contactors could be devised which could bring about essentially instantaneous contact between particles and bubbles, effectively eliminating the downcomer. However, the over-riding objectives mentioned earlier – achieving high grades and recoveries, with small size, minimum capital and operating costs, in equipment which is easy to operate and maintain – will always remain the prime concerns of industrial users. In any new approaches, these objectives must be kept in view.

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Oil and Water Separation

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Development

The process of flotation needs a gas bubble to collide with, and attach to, an oil droplet; because of the hydrophobic nature of the oil droplet, a stable gas–oil matrix is formed. The buoyancy of the oil droplet is increased by the attachment of the gas bubble, causing the oil droplet to rise rapidly through the water. Typically, one gas bubble will attach to one similar-sized oil droplet as described by Leech. As the bubbles in the froth phase burst, an oil layer is formed on the surface of the water. Oil and froth are then removed from the surface on an intermittent or continuous basis, depending on the mechanism used.

Flotation is a kinetic process. While a number of flotation models exist, Klimpel's first-order rate equation has been demonstrated to provide modelling flexibility, ease of physical interpretation and a good fit to the experimental data. The Klimpel model is written as:

$$R_0(t) = \left[1 - \left(1 - \frac{\exp(-kt)}{kt}\right)\right]$$

where $R_0(t)$ is the fractional recovery of oil at time t(s) and k is the characteristic first rate constant (s^{-1}). The key to flotation is the production of air or gas bubbles. The two major techniques are known as dissolved air flotation (DAF) and induced air flotation (IAF). IAF can be further subdivided into mechanically and hydraulically induced flotation.

Mechanically induced flotation has now been used for about 100 years to separate from a suspension in water, particles of valuable mineral from gangue. In the mining industry this process is known as beneficiation. It is now the main method of concentrating copper, molybdenum, iron, phosphate, lead and zinc ores. In the minerals industry the air is dispersed as bubbles, either through an impeller in subaeration cells or through spargers in flotation columns. These and other variants of the air addition to flotation pulps are classified as IAF. In the petroleum industry natural gas, carbon dioxide or nitrogen may be used as the flotation gas, hence the process is termed induced gas flotation or IGF. The use of these gases significantly reduces downstream corrosion problems and possible hydrocarbon degradation caused by the use of air.

Flotation techniques can remove dispersed, but not dissolved oil. As environmental legislation specifies both the limiting oil concentration and also the biological oxygen demand (BOD) in the discharged water, flotation is often the second stage of a three-stage effluent treatment process of gravity separation, flotation and biological treatment. As an example, British Petroleum's Grangemouth facility has achieved discharge concentrations of 2–3 mg L^{-1} oil-in-water using gravity separation in American Petroleum Institute (API) separators, followed by IAF with a final biological treatment stage to remove dissolved BOD materials including ammonia, phenols and sulfides. Limits for oil-in-water discharges vary around the world, typically between 15 and 40 mg L^{-1}. A maximum BOD of 216 mg L^{-1} daily, with a monthly average of 53 mg L^{-1} is considered to be achievable via the application of the best available technology by the United States Environmental Protection Agency.

Process Techniques

Dissolved Air Flotation (DAF)

In this method compressed air or gas (nitrogen, carbon dioxide or methane) is dissolved into all or part, of a process liquid under pressure in a retention vessel. The gas–oil–water mixture is then sent to a flotation cell, where the pressure is reduced, causing bubbles to come out of solution. The bubbles then attach to and are possibly nucleated on the oil and suspended particles.

The solubility of a gas in water is proportional to its partial pressure and inversely proportional to the water temperature. Solubility may be characterized by Henry's law:

$$X_G = \frac{p}{H_G}$$

where X_G is the molecular fraction of the gaseous component in the liquid, p is the partial gas pressure and H_G is a constant. The release of gas following a reduction in pressure is proportional to:

$$\Delta X_G = \frac{1}{H_G}(p - p_{\text{amb}})$$

The Henry's law constants at 25°C for some gases used in DAF are given in **Table 1**.

Flotation efficiency depends on the gas used. The effectiveness of the various gases in terms of their bubble release increases in the following order: nitrogen, oxygen, natural gas (methane) and carbon dioxide. Solubility is also reduced as the dissolved solids content is increased. The amount of gas that can be dissolved ranges from 50% to 90% of its equilibrium solubility depending on the design of the pressurization system.

