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FLOTATION OF FINE OIL DROPLETS IN PETROLEUM PRODUCTION CIRCUITS

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ABSTRACT

The oil and gas industry produces 3-5 barrels of water for each barrel of oil, which must be separated from the hydrocarbon fluids and cleaned for disposal or reinjection. Land based oil field can use mechanical flotation cells that have been developed for traditional mineral processing circuits, however offshore production installations requires smaller, lighter, and motion insensitive flotation cells that have been developed utilizing hydraulic principles only. Hydraulic induced gas flotation (IGF) in the oil industry must remove very fine oil droplets (10-50 microns) from hypersaline water using methane as the bubble gas. This paper will discuss droplet breakup and coalescence, along with droplet-bubble interaction with regards to oil and water fluid properties and hydraulic principles. Also discussed will be hydraulic IGF design with respect to orientation, residence time, gas and solids handling, flow pattern, oil skimming, and gas bubble generation.

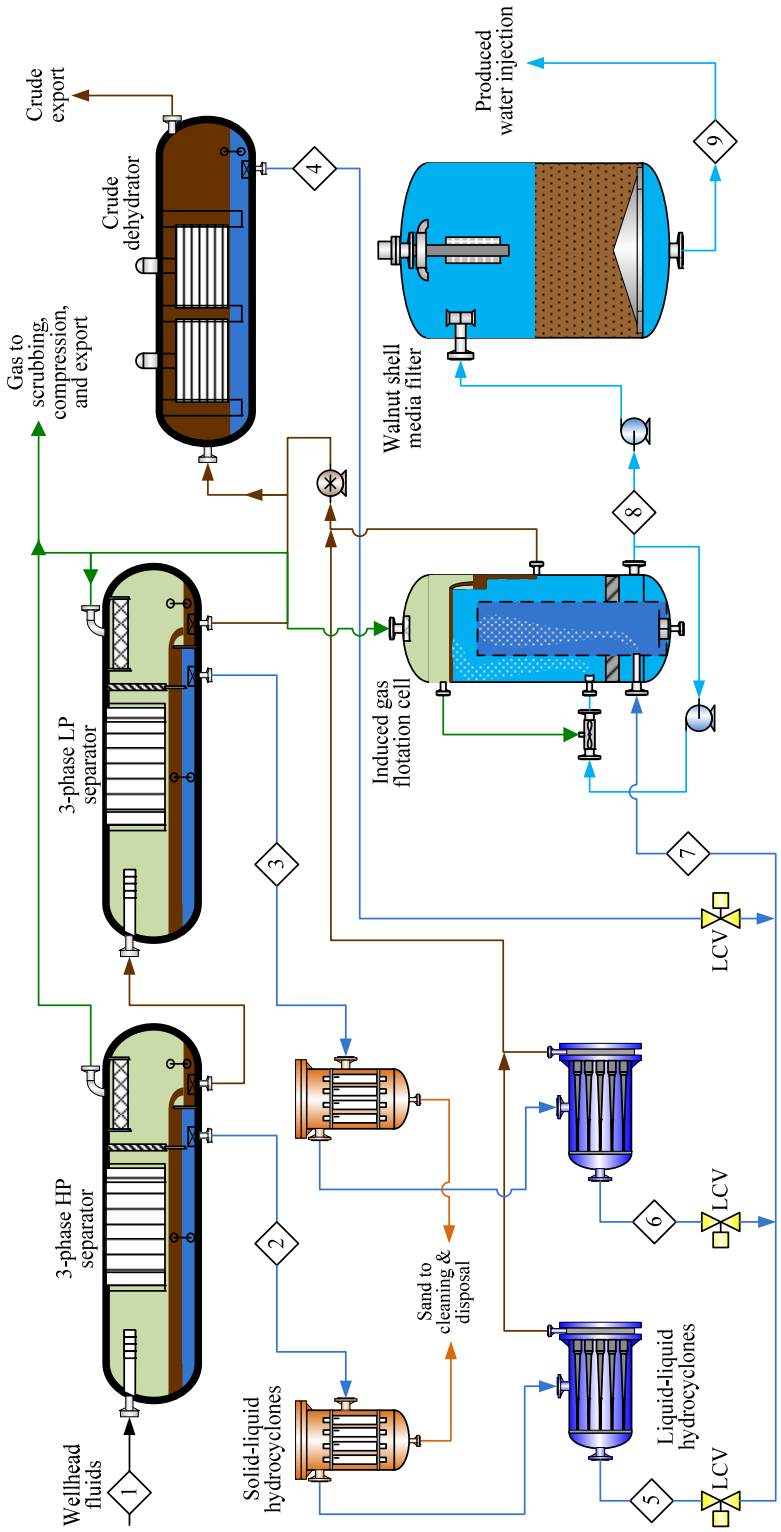
OILFIELD MINERAL PROCESSING

World crude oil production averaged 73.8 million barrels per day (BPD) (3.1 billion gallons per day) in 2008 (DOE/EIA), however, the total amount of water produced along with the crude oil fluids totaled over 194 million BPD (8.15 billion gallons per day) (Veil 2009), resulting in approximately 3 barrels of water produced along with 1 barrel of crude oil. This water may be termed connate, interstitial, or formation water, but is commonly referred to as produced water. Initial well production is designed to minimize or eliminate water production, as this liquid occupies production volume and requires expense for treatment and disposal. However all crude oil wells will eventually generate produced water due to water breakthrough or enhanced oil recovery (EOR) activities, thus a water treatment system is incorporated in most all production systems. The volume of produced water is often the limiting factor for sizing the entire production system.

Produced water treatment is governed by the U.S. Environmental Protection Agency (EPA) through the Clean Water Act. Article 40 CFR 435 of the National Pollutant Discharge Elimination System (NPDES) is entitled "National Effluent Limitations Guidelines for the Oil and Gas Extraction Point Source Category" and sets technology based limits for (overboard) discharge of produced water based on location. Oil and grease discharge limits (in produced water) for territorial seas (0-3 miles) and the outer continental shelf (>3 miles) are 29 mg/l monthly average and 42 mg/l daily maximum. However, petroleum production in onshore or coastal zones has zero discharge of produced water, except under specific instances for agricultural use or stripper wells (<10 BPD). In addition to oil and grease limits, regulations are set on toxicity, hypoxia, as well as other specific components (benzene, lead, thallium, phenol, etc.). The general trend worldwide regarding produced water is to reach zero discharge, thus the primary disposal route will be reinjection into the production formation or a separate zone.

Drilling a disposal well is a sunk cost that adds no fiscal benefit to the operating company, thus maximizing the lift of the disposal well is critical to minimize overall disposal costs. The damaging mechanisms for disposal wells include near well-bore formation plugging, invasive plugging, perforation plugging, or wellbore fill-up which can all be caused by contaminants in the produced water (Barkman and Davidson 1972). These contaminants include suspended silts, clays, scale, oil droplets, and bacteria. The solid and liquid contaminants are removed in a series of steps that utilize many traditional mineral processing unit operations specifically designed for oilfield use. Recovery of the oil from produced water, in addition to protecting the disposal well, also recoups some of the financial burden of treating the produced water. One hundred parts per million by volume (ppmv) of oil has a $0.21 per barrel value (based on $50 per barrel crude spot price) which can cover a significant part of the processing cost.

Using the definition "any naturally occurring homogeneous substance or compound that results from the processes of nature and obtained usually from the ground," crude oil or petroleum can loosely be classified as a mineral. Furthermore, using the American Geologic Institute definition for ore as "a mineral, or aggregate of minerals, more or less mixed with gangue, which from the standpoint of a metallurgist can be treated at a profit" treatment of crude oil can be considered *oilfield mineral processing*. Crude oil is mixed with gangue materials, principally water, formation sand and clay, scale solids, salts, and other precipitates, and must be liberated to produce a crude oil "concentrate". Crude oil in itself is not an end product, much like a sulfide flotation concentrate from a zinc, copper, or lead circuit, but must be refined to produce a final saleable commodity. The offshore platform that receives raw crude and performs the upgrading duty to produce a clean crude concentrate is analogous to a mineral processing plant, and the crude oil refinery which receives the clean crude concentrate to produce commodity hydrocarbon products is analogous to a smelter.



