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# Gas Flotation for Subsea Produced Water Treatment - Development of a Method

Master's thesis in Chemical Engineering

Supervisor: Gisle Øye

Co-supervisor: Martina Piccioli

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Department of Chemical Engineering





## **Abstract**

In oil recovery industry, produced water is the largest waste stream by volume, and the fractions of water to hydrocarbons that are extracted from oil wells tend to increase over time. To ensure proper handling of produced water in accordance with regulations, a series of treatment steps has to be applied. Gas flotation is often included, and it is a common and well established technology for separation of oil and water at topside facilities. However, since produced water is usually either discarded into the ocean or reinjected into wells for pressure maintenance, there could be potential benefits like reduced capital costs and lower energy requirements if the treatment could be applied at seafloor level rather than topside. To explore how gas flotation could be affected by subsea conditions, a range of pressures, temperatures and retention times were tested on batches of synthetic produced water using a high-pressure, high-temperature gas flotation rig. Some gravity separation experiments were also conducted for comparison and to measure the impact of applied gas flotation. It was found that increasing all parameters will probably have a positive impact on separation efficiency, where an increase in temperature seems to have the largest effect. The results range from 24% to 89% oil removal efficiency. This could indicate that the high pressures found on the seafloor could be suitable for potential subsea processing units.

## Sammendrag

I oljeutvinningsindustrien er produsert vann den største avfallsstrømmen målt i volum, og fraksjonene av vann til hydrokarboner som utvinnes fra oljebrønner har en tendens til å øke over tid. For å sikre riktig håndtering av produsert vann i henhold til regelverket, må en rekke behandlingstrinn brukes. Gassflotasjon er ofte inkludert, og det er en vanlig og veletablert teknologi brukt til separasjon av olje og vann ved overflaterigger. Men siden produsert vann blir vanligvis enten kastet i havet eller reinjisert i brønner for vedlikehold av trykk, kan det være potensielle fordeler som reduserte kapitalkostnader og lavere energiforbruk dersom behandlingen kan foregå på havbunnen istedet for på overflaten. For å utforske hvordan gassflotasjon kan bli påvirket av forholdene på havbunnsnivå ble en rekke trykk, temperaturer og retensjonstider testet på partier av syntetisk produsert vann ved bruk av en gassflotasjonsrigg. Noen gravitasjonsseparasjons eksperimenter ble også utført for sammenligning og for å måle virkningen av gassflotasjonen. Det ble funnet at økning av alle parametere sannsynligvis vil ha en positiv innvirkning på separasjonseffektiviteten, og økning i temperatur ser ut til å ha størst effekt. Resultatene varierer fra 24% til 89% separasjonseffektivitet. Dette kan tyde på at det høye trykket på havbunnen kan være egnet for potensiell undervannsbehandling av produsert vann.

## Acknowledgement

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# 1 Introduction

For the continuous development of sustainability in the oil recovery industry, there are countless efforts being made to ensure that operation and evolution of industrial processes are showing improvements in terms of carbon footprints, emissions and the release of potentially harmful substances from the confines of subterranean oil and gas wells into environments at the surface of the earth. One important aspect of this work is related to what is called produced water (PW), that is water extracted from these wells along with the precious hydrocarbons that are of great value to industries and economies all around the globe. One of the separation techniques that are widely used for treatment of PW is gas flotation, which is designed to separate small oil droplets from water.



Figure 1: Photograph of an offshore oil rig

Source: [shorturl.at/ouT35](http://shorturl.at/ouT35)

In this thesis, a high-pressure, high-temperature gas flotation rig was used to pressurize and pass small bubbles of nitrogen gas through an emulsion of oil in water. This emulsion was designed to emulate the properties of PW that would be subject to gas flotation in an authentic offshore industrial setting. The goal was to examine a range of parameters and the effects they have on the oil contents of the samples that are extracted from the flotation cell after the gas bubbles have passed through. To analyze and verify the results, analytical tools like UV-vis spectroscopy and laser scattering were used.

The thesis is largely a continuation of the work done in relation to a project report that was written one semester earlier by the same author. The laboratory work picks up at the point of conclusion from this report and is, in addition to the exploration of applied gas flotation, an attempt to rectify the inherited challenges that were not solved by the end of the previous semester. Some of the work for this thesis is also done in collaboration with the author's co-supervisor, as it is also partly the subject of their forthcoming PhD thesis.

## 2 Background

### 2.1 Oil Recovery and Produced Water

#### 2.1.1 What Is Produced Water?

Produced water is a collective term for water that is extracted along with hydrocarbons during upstream oil recovery processes. It is a complex composition of dissolved hydrocarbons, gases, minerals, sediments, ions, acids, production chemicals and possibly other contaminants. Thus, it can be categorized as an environmental hazard and pollutant and it is the largest liquid waste stream of the entire oil recovery industry (Jiménez et al. 2018, Liu et al. 2021, Nešić and Streletskaia 2018). A significant fraction of the volumes that are extracted from oil wells is actually water, and it is estimated that there is approximately a 3:1 - 4:1 ratio of water to hydrocarbons extracted from oil wells on a worldwide basis (Eftekhardakhah et al. 2015, Fakhru'l-Razi et al. 2009, Skjefstad and Stanko 2017). Over time, the quantity of PW in the production stream from a well will steadily increase until production is no longer financially viable. Figure 2 shows a graph of the outputs of oil and water from a generic oil field:

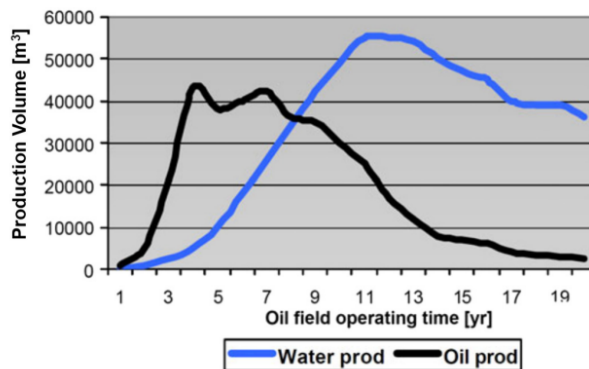


Figure 2: Production profile of a typical oil field

Source: Liu et al. 2021

On the Norwegian Continental Shelf, a total produced water quantity of 190 million m<sup>3</sup> was recorded in 2015, that is more than twice the the amount of produced oil (Skjefstad and Stanko 2017). This underlines the need for proper handling, and PW and as per regulations it must be treated to a certain level of purity before it can be discarded or eventually injected back into other wells. Over the years, the regulations are becoming more and more strict, and as per 2022 the maximum allowed oil concentration in PW before it can be discarded has been set to 30 parts per million (OSPAR 2011). To reach these levels, PW has to undergo a series of treatment steps, each gradually decreasing the

contents of oil and other unwanted constituents.

### 2.1.2 Origin and Production of Produced Water

Naturally occurring rocks in subsurface formations may contain fluids such as oil, gas and saline water (Fakhru'l-Razi et al. 2009). Light hydrocarbons migrate to trap locations where it displaces the water, and over time, the reservoir rocks absorb the fluids. When wells are accessed and production begins, a mixture of all these fluids is extracted simultaneously. Water may be injected during well production and pressure maintenance activities. As such, it is a very important production fluid and it is added in large quantities during oil recovery, not only in offshore wells, but also during recovery from more unconventional sources like shale, oil sands and coal beds (Jiménez et al. 2018). As wells age, the output ratio of water to hydrocarbons tend to increase due to oilfield maturation. During the lifespan of a well, this ratio may increase from a few percent in initial stages up to 95% towards the end of the extractions (Dudek, Kancir, et al. 2017, Fakhru'l-Razi et al. 2009, Nešić and Streletskaya 2018). There are many factors that can contribute to the amount of produced water from an oil well, including for example the method of drilling, location of well within homogeneous or heterogeneous reservoirs, the use of injection water, the mechanical integrity of the well bore and the maturation of different zones in the well over time to name a few. The amount of PW from a well can also be driven down by better management methods and the introduction of new oil fields. The volume of PW has steadily increased worldwide at least since 1990 (Fakhru'l-Razi et al. 2009).

### 2.1.3 Composition of Produced Water

PW is considered waste due to the various components that it contains, some of which are categorized as crude oil. Oil is made up of a number of different hydrocarbons including benzene, toluene, ethylbenzene and xylene (BTEX), naphthalene, phenanthrene, dibenzothiophene, polyaromatic hydrocarbons and phenols (Ekins et al. 2007, Nešić and Streletskaya 2018). Most of these compounds are actually insoluble in water, and the oil can be considered dispersed as droplets in the water phase, though some of the more polar components, like propionic acid and formic acid may dissolve in the water phase. The amount of dissolved organics may increase with pressure, temperature and pH, but is unaffected by salinity (Fakhru'l-Razi et al. 2009). The amount of organics dissolved in water is dependent on oilfield maturation, the composition of the crude oil and the volume of water production. The amount of dispersed oil and the size of the oil droplets depend on the crude oil density, the amount of shear forces that are applied to the droplets, the amount of oil precipitation and interfacial tension between oil and water (Stephenson 1992).

