (best pH at  $7 \pm 2$  units) so the wastewater pH may need to be adjusted to this range;
- ▶ Chemical content of the wastewater and the oil;
- ▶ Correct dosage of chemicals



#### 4.4 Chemical Additives - Surfactants and Polyelectrolytes

The oil in wastewater is usually in the form of oil in water emulsion with most droplet diameters being less than  $20\ \mu\text{m}$  with a median often around  $5\ \mu\text{m}$ . These tiny drops are prevented from coalescing by negative charges on the surface of the oil droplets and gas bubbles due to electrostatic forces created by the electric double layers. These create a repulsive force between the drops or bubbles which keep them apart and thus have a low probability of coalescing. Separation by gravity by letting the wastewater stand (i.e., Stokes Law) can be dismissed as a demulsifying force for industrial purposes, because the small size of the oil drops make this process extremely slow, e.g., estimates [14] for a density difference of  $0.1\ \text{gm/cc}$  predict that a  $10\ \text{mm}$  rise in an aqueous medium will take around 50 sec for a  $70\ \mu\text{m}$  diameter oil drop, 600 sec for  $20\ \mu\text{m}$  and 3000 sec for  $10\ \mu\text{m}$ . Thus, before flotation can be effective industrially, the emulsion must be destabilised and the oil droplets coalesced. To break the emulsion, the accumulated electrical charge on the bubbles and drops must be neutralised by introducing an opposite charge. This is achieved by demulsifiers. In terms of physical interactions, the demulsifier serves

- ▶ To modify the charge on the oil droplet
- ▶ To cause flocculation by anchorage and bridging mechanisms

Surfactants, or surface active agents, are molecules which are able to modify the properties of an interface, e.g., liquid/air or liquid/liquid by lowering the surface or interfacial tension. A surfactant possesses the fundamental characteristic of having two essential portions, one being water repellent, usually called hydrophobic (or oleophilic), the other being water attractive, usually called hydrophilic (or oleophobic). The hydrophobic portion comprises a collection of hydrocarbon groups, some at least of which form a linear chain which may or may not be substituted to varying extents. The hydrophilic portion comprises a solubilising group such as sulphate, sulphonate or ethoxylate.

The number and arrangement of the hydrocarbon groups together with the nature and position of the hydrophilic groups combine to determine the surface

active properties of the molecule. If the hydrophilic portion is high molecular weight, it is termed a polymer surfactant. Surfactants fall into four categories depending on the distribution of electrical charge on the molecule viz:

- ▶ Anionic in which the hydrophobic portion of the molecule carries a residual negative charge,  $\text{RCOO}^- \text{X}^+$  e.g., sodium dodecyl sulphate:  
 $\text{CH}_3\text{CH}_2(\text{CH}_2)_9\text{CH}_2\text{OSO}_3^- \text{Na}^+$
- ▶ Cationic in which the hydrophobic portion carries a residual positive charge,  $\text{R}^+ \text{X}^-$  e.g., cetyltrimethyl ammonium chloride:  
 $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{-N}(\text{CH}_3)_3^+ \text{Cl}^-$
- ▶ Nonionic in which there is no residual electrical charge, e.g., dodecylalcohol ethoxylate:  
 $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2(\text{OCH}_2\text{CH}_2)_n \text{OH}$
- ▶ Amphoteric in which both positive and negative centres are to be found in the molecule, e.g., alkyldimethylbetaine:  
 $(\text{CH}_3)_2\text{N}(\text{CH}_2)_n\text{R}-\text{N}^+ - \text{CH}_2\text{COO}^-$ .

These surfactant molecules orient themselves at the oil-water interface. A flocculant, which is a high weight cationic or anionic polymer, is added after to create macroflocs. Faster flotation results, according to Stokes Law, and a more efficient separation. An emulsion breaker is typically a high charged, low molecular weight, cationic polymer. They have a long chain and in addition to charge neutralisation enables mechanical bridging of oil drops to create flocs. An anionic polymer, which has a high molecular weight, can then be used to promote growth of the floc through further mechanical bridging. An even larger rising velocity will occur according to Stokes Law when the radius of the 'oil drop' increases through such floc formation. This will in turn increase the frequency of its collision with similar molecules of oil, and thus form even larger flocs. It will also increase the collision rate with the gas bubbles in the wastewater flotation tank, further



increasing the chances of oil/bubble attachment. Organic emulsion breakers, in addition to producing better effluent quality, often require less dosage and produce a smaller volume of sludge, than if an inorganic programme was employed.

