Experimental Analysis Of The Hydrogen Sulfide Absortion Phenomena In Brine/oil Mixtures As A Function Of System Pressure And H2s

2008

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EXPERIMENTAL ANALYSIS OF THE HYDROGEN SULFIDE ABSORPTION
PHENOMENA IN BRINE/OIL MIXTURES AS A FUNCTION OF SYSTEM
PRESSURE AND H₂S CONCENTRATION

by

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A thesis submitted in partial fulfillment of the requirements
for the degree of Master in Science in Aerospace Engineering
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ABSTRACT

In underground oil reservoirs, Hydrogen sulfide is usually found coexisting with the oil due to bacteria reduction over a long period of time. The amount of H₂S in the oil varies from place to place around the globe. When the oil extraction process begins, the presence of Hydrogen sulfide becomes noticeable as drilling tools, piping and other equipment suffer from sulfide stress cracking, electrochemical corrosion and corrosion fatigue. For this reason, the oil industry invests millions of dollars per year trying to find better ways to reduce the amount of H₂S in oil.

An important part of the current investigations deals with brine (sea water)/oil mixtures. The reasons are two-fold: 1) one way of extracting the petroleum from the reservoir is by injecting brine into it and since it has a higher density than oil, the latter will be ejected up to the surface. Taking into account the complex fluid flow occurring within the reservoir it is easy to understand that some brine will also be present as part of the ejected fluid; 2) brine is already present in the reservoir, so independent of the extraction method used, there will be a brine/oil mixture in the ejected flow.

When brine and oil have absorbed H₂S under pressure in the reservoir and then suffer a decompression during the extraction process, a certain amount of H₂S is released from the liquid phase. In order to have a better prediction of how much Hydrogen sulfide can be liberated a good understanding of H₂S absorption by these liquids is necessary.
The amount of gas a solvent absorbs is a function of pressure, original gas concentration and temperature as described by Henry’s Law. The purpose of this thesis is to experimentally analyze how much of the corrosive gas is absorbed into different brine/oil mixtures, and brine and oil, separately. In order to find sufficient data for a thorough analysis, different reservoir simulation scenarios were created. The liquids were mixed from pure brine to pure oil, resulting in 33% and 66% water cuts. Data were obtained at 2 pressures of 20atm and 70atm at room temperature. \( \text{H}_2\text{S} \) concentration was also a variable, changing the original gas concentration through different values: 50, 100, and 300ppm. These experiments were conducted in an autoclave system and will better explain the hydrostatic process that occurs inside the reservoir.

It was found that throughout all the water cuts, the role that total pressure plays in the absorption phenomena is of less importance as the original \( \text{H}_2\text{S} \) concentration is increased. In the same manner it was observed that the highest mass-absorption ratios are always found between 50 and 100ppm and the lowest at 300ppm, this is observed for all water cuts and total pressures. Another important finding was that the ability to absorb the corrosive gas decreases as the original \( \text{H}_2\text{S} \) concentration increases and this proves to be true for all water cuts and system pressures.

After conducting these different reservoir scenarios, tests were conducted to simulate 300m of the horizontal section of the pipe that connects the head of the well with the platform. This was done with a high pressure 300-meter long loop. It was found that the
corrosive gas is absorbed at a higher rate when there is a flow, opposite to a hydrostatic case.

Henry’s Law constant was identified for each water cut and each pressure, however, the test procedure could not be validated since the gas being studied was not in its pure form.

Understanding the absorption phenomena of Hydrogen sulfide in different water cuts will definitely be of great help to the oil industry to make better forecasts of \( \text{H}_2\text{S} \) concentrations being ejected from each well.
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INTRODUCTION

Petroleum is a complicated mixture of chemical compounds based mostly on carbon and hydrogen. It can be found in places all around the world, usually near tectonic faults. It is generated after a lengthy process that starts with microscopic sea life digesting carbon-based molecules (from algae and other plants). An abiogenic process follows it, and the crude oil acquires the hydrogen from either water or water vapor and oxygen from the atmosphere. The petroleum is “locked in” between strata (a stratus is a single layer of sedimentary material that presents homogeneous characteristics [1]). Some of these formations can be of epochs as ancient as the Cambrian, from the Paleozoic era (~540 million years ago). Up to 45% of the discovered petroleum is in strata of the Mesozoic era or older, and 20% has been found in reservoirs in formations of the Pliocene or earlier (~12 million years ago) [2].

The petroleum is encapsulated within distinct materials that allow different fluids to flow at diverse rates (modeled by Darcy’s Laws) up until a given distance after which no gases or liquids can flow. This material (that varies from place to place – limestone, sands, etc) then behaves as an impermeable wall that segregates these fluids from the rest of the world. In this case, this is called a closed reservoir [3]. An open reservoir, on the other hand, presents one main distinction: an (either water or brine) aquifer is connected to the reservoir.
In reservoirs there is connate (or innate) water. It is usually found in the interstices or pores along with the oil and gas. This water contains dissolved salts and is called brine [2].

Petroleum entrapments are categorized as anticlines, domes, synclines, monoclines, stratigraphic types, etc. Regardless of the shape of the reservoir, they all have something in common: water, oil and gas (Hydrogen sulfide included) are found in them [16-19].

In order to find these reservoirs a team of experts work together. Geologists suggest where oil may be entrapped based on topographical information, character of the surface rocks (e.g. having an impermeable layer on top of a permeable one), faults, etc. Geophysicists find changes in earth’s magnetic and gravitational fields and conduct tests with seismic (sound) waves. Geochemists analyze the chemicals on the surface, etc. [2].

To find an oil reservoir with small amounts of water or brine is desired. A detailed field study can guide into reducing the water cut while decreasing the required investment prior to oil extraction [4]. If all the data indicate that an acceptable reservoir has been found, ground samples are taken with special drills. Once it has been proven that exploiting that reservoir is a profitable venture, a well is drilled and pipeline to connect a platform with the reservoir is put in place.

Pressure varies from reservoir to reservoir, and also depends on whether it is an open or closed system. In some cases, especially on open systems, the pressure in the reservoir can go up to the hydrostatic pressure at that depth. Two very common pressures found in
reservoirs are 20 and 70 atm. This thesis simulates reservoirs at these two different pressures. It is known that the amount of H₂S that will be absorbed into the liquids will vary with this pressure [5]. The pressure gradient between the inside of the reservoir and the one at the platform (atmospheric) drives the fluids upwards through the piping when the valves are opened. The energy that forces the fluids to go up the tubing is called *reservoir energy* or *reservoir drive* [6]. As the flow starts going up the well pressure decreases. This pressure decrease causes gases to come out of solution [2]. In order to be able to estimate how much of these gases (especially Hydrogen sulfide) will be liberated during this process, it is essential to understand the amount originally absorbed by the liquids while all the species were still at reservoir conditions.