Stream Description & No.		Wellhead Fluids 1	HP Separator Outlet 2	LP Separator Outlet 3	Dehydrator Outlet 4	HP Deoiler Outlet 5	LP Deoiler Outlet 6	Flotation Inlet 7	Flotation Outlet 8	Filter Outlet 9
Flow Condition	Units									
Pressure	(psig)	<1350	675-1350	<260	50-150	100	100	50	45	25
Temperature	(°F)	120-180	120-180	120-180	150-300	120-180	120-180	150-200	100-150	100-150
Oil Concentration	ppm(v)	5-99%	500-2000	500-2000	500-2000	<50	<50	<50	<25	<5
Mean Oil Drop Size	microns	Continuous	100-300	100-300	100-300	<50	<50	<40	<10	<5

Figure 1. Process flow diagram for the raw crude and produced water treating systems for an offshore Gulf of Mexico based crude oil process system.

Offshore Produced Water Treatment

Figure 1 shows a process flow diagram for an offshore Gulf of Mexico based crude oil process system, similar to what would be found on a floating or fixed based platform structure, with emphasis on the produced water treatment system. Wellhead fluids (raw crude) are received through a choke valve into a series of three phase separators. The production separators are large, horizontal, cylindrical pressure vessels with dimensions from 10-15 foot diameter
by 30-50 foot in length. Three phase production separators operate on the principles of pressure let-down and gravity settling. Pressure reduction allows gas dissolved in the crude and water to effervesce, while gravity settling results in the formation of three distinct layers with gas on top, crude in the middle, and water (with solids) at the bottom. The high pressure (HP) and low pressure (LP) separators operate in series with a sequence of pressure let-down to capture natural gas in stages. The recovered gas reports to scrubbing and compression for export to a pipeline. The crude oil goes through an electrostatic dehydrator as a polishing stage to meet the export specification of 0.5% BS&W (bottom sediment and water).

The produced water treatment system is designed to capture and combine all separator water streams and prepare them for common disposal, which in this case is injection into a subsurface formation. Produced water from the HP and LP separators follow parallel paths operating at different pressures. Water from the HP separator exits at 675-1350 psig and 120-180°F while the water from the LP separator exits at <260 psig and similar temperature. Oil in the separator produced water stream is in the form of droplets that have not risen due to buoyancy under Stokesian principles. A concentration range is from 500-2000 ppmv oil-in-water, with a median oil droplet diameter of 100-300 microns. Water discharging from the dehydrator will be at a lower pressure (50-150 psig) and higher temperature (150-300°F), but with similar oil droplet concentration and median droplet diameter. However, the water flow rate from the dehydrator comprises <5% of the total produced water treatment throughput.

Produced water from the separators is first treated with a closed underflow multi-liner solid-liquid hydrocyclone vessel termed a desander. Inorganic solid particles (mainly sand and scale) greater than 15 microns are separated and periodically discharged for cleaning and disposal. The desander operates with a nominal 15-25 psi pressure drop and details of its design and operation are given elsewhere (Rawlins and Wang 2000). The produced water stream is then treated with a multi-liner liquid-liquid hydrocyclone vessel termed a deoiler. Dispersed oil droplets greater than 50-75 microns are captured to form a continuous oil concentrate (<10% oil) reject stream which is sent to the dehydrator or a slop tank for oil recovery. Details of the design and operation of a deoiler system are given elsewhere (Ditria and Hoyack 1994). Produced water exiting the deoiler contains up to 50 ppmv of oil (thus 90-98% removal efficiency by the deoiler) with a median droplet size <75 microns. This stream passes through a level control valve (LCV) which is used to control the liquid level in the production separators. The turbulence created by the pressure drop through a control valve may decrease the median droplet diameter by up to 90%, so the LCV is placed after the deoiler to optimize operation of that unit process. However, droplets remaining in the produced water stream after the deoiler are subject to shearing, but since the overall concentration of oil is much less the net effect is minimized. Oil droplets that are not captured by the deoiler and/or sheared by the LCV are termed fine oil droplets. Under quiescent or laminar conditions fine oil droplets in high concentration will interact and coalesce to increase the median droplet size. However after the deoiler and LCV the total oil-in-water concentration is very low, thus the probability of growth by coalescence is diminished. As a point of reference for this paper the term *fine oil droplets* applies to a median droplet size <50 microns in a very dilute system (<50 ppmv).

A flotation cell is the primary unit operation used to recover fine oil droplets from produced water systems. Both mechanical induced gas flotation (IGF) and hydraulic dissolved gas flotation (DGF) cells have been used for residual oil removal from produced water since the late 1960's (Sport 1970; Bassett 1971). Mechanical IGF cells developed from the WEMCO® multi-cell rectangular-shaped mechanically-driven rotor/stator design. The primary difference from a mineral processing flotation cell is that the flotation chamber is fully encapsulated to prevent hydrocarbon vapor release into the atmosphere. Mechanical IGF cells have found significant use in applications that are not space or motion sensitive such as land-based or fixed-platform fields. However deepwater floating platforms are not suitable for mechanical IGF use as the footprint requirements are too strict and motion of the platform does not allow a fixed skimming level for the oil froth resulting in re-entrainment of the oil or splashing of the produced water. The latest generation of offshore flotation cells are primarily hydraulic IGF or DGF designs with a vertical orientation and no moving parts. The vertical orientation both minimizes footprint, but also allows a thicker oil skim pad which is much less sensitive to platform motion. Vertical hydraulic IGF cells are similar in concept to a column flotation cell, however the length to diameter ratio is normally 3:1, whereas a column cell may be 10:1. These flotation cells rely partly on dissolved gas effervescing from solution (due to pressure letdown), but the primary bubble source is hydraulic entrainment of gas through an eductor, sparger, or shear pump. In all cases the flotation gas is natural gas sources from the facility. Air is never used as the flotation gas, as oxygen in the system can lead to adverse chemical reactions, corrosion, or biological growth. Figure 2 shows a four-stage mechanical IGF cell installed at a land-based oil facility and a vertical IGF cell installed on an offshore fixed-platform. A flotation cell will generally reduce the oil concentration to <25 ppmv and capture oil droplets down to a median size of <10 microns. Currently eight companies provide over twenty different models of flotation cells specifically designed for produced water filtration (Rawlins 2009).

The final stage of produced water treatment before injection is normally deep bed media filtration. These units are designed to remove the residual oil droplets and particulate solids to prevent formation damage. The discharge oil and solids concentration is normally just a few ppmv. Several types of media are used such as garnet or silica, but the preferred bed media is walnut or pecan shells. Typically sized at 12/20 or 20/30 mesh, this bio-media has an excellent combination of oil adhesion and resistance to attrition during the backwash cycle.

Figure 2. (left) Four-stage mechanical IGF cell installed at a land-based oil facility and (right) a vertical IGF cell (gray vertical vessel near center) installed on an offshore fixed-platform.

PROPERTIES OF THE FLUIDS IN PETROLEUM CIRCUITS

In flotation of fine oil droplets in a petroleum production water treating circuit, the continuous phase is produced water. Produced water differs significantly from the fresh/recycled water used in mineral processing circuits in the amount of dissolved solids. All formation (produced) water contains substantial concentrations of dissolved solids, primarily sodium chloride. The concentration and distribution of ions differs greatly from seawater giving produced water unique properties. Total dissolved solids (TDS) concentrations have been reported from 200 ppm to saturation, which is near 300,000 ppm (McCain 1990). Typical values lie in the range of 80,000-120,000 ppm, which is 3-4 times the TDS value of seawater. The most common cations are Na^+, Ca^{2+}, and Mg^{2+}, and the most common anions are Cl^-, SO_4^{2-}, and HCO_3^-.

Properties of Produced Water

In modeling the mechanisms of fine oil droplet flotation in produced water, the properties of the continuous fluid are required. The density and viscosity are needed for a simple Stokesian buoyancy calculation, while further calculations on bubble-droplet interaction require the interfacial tensions (water-oil and water-gas). These thermophysical properties are a function of pressure, temperature, and water composition. Of these factors, temperature and composition are determining while the pressure normally exhibited in a flotation cell (<100 psig) has negligible effect. Figure 3 shows the effect of temperature and salinity on water density and viscosity at atmospheric pressure.