Currently, in oily wastewater industrial practice, cationic and anionic surfactant and polymers are used to tailor the floc size, floating characteristics and shear strength. In practice, the chemicals used to give optimum results typically would be a primary coagulant (emulsion breaker) being a low molecular weight, cationic (i.e., positively charged) polymer which is able to neutralise the negative charge on the oil droplet as it adsorbs at the negatively charged surface of the oil droplet. This is followed by a high molecular weight (~2000) anionic polymer, often derived from ethylene, propylene, vinyl, vinylidene or vinylacetate, which can then be used to promote growth of the floc through mechanical bridging. The preferred size of the polymer molecule is such that several oil globules can become attached to one polymer, which causes them to coalesce into larger particles by a bridging mechanism.

#### **4.5 Jar-Testing**

The maximum amount of surfactant that should be used is that which creates the Critical Micelle Concentration, cmc, at the salinity and temperature of the wastewater [25]. The cmc is the point when a surface is covered by a monolayer of the surfactant. At this point, aggregates of surfactant molecules (micelles) begin to form in the bulk phase. Above this concentration, the surfactant concentration is 'overshot' and causes the droplets to gain increased charge and repel each other so that the separation process loses its efficiency. It can cause the formation of foam between the surfactant and gas bubble. This foam cannot efficiently trap oil drops and the entire purpose of surfactant usage will be defeated. If too little surfactant is used, flotation will be less efficient since the conditions are not optimum (perhaps 20% less effective). Hence, before chemicals are added, their optimum concentration must be determined. This value will vary according to the field conditions including diurnal temperature variations, concentration of wastewater, oil properties, and the salinity of water.

Unfortunately, information on flocculation and surfactant composition used commercially is not often divulged in product literature, much to the disadvantage

of those wishing to minimise their costs or select the optimum flocculants. To select and screen demulsifiers, the effect of various factors that affect oil water separation need to be quantified. These include shear, asphaltene content, water cut, demulsifier dosage and mixing different crudes and temperature. Increasing the temperature decreases the viscosity of the oil and emulsion, increases the frequency of the drop collisions, decreasing the interfacial viscosity, causes a faster film drainage rate which in turn aids coalescence greatly. Experiments must be carried out to identify suitable chemicals (surfactants) and their concentrations. The inlet wastewater stream must be monitored closely, especially if surges in concentration occur frequently. Bottle/jar-testing or some other test is essential. Such tests can identify some chemicals, and eliminate others, which might be effective under the field conditions. Bottle tests involve the mixing of the various chemicals with samples of the contaminated water, shaking and observing the results. It is the normal procedure used in determining the optimum concentration of polymers needed for the flotation unit's treatment fluid at any point in time. It is a relatively quick method for selecting the chemical type, dosages and treatment conditions. It needs a small volume of material, a relatively short testing time and is relatively inexpensive. During full scale operation jar-testing can be used to check chemical feed rates which may lead to a substantial decrease in the amount of chemicals used, the quantity of sludge produced, as well as a better quality effluent. However, a problem can sometimes occur when scaling-up the laboratory test results for application to field operations, because a surfactant's effectiveness is highly dependent particularly on the cmc, which is affected by the current field water characteristics. The field conditions can be very variable due to changes in production rates, stream salt concentrations, rainwater additions and temperature changes caused by weather or simply day and night variations. Any deviations from the field conditions of even a well-planned laboratory jar-testing programme can be ruined by deviations of the field conditions for the laboratory tests, which then have detrimental effects on the flotation efficiency.