The importance of knowing how much H₂S is to be expected up in the platform falls into the fact that this acid gas damages the pipes, valves, separators, etc. H₂S partial pressures of 5% of the total pressure are considered corrosive. It is a catalyst in the absorption of H₂ in steel which leads to sulfide stress cracking [7]. The primary problem it presents is metal embrittlement due to H₂S penetration but several other hindrances such as uniform corrosion, pitting corrosion, corrosion fatigue, sulfide stress cracking, hydrogen blistering, and stepwise cracking are also common [8]. Corrosion products include black or blue-black iron sulfides, pyrite, greigite, mackinwaite, kansite, iron oxide (Fe₃O₄), magnetite, sulfur (S), and sulfur dioxide (SO₂). In order to avoid all these problems, Hydrogen sulfide scavengers are injected to the flow coming through the well. The amount of injected scavenger depends on the H₂S concentration, liquid and gas superficial velocities and water cut, among other parameters.
A horizontal section of the pipi ng that connects the head of the well with the platform was recreated in the laboratory with a 1000ft long high pressure coil. In this system, a hydrogen absorption test was also conducted running the fluids in a slug flow regime.

The oil industry invests millions of dollars per year in order to find ways of reducing the amount of H$_2$S that reaches the platform. It is also important to know what the ideal quantity of this chemical is needed for the flow received. In order to reduce costs and maximize platform efficiency in this regard a close estimate of how much H$_2$S will be received is imperative and a major part of that is to understand how much of this gas is entrapped in the liquids before oil extraction begins. Finally, it is very important to understand how this gas dissolves in the liquids depending on the pressure, water cut and H$_2$S concentration in gaseous state within the reservoir.
MATERIALS AND METHODS

Autoclave System: Hardware

In order to simulate an oil reservoir, an autoclave was utilized. This device is a vessel that can contain fluids at high pressures and temperatures. The autoclave used in the current equipment was built by St. Cloud Welding. It is made of 1010 Carbon Steel and designed for working with pressures up to 78 atm and has a 4 Liters volume. It has five ½” female NPT ports, four on the top, and one on the bottom.

![Figure 1: Autoclave from above](image)

For security purposes, there is a sixth port, which is located in the middle of the top flange of the autoclave. This is a 1” female NPT that connects to a 78 atm corrosive-fluid rated Pressure Relief valve which would activate in case the pressure reaches this limit. The four top ports can be separated in two groups of two ports each: In the first one, each port has an access tube that goes within the autoclave almost all the way to the bottom; each of the ports of the second group has an access tube that reaches to a quarter of the depth. As it can be seen in Figure 2, both ports of the latter group and one of the first ones were used during this set of experiments.
Of the short-tube ports, one was used for delivering the brine and the crude oil, while the second one was used for taking gas samples. One of the ports with a long inner tube was utilized for bubbling the H$_2$S in the liquids, thus temporarily increasing their contact surface with the purpose of simulating the reactions in the reservoir during a longer period of time (Hydrogen sulfide and other gases slowly flow out of the rocks into the reservoir) [6].

The bottom port is used for sample collecting purposes. This port is connected to a 0.5” O.D. 1010 Carbon Steel tube (rated for a maximum pressure of 132atm at 22°C) that connects to Swagelok® 316 Stainless Steel manually operated needle valves that go to the High Pressure Sample Collector (HPSC).
The HPSC is built from carbon steel scheduled 80 nipples, caps, valves and reducers, among other fittings. Every part of the HPSC is rated for at least 78 atm and has a 1L volume (see Figure 4). The same kind of carbon steel tubing permits the fluids to come from the Autoclave to the HPSC through a ½” High Pressure ball valve. The sample collector possesses a second of these valves: it connects the HPSC to the Low Pressure Sample Collector (LPSC) through a pair of Camlock fittings.
The Low Pressure Sample Collector (LPSC) entails a 1.15m long, 6.67cm inner diameter (4L) clear PVC pipe with two PVC caps at the ends. The top cap has two ports; the one on top (see Figure 5) has a ½” O.D. PVC pipe that connects it to a low pressure ½” ball valve. At the same time, this valve is connected through another nipple to a female Camlock that allows the LPSC to be linked to the HPSC. The volume of the LPSC was designed so that it could contain the same volume of liquids and gases of the HPSC but at atmospheric pressure. Based on fundamental hydrostatic relationships, conservation of mass and the law of ideal gas, it was assumed that the gas to liquid volume ratio in the HPSC would be 0.5.

$$70\text{ atm} \approx 7 \text{ MPa}$$

Gas volume in HPSC: $V_{(g)\text{HPSC}} = 0.5L$

$$P_{HPSC}V_{(g)\text{HPSC}} = P_{LPSC}V_{(g)\text{LPSC}}$$

$$V_{(g)\text{LPSC}} = \frac{P_{HPSC}}{P_{LPSC}}V_{(g)\text{HPSC}} = \frac{7\text{MPa}}{0.1\text{MPa}} \times 0.5L = 3.5L$$

Also, treating oil and water as incompressible liquids: $V_{(l)\text{HPSC}} = V_{(l)\text{LPSC}} = 0.5L$
Then,

\[ V_{LPSC} = V_{(g)LPSC} + V_{(i)LPSC} = 4L \]

**Figure 5: Low Pressure Sample Collector (LPSC)**

The pressure in the autoclave system is controlled with an intrinsically safe (for use in Class 1, Division 2, Groups A, B, C, and D locations) Digital Pressure Gauge. It can read pressures up to 136 atm with an accuracy of ±0.05 of its scale. It connects to the loop through a 316 Stainless Steel NPT male and can work in temperatures between -10 to 55°C.

As it can be seen in Figure 3, the Autoclave System possesses 4 Hydrogen sulfide Monitors: Two are part of the experimental procedure and the other two are for leak detection and safety purposes. Depending on the set of experiments being run, sensors with capabilities for reading from 0 to 100 ppm or from 0 to 500 ppm are connected to the Autoclave System. These electrochemical cell sensors are Gas Alert Extreme H₂S Monitors that read and display with 1 ppm increments. They can operate in environments
between -40 to 50°C and 15% to 90% relative humidity. They are intrinsically safe for Class 1, Division 1, Group A, B, C and E locations.