PW will also contain inorganic dissolved materials like ions and heavy metals. Example of cations may include  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Fe}^{2+}$ , while anions may include  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  (Hansen and



Davies 1994). The amounts of these ions vary from 200 ppm to 300 000 ppm, which is saturation, but typical values are located in the range of 80 000 - 120 000 ppm (Rawlins and Ly 2012). This may of course affect the salinity of the water (especially  $\text{Na}^+$  and  $\text{Cl}^-$ ), and may alter the scale potential as well as the viscosity and density (Igunnu and Chen 2012, Rawlins and Ly 2012). Trace amounts of heavy metals like cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc may also be found, and the amounts depend on well age and formation geology.

Although not found naturally in reservoir fluids, production chemicals will also be a constituent of PW when it reaches the surface (Stephenson 1992). These are mainly added to assist the extraction process and prevent flow issues and other production problems. This class of chemicals may include scale- and corrosion inhibitors, emulsion breakers, anti-foam and water treatment chemicals. The concentration of these can be as low as 0,1 ppm.

#### **2.1.4 Handling of Produced Water**

In offshore oil recovery industry, produced water is usually either discarded into the ocean, or injected back into oil wells to maintain well pressure (Clark and Veil 2009). In any case, PW must be treated to meet specific regulations. There are a wide variety of PW processing methods that can be applied which will not be discussed in this thesis like sand filtration, use of bacteria or other biological materials, evaporation, electrochemical processing, demulsification and photocatalytic treatment to name a few (Fakhru'l-Razi et al. 2009). For the purpose of this thesis, a generic system using gravity separation, hydrocyclones and gas flotation separation will be considered. Imagine then a processing setup as illustrated in figure 3:

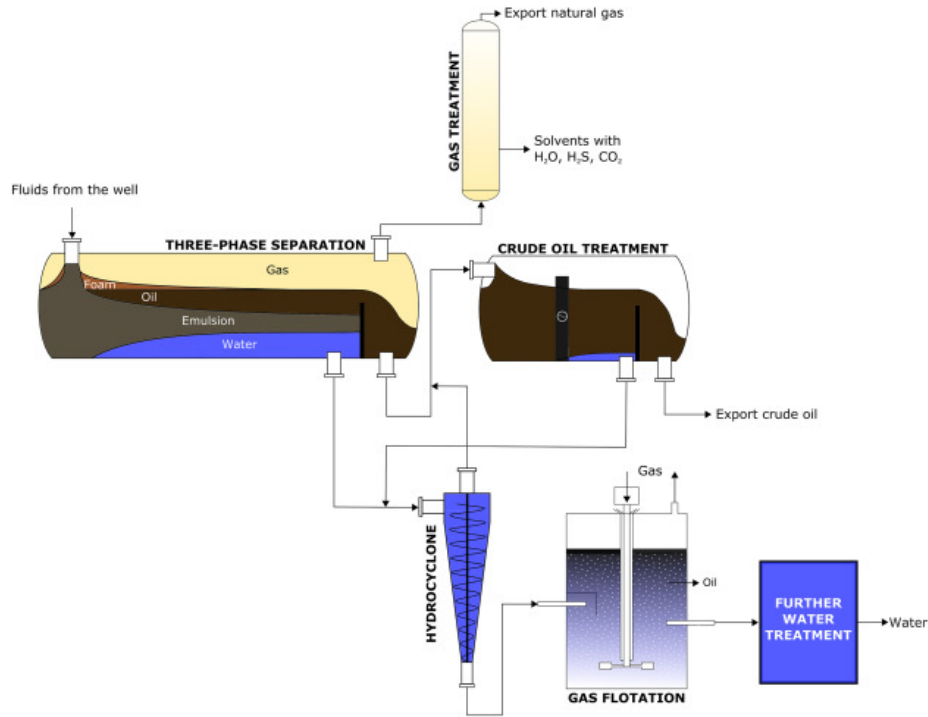


Figure 3: Schematic drawing of an oil/gas/PW processing setup including gravity separators, hydrocyclones and a gas flotation unit

Source: Dudek, Vik, et al. 2020

When fluids from the well first enter the production line, it is fed into large tanks called gravity separators or bulk separators. At this point, the input fluids are a sludgy mix of components as outlined in chapter 2.1. Here the main objective is to separate the bulk volumes of water and oil in addition to the amount of gas that may be present, dissolved or not. Most of the gas will quickly escape the oil/water mixture and will be removed from the top of the separator. The remaining oil and water will have a density difference, so separation will occur over time in accordance with Stoke's law which is shown in equation 1 (Eftekhardadkhah et al. 2015):

$$v = \frac{2 R^2 (\rho_2 - \rho_1) g}{9 \eta} \quad (1)$$

$v$  is the droplet velocity,  $\rho_2 - \rho_1$  is the density difference between the two phases,  $g$  is the gravitational acceleration and  $\eta$  is the viscosity of the continuous phase. This phenomenon is called gravity separation and it is commonly exploited in petroleum recovery industry (Piccioli et al. 2020). As the oil has lower specific gravity, this will separate from the water by creaming to create a bulk phase on top of the water, and can be skimmed off at the end of the separator for

secondary and tertiary processing steps, producing valuable petroleum products. One of the problems with gravity separation in the context of PW treatment is that there are usually very large volumes that need to be separated, and this means the processes have to be fast to maximize the efficiency and minimize the size requirements of equipment. As shown by Stoke’s law, the droplet velocity is heavily dependent on droplet size, which means that the smaller the droplets, the slower they separate from the continuous phase. Due to the high pressures and large amounts of shear forces applied to oil droplets in wells during transport through pipes/valves in production setups, the drop size distribution of oil may consist of droplets that are so small that gravity separation will be ineffective, because the smallest droplets will stay dispersed (Nešić and Streletskaya 2018). To ensure that sufficient amounts of oil are removed from the PW in order to fulfill regulations, there is a need for additional treatment downstream of the gravity separators.

In the following step, the bottom fraction consisting mainly of PW is fed into hydrocyclones. These can remove solid particles and dispersed oil droplets with a diameter equal to or greater than 10 microns (Rawlins and Ly 2012, Kharoua et al. 2010). Hydrocyclones are relatively simple devices designed to utilize centrifugal forces to separate a dispersed phase from a continuous phase, and they can be designed for liquid-liquid or liquid-solid separations (Kharoua et al. 2010). Hydrocyclones can be affected by substantial turndown rates as they are susceptible to frequent blockage and must be back-flushed regularly (Zhao et al. 2020). This is why there are some PW processing setups that do not utilize hydrocyclones at all. In any case, OSPAR regulations will most likely not be met at this level of treatment, and this is the point where gas flotation may be applied.

## **2.2 Gas Flotation**

### **2.2.1 Gas Flotation in Offshore Oil Production**

Gas flotation is a separation technique often used in oil recovery industry (Piccoli et al. 2020, Nešić and Streletskaya 2018). It is largely based on the same principle as both gravity separation and centrifugation, that is Stoke’s law (Eftekhardakhah et al. 2015). The main objective of applied gas flotation in offshore industry is to increase separation of oil and water by passing gas bubbles through produced water (Igunnu and Chen 2012). This method relies on the attachment of oil droplets onto gas bubble surfaces as the bubbles travel through the water. If this attachment is successful, the effective density of the oil is reduced, and Stoke’s law states that separation velocity should be increased as gas and water has a much higher density difference than that of oil and water. Also the gas bubbles may have a larger diameter compared to the dispersed oil droplets, which may also significantly increase separation velocity compared to the oil droplets alone (Rawlins and Ly 2012).

### 2.2.2 Induced and Dissolved Gas Flotation

There are two main methods of gas flotation which are usually used for PW treatment (Piccioli et al. 2020). One is induced gas flotation (IGF), and when using this method, gas bubbles are generated mechanically or hydraulically. This generates gas bubbles in the size range of 100-1000  $\mu\text{m}$ . During mechanical IGF, the gas bubbles are introduced to the water through flow eddies generated by mechanical impellers. During hydraulic IGF, small bubbles are generated as the gas is subjected to shear forces as it passes through some valve or orifice. The generation of bubbles through hydraulic IGF is illustrated in figure 4:

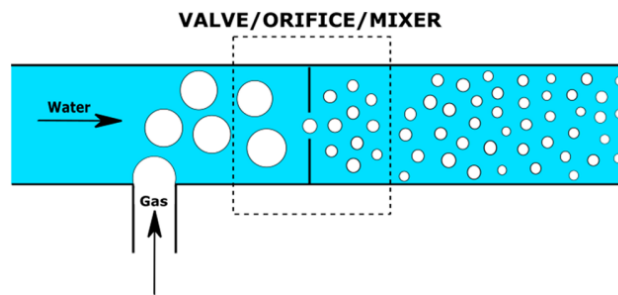


Figure 4: Illustration of bubble generation through hydraulically induced gas flotation

Source: Piccioli et al. 2020

The second method is dissolved gas flotation (DGF) and when using this method, small bubbles in the size range of 10-100  $\mu\text{m}$  are created by reducing the pressure in a tank where gas is dissolved in the fluid. Upon pressure decrease, nucleation occurs and bubbles form.