#### **4.6 Approach of Oil Droplet and Gas Bubble**

As two drops (oil/oil or oil/gas bubble) approach each other in a medium, there is a deformation of the drops,



#### **4.6 Approach of Oil Droplet and Gas Bubble**

As two drops (oil/oil or oil/gas bubble) approach each other in a medium, there is a deformation of the drops, which results in the formation of a dimple (Figure 5c). This gradually disappears, giving way to a thin interstitial water film between the two oil droplets which must drain before it can rupture.

#### **4.7 Drainage**

The interstitial film drains under the combined action of capillary suction and osmotic pressure, balanced by disjoining pressure [26-32]. Disjoining pressure consists of van der Waals dispersion forces and electrostatic forces. The capillary pressure is the pressure difference between the inside of the drops being greater than the pressure outside. Gravity forces play only a minor role in the drainage process; they slightly disturb the shape of the film, although the characteristic dimple is partly caused by the effects of gravity. The dimple induces a pressure distribution in the film, and hence fluid flow. The lifetime of the film is determined by the rate at which drainage takes place; it is the rate-limiting step of the coalescence process. The stability of this film is a crucial factor in determining the efficiency of the oil-water separation process.

The surfaces of the films are mobile and have surfactants within the interfaces [26-31]. The main movement within the fluid film occurs in the radial direction with velocity varying with position in the film (Figure 5d). The concentration of surfactants (natural or added) along the oil/water and gas/water surfaces at the centre falls due to surface expansion caused by the dimpling, creating a concentration gradient between the centre region of the film and its surfaces. The surfactant concentration increases in the flow direction, which in turn causes a reduction in interfacial tension creating an interfacial tension gradient. This gradient along the surfaces produces a force opposite to liquid flow and is known as a Gibbs-Marangoni effect [26, 29]. The movement of the surface from areas of low interfacial tension to the new areas of higher interfacial tension is accompanied by a movement of bulk liquid which attempts to restore the film to its original surfactant concentration. The monolayer of surfactant flows from regions of lower concentration to regions of higher concentration (lower interfacial tension)

creating a drag on the liquid adjacent to it in the thin layer. The velocity of flow of monolayer material is governed by the viscosity of the interface and by the bulk viscosity of the thin layer fluid.

Drainage therefore occurs because the surface of the film is mobile and the surface concentration at the centre falls due to surface expansion. Drainage proceeds slowly and the film thins and the surfactants redistribute themselves such that the concentration at the centre gives an interfacial tension difference (Figure 5d). The role interfacial tension plays in drainage is thus very important.

The lifetime of the film is determined by the rate at which drainage takes place, but all this has to happen in the short period (a few milliseconds) whilst the gas bubble and oil drop are close together.

The ideal surfactant to achieve the specific purpose of enhanced spreading is still uncertain [18]. What is certain is that at surfactant concentrations below or around the cmc, the adsorption of the surface active molecules on the film surfaces and the properties of the adsorbed layers controlling the drainage and stability of the film are optimised [25, 26].

The flow movement is illustrated in Figure 5d. The film, therefore, thins and when the critical thickness is reached, ruptures.

#### **4.8 Oil/Bubble Attachment through Rupture**

When the liquid film reaches a thickness of approximately  $0.1 \mu\text{m}$ , disjoining pressure dominates. Here, very strong intermolecular forces come into effect, which lead to rupture of the film. Normally, the disjoining pressure consists of the electrostatic repulsive forces between the two overlapping surface double layers, the Van der Waals forces among all the molecules of the film and the steric forces due to steric hindrance of closely packed molecules in monolayers [26-32].

#### **4.9 Spreading**

Immediately following the rupture of the thin film, the oil must then spread over the gas bubble for flotation to occur. Fluid/fluid interactions are usually described by the spreading coefficients. The spreading coefficient of a fluid,  $S$ , is the imbalance between the interfacial tensions (forces) acting along a single line (contact line between fluid phases) [33]. For the gas-oil-water



system, the oil spreading coefficient on a water-gas interface is defined as [34]:

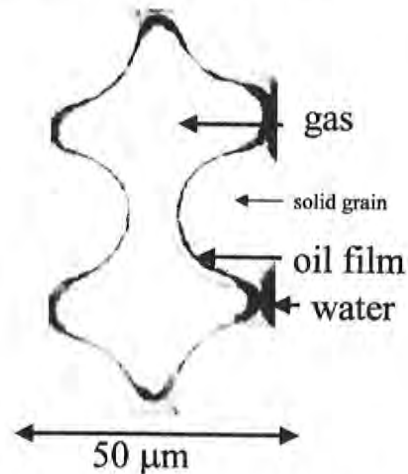
$$S_o = \gamma_{wg} - \gamma_{ow} - \gamma_{og}$$

where  $\gamma_{wg}$  is the water-gas surface tension,  $\gamma_{ow}$  is the oil-water interfacial tension and  $\gamma_{og}$  is the oil-gas surface tension.  $S_o$  needs to be positive for spreading to occur: for oil-water systems, this is generally the case.

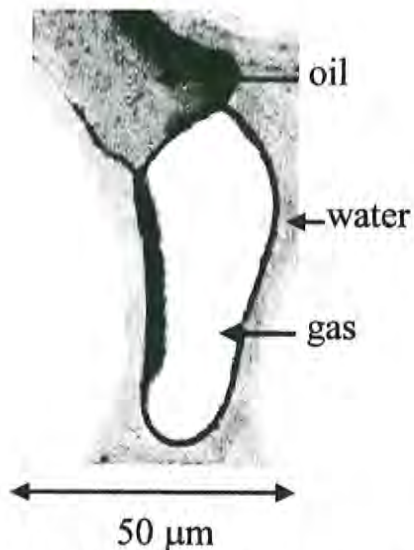
The spreading coefficient is a measure of one fluid spreading spontaneously relative to another on a third phase and therefore as the value of  $S$  increases, the tendency to spread increases. For effective gas flotation,  $S_o$  must be positive and indicates that oil tends to form a spreading continuous film on the water-gas interface because  $\gamma_{wg}$  is larger than the sum of other two interfacial tensions ( $\gamma_{ow} + \gamma_{og}$ ).

Examples of spreading and non-spreading oils on gas are shown in **Figures 6** and **7** [35-38]. These beautiful pictures were taken from a series of experiments performed to visually observe gas and oil depressurisation behaviour in porous media using micromodels and are highly relevant to gas flotation. The sand grains are the spots but do not affect the gas-oil spreading phenomena (only the morphology of the bubbles) so are not relevant to the discussion of the flotation of oily wastewater. A positive value of  $S_o$  means that whenever the three phases of gas, oil, and water come into contact, the oil phase always forms a continuous film between the gas and water (**Figures 5a, 5b** and **6**). Spreading of oil around the gas ensures the attachment of the oil to the bubble is maintained while it rises to the surface. For a gas bubble of  $50\mu\text{m}$  diameter, an oil drop with a diameter of  $20\mu\text{m}$  will form a layer around the bubble of around  $1\mu\text{m}$  and for a drop of diameter  $10\mu\text{m}$ , a film of  $0.15\mu\text{m}$ . Floating oil droplets less than  $3\mu\text{m}$  is therefore not generally successful, as a very thin unstable film around the bubble would be formed, thus, another reason to grow the oil droplets to around  $20\mu\text{m}$  by coalescence before attempting to float them.

If the system is non-oil spreading, the adherence of the oil to the gas bubble is weak and the agglomerate is likely to break up as it rises (**Figure 7**).



**FIGURE 6:** Spreading Oil: Oil enclosing the Gas and Spread around Whole Bubble as a Thin Film



**FIGURE 7:** Non-Spreading Interface: Oil and Gas Touching but not Spreading

#### 4.10 Rise

The oil in the wastewater, now with the attached gas bubbles rises to the top of the flotation chamber to form a froth, and finally is removed from the cell top by skimming of the overflow using paddles and/or adjustable weirs (**Figures 1** and **2**). This scum must be properly disposed of otherwise it becomes a new additional waste hazard which has to be processed. A possible process is keeping the foam in a separate tank to allow it to collapse, letting the oil films drain although some form of biodegradation is another



practical solution. The clean wastewater leaves the system from near the bottom of the tank and any sludge which accumulates on the bottom cleared away occasionally.