When measuring the H₂S concentration, these monitors require being in contact with the gas at atmospheric pressure for approximately 30 sec. When it is desired to read the H₂S concentration in the autoclave at high pressure (70 atm) the gas must flow through a regulator before reaching the monitor. This regulator is a two-stage stainless steel Harris HP 742 designed for corrosive gas applications. It has a 316L stainless steel diaphragm and nozzle and PTFE Teflon® seats and seals. The same device is attached to the H₂S tank for flowing the gas into the Autoclave.

Figure 6: Autoclave System
Vacuum Subsystem

This subsystem is the main mechanism for assuring an appropriate management of any H$_2$S there might be in the cabinet. The gas may come from a leak in the tank, an escape from a fitting (due to failures in the system) or from the gas products from the chemical reactions in the autoclave. This subsystem sucks all the air in the cabinet and bubbles in a bucket with 50%wt NaOH in water. The purpose of this procedure is to force any remaining Hydrogen sulfide react with the Sodium Hydroxide and thus convert it in a non-harmful compound. For security reasons, redundancy was built into the system by incorporating two vacuums (each with its NaOH bucket) instead of one. The first vacuum sucks the air at head-height where most of the tubing and fittings are located. It is then bubbled into the bucket. On this container, a metallic-mesh-filter was installed in order to assure the free flow of gases but not of the Sodium Hydroxide. In case of no-flow, H$_2$S
would settle at the bottom since it has a higher molecular weight than air. Therefore a second vacuum was placed at the bottom.

**300-meter System**

The big loop is a high-pressure system capable of running experiments with corrosive gases and liquids at high pressures (approximately 78atm). Its core is 300 meters of 2.5cm ID stainless steel tubing.

![Core of the loop: 300m of stainless steel tubing](image)

It also has two air-driven Haskel ¾ HP (0.56kW) pumps with a maximum rated output pressure of 100atm and a 2.5gal/min volumetric flow; two forced-air-cooled 4-stroke gasoline pumps with a 123cc displacement, *approximately* 140 gal/min volumetric flow and a 30mt head and a 15HP, 1740rpm max speed multiphase pump. This multiphase pump (MPP) is a 4-stage, gear type joint with a cast steel suction housing and an alloy steel drive shaft and rotor. It is controlled by a MOVITRAC® 07, 3-phase AC 400/500V Driver capable of delivering to a 20HP Pump up to 5500rpm with a 1rpm resolution.
It is also composed of 5 carbon steel tanks rated at 78atm, a 10,000gal double-walled above-surface tank for petroleum storage, a 350gal and two 550gal stainless steel tanks, more than 50 valves, two separators, multiple Good Year® FlexyWing Petroleum-rated hoses, two intrinsically safe pressure transducers and five J-type thermocouples connected to a Data Acquisition System linked to a PC utilizing LabView. The same kind of regulators and H₂S monitors are used both systems.
Figure 11. Double-walled 10,000gal isotank for Petroleum Storage

Figure 12. Big Loop

Figure 13. Stainless steel 550gal tanks with petroleum-rated hoses
**Chemicals used**

**Brine**

Brine is a strong saline solution that contains sodium chloride or other salts, *i.e.* it is water with a high concentration of salt [1]. These experiments are conducted with brine and not plain water since it is brine what is usually found in petroleum reservoirs. In order to recreate brine in the laboratory, every 1L of water was mixed with 43g of salt. This mass of salt (NaCl) was calculated for a 2% volume of this salt in the solution and that salt density of $2170\frac{kg}{m^3}$, as follows:

$$0.02 \times \left(\frac{1000ml}{1L}\right) \left(\frac{1cm^3}{1ml}\right) \left(\frac{1m^3}{100^2 cm^3}\right) \left(\frac{2170Kg}{1m^3}\right) \left(\frac{1000g}{1Kg}\right) = 43\%_L$$  \hspace{1cm} (1)

**De-Emulsifier**

A Xylene-based de-emulsifier was utilized in the HPSC. Before allowing the fluid sample flow towards the HPSC, 10ml of de-emulsifier can be injected into the high pressure vessel to ensure the liquids separation. Xylene is a flammable liquid with a $C_6H_4(CH_3)_2$ formula. It is clear and colorless with a sweet, balsam-like odor [9].

**Hydrogen sulfide (H$_2$S)**

A few breaths of air with levels of 500ppm can cause death. Hydrogen sulfide is a corrosive, colorless, flammable gas with a characteristic odor of rotten eggs. When it is released into the air, it reacts to form sulfur dioxide and sulfuric acid. When one is exposed to lower concentrations of H$_2$S during a longer period of time, one can suffer nose, throat or eye irritation, headaches and fatigue [9].
Sodium Hydroxide (NaOH)

Sodium hydroxide is a white, crystalline odorless solid. In the autoclave system NaOH is utilized in the liquid form in a 10%wt solution in water. When sodium hydroxide is dissolved in water, an exothermic reaction occurs. The amount of heat can be sufficient to ignite combustible materials. This heat releasing process occurs also when NaOH is made to react with acids (e.g. H₂S).

This chemical needs to be handled with extreme caution since contact with skin can cause severe and painful burns with ulcerations. If the eye gets in contact with it, clouding of the eye and blindness can occur. Inhaling this compound can translate into obstruction and loss of measurable pulse, lung inflammation and fluid accumulation in the lungs [9].

Nitrogen (N₂)

This inert gas presents no threat to human beings (it composes more than 78% of our atmosphere). It is colorless, odorless and tasteless [9].

Petroleum

Crude oil or petroleum is a viscous, dark and highly flammable liquid. If it produces vapors due to heating and these gases are inhaled it can cause throat irritation, headache, nausea and dizziness. In the long term it can cause dermatitis: if the liquid gets in contact with clothes or shoes, these must be taken off immediately and the person must shower for at least 20min. It has a 400°C boiling temperature (at 1atm) and a -7°C flash point [10].
**Testing Procedure and Calculations**

Every test must start by having a clean Autoclave System in order to avoid having memory from previous experiments. The autoclave, hoses and HPSC are cleaned by running 1L of Kerosene and 1L of water with a Haskel, air-driven single-piston pump that is connected to the system on a loop mode, *i.e.* it takes the liquids out from the bottom of the Autoclave and then returns them in from the top, using the fourth and yet unutilized ½” female NPT port (as seen on *figure 14*). After running the Kerosene for 5 minutes the liquid is removed and 2L of water are run in the same mode, but this time with Nitrogen at 5atm. These liquids are taken away from the system (through the pressure gradient) through the HPSC.