### 2.2.3 Gas Bubble and Oil Droplet Attachment

Beyond the simple Stokesian buoyancy calculation, the bubble-droplet attachment mechanisms in the system can be examined as this is generally considered to be the rate determining step in flotation (Oliveira et al. 1999). There are four different attachment mechanisms that can occur between the two phases; full or partial encapsulation, formation of buoyant mats due to bubble clustering, gas nucleation on oil droplets and transport of oil in the turbulent wake of gas bubbles (Rawlins and Ly 2012). Given sufficient droplet size, the gas and the hydrocarbons will come in contact, and after water film thinning and breakage, the two can merge to form either an oil film, an oil lens or a point attachment. The steps involved in gas bubble encapsulation are illustrated in figure 5:

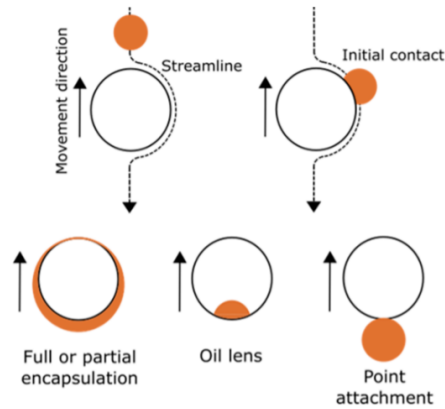


Figure 5: Attachment mechanism between oil droplet and gas bubble to form either an oil film, oil droplet or a point attachment

Source: Rawlins and Ly 2012

There are several sub processes that are taking place during the water film breakage: the approach of gas bubbles and oil droplets and the thinning and rupture of the film upon approach before the subsequent rise of the coalesced phases. The time required for the film to reach critical thickness, that is the thickness at which point the film breaks, is called the drainage time (Piccioli et al. 2020). This is the most important factor affecting the attachment, and is therefore a crucial parameter for successful gas flotation (Yan et al. 2020, Ralston et al. 1999). The film should drain and rupture as fast as possible to form a stable bubble-droplet aggregate, which in turn causes greater separation efficiency (Eftekhardakhah et al. 2015). It has been reported that the critical film thickness is close to  $0,1 \mu\text{m}$ , at which point strong molecular forces come into effect, causing the film to rupture (Oliveira et al. 1999). A study by Yan et al. showed that the main driving force behind film drainage is the Laplace pressure, indicating that smaller bubbles, which have a higher Laplace pressure, will increase film discharge velocity and lower the drainage time (Yan et al. 2020). Smaller bubbles can also lead to a larger surface area for attachment between droplets and bubbles, and may also increase the collision frequency (Strickland 1980). These effects will all have a positive influence on separation efficiency. Experiments have shown that larger droplet sizes will also lower the drainage time and increase separation (Eftekhardakhah et al. 2015). As such, it can be concluded that the relative size difference between the droplets and the bubbles play a central role in flotation efficiency.

The attachment is governed by the oil spreading coefficient, which is a function of the surface tension between the phases, and free energy minimization. The spreading coefficient is given by equation 2:

$$S_0 = \gamma_{wg} - \gamma_{ow} - \gamma_{og} \quad (2)$$

$\gamma_{wg}$  is the surface tension between water and gas,  $\gamma_{ow}$  is the surface tension between oil and water and  $\gamma_{og}$  is the surface tension between oil and gas. If the condition of complete wetting is fulfilled (i.e.  $\gamma_{wg} = \gamma_{ow} + \gamma_{og}$ ), full encapsulation of the film across the droplet surface will occur. This will be the most optimal condition for separation, as this causes the strongest interaction between oil and gas. This makes the coalesced phases more resilient to detachment due to shear forces from the fluid streams compared to other forms of attachment (Piccioli et al. 2020).

#### 2.2.4 Compact Flotation Units

In offshore installations, the Compact Flotation Unit (CFU) is used when applying gas flotation and this is usually placed downstream of the gravity separators and the hydrocyclones. CFUs combine both induced and dissolved gas flotation as a combination of the methods are shown to be the most effective (Eftekhardakhah et al. 2015, Piccioli et al. 2020). CFUs are designed for minimal weight and motion sensitivity, and also for optimal oil removal efficiency and simple operation. Most CFUs are continually fed and have a retention time of less than one minute, making them able to handle a throughput of up to 900 m<sup>3</sup>/h (Piccioli et al. 2020).

#### 2.2.5 Subsea Produced Water Treatment

Although the use of CFUs is a well-established practice on topside offshore rigs since the early 2000s, there is increasing interest in developing subsea processing units with the aim of processing PW at the seafloor. This is due to several potential benefits of being closer to the wells (Zhao et al. 2020, Bhatnagar and Sverdrup 2014). There are costs both in terms of capital investments and energy demand related to the transportation of the vast volumes of water to the topside installations. Also, there are major costs and challenges related to revamping old topside facilities to adapt to the increasing fractions of PW as time passes. This includes limited access, available space and load capacity of production units (Skjefstad and Stanko 2017). If PW could be treated completely at the seafloor, it could reduce the CO<sub>2</sub> footprint as well as operational and capital costs and it could increase lifetime of installation, production rates and generate increased returns for the operators. In addition, a subsea unit could be beneficial for reinjection of produced water to prevent loss of well pressure (Zhao et al. 2020). Especially in regards to the new regulations per the European Commission for new installations, reinjection of fluids into wells would be the most feasible technology if a zero-emission goal is to be met (European Commission 2019). There are some projects that have explored subsea technology for PW treatment. Hydrocyclones for subsea treatment is currently used on Marlim, while Troll Pilot and Tordis installations use horizontal gravity separators (Skjefstad and Stanko 2017). Gas flotation and the topside CFU has been

considered promising for subsea development, but has not been demonstrated in large-scale setups with relevant subsea pressures (Zhao et al. 2020). This is why pressurized gas flotation in combination with varying temperatures is the main goal of the experimental work conducted in relation to this report.

Zhao and colleagues have conducted high pressure flotation experiments using a pilot subsea CFU (Zhao et al. 2020). A continually stirred and continually fed unit was used to subject PW to gas flotation at pressures of 16, 53 and 90 bar. Working criteria of their experiments include temperature set to 52°C, Dv50 in the range of 10-20  $\mu\text{m}$  and an inlet PW oil concentration of minimum 100 ppm. The average oil removal efficiency was shown to increase quite dramatically by increasing the pressure from 16 bar to 53 bar, going from approximately 27% removal up to 52%. The trend curve then flattened when pressure was increased further to 90 bar, resulting in an oil removal efficiency of approximately 55%. The conclusion was that operating a flotation unit at elevated pressure seemed to increase the oil removal efficiency, which indicates that the CFU could be a viable solution in treating PW at subsea conditions.

### **2.2.6 Effect of Pressure and Temperature on the System**

As higher pressure is applied, the thermodynamic equilibrium of the fluid system is shifted (Zhao et al. 2020). Gas solubility increases with pressure, and since gas is added during flotation, this has to be taken into account. An increase in pressure is expected to have some influence on gas flotation separation efficiency as it can not only affect solubility, but also alter densities, viscosities, interfacial properties, and the size of the bubbles and droplets (Piccioli et al. 2020). The effect on interfacial tension is relatively low, but the effect on gas density is substantial when pressure is increased. This causes an increase in breakage and stability of nitrogen gas bubbles, and decreasing bubble velocity, causing higher chances of droplet-bubble interactions.

An increase in temperature can also have an impact on several properties of the system. A change in temperature can influence density, viscosity, interfacial tensions, solubility of gas and oil components, and dimensions of gas bubbles (Piccioli et al. 2020). Raising the temperature decreases the viscosity and density of all phases, which are determining factors in separation velocity as stated by Stoke's law. It can also cause an increase in coalescence frequency, shifting the drop size distribution and thereby destabilizing the emulsion. The net effect of an increase in temperature has been shown to have a positive effect on separation efficiency (Aliff Radzuan et al. 2016). However, there may be some conflicting phenomena, as the changes in interfacial tension between the phases may cause droplet breakage to occur more frequently subsequently causing separation to decrease (Rawlins and Ly 2012). In addition, an increase in temperature can cause some adsorption of dissolved components at bubble surfaces which could alter the bubble-droplet interactions (Eftekhardadkhah et al. 2015).

## 3 Method

### 3.1 UV-Vis Spectroscopy

In the analytical stage of the experimental work, UV-Vis molecular absorption spectroscopy was used to find concentrations of oil in dichloromethane. This was done through the application of an Agilent Cary 3500 UV-VIS Double beam Spectrophotometer. This instrument passes ultraviolet and visible light through cuvettes, one containing pure solvent for reference, and one or more extracted samples subject to analysis (Skoog et al. 2017). When light passes through the liquids, some of the light will be absorbed due to the presence of certain molecules in the sample. The difference in intensity between light output and input is recorded as absorbance by a spectrophotometer at the other end in accordance with Beer's law, which is shown in equation 3:

$$A = \log \frac{P_0}{P} \quad (3)$$

$A$  is absorbance,  $P_0$  is the incident radiant power, also called the incident beam, and  $P$  is the transmitted radiant power, or the emergent beam. It is based on the principle that light passes into the sample with a certain strength, and comes out with reduced intensity due to molecular light absorption and scattering. The useful information from these experiments will be the absorbance of the solute, not the absorbance of the solvent or the container. A reference sample of pure solvent is analyzed parallel to the sample containing solute such that "ambient" absorption or scattering can be accounted for. It can be shown that the absorbance of the sample has an approximate linear correlation to the concentration of dissolved components in the sample. As such, higher concentrations of components in the sample will cause more light to be absorbed. However, this is only accurate to a certain extent. Beer's law has limitations, and one of the conditions for validity is that the sample must have sufficiently low concentration (usually less than 0,01M), such that solute-solvent, solute-solute and hydrogen bonding interactions do not affect the absorption rate, which would subsequently affect the linear relationship.