## 5. Discussion

The physics behind cleaning oily wastewater by gas flotation is not yet fully understood by the oil industry. Flotation is dependent on hydrodynamic forces, thermodynamic forces and physicochemical interactions. The essential stages are:

- ▶ Approach
- ▶ Drainage
- ▶ Rupture
- ▶ Spreading

These stages must occur in this systematic order to achieve efficient flotation. The role of polymers in the drainage for floc formation and agglomeration processes can be crucial to flotation. A critical stage is the charge neutralisation on the oil drops and gas bubbles. This is carried out with molecules oppositely charged to the oil, and are usually polyelectrolytes or other similar type surfactants. The rate determining stage is the drainage of the film. The thinning rate of the thin lamella/film is governed by the hydrodynamic and thermodynamic interactions between the two film surfaces. It is also clear that the controlling factor in the flotation of the oil is bubble/oil attachment. The spreading stage is vital for efficient bubble/oil rise and a positive spreading coefficient is needed for spreading to occur.

The purpose of chemical addition is two-fold with respect to aiding the flotation process. They must assist demulsification and floc formation. The surfactants must enable the drop and bubble to approach each other and remain sufficiently close long enough to establish drainage, rupture and allow spreading. If they cannot perform this job (perhaps not using the right concentration of surfactant to get it near the cmc under local conditions), the bubble will rebound and spreading will not occur. The maximum amount of surfactants that should be used to enhance the approach, drainage and rupture process is the cmc.

Spreading is controlled by the interfacial tensions which are themselves influenced by the temperature, the salt concentration of the aqueous medium and the surfactant concentration. Oil droplet size, gravitational

acceleration, density difference between oil drop and continuous phase, viscosity of continuous phase, chemical concentration, chemical type and turbidity all affect flotation efficiency. The small oil drops must be coalesced (flocculated) and not broken up again by agitation. Thus, the vessel must have only gently shear.

The main problems with floating oil droplets are with their charge, deformability and elasticity. The collision between two elastic bodies, such as oil and gas, leads to deformation and rebound which can prevent the surface forces being effective to give attachment. Growing the bubble directly on the oil surface from a supersaturated solution can solve this problem. However, this can only be achieved if the gas nuclei are already on the oil drop surface possibly by having solid particles on the oil drop surface which are made of sandstone or long-chain polymers and can be adsorbed onto the oil surface.

## 6. Conclusions

1. Gas flotation units are necessary for treating oily wastewater because:
  - ▶ The amount of oil, which is still within the water after separation by normal skimmers, is not low enough to meet the new environmental standards.
  - ▶ The oil droplet size is often less than  $20\ \mu\text{m}$  caused by shear when passing through flow lines and production equipment.
  - ▶ It is the only possible method for heavy oils, i.e., where the density of oil is close to that of the water phase, and for emulsions where the median droplet size is of the order of  $2\text{-}20\ \mu\text{m}$ .
2. Flotation works well with drops  $20 < d < 150\ \mu\text{m}$ , but has little effect when the droplets are less than  $3\ \mu\text{m}$ .
3. For efficient oil - water separation, the following must be accomplished:
  - ▶ Good flotation
  - ▶ An appropriate chemical programme



- ▶ Efficient skimming of the oil that is floated to the surface
- 4. There are many physical factors that influence the flotation of oily wastewater. These include inlet concentration of oil, density of oil, salinity and viscosity of the aqueous phase, droplet and bubble sizes and chemical interventions. The attachment efficiency is affected by many parameters and requires further study. Currently, interrelationships between cell design and feed parameters determine the separation efficiency. Thus, the flotation unit has to be optimised locally on site.
- 5. The effective operation of the gas flotation process requires an understanding of the mechanisms behind the process, particularly the gas attachment to oil droplets. The physics to aid in the finding of the optimum parameters of the flotation process covers oil/bubble contact, the interactions of surfactants in aiding this contact, and the spreading of the oil around the gas bubble.
- 6. Further study must be carried out on the identification of suitable surfactants, their concentrations and effectiveness under the variable field conditions so that the chemical costs can be reduced and efficiency increased in the flotation process.

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