The first step to run a test is to input the liquids. It must be made sure that all valves are closed except those that need to remain open for the liquid introduction. The details of which valves are open and in which order etc., can be found in Appendix A. Autoclave System Operation Checklist. Depending on the water cut of the experiment being conducted it is decided how much volume of brine and how much of petroleum is input, *e.g.* in the case of 33%WC, 0.66L of brine and 1.33L of petroleum are input:

\[
0.33 \times 2L = 0.66L \quad (2)
\]

\[
2L - 0.66L = 1.33L \quad (3)
\]
Once the liquids are in, Hydrogen sulfide must be injected. If, for example, the experiment being run has the H$_2$S concentration parameter set at 100ppm at a total pressure of 70atm, a 100ppm of H$_2$S-in-Nitrogen Tank will be used. It is connected to the system and the proper valves and regulator are open in order to let enough gas get in the autoclave until the pressure in the system has reached 70atm. In order to allow the absorption process to occur and equilibrium to be reached, 5 minutes are allowed to pass. Next, a H$_2$S in gaseous form concentration reading is done. The valve that allows gas flow into the autoclave’s regulator is open and this allows the H$_2$S monitor to get a constant flow for approximately 30sec and thus a reading. This gas flow translates into a 30psi pressure drop in the autoclave. There is a concentration difference between the input value and the measured value at this point. This change in concentration is the amount of H$_2$S absorbed by the liquids.

The original planned procedure entailed taking a sample in order to learn how much of this change was due to oil and how much due to water. At this point, in the original plan, the HPSC is still at atmospheric pressure from the recently completed cleaning process. Before sending a fluid sample at high pressure from the autoclave into the collector, 10ml
of de-emulsifier were to be injected into the HPSC in order to guarantee a proper brine-oil separation. Once the HPSC was ready, the appropriate valves would be opened to allow the fluids to travel to the HPSC (See Figure 3).

In this first plan, all the valves were closed and one minute was allowed for the liquids and gases to settle in the HPSC, as well as for the de-emulsifier to increase the superficial tension of the water and oil phases. Next, the LPSC was connected to the HPSC through a 136atm petroleum-rated flexible hose with Camlock fittings. The bottom valve of the HPSC was then very slowly opened in order to let the water in the bottom drain out to the larger volume of the LPSC. The clear PVC pipe of the LPSC indicated the water level. When the brine pressure is reduced from 70atm to atmospheric pressure, it releases the previously absorbed gases. These gases were entrapped in the LPSC. The lateral valve in the LPSC was then opened to allow those gases to come in contact with the H$_2$S monitor and thus a second concentration reading was acquired.

Once this measurement was recorded, the LPSC was disconnected from its high pressure counterpart. The H$_2$S monitor was then unplugged from the LPSC and the hose was directed into the vacuum system. Thus, the Hydrogen sulfide was scrubbed in the NaOH canister.

When brine is let out of the HPSC (only petroleum and H$_2$S are withheld) there is a pressure drop inside the collector (it decreases from 70atm to an unknown $P_x$); now gases would be allowed to occupy the volume recently vacated by the brine. This pressure
decrease translated into gas release by the petroleum. When the HPSC-LPSC connection procedure was repeated with the crude oil, the linking valve was closed when all the oil had been released and gases started to flow. In order to discover how much of the gas was absorbed by the petroleum, a third H₂S concentration reading was taken. Lastly, after removing the petroleum and its liberated gas from the LPSC, the remaining gases in the HPSC were allowed to fill the LPSC and a fourth (and last) concentration measurement was taken. This last measurement would differ from the one taken on the first reading. This difference was what was liberated by the crude oil when its pressure was decreased from 70 atm to \( P_x \). Knowing these concentrations and volumes, it was then calculated how much H₂S was released inside the HPSC and this was added to the third concentration reading then having the real data of how much Hydrogen sulfide was absorbed by the crude oil. Finally, at this point it would be known how much Hydrogen sulfide was absorbed by the brine, and how much by the petroleum.

This original procedure could not be implemented in practice: the H₂S monitors require approximately 30 sec flow in order to give a concentration reading, and the gases that came out of the LPSC lasted for 2 or 3 seconds. This meant that the LPSC could not be used for the purpose it was designed and built.

In order to solve this problem a new approach was adopted. The liquids were to be input into the system followed by the H₂S and the desired concentration and pressure. A concentration reading would then be acquired and this concentration would differ from what was input by \( \Delta c_{H_2S} \) (H₂S concentration difference). This difference is what was
absorbed by the mixture. Instead of trying to identify how much was absorbed by each of the liquids, the Hydrogen sulfide absorption ratio by the mixture is obtained, which is a more useful information for the oil industry. According to Henry’s Law of dilute solutions or gas absorption in liquids, the solubility depends on both the solute and the solvent [13]. In this case the solute remains the same (H₂S) whereas the solvent (mixture) will change its properties as the water cut varies. Then, with this new approach these absorption ratios are found experimentally and analytically (utilizing chemistry and gas equilibrium knowledge).

From the operational perspective, this new procedure meant skipping phases D, E and F of the Checklist (Appendix A). The rest of the process would remain the same.

As previously mentioned, after 5min of the beginning of the gas-liquids interaction a Hydrogen sulfide concentration is acquired \( c_{H_2S, new} \). This concentration is compared with the original one \( c_{H_2S, o} \) thus finding the amount that was absorbed by the liquids:

\[
\Delta c_{H_2S} = c_{H_2S, o} - c_{H_2S, new}
\]

This value is in molar ppm, i.e. it shows how many moles of H₂S there are in the mixture per every million moles of Nitrogen. Knowing that the volume the gases will be contained in the autoclave is 2L, it can be found how many moles of Hydrogen sulfide there are within the system.

In order to state the physical and chemical relationships that are used in the calculations, it is necessary to declare the basic equations based on the assumption of an ideal gas:
Mole fraction is defined as

$$x_i = \frac{n_i}{n_{tot}} = \frac{P_i}{P_{tot}} \quad (5)$$

Then, for Hydrogen sulfide:

$$P_{H_2S} = x_{H_2S}P_{tot} \quad (6)$$

where \(P_{tot}\) is the total pressure.