There are a number of ways of dissolving gas under pressure. The gas can be sparged into the liquid in a pressure vessel, liquid can be trickled over a packed bed or sprayed into an unpacked vessel, gas can be entrained with ejectors or gas can be injected into the suction side of the recycle pump.

Table 1 Henry's law constants at 25°C for various gases used in DAF

Gas	*H (atm/mol fraction)*
Nitrogen	9.08×10^4
Oxygen	4.38×10^4
Methane	4.13×10^4
Carbon dioxide	1.64×10^3

Full flow pressurization transfers gas to the whole feed flow at a relatively low pressure of between 30 and 40 psi. This technique is suitable when sufficient gas can be dissolved to effect flotation, and the passage of the whole flow through a centrifugal pump will not impair the subsequent flotation process through floc shearing.

Partial flow pressurization passes a proportion of the full flow through the pressurization system at 60–75 psi. This method reduces the size of the pressurization system, resulting in significant cost savings. This technique is suitable when sufficient gas can be dissolved to effect flotation, and passage of the partial flow through the pump will not impair flotation.

Recycle flow pressurization is used when a natural or chemically formed floc is to be separated from a wastewater. A portion of the clarified flotation effluent is recycled and used as the carrier of the dissolved gas. This latter technique is the most efficient and accounts for the majority of installations.

Figure 1 shows a flowsheet of a system operating with recycle flow, a flotation cell operating at atmospheric pressure, a pressurized retention vessel, feed and recycle pumps and a backpressure valve.

A level controller controls the flow into the pressurization vessel and excess gas may be vented. There is adequate residence time (typically 1–3 min) in the pressurization vessel for sufficient gas dissolution to take place (50–90% saturation). The pressurized liquid from the vessel is mixed with fresh feed, and is discharged through a back pressure valve to the flotation tank.

In the flotation tank, which may be circular or rectangular, the pressure is typically reduced to atmospheric pressure, and this reduction or let-down causes bubbles between 1 and 120 μm in diameter to come out of solution. Bubble size depends on the operation of the pressure let-down valve.

Gas bubbles may form by nucleation on an oil droplet or solid particle, or they may come out of solution and then attach to oil droplets and suspended solids by collision, or they may become trapped in a solid–chemical or oil droplet–chemical floc. Chemical usage is determined by the total chemistry of the system, and a series of bottle tests at site will be necessary to optimize performance.

Floated oil and suspended solids are removed by skimmers, while non-floatable settlings are removed from the bottom of the cell by a grit scraper. The efficiency of the removal process depends on the ratio of air to solids and/or oil in the water. Too little air and separation will not be achieved. Too much air and the additional turbulence may actually reduce separation performance by causing floc re-entrainment, resulting in a reduction in energy efficiency.

The DAF machine can be characterized by being a relatively quiescent, high retention time device (15–30 min), using small volumes of dissolved gas (35–180 L m^{-3} of throughput). Depending on gas type, dissolution pressure, stream temperature and suspended solids loading, DAF may achieve 80–95% removal of free and emulsified oil and suspended solids.

Induced Gas Flotation (IGF)

In the induced gas flotation (IGF) (or IAF) process, which resembles the design of a subaeration minerals flotation cell (see **Figure 2**), bubbles are induced mechanically.

IGF uses a star-shaped impeller to generate intense local turbulence. This results in subatmospheric pressures being generated in the region surrounding the impeller which causes gas to be induced from the gas space at the top of the compartment via gas inlet