### 3.2 Calibration Curve

To know what concentration an unknown sample had by reading the absorbance, a calibration to obtain a reference curve had to be made. This was done by analyzing a range of samples with known concentrations, and using the results to conduct a linear regression. A stock solution of approximately 1000 ppm crude oil in DCM was made, and this was used to make 13 standards used for the calibration. This was done by weighing a certain amount of the stock solution and adding DCM to reach a total sample weight of approximately 10 grams. The concentration of each standard is shown in table 1:



#	Added stock (g)	Sample weight (g)	Sample conc (ppm)
1	0,104	9,993	10,404
2	0,202	10,000	20,194
3	0,301	10,002	30,085
4	0,400	10,001	39,984
5	0,506	9,999	50,589
6	0,598	10,003	59,764
7	0,796	10,096	78,819
8	1,004	10,016	100,209
9	1,207	10,007	120,578
10	1,405	10,008	140,344
11	1,706	9,997	170,599
12	2,017	10,006	201,517
13	2,307	9,998	230,675

Table 1: Concentrations and contents for each of the standards used for calibration

These concentrations were input in the spectrophotometer software, and each corresponding sample was scanned to measure the absorbance in the range of 200-900 nm. The absorbance is measured for each wavelength, and the absorbance for each standard as a function of the wavelength is shown in figure 6:

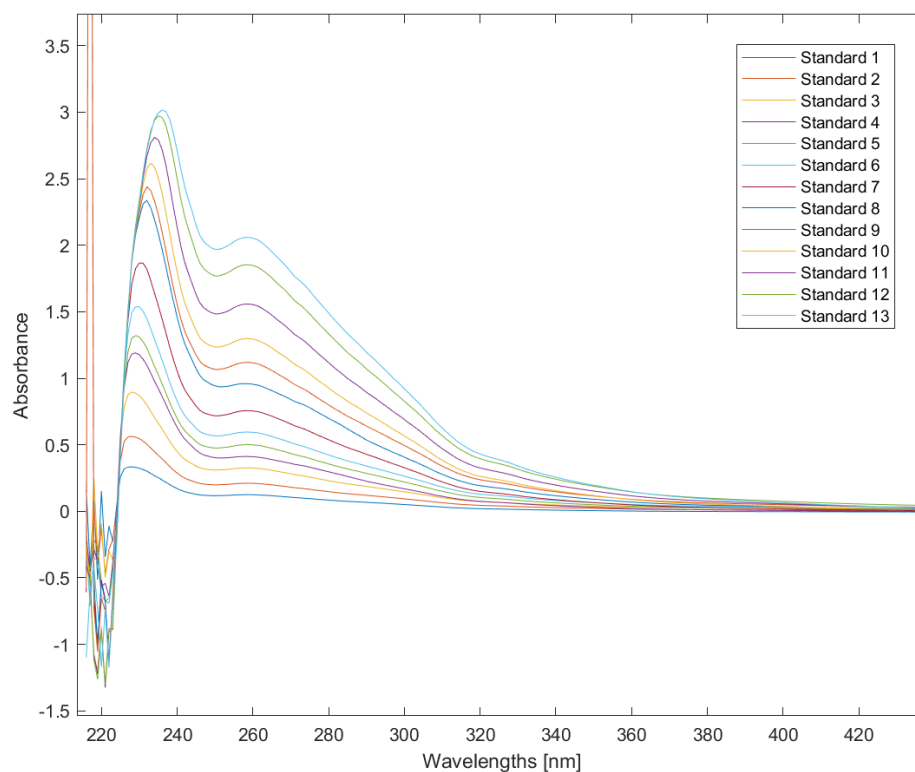


Figure 6: Absorbance profiles for all standards as a function of wavelengths of light

According to the literature, the sensitivity of the instrument is usually highest at local absorbance maxima because the change in absorbance per unit of concentration is greatest at these points (Skoog et al. 2017). As such, a wavelength of 260 nm was chosen for analysis. Linear regression was done to obtain the reference curve on the form  $f(x) = ax + b$ , where  $f(x)$  is the concentration and  $x$  is the sample absorbance. The instrument was then ready for use. A graph showing the reference curve is shown in figure 7:

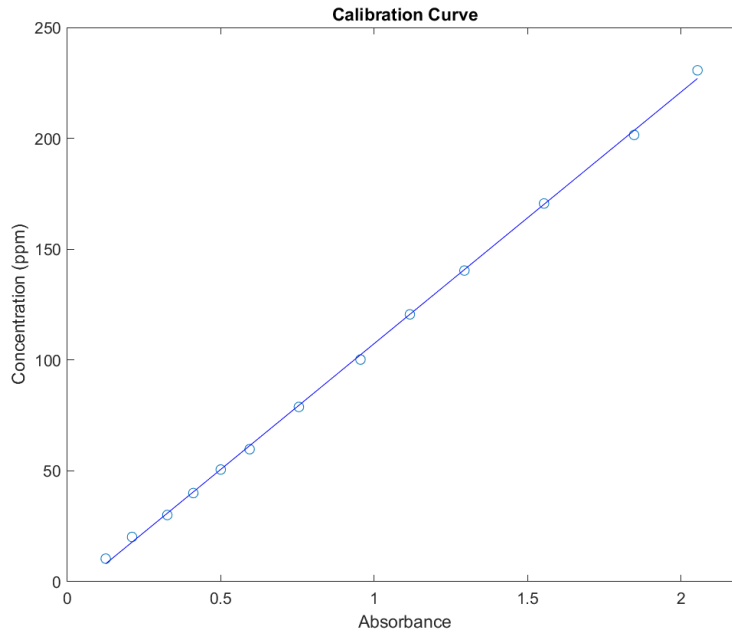


Figure 7: Calibration curve obtained from linear regression.  $R^2=0,9994$

### 3.3 Laser Scattering

To find oil droplet size distributions in synthetic PW emulsions, a laser scattering technique was applied. A Mastersizer 3000 was used to plot the volume distribution (%) of droplets in a sample as a function of their discretized size classes ( $\mu\text{m}$ ). The instrument works by exposing a sample to a beam of light, and sensing the angular patterns of the light as it is scattered by droplets of different sizes (Skoog et al. 2017). The patterns that are produced by the scattering of the light are highly characteristic of the droplet size, and this can be used to create a plot of the size distribution of droplets in a sample. Pure continuous phase, in this case 3,5 wt% NaCl brine without oil droplets, was used for reference calibration.

## 4 Experiment

### 4.1 Main Objective

The main goal of the experimental work was to perform gas flotation and gravity separation on batches of synthetic PW at a range of pressures, temperatures and retention times, to find how this affects oil removal efficiency. In addition, a functional and robust method to ensure reproducibility of the results had to be developed. Oil-in-water emulsions were prepared to emulate the conditions of PW at the point of injection into a industrial flotation unit in terms of salinity,

oil content and drop size distribution. In addition to gas flotation experiments, some gravity flotation experiments were to be carried out such that the results of the two separation methods could be directly compared.

## 4.2 Preparation of Emulsions

Diluted emulsions were prepared by dispersing crude oil in 3,5 wt% NaCl solution. The total volume of the solution was 250 mL. The properties of the crude oil is shown in table 2:

Density at 20°C (g/cm <sup>3</sup> )	0,85
Viscosity at 20°C (mPa*s)	12,4
TAN (mg/g)	0,2
TBN (mg/g)	0,6
Saturates (Wt%)	83,4
Aromatics (Wt%)	14,0
Resins (Wt%)	2,4
Asphaltenes (Wt%)	0,2

Table 2: Properties of crude oil G

The amount of oil weighed and added to the brine was dependent on the desired initial concentration. The initial oil concentration was set to ca. 200 ppm, as this is approximately the concentration of oil in actual PW at the point where it would be subjected to gas flotation in a topside CFU unit. In a realistic scenario this concentration will of course vary depending on many parameters related to the natural composition of the well fluids and the treatment prior to flotation, but similar studies done by Maelum & Rabe and Zhao et. al. involve concentrations in the range of 0-500 ppm, while Eftekhhardadkhah et al. tested inlet concentrations of 200-300 ppm, providing a decent basis for comparison (Maelum and Rabe 2015, Zhao et al. 2020, Eftekhhardadkhah et al. 2015). To determine the actual concentration of crude oil in the emulsion, the mass of oil was noted before the brine was added. The oil/water mixture was then emulsified at 15 000 RPM using an Ultra-Turrax stirrer for five minutes.