From the ideal gas equation of state:

$$Pv = RT \quad (7)$$

The gas constant \(R\) is defined as

$$R = \frac{R_u}{\bar{m}} \quad (8)$$

where \(R_u = 8.314 \frac{kJ}{Kmol \cdot K}\) and \(\bar{m}\) is the species’ molecular mass.

This value is found for Hydrogen sulfide as:

$$H_2S \rightarrow 2H + S \iff 2(1.008 \frac{kg}{Kmol}) + (32.065 \frac{kg}{Kmol}) = 34.081 \frac{kg}{Kmol} = \bar{m}_{H_2S} \quad (9)$$

then

$$R = \frac{8.314 \frac{kJ}{Kmol \cdot K}}{34.081 \frac{kg}{Kmol}} = 0.244 \frac{kJ}{kg \cdot K} \quad (10)$$

Since all tests are run at room temperature (298K) and from equations (6) and (7)

$$V_{H_2S} = \frac{RT}{P_{H_2S}} = \frac{RT}{x_{H_2S}P_{tot}} = \frac{(0.244 \frac{kJ}{kg \cdot K})(298K)}{x_{H_2S}P_{tot}} \quad (11)$$

$$V_{H_2S} = \frac{72.71 \frac{kJ}{kg}}{x_{H_2S}P_{tot}} \quad (12)$$

In order for this equation to make dimensional sense \(x_{H_2S}\) must be given in \(\frac{mol}{mol}\) while \(P_{tot}\) in KPa.
The number of moles of a species in a system can be found as

\[ N = \frac{m}{M} \]  \hspace{1cm} (13)

where \( N \) is the number of moles.

In order to find the mass of Hydrogen sulfide that is originally input in each experiment, the system’s volume is required to be known. This is visible from the following equation:

\[ m_{H_2S} = \frac{\nu_{gas}}{V_{H_2S}} \]  \hspace{1cm} (14)

\[ \nu_{gas} = 2L = 2000mL = 2000 \text{cm}^3 \left( \frac{1m^3}{100^3 \text{cm}^3} \right) = 0.002m^3 \]  \hspace{1cm} (15)

Then,

\[ m_{H_2S} = \frac{0.002m^3}{72.71 \frac{kJ}{kg}} \]  \hspace{1cm} (16)

\[ m_{H_2S} = \left( 2.75 \times 10^{-5} \frac{m^3}{kg} \right) \nu_{H_2S} P_{tot} \]  \hspace{1cm} (17)

After taking a concentration reading, a new \( x_{H_2S} \) is found: \( x_{H_2S, new} \). By the time this reading has finished taking place the pressure in the system has changed, this new pressure is called \( P_{new} \). When,

\[ m_{H_2S, new} = \left( 2.75 \times 10^{-5} \frac{m^3}{kg} \right) \nu_{H_2S, new} P_{new} \]  \hspace{1cm} (18)

Based on equation (4) it can now be stated that the mass of Hydrogen sulfide that has been absorbed by the oil/brine mixture is

\[ m_{H_2S, absorbed} = \Delta m_{H_2S} = m_{H_2S} - m_{H_2S, new} \]  \hspace{1cm} (19)
In order to give a dimensionless value that will help relate one result with the other, a percentage will be quantified in the following manner:

\[
\% \text{ absorbed mass} = \frac{m_{H_2S, \text{absorbed}}}{m_{H_2S, \text{original}}} \quad (20)
\]

Following equation (13) the amount of moles that have been absorbed is given by

\[
N_{H_2S, \text{absorbed}} = \frac{m_{H_2S, \text{absorbed}}}{0.034 \text{ Kg/mol}} \quad (21)
\]

Finally, keeping in mind that the volume the liquids occupy is \( V_{\text{liq}} = 0.002 m^3 \) the molar solubility \( M \) (parameter used for describing dilute solutions) is

\[
M_{H_2S} = \frac{N_{H_2S, \text{absorbed}}}{V_{\text{liq}}} \quad (22)
\]

\[
M_{H_2S} = \frac{m_{H_2S, \text{absorbed}}}{0.002 m^3} \quad (23)
\]

\( M_{H_2S} \) is a function of \( m_{H_2S, \text{absorbed}} \), the latter is a function of \( V_{H_2S} \) which at the same time is a function of \( P_{H_2S} \), thus

\[
M_{H_2S} = f(P_{H_2S}) \quad (24)
\]

**Propagation of error analysis**

From equations 17, 18, 19 and 20 it can be said that

\[
\sigma_{m_{H_2S}} = \sqrt{\left( \frac{\partial m}{\partial x} \right)^2 \sigma_x^2 + \left( \frac{\partial m}{\partial P} \right)^2 \sigma_P^2} \quad (25)
\]
Where

\[ \sigma_x = 3\% = 0.03 \text{ (uncertainty from gas tank manufacturer)} \]  \hspace{1cm} (26)  

\[ \sigma_p = 0.1 \text{psi} \approx 0.0068 \text{atm} \approx 0.03\% \text{ (for 20atm tests) or 0.01\% (for 70atm tests)} \]  \hspace{1cm} (27)  

(uncertainty from digital pressure gauge)

Also, from equation 17

\[ \left( \frac{\hat{m}}{\hat{x}} \right) = \left(2.75 \times 10^{-5} \frac{m^3 \text{kg}}{\text{KJ}}\right) P_{\text{tot}} \]  \hspace{1cm} (28)  

\[ \left( \frac{\hat{m}}{\partial P} \right) = \left(2.75 \times 10^{-5} \frac{m^3 \text{kg}}{\text{KJ}}\right) x_{H_2S} \]  \hspace{1cm} (29)  

The uncertainty for water cut measurements was measured in the lab as

\[ \sigma_{\% WC} = 40 \text{ml} = 2\% = 0.02 \]  \hspace{1cm} (30)  

**300-meter horizontal pipe simulation test**

When the liquids leave the reservoir they are usually transported through either vertical or highly-tilted tubing until it reaches the surface. Especially for platforms in the sea, the vertical section leads to a horizontal section. It connects again to a vertical or highly-tilted tube that finally reached the platform. As a part of this thesis, a larger system was utilized to simulate this section of horizontal tubing and analyze the absorption phenomena when there is a slug regime flow in the piping.
An 80%WC mixture was prepared in a stainless steel, 350gal tank. This mixture was stirred for 10 minutes to assure a good blend. Next, a Haskel, air-driven pump was utilized to introduce 19gal of this solvent into the system. This is a 45gal system so a \textit{approximately} 40% volume of liquids was input. The liquids were allowed to settle within the system for proper species separation, with the petroleum on top. Following this step, H$_2$S at 353ppm was input until a 20atm pressure was reached within the system.