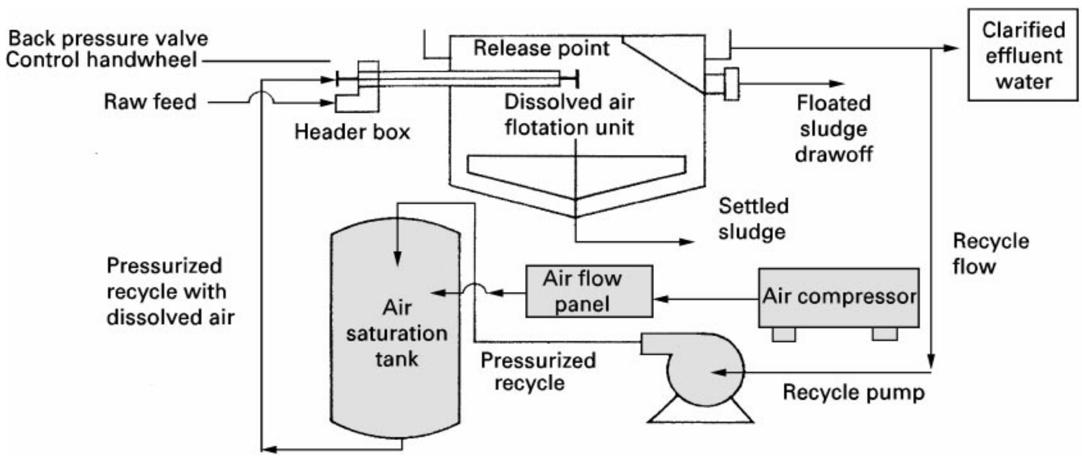

Figure 1 Flow diagram for a dissolved air flotation system. Courtesy of Baker Process.

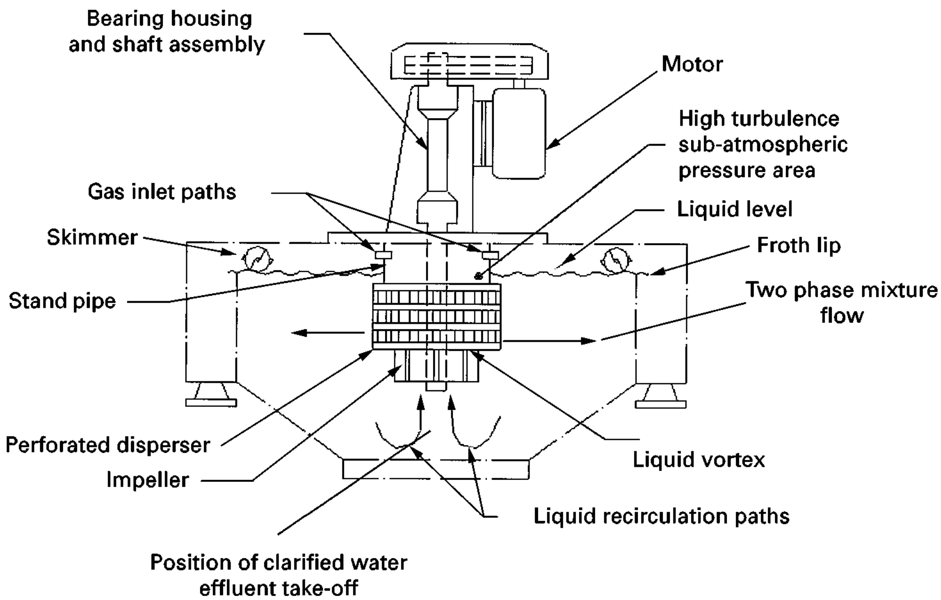

Figure 2 Transverse cross-section of mechanical induced gas flotation machine. Courtesy of Baker Process.

ducts. Impeller rotation also causes an upward circulation from the bottom of the vessel. The gas and liquid mix to form a relatively homogenous two-phase (gas–liquid) dispersion which leaves the impeller with a mainly tangential velocity. The impeller is shrouded by a perforated cylindrical disperser, which separates the intensely turbulent inner zone from the relatively quiescent outer region of the rest of the cell. The dispersion passes through the disperser, which, because of the shear resistance to the flow through its wall, reduces the size of the bubbles and improves the uniformity of their radial distribution through the main cell volume, thereby increasing the probability of a bubble–droplet collision. After attachment of the bubble to the droplet or suspended particle, separation of oil and solids occurs by flotation. The surface of the cell remains relatively quiescent as a result of the baffling effect of the disperser and hood, which minimize re-entrainment of floated oil and solids. Since the upward surface flow is uniform in the outer quiescent region surrounding the impeller, the loaded bubbles which form a froth layer at the upper surface of the cell are usually removed simultaneously from both sides of the cell.