## 4.3 Oil Mass Balance - Developing the Method

One of the challenges passed on from the work that was done for the project was to find how the separation efficiency of the gravity separation and flotation experiments were seemingly close to independent of parameter combinations. In addition, the calculated efficiencies were unreasonably high (approximately 80%) for many of the experiments at lower temperatures, pressures and retention times. It was suspected that some of the oil was not recovered due to reasons other than the separation itself. Two main reasons were identified: (i) all of the oil was not extracted during the extraction procedure or (ii) oil was lost during emulsification. After mixing with the Ultra-Turrax, it was found

that some oil was left on the surface of the stirrer, as wiping it with tissues left brown spots on the paper. To determine how much oil was lost during preparation and to determine whether the DCM was able to extract all of the oil, emulsions with a range of initial weighted concentrations were made. The weighted concentration was found by noting the mass of added oil rather than pipetted volume. The yield of oil recovered from the emulsion was found, and the surface of the stirrer was washed with DCM. The recovered oil yield from the stirrer was then also found. The mass balance of oil was examined by summing the two yields to see if all of the oil could be accounted for. The range of different concentrations was prepared to see if the detected concentration was linear across the range, revealing whether the extraction yield was constant. To ensure maximum extraction of the oil, the volume of DCM was changed from 10 mL to 50 mL. Some experiments exploring different crude oils and scrubbing agents were done, but the results were not fruitful. The results of the mass balance experiments are presented and discussed in chapter 5.1. As a consequence of what was learned from this, the initial weighted concentration for gravity and flotation experiments was set to 240 ppm, as an oil loss of approximately 10-20% would give a well mixed emulsion a concentration of no less than 200 ppm after oil had been lost to the stirrer.

#### 4.4 Extraction of Oil From Emulsions

To estimate the oil concentration left in the flotated samples, the oil had to be extracted from the brine and dissolved in a suitable solvent. To do this, 50 mL of dichloromethane (DCM) was added to approximately 100 mL of emulsion in a separation flask. This volume of DCM was adjusted up from 10 mL in the project work, to ensure sufficient ability to dissolve all of the oil present in the sample. The masses of both DCM and emulsion were noted. The mixture was swirled and shaken thoroughly, and the organic phase was collected in a separate container. To find the oil left on the stirrer of the Ultra-Turrax, a certain amount of DCM was pipetted out and used to wash the stirrer, thus collecting the oil left on the surface. This volume was stored in a container and the mass of DCM was noted.

#### 4.5 Sample Analysis

The oil-containing volumes of DCM obtained from scrubbing the emulsions and washing the stirrer were inserted into cuvettes and analyzed using UV-vis spectroscopy. A calibration curve generated by linear regression of data from 13 standard samples as outlined in chapter 3.2 were used to find unknown concentrations of oil in the samples. The calibration curve, also illustrated in figure 7, is shown in equation 4:

$$\text{Concentration} = 113,636 * \text{Absorbance} - 6,136 \quad (4)$$

This was used by the instrument to convert from measured absorbance of light at wavelengths of 260 nm to concentration of solute in the sample.

When examining the oil mass balance, the yield of the samples were found using equation 5:

$$\text{Yield [\%]} = \frac{\text{Mass of oil in solvent [g]}}{\text{Mass of oil in 100 grams of emulsion [g]}} * 100 \quad (5)$$

To find the yield of oil in the DCM used to wash the stirrer, equation 6 was used:

$$\text{Yield [\%]} = \frac{\text{Mass of oil in solvent [g]}}{\text{Mass of oil added in 250 grams of brine [g]}} * 100 \quad (6)$$

Mass of oil in the solvent was easily found from the concentration given by the spectrophotometer and the noted amount of solvent added to the separation flask. The total yield was found by summing the two yields from the corresponding parallel sample. In the case of gravity and gas flotation separation experiments, the results were evaluated on the basis of the separation efficiency, which is calculated as shown in equation 7:

$$\text{Efficiency [\%]} = \frac{\text{Init weighted conc [ppm]} - \text{Detected conc [ppm]}}{\text{Init weighted conc [g]}} * 100 \quad (7)$$

## 4.6 Drop Size Distribution

Oil droplet size distribution obtained during emulsification was analyzed using laser scattering and diffraction. Emulsions were made as described in chapter 4.2 and inserted into a Mastersizer 3000, which outputs the volume distribution of oil in the emulsion [%] as a function of discretized droplet diameter size classes [ $\mu\text{m}$ ]. Emulsification parameters like Ultra-Turrax RPM and mixing time was determined on the basis of drop size distribution data obtained by these experiments.

## 4.7 Gravity Separation and Gas Flotation

A high-pressure, high-temperature separation rig was used for both gravity separation and gas flotation separation experiments. The cell consists of an upright sapphire glass cylinder with a volume of 360 mL, and it is surrounded and contained by a metal chassis. Three stainless steel metal spargers are located at the bottom of the cylinder for the hydraulic generation of gas bubbles in the size range of 100-200  $\mu\text{m}$ , which is similar to sizes generated hydraulically in topside CFUs (Piccioli et al. 2020). The droplet sizes were verified by image analysis software. Different inlets at the top allow for sample insertion and cell pressurization, and an outlet at the bottom allows for extraction of the liquid

inside the cell. The device is placed inside of a heating cabinet where the temperature can be adjusted when needed. An image of the flotation cell is shown in figure 8:



Figure 8: An image of the flotation cell used to conduct the gas flotation experiments

Gravity separation experiments were done by pouring a freshly made emulsion into the cell using a funnel at the inlet on the top of the device. The stirrer of the Ultra-Turrax was washed with DCM to find how much of the oil was left on the surface, in the same manner as for the experiments outlined in chapter 4.3. The cell was sealed and pressurized using nitrogen gas. The emulsion was left inside the cell for a certain amount of time, before a sample could be extracted from the bottom. Approximately 150 mL of the sample volume was extracted using a glass container, leaving some of the emulsion as well as the creamed oil floating at the surface. The oil in the sample taken from the cell was extracted as described in chapter 4.4, and analyzed as described in chapter 4.5. The cell was cleaned by filling the column first with xylene, then isopropanol and then three separate washes with deionized water. Gas bubbles of compressed air were passed through the liquid at each step of the cleaning process to properly extrude any residual materials left in the spargers. After the solvents were removed and the cell was clean, it was flushed and dried with compressed air.

During flotation experiments, emulsions were added in the same manner as for the gravity separation experiments. The cell was pressurized and nitrogen gas was fed through the spargers through the use of a flow controller to generate bubbles. These bubbles were distributed and passed through the liquid in the cell to accelerate the creaming of the oil. Samples were extracted and the cell was cleaned in the same manner as for the gravity separation experiments. A schematic of the flotation cell setup is shown in figure 9:

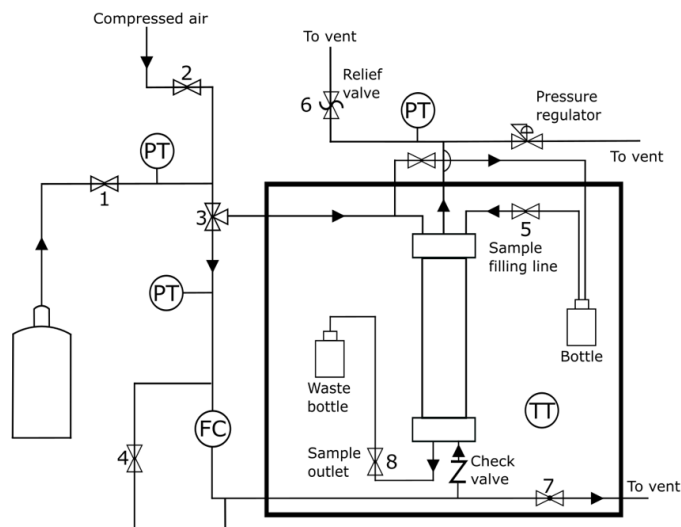


Figure 9: Schematic drawing of the flotation cell with numbers 1-8 indicating the numbers assigned to each valve

The schematic shows the flotation cell in the center, and the thin lines indicate the flows of gas or liquids, which are controlled by valves. The thick line indicates the confined space of the heating cabinet which the cell is placed in. Pressure (PT) and temperature (TT) sensors as well as the flow controller (FC) are all indicated by the circles in the grid. Samples are inserted through valve 5 and taken out through valve 8. The schematic also shows how gas can be directed either to the spargers for bubble generation or to the top inlet for pressurization. The gas is vented through the top of the cell. Pressure and temperature sensors are connected to a C Series current input module (NI-9203, National Instrument) and a C Series temperature input module (NI-9217, National Instrument), respectively. The analog signal from the C Series Modules is converted into digital through a Compact DAQ USB Chassis (NI-9171, National Instrument). Temperature and pressure values during the experiment are tracked through the custom-written script in LabVIEW software. Software is also used to adjust flow controller setpoint.

## 4.8 Experimental Design

The overall objective of the experimental work was to perform gas flotation, changing several parameters, namely temperature, pressure and retention time. Temperature and pressure combinations are summarized in the experimental matrix, which is illustrated in table 3:



Experiments		
P1T1	P1T2	P1T3
P2T1	P2T2	P2T3
P3T1	P3T2	P3T3
P4T1	P4T2	P4T3

Table 3: Experimental matrix illustrating the combinations of temperature and pressure that are applied in separation experiments using the flotation cell

Each cell in the table refers to a pressure value (P) and a temperature value (T), each distinguished by the following number. P values were set to: 2 bar (P1), 20 bar (P2), 40 bar (P3) and 80 bar (P4). Temperature values were set to 25°C (T1), 50°C (T2) and 80°C (T3). Each of the combinations were to be run at retention times of 3, 10 and 20 minutes, these being the intervals of time during which the emulsions were subject to pressurization and separation in the flotation cell. Three parallels of each parameter combination were conducted to examine of the scope of error and reproducibility of the results. It was also the intention to do gravity separation using the same parameter combinations for comparison, but due to time restrictions the gas flotation was prioritized and gravity separation was only carried out for all pressures and retention times at 25°C.