Temperature and salinity have competing effects on both density and viscosity. An increase in temperature decreases both properties, while an increase in dissolved solids has a direct proportional effect. Produced water containing 15% NaCl at 50°C has density of 1099 kg/m^3 and viscosity of 0.74 cP. Temperature has a stronger effect on viscosity and dissolved solids content a stronger effect on density. In terms of Stokes' Law, both density and viscosity have unity exponent however the density term is a relation between oil and water (ρ_{water}-ρ_{oil}) while viscosity is a direct factor. Temperature has a slightly stronger effect on viscosity than salinity. For a given droplet diameter, doubling the temperature (at a fixed salinity) increases the rise velocity by ~50% and doubling the salinity (at a fixed temperature) decreases the rise velocity by ~10%, therefore temperature is the prevailing parameter. While this discussion has primarily focused on the rise of oil droplets in produced water a similar relationship exists with the rise of gas bubbles in produced water. The density difference between water and gas is several orders of magnitude higher than that between water and oil, but the viscosity effect of the water phase is the same. The net effect is that gas bubbles rise about one order of magnitude higher velocity compared to a similar diameter oil droplet.

The interfacial tension (IFT) between gas-water (γ_{gw}) and oil-water (γ_{ow}) is a key factor in determining droplet/bubble stability. Figure 4 shows the effect of temperature and salinity on these parameters at ambient pressure. The air-water IFT curve is given as a point of reference and shows that increasing temperature decreases IFT. Methane has a slightly lower IFT (3-7%) to fresh water compared to air showing that methane bubbles in water are slightly less stable than air bubbles and the driving force for bubble coalescence is enhanced (Jennings and Newman 1971). The effect of dissolved solids is to increase surface tension. The data shown for methane-water IFT at various salinities is estimated from data for air-water IFT with NaCl molality given at ambient pressure and temperature (Argaud 1992). Increasing the salinity to 10 wt.% solids (NaCl) brings the methane-water IFT to near the same values as air-water. Salinity has the effect to stabilize gas (methane) bubbles and work against bubble coalescence. The magnitude of temperature and salinity effect on methane-water IFT is approximately the same, but working in opposite direction.

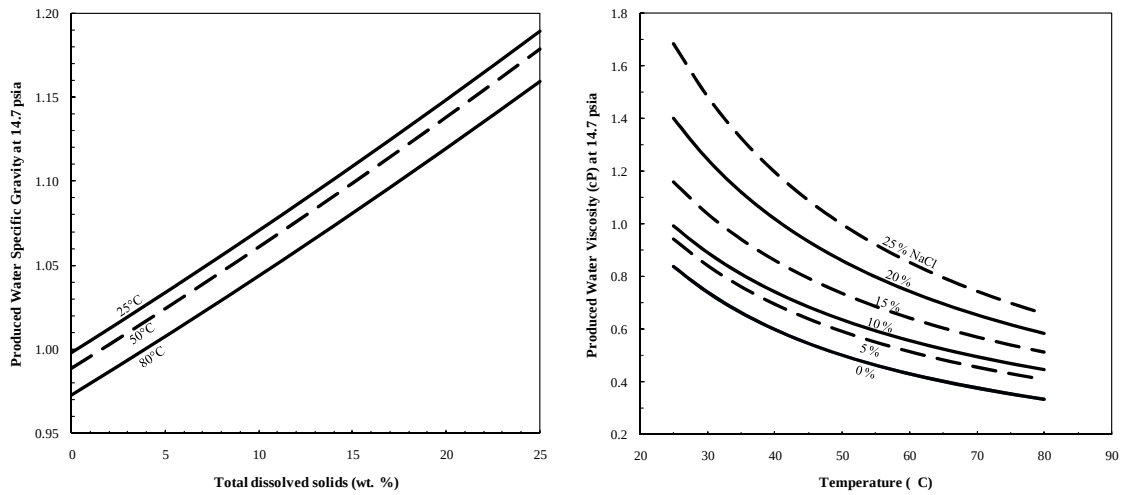


Figure 3. (left) The effect of dissolved solids (as salinity) and temperature on the specific gravity of produced water (data from McCain 1990 and Street et al. 1996) and (right) the effect of salinity and temperature on the viscosity of produced water (data from McCain 1990).

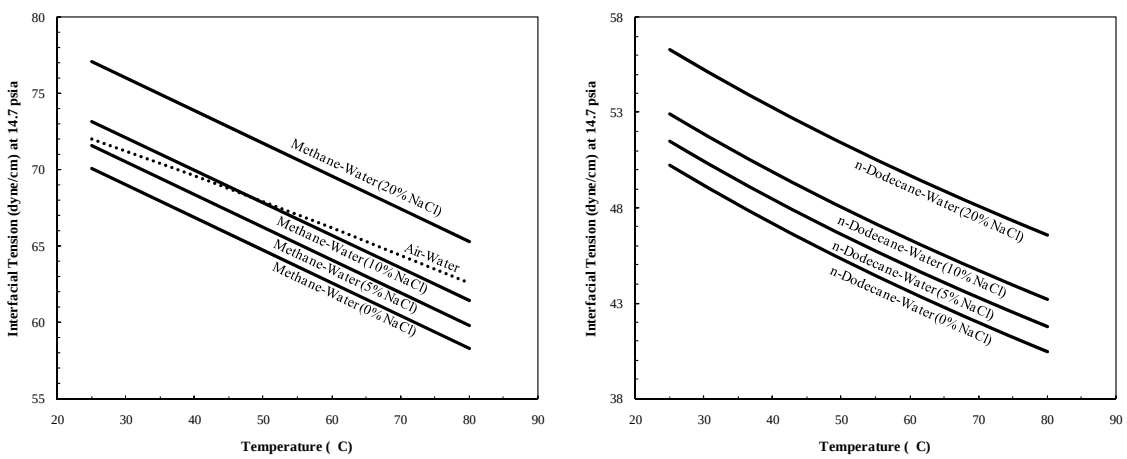


Figure 4. (left) The effect of dissolved solids (as salinity) and temperature on the interfacial tension between methane and water at ambient pressure (data from Jennings and Newman 1971; Street et al. 1996; Argaud 1992) and (right) the effect of salinity and temperature on the interfacial tension between n-dodecane and water at ambient pressure (data from Street et al. 1996; Argaud 1992).

Figure 4 also shows the interfacial tension between oil and water. While methane is a single component gas and is the most prevalent component of flotation gas used in hydraulic IGF cells, crude oil has a widely varying composition. As a reference, data is presented for n-dodecane ($C_{12}H_{26}$) which has the characteristics of a light crude-oil condensate. It has a specific gravity of 0.80 (46 API) and is a neutral (non-polar) oil. The IFT range for n-dodecane and pure water is about 30% less than the IFT for methane pure water. Oil droplets are less stable and have a stronger driving force for coalescence compared to bubble-bubble coalescence. The effect of temperature is to decrease IFT, while salinity increases IFT. Compared to methane-water, the magnitude of temperature and salinity on IFT are very similar.

As both methane and n-dodecane are neutral hydrocarbons, the IFT between these compounds is lower than that between either of them and water. Figure 5 shows the IFT between methane gas and n-dodecane liquid across the temperature range 25-80°C (ambient pressure). The IFT value is about 50% less than the IFT between n-dodecane and water. Temperature has a small decreasing effect on IFT over the observed range, reducing the value about 9%. These values disregard the effect of polar hydrocarbons that may be present at the liquid-gas interface, and the effect of dissolved or dispersed solids in the water. All of these factors will increase the IFT between methane and n-dodecane. Decreasing the carbon content of the alkane (C_n) decreases the oil-gas IFT (γ_{og}). Liquid i-Pentane (C_5H_{12}) has approximately half the IFT with methane compared to liquid n-dodecane. Raw crude oil is a mixture of at least 30-40 hydrocarbons (C_1, C_2,…C_n) and the real γ_{og} is often lower than that shown in Figure 5.

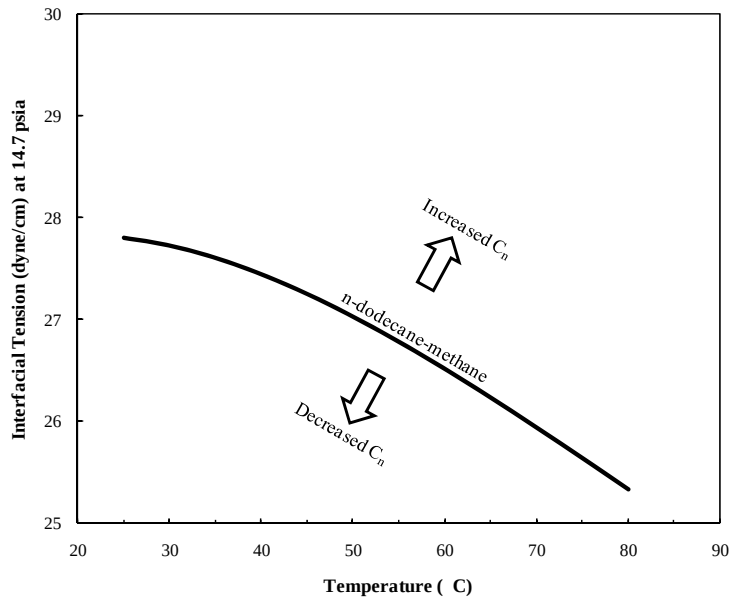


Figure 5. The effect of temperature on the interfacial tension between methane and n-dodecane (data from McCain 1990).