A reduction in bubble size reduces gas flow requirements because of the more favourable surface area-to-volume ratio of the smaller bubbles. There is, however, an optimum bubble size of about 10 μm as the collision efficiency is reduced below this size. Design considerations require a balance between impeller power input and hence total gas flow, mixing region shear turbulence, surface and flotation zone quiescence, oil droplet re-emulsification and gas bubble size.

An IAF usually has four or more cells in series with a 1 min residence time per cell. This reduces flow short-circuiting, thereby improving separation efficiency. Water enters the first active flotation cell via a feedbox, and passes from cell to cell via underflow weirs in the connecting bulkheads. Floated oil is removed separately from each cell. Dispersed oil droplet concentration in the influent should typically be no greater than 500 ppm on a long-term basis of which approximately 50% is removed by each cell, the percentage removal efficiency increasing with the influent oil droplet concentration for a fixed residence time. The treated water finally enters a quiescent discharge cell with an approximately 1 min residence time where separation continues as gas bubbles, still entrained in the water leaving the last cell, rise to the surface. Individual IGF machines are typically available in different sizes to treat feed flows of between 50 and 5000 gpm (**Figure 3**).

The performance of the IGF process has been extensively investigated, and proprietary predictive mathematical models derived. In the context of the trials, the most influential variables in IGF, listed in order of decreasing importance, are:

- water-treating chemical concentration;
- feed water flow rate (relates to residence time);
- impeller speed (increasing the speed will ingest more air and increase power consumption with relatively little change in fluid circulation);
- impeller submergence (distance between the liquid surface and the top of the rotor. Increased submergence increases power draw, whilst reducing

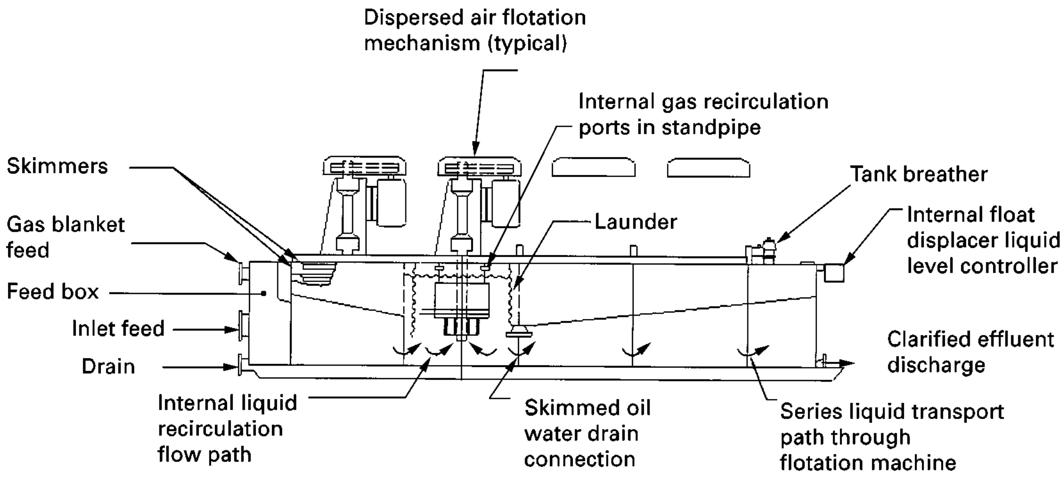

Figure 3 Longitudinal cross-section of mechanical induced gas flotation machine. Courtesy of Baker Process.

gas injection and increasing the liquid recirculation rate. Typically 200 mm);

- impeller engagement (distance from bottom of the impeller to top of draft tube. Engagement is positive if the rotor is in the tube and negative if it is above the draft tube. Influences liquid circulation. Typically 50 mm.

The order of this list may vary for different applications since removal efficiency is a strong function of the type of crude oil and the chemical composition of the feed water.

The IGF is a relatively low retention time (4–6 min) device using relatively large volumes of gas (compared to DAF) at near ambient pressure. The gas dispersion in these cells is so effective that retention times are relatively short, allowing a reduction in equipment size compared to the DAF method. The process operates at near atmospheric pressure. Both these factors give the IGF process a significant economic advantage over the DAF.