#### 4.9 Additional Notes Regarding Experimental Procedures

The flow of gas going into the spargers needed to be adjusted for each of the column pressure settings, as an increase in pressure alters the solubility of nitrogen gas in the liquids inside the cell (Sun et al. 2001). Based on earlier work done by Martina Piccioli, the flow controller setpoints for each pressure setting is shown in table 4:

2 bar	20 bar	40 bar	80 bar
50 ml/min	300 ml/min	600 ml/min	1200 ml/min

Table 4: Flow rates of nitrogen gas for each pressure setting

These values are based on experimental data and are set to keep the amount of bubbles passing through the column as constant as possible for all pressures. The values were found by measuring the intensity of light passing through the column while samples of brine were subject to combinations of pressures and gas flow rates. Pictures were taken with a high-speed camera, and the mean intensity and standard deviation was found using ImageJ. The results were compared to find the gas flow settings that would keep the number of bubbles in the system constant across different pressures.

It is worth to mention that that for all gas flotation experiments, some gravity separation will have taken place as some time is passed between sample mixing

and the point where gas starts flowing through the sample. On average, it took  $1:49 \pm 0:14$  to insert the sample into the column, seal it, pressurize and activate the flow controller. After this, pressure needs to build in the pipe between the flow controller and the spargers such that bubbles can be generated. The amount of time needed to achieve this is determined by the pressure at which experiments are carried out. This is due to how the system is set up, and the fact that for higher pressures, the gas flow through the flow controller needs time to reach target pressure as it builds. At 2 bar, the average time recorded between activation of flow controller and the generation of gas bubbles is 34 seconds. For 20, 40 and 80 bar experiments, the average times are 0:59, 1:01 and 1:51 respectively. These times were minimized by setting a higher setpoint flow rate for the controller during the time which it builds pressure, and then adjusting the setpoint to the correct value just before target pressure is reached and flotation is started. This reduces the time it takes for pressure to build in the pipe and flotation starts earlier.

When working at 50°C and 80°C, additional measures had to be made to ensure that the temperature remained sufficiently high throughout the duration of the experiments. This mostly involved preheating the flotation cell, emulsions, cleaning water, glassware and other objects used to carry out the experiments.

## 5 Results & Discussion

### 5.1 Results of the Oil Mass Balance

Figure 10 shows the detected concentration as a function of the weighted concentration.

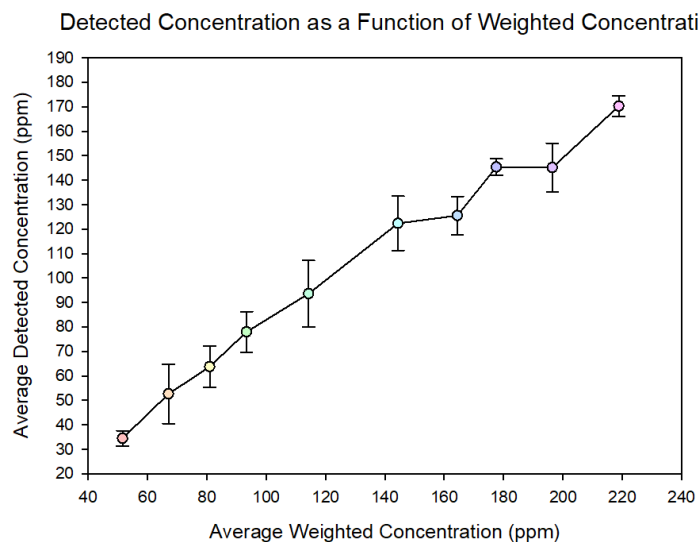


Figure 10: Detected concentration as a function of the weighted concentration

The figure shows a relatively linear variation in detected concentration, which could indicate: (i) the extraction yield of the scrubbing is constant, which could mean that not all of the oil is scrubbed from the sample. Since the detected concentrations are lower than their corresponding weighted concentrations, it could also indicate: (ii) that some oil is lost to the stirrer, or some other part involved in the process. If then the oil recovered from the surface of the stirrer along with the oil recovered from the samples after separation adds to 100%, then all of the oil would be accounted for. Figure 11 shows the sum of oil yields and the fraction of which is restored from the surface of the stirrer.

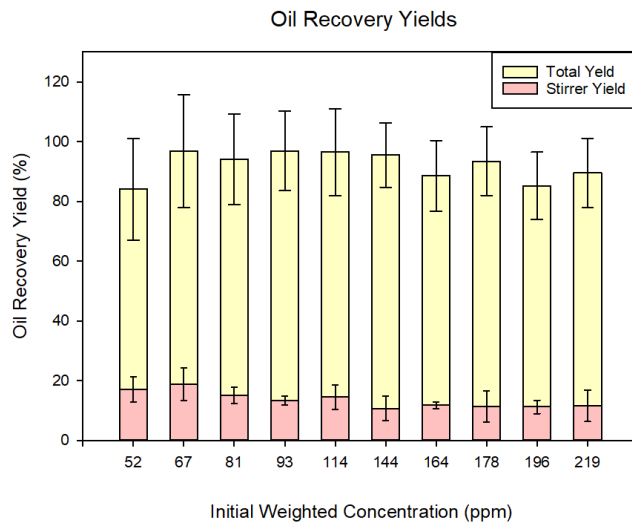


Figure 11: Total oil recovery yield and fraction of yield recovered from the surface of the stirrer after mixing

It can be seen that for most concentrations, the total yield is in the vicinity of 90%, although the error bars are substantial. However, for every concentration, a fraction of oil in the range of 10-20% is recovered from the stirrer, indicating that there was indeed an oil loss during mixing of the emulsions. With this magnitude of error for the total yields, it was difficult to determine with certainty how well all of the oil could be accounted for, but the conclusion from this was that for each experiment, the stirrer was to be washed with DCM to record the oil loss. In addition, the weighted concentration for emulsions used in separation experiments were set to 240 ppm to keep the concentration from dropping below 200 ppm after oil had been lost to the stirrer. The 10% or so of oil that was not accounted for could perhaps be explained by the use of UV-spectroscopy, as there is a possibility that some compounds of the oil are not detected by the instrument.

From this experiment it was also learned that the magnitude of error in the work done for the project was related to the amount of oil added during preparation. Before measuring the mass of the added oil was a part of the method, the pipetted volumes were instead used to assume the concentrations of the emulsions. As discovered while weighing oil for a substantial amount of emulsions over the duration of the semester, tiny changes in volume can have significant impacts on the concentration when aiming for a range of 200-250 ppm, meaning

that the mass of oil is needed to be sure of the actual concentration. The level of inaccuracy introduced by trusting the pipetted volume without noting mass may well explain a large fraction of the poor results obtained for the project work. As such, this experiment provided massive help in diagnosing a faulty method.

## 5.2 Drop Size Distribution

Figure 12 shows the average drop size distributions of emulsions immediately after mixing. Four parallels were made at each temperature, where each set of emulsions were preheated to 25°C, 50°C and 80°C respectively before mixing.

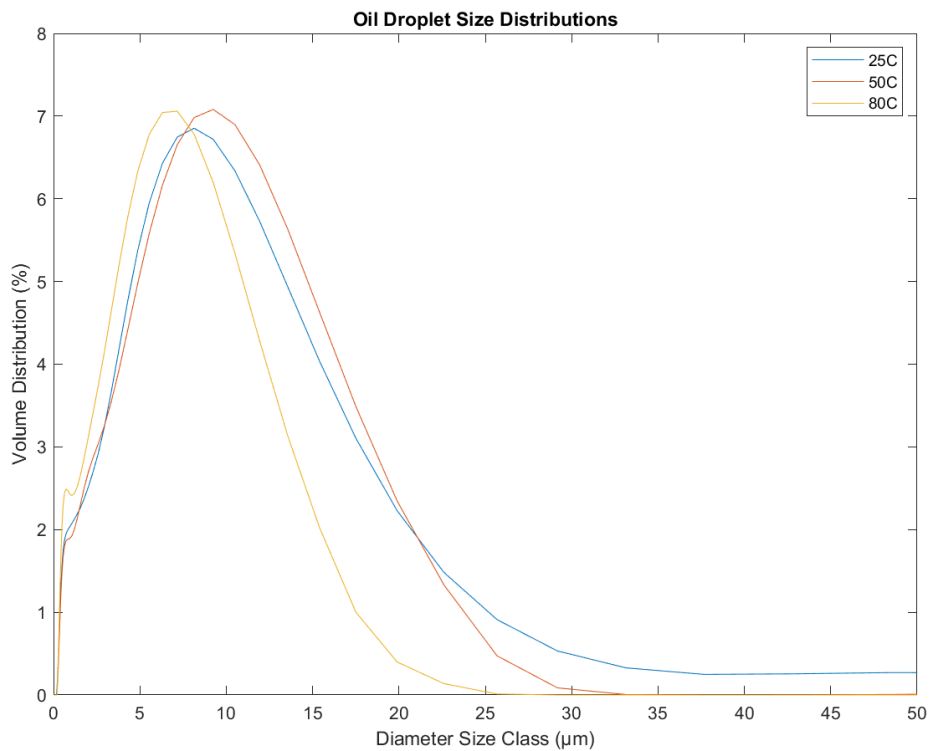


Figure 12: Average drop size distributions of emulsions mixed at 15 000 RPM for five minutes at different temperatures

The figure shows that for all temperatures, the highest peak of each distribution is located between 5 and 10 microns. The shift of the peak at 80°C may be due to the lower viscosity of oil as temperatures are increased. This can make dispersing easier at the same mixing condition. These distributions were considered acceptable in terms of emulating PW from a realistic scenario. As reported by literature, droplets of 10 microns and above would have a decent chance of being removed by hydrocyclones in steps prior to gas flotation. Maelum and

Rabe examined gas flotation with droplet sizes ranging between 3-40  $\mu\text{m}$ , while Zhao et al. used drop size distributions with  $D_{v50}$  values of 5, 15 and 25  $\mu\text{m}$  (Maelum and Rabe 2015, Zhao et al. 2020).