Spreading Coefficient and Free Energy

One method to estimate the efficacy of oil droplet flotation by methane bubbles is to evaluate the spreading coefficient. The spreading coefficient of a fluid (S) is the imbalance between the interfacial tensions acting along the contact line between the fluid phases (Grattoni et al 2003). For the water-oil-gas system, the oil spreading coefficient at the water-gas interface (S_o) is given by Equation 1.

$$S_o = \gamma_{wg} - \gamma_{ow} - \gamma_{og} \tag{1}$$

If ($\gamma_{ow} + \gamma_{og}$) is less than γ_{wg}, then S_o will be positive which indicates spreading of the oil layer to form a boundary between the gas and water. A negative S_o indicates a non-spreading condition, in which the oil will form a finite contact angle with the gas and water interface. Spreading of the oil droplet along the gas-water interface (i.e. formation of an oil coating on the gas bubble) will only happen if the balance of interfacial tensions yields a positive spreading coefficient, therefore gas flotation is more effective with a positive S_o.

Figure 6 shows the effect of temperature and salinity on the spreading coefficient of the dodecane-methane-water system. In pure water a dodecane droplet has a S_o of -7.93 dyne/cm at 25°C. Temperature has a small increasing effect on S_o, raising the value by ~4% when the temperature doubles to 50°C. Salinity has a slightly greater effect increasing S_o by 7% as the salinity doubles from 10% to 20%. In all cases shown S_o is negative indicating that n-dodecane will not spread (or wet) the interface between methane and water, but will form a definite contact angle. Decreasing the carbon content of the alkane (C_n) will increase the spreading coefficient such that light oils (i.e. propane and ethane) or raw crude oils that contain a high content of these light hydrocarbons will actively coat bubbles of methane in a saline-water system. Chemical additions are not commonly used in oil droplet flotation in order to minimize treatment cost, however a surfactant that lowers the oil-water interfacial tension (γ_{ow}) will increase the spreading coefficient to enhance bubble coating by the oil droplet.

Further analysis with the spreading coefficient is to evaluate the overall change in system energy involved with oil coating a gas bubble. The free energy (G) of the interface between a gas bubble and water or an oil droplet and water can be determined from the interfacial tension (γ) and bubble/droplet surface area (A), as shown in Equation 2.

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{P,T,n} \tag{2}$$

For constant pressure, temperature, and composition then G is a product of γ and A. If the system energy is reduced ($\Delta G<0$) by converting a discrete oil drop and a discrete gas bubble into an aggregate, then the oil will coat the gas bubble. The creation of an aggregate from the discrete particles can be represented by Equation 3.

$$\left(\gamma_{og} A_{bubble} + \gamma_{ow} A_{oilfilm}\right) - \left(\gamma_{ow} A_{drop} + \gamma_{wg} A_{bubble}\right) < 0 \tag{3}$$

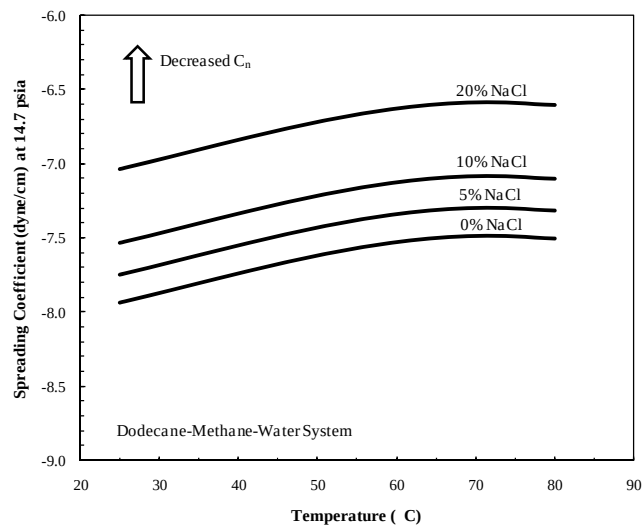


Figure 6. The effect of temperature and salinity on the spreading coefficient of the dodecane-methane-water system.

Critical Diameter Ratio

If the energy of the discrete oil droplet ($\gamma_{ow}A_{drop}$) plus the discrete gas bubble ($\gamma_{wg}A_{bubble}$) is greater than the energy of an oil coated bubble, then the droplet will coat the bubble. The oil acts to replace the water-gas interface with an oil-gas interface plus oil-water interface with a net reduction in free energy. The reduction in energy is both interfacial tension and bubble/droplet size dependent. As the surface area of the bubble is in both terms, changing the bubble size alone has less effect than changing the droplet:bubble ratio. Holding the interfacial tension values constant, a droplet/bubble diameter ratio can be determined below which the droplet will not coat the bubble, but attach through a different mechanism. This diameter is called the critical diameter ratio (D_{cr}). Figure 7 shows the net energy curve for 50 µm, 100 µm, and 200 µm diameter methane bubbles in water (0% salinity) at ambient temperature and pressure in contact with a n-dodecane droplet of varying diameter.

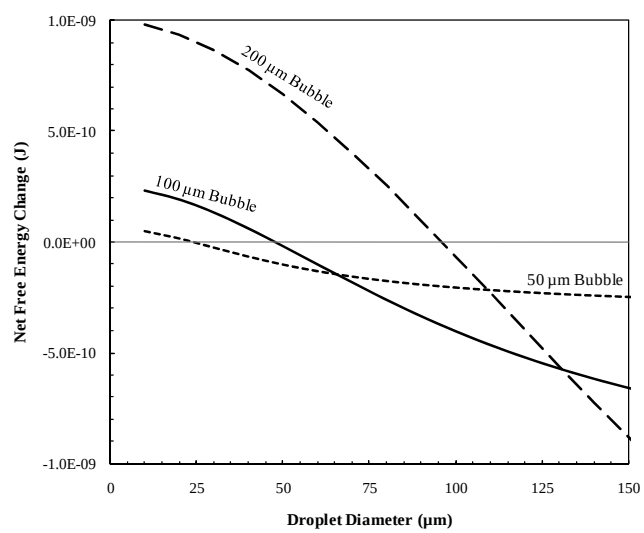


Figure 7. Net surface energy change for coalescence of oil droplet (n-dodecane) of varying diameter onto gas bubble (methane) in water (0% salinity) at ambient pressure and temperature.

The critical diameter ratio is determined for each bubble size at the point where the net energy change goes below zero. At $\Delta G<0$ the reduction in energy drives the coating of the gas bubble with the oil droplet. For the scenario depicted in Figure 7, D_{cr} has a constant value of 0.48 independent of bubble diameter. A 100 micron methane bubble will capture (by coating) n-dodecane droplets 48 microns and larger. Droplets smaller than this diameter may be captured by a different mechanism.

The value of D_{cr} will change with water salinity and temperature. Figure 8 shows the effect of salinity (0-20%) at a constant temperature and pressure and the effect of temperature (25-80°C) at a constant salinity and pressure for the dodecane-methane-water system. Salinity has a moderate decreasing effect on D_{cr} reducing the value by 0.065 (~13.6%) across the range of 0-20% NaCl content. Temperature has a slight increasing effect on D_{cr}, raising the value by 0.052 (~10.9%) as the temperature is increased from 25° to 80°C.