Induced Static Flotation Unit (ISF)

Since the IGF was originally developed for the mining industry, the power required by the impeller needed to be sufficient to suspend solids of perhaps 0.2–0.3 mm in diameter at concentrations of 30–40% solids. As solids removal is not the dominant process in oily water treatment, solids suspension capability can be reduced in order to achieve low turbulence in the flotation vessel at reduced power. This has led to the development of hydraulic rather than mechanical induction of bubbles (see **Figure 4**). The ISF generates bubbles hydraulically using an eductor operating under pressure, usually 60 psig rather than mechanically. Feed is added directly to the flotation vessel. Clarified effluent water is recycled through a header, and gas is drawn from the vapour space by a Venturi effect. The resultant gas–liquid mixture is directed against a striker plate, which causes the formation of numerous small bubbles that are distributed across the full cross-section of the cell. The circular cross-section of the vessel improves the uniformity of the bubble distribution in the flotation vessel, which improves the probability of bubble–droplet collision.

Unlike the IGF, the ISF operates under pressure. Pressure operation has the advantage that hazardous (hydrogen sulfide) or environmentally sensitive gases (hydrocarbons, carbon dioxide) are contained. It has also eliminated the need for transfer pumps for the clarified water effluent and the requirement for mechanical skimmers to remove the floated oil.

The ISF design reduces the number of moving parts, while maintaining performance similar to the industry-standard mechanical units. Operation of the ISF with a centrally mounted skim trough and skim cycle timers has provided the means to reduce the skim volume to less than 1% of the forward flow in most cases. It also uses less power than the mechanical IGF. All machine adjustments are external to the vessel, thereby ensuring operator safety in hazardous applications.

The use of eductors for inducing gas to generate gas bubbles in the flotation process was first patented in the mid-1970s. Initially, ISF performance was poor compared to mechanical flotation units. The design was improved by employing a cylindrical pressure vessel, centrally mounted skimmings trough for use on floating platforms and an improved eductor configuration. The most common version of the ISF has four cells, hydraulically connected in series. Increases in the clean water recycle rate will cause

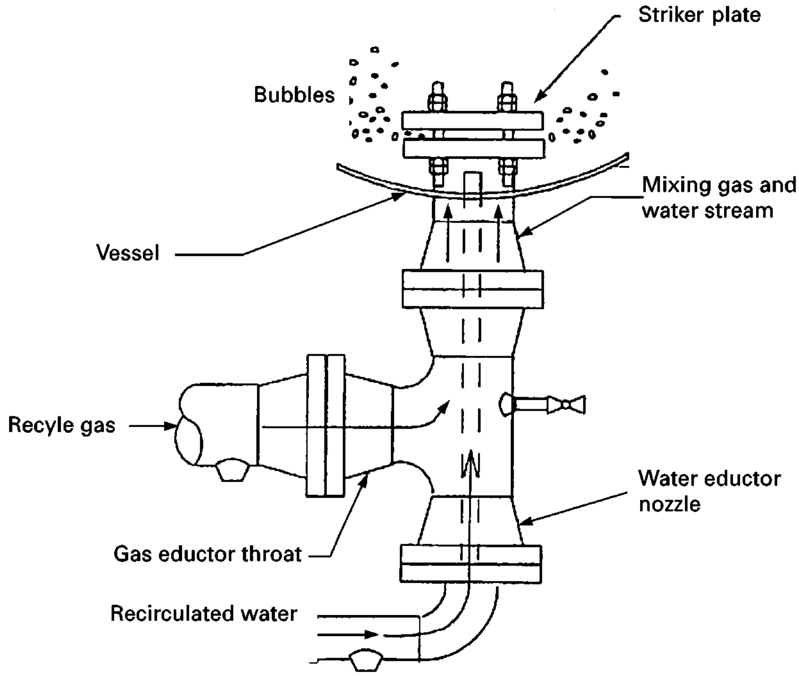

Figure 4 Eductor for hydraulic induced static flotation machine. Courtesy of Baker Process.

a progressive reduction in residence time throughout the unit, which may result in reduced bubble–droplet collision efficiency. The clean water recycle rate may be reduced by operating at a high nozzle pressure (50–100 psi).

The key features of the hydraulic flotation machine are shown in the cut-away view in **Figure 5**.

Comparison of DAF and Induced Processes

Dissolved and induced processes differ in a number of key parameters.