## 5.3 Results of Gravity Separation and Gas Flotation

### 5.3.1 Experiments at 25°C

Figure 13 shows the results from gravity separation experiments done at all pressures and retention times at 25°C.

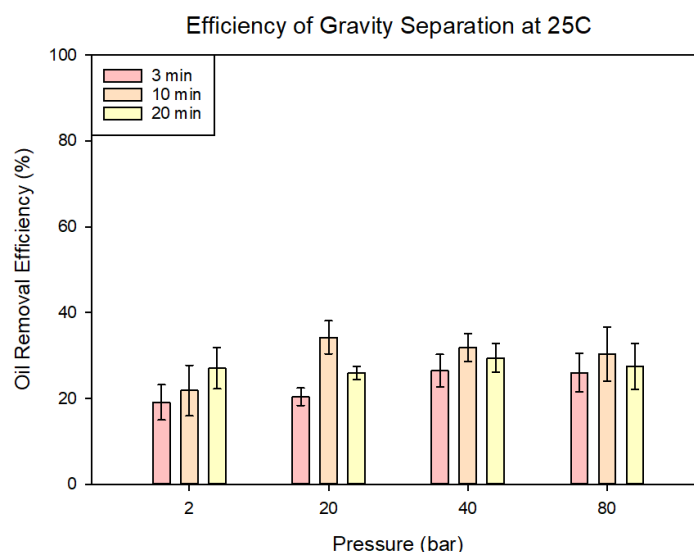


Figure 13: Oil removal efficiency of gravity separation as a function of pressure and retention times at 25°C

Perhaps the most peculiar observation is that for pressures above 2 bar, the separation efficiency is higher for experiments done at 10 minutes retention time compared to those at 20 minutes. This is quite counter-intuitive, as gravity separation for a longer period of time should increase separation. The set of results at 2 bar, showing an increase in separation with each increase in retention time, seem reasonable. For experiments at 3 minutes retention time, we can see a slight increase in efficiency when pressure increases. Overall, oil removal efficiency is located in the range of 20-35% for gravity separation, and this gives a reasonable basis for comparison with gas flotation experiments. It could be interesting to try inserting a sample and afterwards sample immediately without applying any residence time under pressure. This could perhaps reveal how much of the removal efficiency is due to actual gravity separation, or rather due to the oil sticking to the walls of the glass cylinder in the same manner as it sticks to the surface of the stirrer.

Figure 14 shows the results from gas flotation experiments at all pressures and retention times at 25°C.

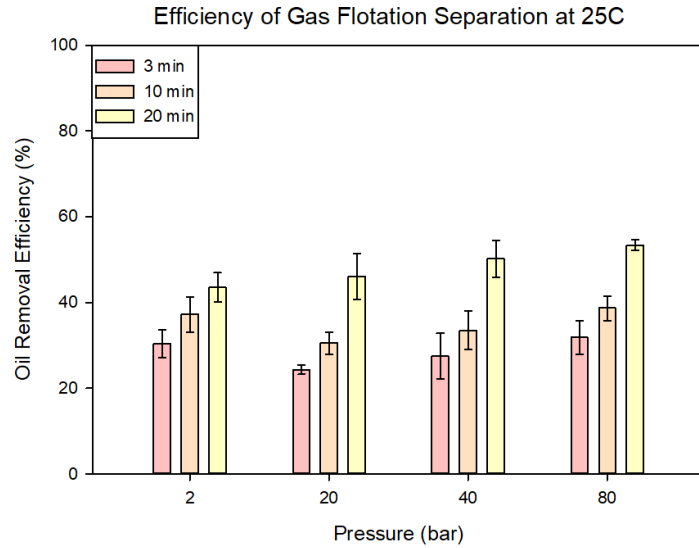


Figure 14: Oil removal efficiency of gas flotation as a function of pressure and retention times at 25°C

The figure shows a clear trend of increased separation efficiency as a function of the retention time for all pressures. Increased pressure seems to promote an increase in oil removal efficiency also, with an increase of 10% in the 20 minute experiments between 2 and 80 bars. Exceptions are set of results at 2 bar, 3 and 10 minutes retention time. For some reason, these parameters yield a higher efficiency compared to the corresponding retention time experiments at 20 and 40 bar. At this time, two explanations spring to mind: (i) the order at which the experiments were conducted may have had an impact. 2 bar experiments at all retention times were done first before moving on to higher pressures. Perhaps the sets of initial experiments yielded somewhat higher separation results due to lack of training with the method, as there are several steps of manual intervention needed when conducting the flotation experiments. It is unknown whether repetition of the 2 bar experiments would yield lower removal efficiencies if they were to be repeated after drilling the method over the course of all 25°C experiments. Another possible explanation is: (ii) the presence of some thermodynamical property of the system was causing a negative effect on the removal efficiency when applying lower pressures, and that this is overcome by a separate and positively contributing effect when reaching pressures of 20 bars and higher. Comparison with flotation results at higher temperatures could perhaps reveal a pattern, or a lack thereof, to help explain these results.

### 5.3.2 Experiments at 50°C

Before experiments at elevated temperatures were started, the temperature decay of approximately 250 mL of NaCl brine heated to 50°C when placed in room temperature was recorded, and the decrease in temperature was found to be 4,5°C over an interval of 7 minutes. This temperature drop was then assumed to be similar to that which would occur during the mixing of preheated emulsions before insertion into the flotation cell when doing separation experiments.

Figure 15 shows the results from gas flotation experiments at all pressures and retention times at 50°C.

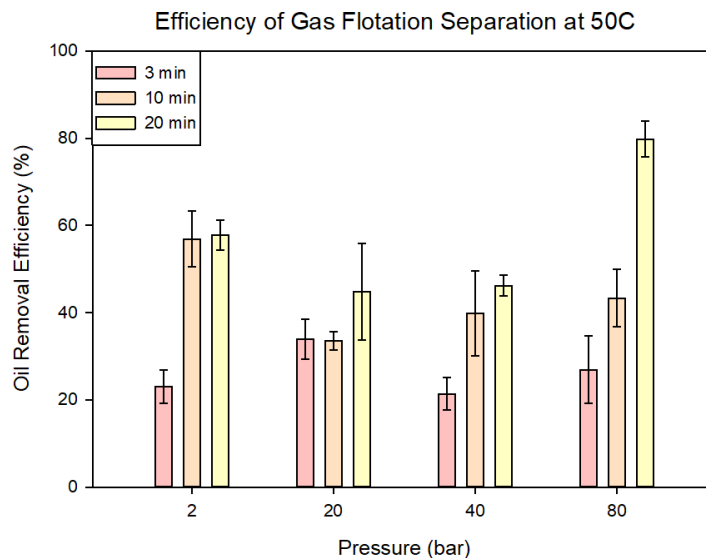


Figure 15: Oil removal efficiency of gas flotation as a function of pressure and retention times at 50°C

While the trends in the data are somewhat more erratic compared to the 25°C experiments, the tendency of the removal efficiency to increase with retention time is more or less present for all pressures. Also, these results show clearly that a combination of higher pressure, retention time and temperature is definitely advantageous for increasing separation efficiency, as 80 bar, 20 min shows a removal efficiency of approximately 80%. In addition, we can see the same effect of higher efficiency for 2 bar, 10 min and 2, bar 20 min than for their corresponding results at 20 and 40 bar (even 80 bar for the 10 min experiments). For 3 minute experiments, the highest efficiency is achieved at 20 bar. While the trends were somewhat difficult to understand completely at the time, the reproducibility of the results seemed reasonable enough to continue. It was however found later that the method had some flaws, and this was adjusted for



the 80°C experiments. This will be explained in chapter 5.3.3.