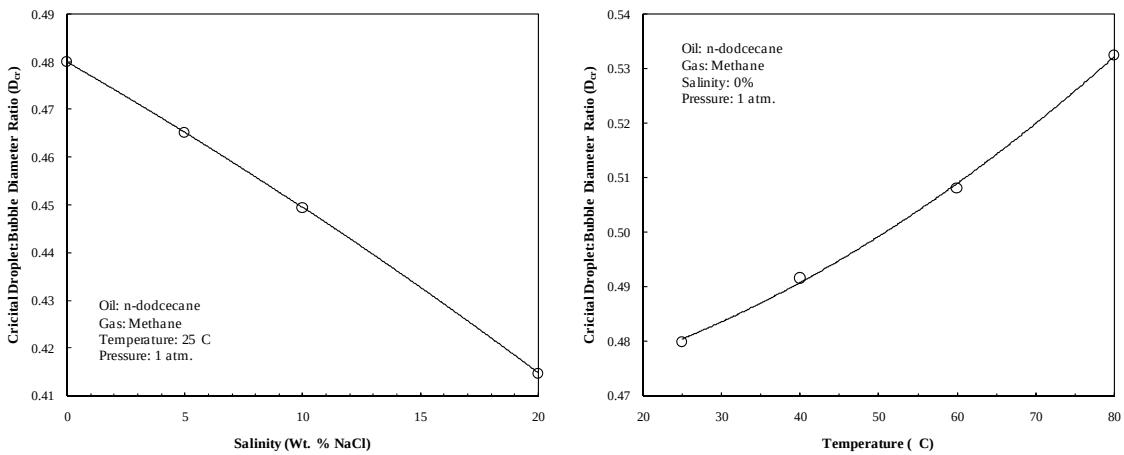


Figure 8. Effect of salinity (left) and temperature (right) on critical droplet:bubble diameter ratio (D_{cr}) for the dodecane-methane-water system at ambient pressure.

Capture of a distribution of oil droplets by coalescence (coating) of methane bubbles is promoted by increased salinity and lower temperature. Minimization of D_{cr} allows capture of smaller droplets with the gas bubbles. Typically these factors are not adjustable within the system, however changes to the IFT, bubble diameter, or droplet diameter can be undertaken to improve oil droplet capture. The most important factor is to decrease methane bubble size or increase the oil droplet size, as droplet capture is a ratio of the bubble diameter. To capture a 10 micron droplet, an approximate 20 micron gas bubble is the largest that can be used. Another important factor is to maximize the methane-water interfacial tension. The magnitude of γ_{wg} is larger than γ_{og} or γ_{ow}. Impurities in methane such as higher hydrocarbons, oxygen, or carbon dioxide will all decrease γ_{wg} thus the methane used should be kept clean and pure

GAS BUBBLE AND OIL DROPLET BUOYANCY

Small gas bubbles and oil droplets in an aqueous system can be assumed to have a spherical shape, thus their buoyant rise velocity can be approximated using Stokes' law. The common form of Stokes' relationship is given in Equation 4, where u_∞ is the terminal velocity (cm/s), g is gravitational acceleration (981 cm/s²), d_p is the bubble/droplet diameter (cm), ρ_l is the liquid density (g/cm³), ρ_p is the bubble/droplet density (g/cm³), and μ_l is the liquid viscosity (g/cm·s).

$$u_\infty = \frac{g d_p^2 \left(\rho_l - \rho_p\right)}{18 \mu_l} \tag{4}$$

Stokes' law is valid for dilute suspensions and where the rising droplet or bubble has a Reynolds number (Re) <0.1. For Reynolds numbers up to unity Stokes' law has a 9% error, thus it can be termed approximately valid for Re<1.0. The Reynolds number for a rising spherical particle in a fluid can be determined from Equation 5.

$$\mathrm{Re} = \frac{\rho_l u_\infty d_p}{\mu_l} \tag{5}$$

Produced water treated by flotation normally has <100 ppmv oil content thus the suspension can be approximated as dilute. The oil droplets will be distributed amongst a size distribution that is dynamic due to continual droplet breakup and coalescence, but the average droplet size is <40 microns. As a population of gas bubbles is introduced into the system they will interact with the distributed oil droplets to capture and coalesce forming an aggregate particle. Assuming a coating-capture mechanism where the oil forms a film on the gas bubble, the aggregate will take the shape of the gas bubble, thus the aggregate will have a spherical shape and the resultant rise velocity be approximated by Stokes' law.

Figure 9 shows the calculated rise velocity for methane gas bubbles, n-dodecane oil droplets, and methane-dodecane aggregates in water (0% salinity) at ambient pressure and temperature. The velocities were calculated using Equation 4, and the aggregates were assumed to be methane bubbles coated with an even film of n-dodecane. At the given conditions, methane bubbles rise at 3.8 times the rate of dodecane droplets. The valid Stokes' region for methane bubbles is <120 µm and for n-dodecane droplets is <190 µm. An aggregate made from the coalescence of a 100 µm methane bubble and 100 µm n-dodecane droplet has a diameter of 126 µm, with an intermediate velocity and is within the Stokes' region (<150 µm). Attachment of the gas bubble increased the droplet velocity from 13.6 cm/min to 32.7 cm/min, which represents a factor of 2.4. For an n-dodecane droplet at the D_{cr} size (48 µm), attachment of a 100 µm bubble will result in a velocity increase factor of 16.4. Maximum flotation effect will be achieved by selecting a bubble size such that the oil droplet mean size is the corresponding D_{cr}. If the bubble size has a D_{cr} larger than the oil droplet size then the oil droplets may not be captured. If the bubble size has a D_{cr} smaller than the oil droplet size the oil droplets will be captured, however the rise velocity of the aggregate will be less than the optimum value.

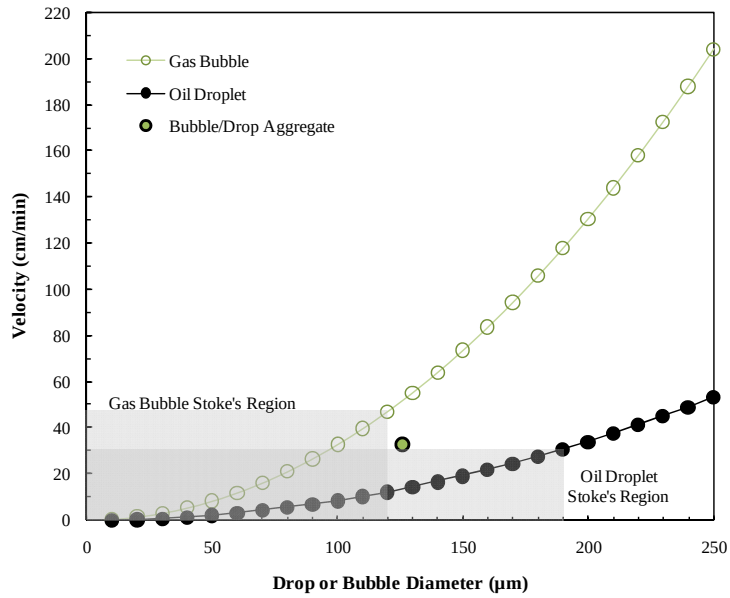


Figure 9. Stokes' buoyant rise velocity of methane gas bubble, n-dodecane droplet, and gas-bubble aggregate in water (0% salinity) at ambient pressure and temperature.

Increasing the produced water salinity (higher density) and mean oil droplet size aid flotation, while increasing the water viscosity, oil density or gas density hinder flotation. Pressure and temperature effects on flotation are reflected in the water, oil, or gas density and viscosity.

The primary purpose of oil droplet flotation is to reduce residence time. Whereas mineral flotation seeks to separate and concentrate a specific mineral in a mixture of other minerals, oil flotation seeks to separate and concentrate the oil from a bulk liquid phase. Most oil will naturally float by itself (heavy oils and bitumen may have a specific gravity >1), and given enough residence time in a gravity separating vessel the produced water will be cleaned of the dispersed oil phase. A very fine oil droplet however may have such a low velocity that the required vessel residence time may be impractical. A 25 µm droplet of n-dodecane in fresh water has a rise velocity of 0.55 cm/min. In a flotation vessel with a 2 meter reaction zone, the droplet will take 6.1 hours to rise that distance in quiescent conditions. Attaching that droplet to a 50 µm gas bubble increases the velocity to 8.2 cm/min, which reduces the rise time to 24.4 minutes. If the droplet can be attached to a 100 µm bubble, then the rise time is further reduced to 6.1 minutes. The bubble rise velocity must be matched with the direction and velocity of the bulk flow in the vessel. Downward bulk (plug) flow will act counter to the rising droplet or bubble, and generate a cutoff size below which the bubble or droplet will not separate, but travel with the bulk fluid flow. Upward plug flow will assist oil droplet and gas bubble flotation, however there are challenges to removal of the clean water.