1. The amount of gas transferred to the process water is relatively small in the DAF process, approxim-

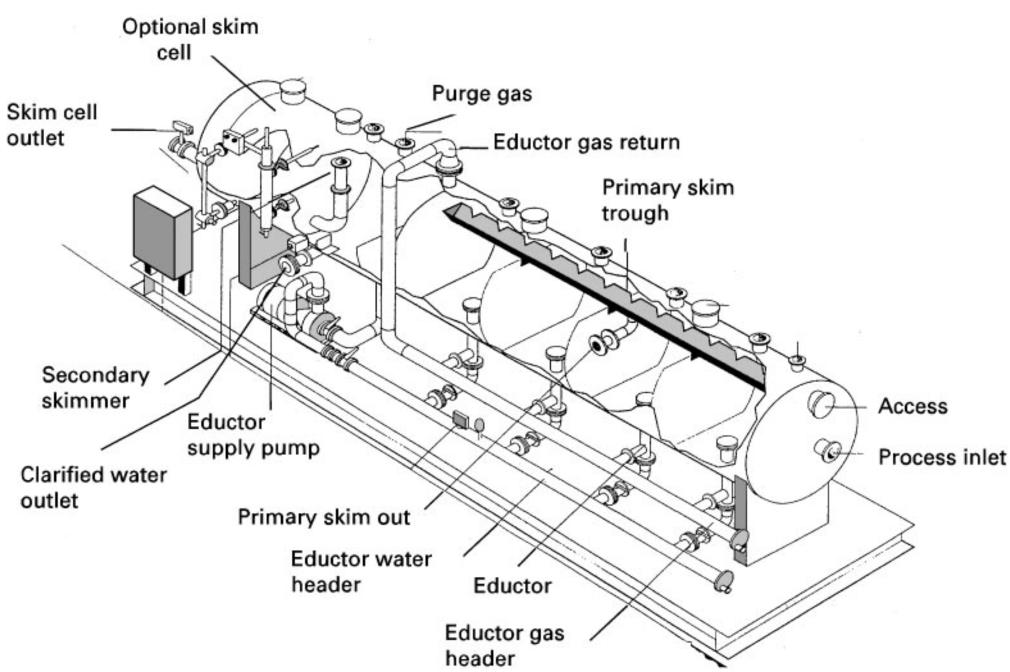

Figure 5 Hydraulic induced static flotation machine. Courtesy of Baker Process.

ately 20–40 times less than that used by the IGF process.
2. Because the DAF works by dissolution of gas in water it is sensitive to water temperature (increased temperature reducing gas solubility). By comparison, induced processes are relatively temperature insensitive. In fields where hot water or steam floods are used to recover oil, temperatures above 40°C will significantly reduce the performance of a DAF unit.
3. The means of bubble generation and mixing differs (pressure let-down in DAF vs mechanical or hydraulic induction in the IAF and ISF, respectively). Gas dissolved in the water is insignificant in process terms in the induced mechanisms since there is no pressure let-down.
4. When scaling up the process, residence time is the key variable for the IGF. For the DAF it is hydraulic loading (total process water feed divided by the vessel surface area). Hydraulic loading is related to plant floor space.

The advantages of DAF are:

1. Often lower power requirement than IGF.
2. Lower volume of skimmings as a percentage of the forward flow (1–5% for DAF systems as compared with 2–10% for mechanically induced gas systems. ISF skimmings volume compares favourably with that of DAF, being approximately 1% of the forward flow).
3. Smaller volumes of sludge may be formed than with IGF, especially where organic rather than inorganic (metallic) polyelectrolytes are used to aid flotation.
4. Better handling of suspended solids. DAF will allow the use of metal salts for coagulation and flocculation. The DAF flotation cell can also be fitted with a bottom skimmer for solid that can settle.

Advantages of induced processes are:

1. Relatively low capital cost.
2. Relatively small equipment footprint (single skid-mounted unit vs a multicomponent system).
3. Volatile organic carbons (VOC) are contained within the flotation cell. Not all DAF units use closed top flotation cells.
4. Varied flows can be handled easily.
5. Due to their high mechanical reliability, no standby capacity is required.
6. Loss of one cell will not significantly reduce separation efficiency, allowing on-line maintenance of impeller mechanisms.
7. Lower chemical consumption, since flocculation is not necessary.