At this time, the multi-phase pump was turned on at 680rpm which yields a total superficial velocity of 6m/sec according to previously done calibrations. With this value, and the liquid volume percentage the corresponding liquid and gas superficial velocities can be calculated:

Liquid volume percentage = 40%

Total superficial velocity = 6m/sec

\[
\text{Liquid Superficial Velocity: } V_{SL} = (0.4) (6 \text{ m/sec}) = 2.4 \text{ m/sec} \tag{31} \\
\text{Gas Superficial Velocity: } V_{SG} = (0.6) (6 \text{ m/sec}) = 3.6 \text{ m/sec} \tag{32}
\]

These superficial velocities pertain to a slug regime flow. The flow continued for 5 minutes before an H$_2$S concentration reading was conducted.
RESULTS

Tests were run to determine several mass-absorption ratios. Four different solvents were utilized as given in Figure 15:

For each solvent six different mass-absorption ratios are found, three at 20atm and three at 70atm. The 3 H₂S concentrations used in this study are: 50ppm, 100ppm and 300ppm.

As previously mentioned, the experimental analysis entailed 60 tests with three different parameters:

- Total Pressure (20, 70atm)
- H₂S Concentration (50, 100, 300ppm)
- Water Cut (0, 33, 66, 100%WC)

as can be seen in the following table:
Table 1: Test Matrix

<table>
<thead>
<tr>
<th>WC</th>
<th>Test</th>
<th>Brine</th>
<th>Crude Oil</th>
<th>Pressure (atm)</th>
<th>Original H2S ppm</th>
<th>New H2S ppm</th>
<th>ANSEROX ppm</th>
<th>( V_e ) ppm</th>
<th>( V_{T} ) ppm</th>
<th>( M_{E} ) ppm</th>
<th>( V_{T} ) ppm</th>
<th>( M_{E} ) ppm</th>
<th>( y_{T} ) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1a</td>
<td>0.0</td>
<td>2.0</td>
<td>20</td>
<td>0.00000</td>
<td>19.0</td>
<td>40</td>
<td>2.1413E+01</td>
<td>51.9</td>
<td>1.68E+01</td>
<td>33.2</td>
<td>1.62E+01</td>
<td>33.2</td>
</tr>
<tr>
<td></td>
<td>2a</td>
<td>0.0</td>
<td>2.0</td>
<td>20</td>
<td>0.00000</td>
<td>19.0</td>
<td>40</td>
<td>2.1413E+01</td>
<td>51.9</td>
<td>1.68E+01</td>
<td>33.2</td>
<td>1.62E+01</td>
<td>33.2</td>
</tr>
<tr>
<td></td>
<td>3a</td>
<td>0.0</td>
<td>2.0</td>
<td>20</td>
<td>0.00000</td>
<td>19.0</td>
<td>40</td>
<td>2.1413E+01</td>
<td>51.9</td>
<td>1.68E+01</td>
<td>33.2</td>
<td>1.62E+01</td>
<td>33.2</td>
</tr>
<tr>
<td></td>
<td>4a</td>
<td>0.0</td>
<td>2.0</td>
<td>20</td>
<td>0.00000</td>
<td>19.0</td>
<td>40</td>
<td>2.1413E+01</td>
<td>51.9</td>
<td>1.68E+01</td>
<td>33.2</td>
<td>1.62E+01</td>
<td>33.2</td>
</tr>
<tr>
<td></td>
<td>5a</td>
<td>0.0</td>
<td>2.0</td>
<td>20</td>
<td>0.00000</td>
<td>19.0</td>
<td>40</td>
<td>2.1413E+01</td>
<td>51.9</td>
<td>1.68E+01</td>
<td>33.2</td>
<td>1.62E+01</td>
<td>33.2</td>
</tr>
<tr>
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<td>0.00000</td>
<td>19.0</td>
<td>40</td>
<td>2.1413E+01</td>
<td>51.9</td>
<td>1.68E+01</td>
<td>33.2</td>
<td>1.62E+01</td>
<td>33.2</td>
</tr>
<tr>
<td>1a</td>
<td>0.0</td>
<td>1.3</td>
<td>32.2</td>
<td>216.0</td>
<td>20.0</td>
<td>157.6</td>
<td>165</td>
<td>4.50E+02</td>
<td>61.6</td>
<td>5.26E+01</td>
<td>105.6</td>
<td>5.11E+01</td>
<td>105.6</td>
</tr>
<tr>
<td></td>
<td>2a</td>
<td>0.0</td>
<td>1.3</td>
<td>32.2</td>
<td>216.0</td>
<td>20.0</td>
<td>157.6</td>
<td>165</td>
<td>4.50E+02</td>
<td>61.6</td>
<td>5.26E+01</td>
<td>105.6</td>
<td>5.11E+01</td>
</tr>
<tr>
<td></td>
<td>3a</td>
<td>0.0</td>
<td>1.3</td>
<td>32.2</td>
<td>216.0</td>
<td>20.0</td>
<td>157.6</td>
<td>165</td>
<td>4.50E+02</td>
<td>61.6</td>
<td>5.26E+01</td>
<td>105.6</td>
<td>5.11E+01</td>
</tr>
<tr>
<td></td>
<td>4a</td>
<td>0.0</td>
<td>1.3</td>
<td>32.2</td>
<td>216.0</td>
<td>20.0</td>
<td>157.6</td>
<td>165</td>
<td>4.50E+02</td>
<td>61.6</td>
<td>5.26E+01</td>
<td>105.6</td>
<td>5.11E+01</td>
</tr>
<tr>
<td></td>
<td>5a</td>
<td>0.0</td>
<td>1.3</td>
<td>32.2</td>
<td>216.0</td>
<td>20.0</td>
<td>157.6</td>
<td>165</td>
<td>4.50E+02</td>
<td>61.6</td>
<td>5.26E+01</td>
<td>105.6</td>
<td>5.11E+01</td>
</tr>
<tr>
<td></td>
<td>6a</td>
<td>0.0</td>
<td>1.3</td>
<td>32.2</td>
<td>216.0</td>
<td>20.0</td>
<td>157.6</td>
<td>165</td>
<td>4.50E+02</td>
<td>61.6</td>
<td>5.26E+01</td>
<td>105.6</td>
<td>5.11E+01</td>
</tr>
</tbody>
</table>