### 5.3.3 Experiments at 80°C

In the same manner as for 50°C experiments, brine was heated to 80°C, and the decrease in temperature was found to be 7,1°C over an interval of 7 minutes. The results of gas flotation experiments carried out at all pressures and retention times at 80°C are shown in figure 16:

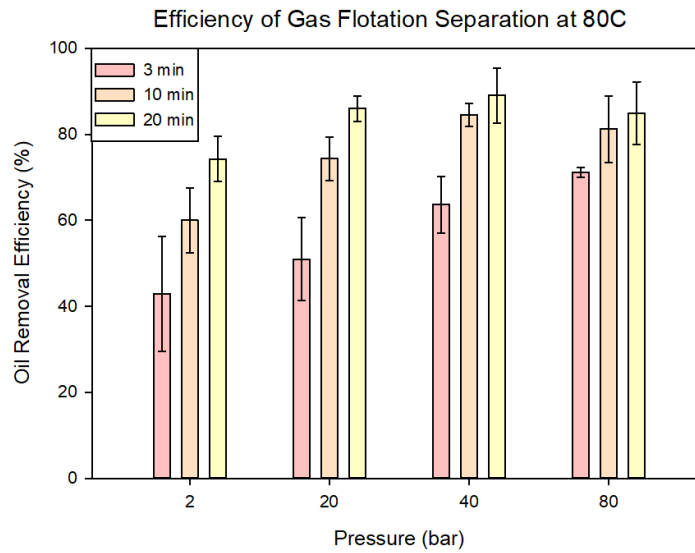


Figure 16: Oil removal efficiency of gas flotation as a function of pressure and retention times at 80°C

The data shows a clear tendency of increased removal efficiency with increased retention time for all pressures. For pressures above 2 bar, the 20 min experiments yield removal efficiencies in the vicinity of 90%. Most of the results obtained at 80°C exhibit close to or higher separation efficiency than that obtained by Zhao et al. who were using a continually fed pilot CFU at close to similar pressure and slightly lower temperature (Zhao et al. 2020). However, one should be careful in comparing these experiments as the methods of applying gas flotation are quite different. There is also a tendency of increased separation with pressure, except for the 10 min and 20 min experiments when increasing from 40 to 80 bar, but this could very well be due to small variations in the manual steps of the method rather than some thermodynamic phenomena. It would not be a surprise if a larger sample size ensured even higher efficiency for the 80 bar experiments. There is a substantial range in efficiency from the lowest to the highest values, where 3 min, 2 bar experiments averaged approximately 43% efficiency and 40 bar, 20 min experiments averaged close to 90% efficiency. Compared to results at other temperatures, the separation efficiency is greater

for 80°C for all parameter combinations, indicating that higher temperature is advantageous for increasing separation, but combining it with higher pressure seems to give the best results. The reproducibility seems quite robust for most of the experiments, and the results overall seem to indicate a relatively refined method. This robustness may be due to some changes that were implemented during the initial stages of 80°C experiments. The process of identifying and mitigating weaknesses in the method for experiments at elevated temperatures will be laid out in the following paragraphs.

Suspicion was raised regarding potential sources of error during the initial stages of carrying out 80°C experiments. It was shown that for some of the experiments that were done as the first experiment of the day, the separation efficiency was well above 80%, even though retention times were set to 3 minutes and the pressures were set to 2 and 20 bar. These values seemed severe compared to results at lower temperatures, but also compared to other experiments which were carried out shortly after in the same day. It was suspected that, since these were the first experiments carried out in their respective workdays, the cell was hotter before and during these experiments relative to the experiments that were done later in the day. It may be explained due to the heat loss of the column as solvents and water was added in several rounds when washing after experiments were done. Also, for the first experiments of the day, the cell was left to preheat usually for 1-2 hours before it was slightly wetted with acetone and water to ready the cell for experiments. This first washing of the day differed from washings between experiments in that smaller volumes of water and solvent was used, thereby stealing less heat from the column compared to using larger volumes for washing. This could indicate that the cell was overall hotter for the first experiment of the day than for subsequent experiments that were conducted later.

In the time before this realization, there was no available method to reliably measure the temperature of the cell itself, and the only available temperature data was provided by a thermometer placed in the atmosphere of the heating cabinet. This was, maybe somewhat naïvely, used to confirm that the temperature conditions were fit to carry out the experiments at proper temperature, with the allocated time for cell heating between experiments were set to 10 minutes approximately. This was also done for all 50°C experiments. To examine this further, the temperature of emulsions were measured before and after completed flotation experiments at 80°C. Emulsions were of course preheated before mixing, and every emulsion had a recorded temperature in the range of 77-78°C before insertion into the cell. After three experiments at 20 minutes retention time were conducted, it was found that extracted samples in preheated containers had a recorded temperature of approximately 65°C, revealing a temperature loss of 12-13 degrees, and thereby also revealing that experiments were not conducted close to 80°C as previously assumed. To solve this, the amount of time allocated between experiments to allow the cell to reheat properly was increased to approximately one hour. Additionally, water was also preheated in

order to minimize the heat loss during cleaning between experiments. However, without a method to directly measure the temperature of the cell, there was no way of knowing if or when the cell reached target temperature before a new experiment could be initiated.

An additional explanation for the outlying values of the separation efficiencies that were detected at the start of 80°C experiments may be due to some of the oil boiling off during sample insertion into the column. In these cases, the funnel used for insertion was preheated for 1-2 hours with the column, and when the samples were poured into this funnel, there was a distinct hissing sound followed by a small rush of steam, indicating that some of the liquid got boiled off when it came in contact with the hot metal surface. This does not seem likely to explain the extreme separation values by themselves, as there were visual clues like high transparency of the water phase and a relatively high volume of creamed oil at the surface, indicating that the separation in the column due to the gas flotation had been very effective. However, if some of the oil was boiled off during insertion, this could partially cause the value of the separation efficiency to rise. To mitigate this, the funnel was only preheated for 5-10 minutes as to not cause any sudden spikes in temperature of the sample when contact was made.

#### **5.3.4 Other Potential Sources of Error**

When DCM was added to the separation flask containing samples that had recently been taken from the cell after 80°C experiments, the temperature was high enough to boil some of the DCM immediately after contact. It is not known if this had any effect on the oil content of the volumes in the flask, but it certainly had an effect on the volume of DCM that was added, thus possibly affecting the ability to extract the oil from the water phase. The solution was to let the emulsion cool down for about an hour after sampling and to add the DCM after the temperature had dropped, to minimize the amount that would boil off.

In regards to the gravity separation that will take place between mixing and the start of gas flotation during experiments, it is suspected that the effect of this will be negligible with the drop sizes that are recorded. From the results showing that oil is left on the stirrer during mixing, it is suspected that similar effects like oil sticking to other surfaces during transfer of the liquids will be a stronger contributor to increased separation rather than a few minutes of extra gravity separation.

#### **5.3.5 Summarizing Discussion and Recommended Further Work**

After finishing laboratory work and obtaining the results of 80°C experiments, it seemed clear that the measures made to ensure greater temperature control and proper heating of the cell was essential for the method to function properly at elevated temperatures. If this is the case, it might be worthwhile to

redo experiments at 50°C as this could ensure clearer trends and possibly also higher separation efficiency values. When comparing the results obtained from 50°C and 80°C, there seems to be no doubt that higher temperature increases separation. Although it is suspected that would also be the case if 50°C experiments were redone with the proper method, the difference might not be as clear as it appears now. Seeing as the experiments carried out at 25°C did not involve any substantial deviations from ambient temperature, there does not seem to be any major question marks regarding the method for these experiments, and it can serve as good comparison with the 80°C experiments to evaluate the impact of the experimental parameters. As such, it seems to be obvious that increasing pressure, temperature and retention time will all contribute to greater separation efficiency, with temperature being the most influential factor.

The lowest efficiency of the gas flotation results were recorded for 20 bar, 3 min, 25°C experiments and averages 24%, even lower than some of the gravity separation experiments. The highest efficiency was recorded for 40 bar, 20 min, 80°C experiments, averaging 89%, although with some error. This difference substantiates the overall trends in the data which makes it possible to conclude that a combined increase of the experimental parameters has a positive impact on oil removal efficiency for gas flotation, which is very exciting in regards to potential development of subsea flotation technology. With knowledge from literature, it is possible to assume then that the increase in separation may be due to: (i) increased breakage and stability of the nitrogen bubbles as pressure increases, (ii) increased coalescence frequency and shifting of the droplet size due to increased temperature which lowers drainage time and (iii) increased number of bubble-droplet interactions at longer retention times. There is probably also a vast range of different thermodynamic phenomena taking place which are contributing either positively or negatively to the separation efficiency when increasing pressure and temperature, but the overall effect over the explored ranges is clearly positive.

To obtain an even fuller image of the impact of applied gas flotation, the completion of gravity separation experiments at 50°C and 80°C would also be recommended for comparison. And although gravity separation experiments were only carried out at 25°C, it seems safe to conclude that gas flotation definitely has a positive influence on the oil removal efficiency compared to only using gravity separation. It could also be of relevant interest to observe how the addition of surfactants would affect the results.

## 6 Conclusion

A method for the successful separation of oil droplets from water using a high-pressure, high-temperature gas flotation rig was developed. Emulsions of approximately 240 ppm of crude oil G in NaCl brine with drop size distributions similar to those found in produced water were mixed and subjected to nitrogen gas flotation at temperatures of 25°C, 50°C and 80°C, pressures of 2, 20, 40 and 80 bar as well as retention times of 3, 10 and 20 minutes with the intention of finding how these parameters affect oil removal efficiency. Gravity separation was also carried out at 25°C and all of the aforementioned pressures and retention times to provide data for comparison. Three parallels of every parameter combination were tested to ensure reproducibility of the results. Although with some deviations, it was found that for gas flotation experiments the overall data indicates that an increase in either parameter had a positive impact on separation efficiency, with results ranging from a minimum of 24% efficiency up to a maximum of 89%. The stabilization of the erratic trends in the results from 50°C to 80°C experiments may indicate that the changes in the method made to control temperature and minimize heat loss were effective. This may also underline the effect of temperature on the separation efficiency. It was shown that at 25°C, gas flotation is overall more efficient than gravity separation.

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