The reduction in residence time results in a corresponding reduction in vessel volume, and for offshore platform based produced water treatment vessel size and weight are limited by platform space and load capability. A vertical vessel with a 2 meter quiescent reaction zone treating 25,000 BPD (730 gallons per minute) will have a 17.9 m diameter for a 25 µm n-dodecane oil droplet, 4.6 m diameter for a 25 µm n-dodecane droplet with 50 µm methane gas bubble, and 2.3 m diameter for a 25 µm n-dodecane droplet with 100 µm methane gas bubble.

ATTACHMENT OF OIL DROPLET TO GAS BUBBLE

Effective flotation relies on attachment of the introduced gas bubble to the dispersed oil droplet. There are numerous factors involved in successful collision and attachment including bubble/droplet size ratio, bubble swarm density, mean bubble size, and

bubble distribution, produce water salinity, oil viscosity, spreading coefficient, fluid velocity, and turbulence. Of these factors gas bubble size, distribution, and dispersion are the most important for flotation efficiency. Oil droplets can attach to gas bubbles by four mechanisms, which are depicted graphically in Figure 10.

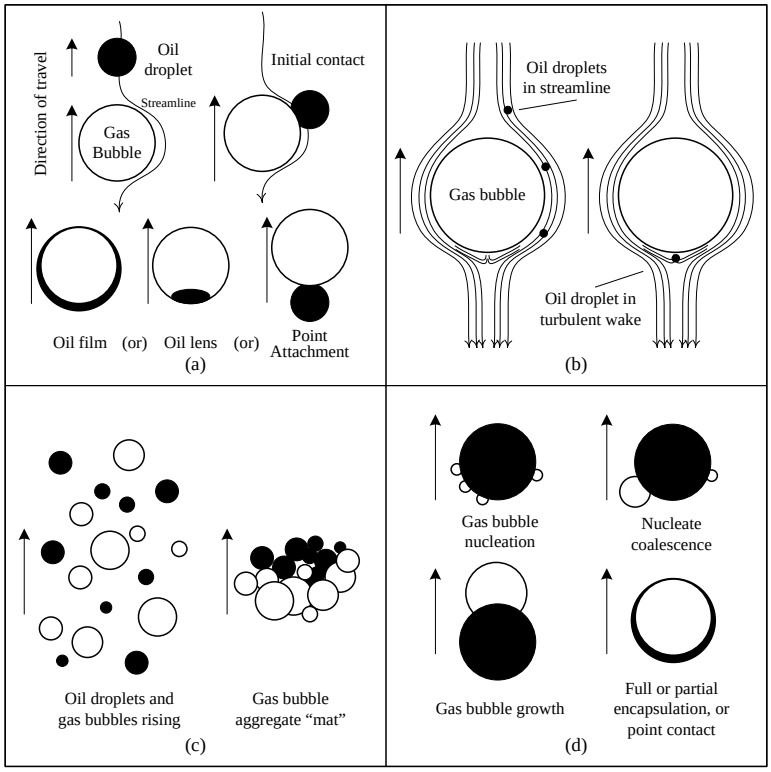


Figure 10. Mechanisms for gas bubble capture of oil droplets suspended in water: (a) direct impingement with full or partial encapsulation by chemical adhesion, (b) hydrodynamic capture of oil droplets in the wake of a rising gas bubble, (c) clustering of gas bubbles to form a buoyant mat, and (d) gas bubble nucleation, coalescence, and growth on the surface of an oil droplet to result in full or partial encapsulation.

The primary mechanism for oil droplet flotation is full or partial encapsulation of the gas bubble by the oil droplet as shown in Figure 10a (Strickland 1980; Oliveira et al. 1999; Grattoni et al. 2003; Moosai and Dawe 2003; Niewiadomski et al. 2007). In this mechanism both the oil droplet and gas bubble exhibit buoyant rise in the fluid in the opposite direction of gravity. The velocity of the gas bubble is sufficiently higher than that of the oil droplet due to diameter and density, thus from the gas bubble inertial frame of reference the oil droplet is settling downward as if under gravitational influence. Because the oil droplet has lower inertia than the surrounding water it will not directly impact the gas bubble, and water streamlines formed from the rising bubble tend to direct the approaching droplet around the bubble. As the droplet passes around the bubble the trajectory in the rising wake pulls the droplet towards the bubble, and if the droplet has sufficient diameter the droplet will touch the gas bubble surface. Once the droplet has touched the bubble surface the intervening water film thins then breaks to allow the hydrocarbon liquid and gas to come in contact (Niewiadomski et al. 2007). Attachment of the oil droplet to the gas bubble is governed by the spreading coefficient and free energy minimization (D_{cr}) as detailed previously. Full encapsulation, where the oil completely covers the gas bubble surface provides the strongest bond between the hydrocarbon liquid and gas thus prevents removal of the oil by shear forces. In addition, an oil coated bubble may more easily attract a free oil droplet thus multiplying the flotation effectiveness (Strickland 1980). Should the droplet size be insufficient for full encapsulation, the oil droplet may form a lens at the aft of the bubble to minimize contact with the aqueous phase, or if the spreading coefficient is negative the oil droplet may form a point contact with the gas bubble. Lens formation is a stronger bond than point contact.

A second mechanism was shown (Sylvester and Byeseda 1980) when gas bubbles 200-700 microns diameter were observed to capture oil drops 1-15 microns diameter in the hydrodynamic wake of the rising bubble, instead of chemical adhesion to the surface. This mechanism is depicted in Figure 10b. The "falling" oil droplet follows the water streamline around the rising bubble. The droplet has insufficient diameter to break the water layer at the bubble surface, however the droplet is small enough to become trapped in the turbulent wake at the aft-end of the rising bubble thus follow the bubble in its upward trajectory. This mechanism does not create a strong bond between the hydrocarbon gas and liquid however this does provide a mechanism by which large bubbles can capture droplets smaller than the D_{cr}.

A third mechanism postulated is shown in Figure 10c, whereby bubble clusters form a buoyant "mat" to assist in droplet entrapment along with hydrophobic binding (Rodrigues and Rubio 2007). The formation of bubble clusters has been observed in mineral flotation, in which case the bubbles are held together by bridging particles that are simultaneously attached to two or

more particles (Fuerstenau et al 2007). In oil flotation, the oil droplets, especially in the case of point attachment, or suspended solids, can act as a bridging structure to form a cluster or mat of bubbles. The bubble mat sweeps upward with a wider diameter than single particles and is able to more effectively sweep the water phase. Bubble coalescence is retarded by high ionic content of the water, plus stabilizing chemicals in the water, thus the bubbles attach to particles (liquid or solid), but do not form a larger bubble. Bubble cluster formation is promoted by high density of small diameter bubbles and a high density of finely disseminated hydrophobic particles.

The fourth mechanism, shown in Figure 10d, is a product of the dissolved gas flotation (DGF) mechanism in that gas bubbles nucleate on particle/droplet surfaces, then grow to sufficient size to aid in flotation as the gas comes out of solution (Oliveira et al. 1999; Rodrigues and Rubio 2007). For this mechanism to take place, sufficient gas must effervesce from solution, which usually coincides with a fairly large pressure drop at the inlet of the flotation cell. Unlike a DGF cell, a separate mechanism for dissolving gas is not utilized, but the gas is forced into solution while the fluids are in contact in the reservoir. Gas will flash from solution at all stages of pressure let-down including well-bore inflow, pipe transport, choke let-down, and inside three-phase separators. The solubility of methane, and other hydrocarbon gases, in water is several orders of magnitude lower than the solubility in hydrocarbon liquid, therefore most of the gas effervescing from solution will come from the oil droplets. The gas bubbles will nucleate within the droplets or at the droplet surface, and continue to grow in diameter as long as the partial pressure is lower in the gas phase compared to the liquid phase. Eventually the nucleating bubbles will contact, and may coalesce to form a larger discrete bubble. The coalesced bubble will form full or partial encapsulation or point contact depending on the volume of the bubble and the spreading coefficient, which is similar to the mechanism in Figure 10a. The amount of gas effervescing depends primarily on the pressure and temperature difference between the upstream piping and the operating conditions of the flotation cell, and the composition of the hydrocarbon fluid. These factors determine the bubble-point pressure.