The first set of columns describes the water cut. For example, a test with a 0%WC requires the Autoclave system to be filled with 0L of brine and 2L of crude oil. The second set of columns states the pressures in atmospheres: first, the initial pressure of the experiment; second, the partial pressure of Hydrogen sulfide as described by Equation 6 and the third one the pressure after the concentration reading took place: \( P_{\text{new}} \).
The third set of columns lists the original amount of Hydrogen sulfide that was input. Here, the first column is the concentration in ppm in Nitrogen. This concentration is acquired from the documentation that corresponds to that gas tank. The second column is the mass of Hydrogen sulfide. This value is obtained from Equation 17 and takes into account the volume where the gases are contained and the molecular mass of the species.

The fourth set represents the amount of \( \text{H}_2\text{S} \) after the 5 minutes of interaction between the fluids. The ppm column is filled by the experiment operator based on the results from the \( \text{H}_2\text{S} \) concentration monitor. The mass column is filled utilizing Equation 18.

The last column set entails all the calculations of how much Hydrogen sulfide was absorbed. The first column is the concentration difference as stated in Equation 4. The second one is how much was absorbed in Kg using Equation 19. The third one is the mass-absorption ratio calculated using Equation 20. The molar solubility is also calculated using Equation 23 and can be found as the last column of the table.

Inspecting the table, it is easy to see that there are four divisions with two sub-divisions each. Each division is a different water cut and each sub-division is a group of tests with the same original pressure.

Each one of these sub-divisions has three original \( \text{H}_2\text{S} \) concentration which yield a different mass-absorption ratio individually. This is the value that is being looked for and the one that is plotted.
Table 2: Mass-absorbance ratios

<table>
<thead>
<tr>
<th>WC</th>
<th>Pressure (mm)</th>
<th>Original ICS ppm</th>
<th>Mass Absorbance in mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>49</td>
<td>61%</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>105</td>
<td>64%</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>312</td>
<td>66%</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>105</td>
<td>65%</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>312</td>
<td>68%</td>
</tr>
<tr>
<td>33</td>
<td>20</td>
<td>49</td>
<td>55%</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>105</td>
<td>59%</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>312</td>
<td>59%</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>49</td>
<td>64%</td>
</tr>
<tr>
<td></td>
<td>70</td>
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<td>67%</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>312</td>
<td>64%</td>
</tr>
<tr>
<td>66</td>
<td>20</td>
<td>49</td>
<td>54%</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>105</td>
<td>68%</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>312</td>
<td>59%</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>49</td>
<td>73%</td>
</tr>
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<td>70</td>
<td>105</td>
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</tr>
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<td>71%</td>
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<td>75%</td>
</tr>
<tr>
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<td>20</td>
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<td>59%</td>
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<tr>
<td></td>
<td>70</td>
<td>49</td>
<td>65%</td>
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<td>105</td>
<td>65%</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>312</td>
<td>65%</td>
</tr>
</tbody>
</table>

In the same manner, each subdivision yielded a particular value for Molar Solubility as can be seen in Table 3:

Table 3: Molar Solubility

<table>
<thead>
<tr>
<th>WC</th>
<th>Pressure (mm)</th>
<th>Original ICS ppm</th>
<th>Molar Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>49</td>
<td>0.00242</td>
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<tr>
<td></td>
<td>20</td>
<td>105</td>
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<td>30</td>
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<td>20</td>
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<td>70</td>
<td>49</td>
<td>0.00981</td>
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<td>0.00342</td>
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<td>70</td>
<td>312</td>
<td>0.01410</td>
</tr>
</tbody>
</table>

The calculated x and y variances are presented in Table 4:
Table 4: Variances in the $x$ and $y$ axis

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>Original H2S ppm</th>
<th>$x$ ppm</th>
<th>Variance</th>
<th>$y$ ppm</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
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<td>33</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>66</td>
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<td>100</td>
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In the 300-meter system, after 5 minutes of slug regime flow through the 300m coil at 20atm and an original amount of 353 ppm an H2S concentration reading was taken. The result was that 0 ppm was left in the gaseous state, i.e. a 100% absorption ratio was achieved for this flow condition.

The main source of error with regards to the volume measurements is the petroleum input into the autoclave. Due to the high viscosity of the fluid, a certain amount tends to stay on the transport vessel walls. The uncertainty was determined to be 40ml. In order to improve the uncertainty, it is recommended that the oil is input first and then brine so the latter will wash the oil down into the autoclave.
Figure 16: Results from all tests with 0%WC at both pressures

Figure 17: Averages of all results with 0%WC at both pressures
Figure 18: Results from all tests with 33%WC at both pressures

Figure 19: Averages of all results with 33%WC at both pressures
Figure 20: Results from all tests with 66%WC at both pressures

Figure 21: Averages of all results with 66%WC at both pressures
Figure 22: Results from all tests with 100%WC at both pressures

Figure 23: Averages of all results with 100%WC at both pressures
DISCUSSION

**Role of System (or total) Pressure in H₂S mass-absorption phenomena**

Figures 16 to 23 show plots of the results of the test matrix of Table 1 with uncertainties marked as calculated by Equations 25 to 30. Each water cut has two graphs, the second one has the same data as the first one but only the average values are being plotted, and these points are connected by smooth lines. Tests at 0%WC, i.e. with pure petroleum show that for lower original H₂S concentration (50ppm) having a lower pressure increases the mass absorption ratio by a 6%. As the original H₂S concentration is increased to 100ppm and above, total pressure seems to have little role on the absorption phenomenon, having differences of only 2% (between 20 an 70atm), higher pressures demonstrating higher absorption ratios.

Analyzing the results of the 33%WC experiments it is easy to observe the same trend as the tests at 0%WC: a maximum absorption ratio is reached near the 100ppm H₂S concentration and the difference in absorption ratio for the two different pressures decreases as the H₂S concentration increases. The greatest difference occurs at 50ppm (9%). In the 33%WC case, the absorption is higher at 70atm throughout the whole region.