In certain applications, such as removal of mineral oils from a steel rolling mill effluent, induced and dissolved process have been used in series.

Chemical Selection

From a chemical addition standpoint the two types of flotation differ due to the size of the bubble each creates:

- induced gas typically creates a relatively large gas bubble in the 10–2000 μm range;
- dissolved gas typically creates a relatively small gas bubble in the 1–100 μm range.

Dissolved Gas

In this instance, chemical treatment is used to flocculate the oil droplets and solid particles. The larger the floc, the more gas bubbles are trapped underneath the floc structure. The flotation process is significantly more quiescent than the induced processes, hence does not tend to break up flocs. Separation is therefore based on the amount of bubbles that are trapped underneath the floc, and the maintenance of uniform flow distribution to avoid floc shearing. The influent/gas bubble carrier flow distributor and mixing chamber design determines the efficiency of a DAF unit.

Ferric compounds work in a similar way to cationic polymers except where polymers are specific to the charge on the oil droplet; metal salts swamp the bulk solution leading to charge destabilization by dissociating on addition to water. As a result, the dose rate is typically higher than for a solution polymer. The solubility of metal ions is limited and hence they tend to generate weak flocs, which means that they are better used as part of a two-stage treatment, usually in conjunction with an anionic polymer. As an example, one facility described by Berne and Cordonnier uses 10 mg L^{-1} aluminium sulfate with 1 mg L^{-1} anionic polyelectrolyte. However, this does result in a large volume of sludge, 10–30 m^3 day^{-1} in this case. Use of organic coagulants alone can significantly reduce sludge volumes (3–5 m^3 day^{-1} in this example).

Induced Gas

The objective of chemical treatment is to change the surface charge of either the gas bubble or the oil droplet in order to cause adhesion between them after collision. The size ratio of the bubble-to-oil droplet is usually $\leq 1:1$. The only solids that are floated are those whose surface charge is opposite to that on the bubble surface, or those that are associated with, and contained in, the oil droplet. For this reason, induced processes may only remove 55–75% solids from the forward flow as compared with 95–98% oil droplet removal. No attempt is made to flocculate oil droplets and solid particles, because the mixing intensity in the units will tend to break up any floc structure that has been formed.

In general, oil droplets and other suspended material will be negatively charged. Addition of cationic polymer neutralizes the charge on the oil–gas species, while a long-chain polymer collects the contaminant in preparation for removal. Most cationic polymers work best in the pH range 6–9. If the pH falls outside this range, pH adjustment of the wastewater may be required. Overall removal rates are around 90% without chemicals up to 98% with chemicals. In order to size a unit for commercial use, laboratory studies are conducted to determine the effect of variables such as rotor speed, chemical addition and feed rate on oil removal, all of which have an impact on the rate constant K. The data are then fed into proprietary models based on the Klimpel model, which contain correction factors for scaling up the equipment. The models have been validated using numerous sets of data from commercial installations. Oil–water separation is enhanced by using an emulsion breaker, a cationic high charge density, low molecular weight coagulant polymer. The polymer is distributed throughout the continuous (water) phase where it neutralizes the anionic charge at the oil–water interface. This destablizes the emulsion, allowing oil droplets to coalesce by collision with one another.

Cationic solution polymers would usually be applied as a 1–10% solution with a dose rate of 2–30 ppm. Emulsion polymers (tightly coiled polymer molecules entrapped in solvent, activated by dilution in water) are applied at concentrations no greater than 1–2% at dose rates of 0.5–5.0 ppm.

Future Developments

Hydrocyclones and Flotation

Flotation was practised extensively on fixed offshore platforms throughout the 1970s and 1980s to clean-up produced water prior to overboard discharge. As the volumes of produced water have increased with field life, water-handling facilities have become constrained. Operators have retrofitted produced water processing capacity using hydrocyclones rather than flotation machines, because the former have a smaller footprint per volumetric flow rate of produced water treated. However, flotation oil–water separation technology has a place on offshore platforms as a polishing stage for produced water clean-up following initial treatment by hydrocyclones. One design uses what is in principle a dissolved air flotation vessel downstream of the oil–water separation hydrocyclones.