OIL FLOTATION UNIT PROCESS

The design of oil flotation in produced water systems as a unit process is governed by location and discharge regulations. Geographic location, primarily onshore or offshore, dictate the size and weight restrictions, while regulations govern the discharge method and oil content limits. Onshore produced water treatment, due to lack of space and weight constraints, may use a gravity settling tank (e.g. API tank) with long residence time, but due to injection requirements will often use deep bed media filtration to reduce the oil content to very low levels. Flotation cells are not used frequently for onshore produced water treatment. Offshore produced water treatment will commonly use liquid-liquid hydrocyclones followed by a vertical flotation cell to meet discharge specifications, as these two unit processes have high throughput to footprint ratio. A gravity settling tank or deep bed media filter are rarely used offshore. An offshore flotation cell must be designed for minimal footprint, minimal weight, high single pass efficiency, gas and oil slugs, suspended solids, motion sensitivity, high uptime, and simplistic operation. These requirements have led to the evolution of the compact flotation unit (CFU), which is a vertical hydraulic single cell, as the primary choice for fine oil droplet removal from produced water in offshore operations. This design is similar in operation to a column flotation unit used in mineral and coal processing. Aspects of this design are discussed as follows.

Orientation: The preferred orientation for the primary reactor in a flotation cell should be vertical, as opposed to horizontal. Vertical orientation minimizes footprint for offshore use, and minimizes liquid level surface area subjected to motion from the facility or gas slugs. Distribution of gas bubbles in a radial pattern to flow vertically in a cylindrical shell is more homogenous compared to distributing bubbles along the length of a horizontal partially filled cylindrical vessel (Smith et al 1996; Lee and Frankiewicz 2004). Plug flow pattern and velocity can also be maintained more homogenous to prevent short circuiting, and skimming of oil from a cylindrical cross section is more efficient than along the length of a rectangular section (Owens and Lee 2007). A vertical orientation allows introduction of the feed water to form a swirling flow pattern, which cannot be accomplished in a horizontal flotation cell. Unlike a mineral or coal column flotation cell which may have a 10:1 or 15:1 height to diameter ratio, the produced water flotation cell most commonly has a 2:1 to 3:1 height to diameter ratio.

Cell Type: The preferred method of flotation action in the flotation cell reaction zone should be induced/dispersed gas, as opposed to mechanical or cyclonic. Mechanical and cyclonic flotation cells introduce high shear forces that can break apart the existing oil droplets, or break apart the droplet/bubble aggregate (Sylvester and Byeseda 1980; Van der Zande et al. 2001; Tavera and Escudero 2003; Welz et al. 2007; Niewiadomski et al. 2007). An induced/dispersed gas flotation cell (including dissolved gas type) has much more flexibility in customizing the bubble distribution and size, as well as introduction location for the gas stream, without creating high shear forces that are detrimental to the oil droplet or droplet/bubble aggregate. Cyclonic flotation cells, while having the smallest footprint, lack the residence time necessary to handle process upsets.

Residence Time: The residence time, or hold-up volume, of the flotation cell should be designed to handle process upsets. These upsets could include oil carry-under from upstream separation equipment due to improper operation, or due to introduction of non-normal fluids into the produced water stream. In some oil and gas facilities the flotation cell may be viewed as the “catch all” for liquids drained from other vessels. Under these abnormal conditions the residence time should be sufficient to maintain the appropriate outlet oil concentration, except in extreme cases. Column flotation cells have low residence time due to small hold-up volume, while the more common oil and gas vertical flotation cells have at most a 3-4 minute residence time. The residence time will determine the height of the vertical flotation cell.

Gas Slug Handling: Gas breakout due to pressure or temperature changes upstream of the flotation cell will result in the presence of free gas as part of the inlet flow stream entering the flotation cell. Small amounts of gas may be beneficial in providing introductory flotation action, but large slugs may lead to high inlet velocity or churning flow, which can lead to oil droplet shearing and/or large disturbances in the oil/water interface, both of which lead to oil droplet carry under, or disturbances in the oil froth collection zone, which will lead to water carryover (Lee and Frankiewicz 2004). Gas slugs of 25-50% gas void fraction (GVF) are common. One method used to accommodate gas slugs is an inlet gas/liquid cyclone. A gas-liquid cyclone

requires introduction of the feed (contaminated) stream at or near the circumferential center of the vertical flotation cell, which may preclude introduction of the bulk fluid flow in a tangential or swirling pattern.

Flow Pattern: The flow pattern can be counter-current, co-current, or swirling, as illustrated in Figure 11. In a counter-current flow pattern the contaminated feed water is introduced at or near the top of the flotation cell reaction zone, thus the oil droplets are introduced near their exit point. The bulk water flow is thus forced down in the direction of gravity, which goes against the natural direction of travel for the oil droplets. The gas bubbles rise against the bulk water flow leading to a natural "filtering" action of the water by the rising bubble swarm due to increase probability of collision between the droplet and bubble (Tavera and Escudero 2003). Free gas in the feed fluids introduced near the top of the flotation cell will have less disruptive effect on the reaction zone, if a gas/liquid cyclone or slugging knock-out device is not used. In addition, free solids settling through the reaction zone may be cleaned on their travel downward. Downward bulk flow does limit the size of gas bubbles and oil droplets that will report to the froth layer, as the rising bubbles/droplets must reach a terminal velocity higher than the downward plug flow velocity (Reay and Ratcliff 1973; Gutkowski et al. 1981; Lee and Frankiewicz 2004).

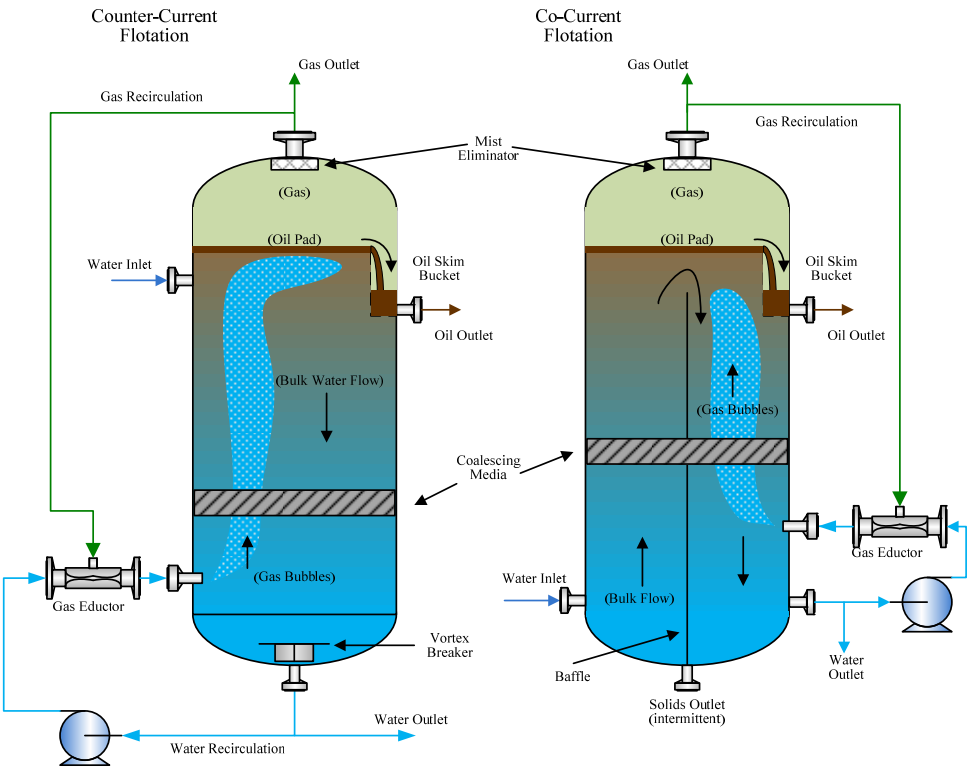


Figure 11. Vertical compact flotation unit for oil flotation in produced water with counter-current flow pattern (left) and co-current flow pattern (right).

A co-current flow pattern, where the feed fluids are introduced at or near the bubble source, allows longer time of contact between the concentrated contaminated stream and the bubble swarm, and forces all flow upward (initially) towards the froth layer such that the bulk flow and natural inertial flow of the droplets coincide. However, the resulting clean water phase must then be reversed to eventually exit near the bottom of the reaction zone and shown in Figure 11. The internals required for this clean water reversal must be designed to prevent disruption of the oil/water interface, and high downward velocities that may entrain small oil droplets (if part of the vessel cross sectional area is taken up by upward feed flow, the returning downward clean water will have a smaller area through which to flow compared to a counter-current design, hence the downward velocities will be higher for the same diameter vessel).