Motion Insensitive Flotation

With the increased use of floating production facilities, the motion experienced by flotation devices

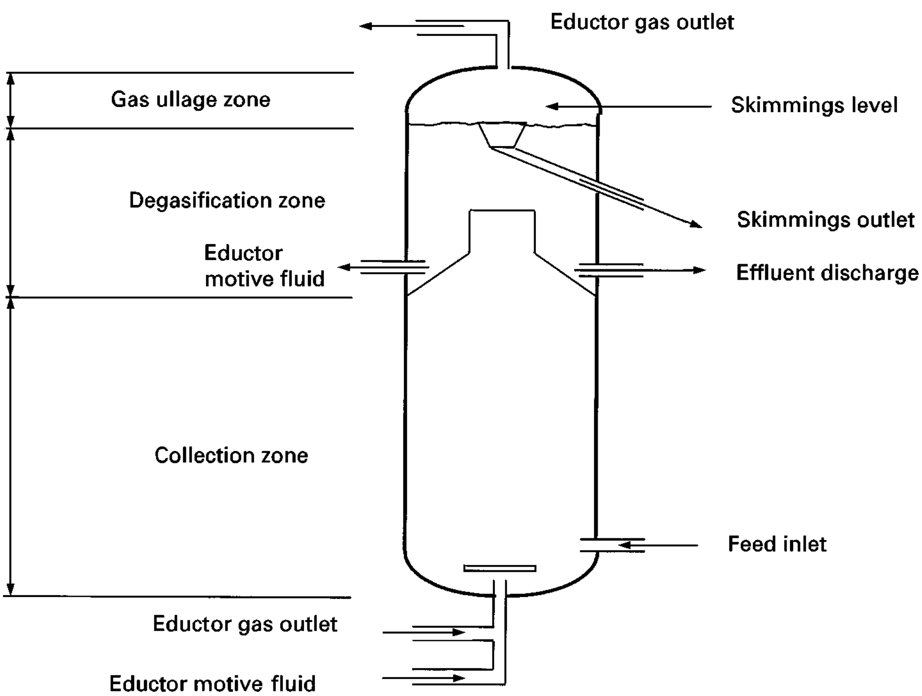

Figure 6 Single cell ISF. Courtesy of Baker Hughes Process Systems.

inhibits separation. A 2° tilt results in one end of a 12 m long flotation machine being approximately 350 mm higher than the other end of the vessel. This results in one end of the machine flooding while the other end will not remove floated oil. To overcome this problem, one manufacturer has designed a flotation column ISF machine that reduces the impact of pitch and roll to 10 mm at 2° tilt.

The method of bubble generation (eduction) is the same as that used for the four-cell ISF. Sparging was investigated as an alternative, however the bubbles were larger and moved in a linear fashion to the surface. Educed air forms smaller bubbles and exhibits random movement. Both these latter characteristics are desirable as they increase the chance of an air bubble–oil droplet collision.

Since the single-cell ISF has one rather than four cells, theory would predict that its contaminant removal efficiency would be reduced from approximately 90–98% for a four-cell unit to 80–90% for a single cell unit, primarily because the residence time in the single cell unit is some 65% of that in the traditional four cell design. In trials, however, the unit has operated successfully with inlet oil concentrations of between 50 and 1300 ppm, and suspended solids concentrations of 10–50 ppm, and has achieved oil removal efficiencies comparable to the four-cell model, taking into account the reduced residence time in the single cell. In service, actual efficiencies will depend on optimization of flow regime and chemicals (see **Figure 6**).

See Colour Plate 45.

See also: **II/Flotation:** Column Cells; Cyclones for Oil/Water Separations; Historical Development.

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Pre-aeration of Feed

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Introduction

Aeration of slurry is a key element in a flotation system. The extent of aeration influences the performance of flotation machines and the overall recovery process. Flotation can, in general, be divided macroscopically into two subprocesses: selective collection of hydrophobic particles by air bubbles, and separation of bubble/particle aggregates from the pulp containing hydrophilic particles. The method and location of aeration or bubble generation control the mechanism of particle collection by either collision with and subsequent attachment to bubbles, or *in situ* bubble formation on hydrophobic particle surfaces. A flotation machine should be designed to provide an