Swirling flow is a regime that is added to the co-current or counter-current flow pattern. An advantage of swirling flow is that it forces the oil droplets and gas bubbles towards the axial center of the vessel for easier collection, and allows longer contact time between the oil droplets and gas bubbles, compared to straight axial flow. In addition, a low velocity swirl introduces a slight turbulence into the bulk flow that may prove advantageous to oil droplet and gas bubble collision efficiency (Strickland 1980; Smith et al. 1996; Grattoni et al. 2003) by imparting inertia to the oil droplet and gives more time for the droplet/bubble to interact due to turbulent flow eddies (Sylvester and Byeseda 1980; Niewiadomski et al. 2007). The swirling flow pattern must be kept near laminar to prevent gas vortexing and droplet/bubble breakup. In a swirling flow pattern collection of the oil froth layer is best accomplished at the center of the swirl. A swirl pattern can be induced by internal nozzles or tangential inlet.

Solids Handling: Produced water entering the flotation cell will contain a small amount of suspended solids. These solids may be free flowing in the water phase, or encapsulated in the oil or oil/water boundary. During the flotation reaction, some of

the solids will become liberated and settle into the bottom of the reaction chamber. Small solids may stay encapsulated with the oil phase and report to the oil froth. The settling solids must be accounted for in the flotation cell design, as their build up in the bottom of the vessel can be detrimental to the flotation cell. Settled solids may lead to corrosion or reduction in vessel residence time. These settled solids must be periodically or continuously removed to prevent adverse effects. An axial flow exit of the clean water (i.e. center of the bottom dished head) allows the solids to continuously exit the flotation cell with the discharge water and prevents accumulation. However these solids have a coating of oil which may lead to higher oil-in-water values in the discharge stream. In addition an axial flow discharge must have a vortex breaker (especially with swirling inlet flow) to prevent gas and oil ingress into the outlet stream and the vortex breaker must be designed to prevent solids build-up. A non-axial discharge (i.e. side of the vessel) prevents oily solids from discharge, but then requires a second discharge point for intermittent solids removal.

Oil Skim Method: Oil and gas bubbles report to the surface of the water phase to form a froth layer or oil pad. The method of removal depends partly on the inlet flow stream design. An inlet gas/liquid cyclone prevents a central oil bucket, and may require a circumferential or chord shaped weir. A tangential/involute inlet allows a central oil bucket, which requires more complicated piping for oil removal. In all cases a non-mechanical froth removal system is desired to reduce complexity and cost. A non-mechanical typically involves an overflow weir system that relies on the overall liquid height and thickness of the oil layer. The thickness of the oil pad is part of the design methodology for oil skimming. A thin pad skims the oil continuously to prevent re-entrainment, but may allow excess water into the discharge oil stream. A thick pad minimizes water carryover, but in upset conditions may allow oil droplets to be re-entrained in the water phase. Thick pad methodology is the preferred design for column flotation and allows better responsiveness to active interface control.

Gas Introduction Location: Flotation gas may be introduced external or internal to the flotation cell. An external design introduces the bubble gas into the inlet piping of the flotation cell then passes the mixture through a mixing zone, such as an in-line auger or static mixing element. The claim is to provide intimate bubble/droplet mixing, however the mixing device is probably detrimental to the inlet stream by promoting droplet breakup (Sylvester and Byeseda1980; Van der Zande et al. 2001; Tavera and Escudero 2003; Welz et al. 2007; Niewiadomski et al. 2007). Introduction of the gas bubbles into the bottom of the flotation cell reactor (internal) allows generation of controllable bubble size distribution and development of a full dispersion of these bubbles across the area of the reaction chamber. In addition the (near) laminar flow in the reaction zone aids in directing the bubbles towards the most advantageous path for interaction with the oil droplets.

Gas Introduction Method: The method of introducing gas flow into the bulk fluid stream to generate flotation bubbles has undergone the most investigation. Methods investigated include porous frit plate, sintered tubes, sparge nozzle, shear orifice, shear pump, dissolved air, electrolysis, and mechanical impeller. A porous glass/metal device (plate, tube, sparger, etc.) has been used successfully in the mineral flotation industry, but shown to have many operational difficulties in produced water flotation. These difficulties include plugging/fouling by contaminants in the gas stream and build up of precipitated scale on the pore throat (Lee and Frankiewicz 2004). While these devices are simple to operate and relatively inexpensive, they are limited on the bubble size produced and gas throughput (Rubio et al. 2002). A gas eductor is the primary method used for produced water flotation due to low price, simplistic operation, and relative efficiency at bubble generation. This mechanism, usually in combination with a shear plate or orifice, is capable of generating bubbles down to 200-300 micron median size (macro-bubbles). For micro-bubble generation (<100 microns) devices include electroflotation (10-20 microns), cavitation tube sparger (20-30 microns), and dissolved air flotation (40-50 microns). In addition a system comprised of an eductor, shear nozzle, and Stokes settling chamber is capable of generating bubbles down to 5 micron diameter (Owens and Lee 2007). The device or system used must be able to accommodate methane gas with possible liquid contamination and water with very high total dissolved solids and small amounts of suspended solids.

Gas Recirculation: Recirculation of the bubble gas is often undertaken to minimize the amount of field gas consumed by the flotation cell. This gas is taken off the top of the flotation cell, above the froth zone, and recaptured for introduction as the bubble gas. An eductor device accomplishes this task well due to the vacuum created in the eductor throat. Relatively little mist carryover is observed as the gas exit velocities are very low. The primary concern with gas recirculation is possible contamination by hydrogen sulfide stripped from the water and saturation of the recycle gas by water however no detrimental performance on the flotation cell is documented (Hubred et al. 1998). From a mechanical view a recycle line provides minor added complexity of design or cost, and the major concern is the supply of field gas from the end user.

Coalescing Media: Most of the second and third generation vertical flotation cell designs contain a section of coalescing media in the flotation reaction zone. These may be placed in the inlet stream (co-current flow), or across the mid to lower section of the main reaction chamber (counter-current flow). Coalescing media type include balls, saddles, parallel corrugated plate, and cross-flow corrugated plate. In a counter-flow design the oil droplets are introduced in the upper part of the reaction chamber and flow downward to impact the coalescing media, while the gas bubbles are introduced below the media to flow upward. The coalescing media helps capture very small descending oil droplets and allows them to grow to a larger size that are more easily floated.

SUMMARY

Treatment of oil well fluids requires the same approach methodology as traditional mineral processing, and uses much of the same unit processes. Approaching the treatment of crude oil as oilfield mineral processing allows technology transfer with the goal of finding optimum solutions for both industries based on two viewpoints. An example is water treatment in the petroleum which requires the removal of small (<100 µm diameter) oil droplets, for which induced gas flotation is commonly employed. Oil flotation differs from mineral flotation in that oil droplets are naturally hydrophobic, have a lower density than water, and have a spherical shape. Unlike mineral particles, oil droplets have a very low energy of cohesion (35-56 erg/cm² for oil vs. 2000-5000 erg/cm² for minerals) and are subject to breakup from water shear forces, or may coalesce upon contact with other oil droplets (Gutkowski et al. 1981). Produced water has increased density, viscosity, and IFT with hydrocarbon fluids due to the high

content of dissolved solids (mainly NaCl). The IFT between the three phases drives the spreading coefficient and critical bubble:droplet diameter ratio to determine how oil and gas bubbles will interact. Once a oil droplet contacts a methane gas bubble it will attach through one of four mechanisms, of which complete encapsulation provides the strongest bond. Complete encapsulation occurs when the droplet diameter is at least 0.4-0.5 times the diameter of the gas bubble. The droplet-bubble aggregate then rises faster than the oil droplet alone, which provides the impetus for using gas flotation. The rise velocity of oil droplets or gas bubbles is governed by Stokes relationship, and because of the several of orders of magnitude increase in rise velocity, the residence time and size of the flotation cell can be significantly reduced compared to gravity separation. Offshore produced water treatment uses primarily a vertical hydraulic single cell flotation unit that is similar in concept to a mineral flotation cell, but must be designed for minimal footprint, minimal weight, high single pass efficiency, gas and oil slugs, suspended solids, motion sensitivity, high uptime, and simplistic operation.

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