The results for the 66%WC solvent are quite similar to the previous two, and the curve seems to flatten as the pressure increases. Again, higher pressure results in a higher mass absorption ratio and the difference in absorption decreases with an original H₂S concentration decrease. The smallest difference is at 300ppm (1%) and the largest is at 50ppm (14%). The data for the 50ppm, 70atm tests was not repeated due to time
constraints while most other tests were done up to five times each. The curve again flattens in the 100%WC solvent (pure brine). Here, the lower pressure shows a flatter profile whereas the higher pressure still shows the same trend as the lower water cuts.

It was consistently observed in all experiments that total pressure played a lesser role in the absorption phenomena is as the H₂S concentration is increased. In addition, the highest mass-absorption ratios are always found between 50 and 100ppm and the lowest at 300ppm, this is observed for all water cuts and total pressures. It was also observed that from 0 to 66%WC, having a higher total pressure translated into having higher mass-absorption ratios. Nevertheless, this order is reversed when the solvent is pure brine.

The lowest absorption ratios were found when the solvent is pure petroleum and the original H₂S concentration is the highest. These results are strongly independent of the total pressure, as the percentages were 36% and 38% for 20 and 70atm, respectively. This means that when a reservoir with a petroleum-rich water cut (low amount of brine) and high concentration of H₂S in gaseous state is found, it can be expected that the amount of Hydrogen sulfide that will be liberated by the liquids during the decompression process will be lower. This also translates into less necessity of H₂S scavenger injection at the beginning of the piping.
Role of Original $H_2S$ concentration and Water Cut % in the phenomena

Figure 24: Mass-absorption as a function of the Water Cut - 20atm

Figure 25: Mass-absorption as a function of Water Cut - 70atm

Figures 24 and 25 illustrate all the results at each total pressure. Each figure has three curves – each one representing $H_2S$ concentration. They show how the absorption ratio changes as the solvent varies from pure petroleum (0%WC) to pure brine (100%WC). All six curves present the exact same behavior where the minimum mass-absorption rate is found at 0%WC and the maximum at 100%WC going through an inflexion point in between. This inflexion point usually found at *approximately* 50%WC. Five out of six of
the curves have a positive slope at this inflexion point, while the curve for 50 ppm at 20 atm has a negative value at this point. This seems to be a real behavior since the experiments represented by 50 ppm were conducted from three to five times each.

The 300 ppm original H₂S concentration curve always yields the lowest mass-absorption ratios at all water cuts and all system (or total) pressures. In the same manner, the 100 ppm curve always presents the highest mass-absorption ratios except for the 66% WC, 70 atm scenario. In this environment in particular, the 50 ppm result showed a higher mass-absorption ratio. This test needs to be repeated.

In these figures, the results on the x axis correspond to a 2% (or 40 ml) error. This is due to the viscous liquid film (especially petroleum) on the wall of the flasks. Comparing the 20 atm and 70 atm curves of the 300 ppm experiments it can be seen that the uncertainty in the y axis is greater for the 20 atm condition. In the same manner, the \( \sigma_p \) for the lower pressure is 0.03 whereas the one for the higher pressure is 0.01. This value is squared to get the final sigma, and thus the uncertainty for the lower pressure is greater.
Importance of each parameter in the phenomena

At low system pressure (20atm), the mass-absorption ratio is the highest for pure solvents and decreases when there is a mixture of brine and crude. The overall highest values for this system pressure are found when the solvent is pure petroleum (for all original H\textsubscript{2}S concentrations). The largest value is 75\% for the 50ppm original H\textsubscript{2}S concentration, 100\%WC scenario.

The ability to absorb the corrosive gas decreases as the H\textsubscript{2}S concentration increases and this proves to be true for all water cuts. As mentioned before, the best absorptivity is observed at the lower original H\textsubscript{2}S concentrations.
For the 70atm system pressure condition, some changes in absorption are observed. It is seen that the role of the water cut is opposite from to the one at lower pressure. In this case, the pure solvents (brine or crude oil) usually present the lowest mass-absorption ratios: now the mixed solvents absorb the best. The 66%WC yields the highest ratios for lower original H₂S concentrations. When the original H₂S concentration is 300ppm, there is an increasing linear behavior of mass-absorption ratios from 0%WC to 100%WC. The highest percentage is found on the 50ppm original H₂S concentration and 66%WC (78%).

For both system pressures, the poorest absorption ratio is always found when the solvent is pure petroleum and the original H₂S concentration is the highest.
As for the 300 m flow loop, the system was filled with a 80%WC mixture. Only one test was conducted in this loop to check the difference between the autoclave results and the flowing loop results. Since any test at 70atm would require at least 3 tanks of H₂S, the test was conducted at low pressure and 80%WC.

The 300-meter system yielded a 100% absorption result for the 20atm, 353ppm, 80%WC test. This results is plotted in figure 21 thus creating figure 28:

![Figure 28: Result of the 300-meter system](image)

The 66%WC plot was utilized since it is the closest one to the 80%WC utilized in the 300-meter loop. It can be seen that having a flow increases the gas absorption ratio since the gas is fully entrapped within the liquid. This is definitely the case for slug regime, and it is suggested for future studies to investigate how this phenomenon changes at different points of the regime flow map.
CONCLUSIONS

- In order to be able to scavenge H₂S along the reservoir-platform piping, it is important to know how much Hydrogen sulfide will be liberated from the aqueous phase as pressure decreases.

- The Molar Solubility of H₂S in the Autoclave System is given by:

\[ M_{H_2S} = \frac{m_{H_2S, absorbed}}{6.8 \times 10^{-5} \text{ Kg m}^3/\text{mol}} \]

- When dealing with petroleum, Molar Solubility is used due to the fact that petroleum’s molecular mass can only be acquired as an estimate and this can affect the reliability of the results. In the same manner, maintaining all calculations in molar solubility units \((mol/m^3)\) permits the results of this investigation to be utilized on a broader range of types of crude oil.

- In all experiments and for all water cuts, the total pressure does not play a strong role in the absorption phenomena as the original H₂S concentration is increased.

- The highest mass-absorption ratios are always found between 50 and 100ppm and the lowest at 300ppm, this is observed for all water cuts and total pressures.

- It was also observed that from 0 to 66%WC, having a higher total pressure translated into having higher mass-absorption ratios. This order is reversed when the solvent is pure brine.

- At low system pressure (20atm), the mass-absorption ratio is the highest for pure solvents and decreases when there is a mixture of brine and crude. The opposite is true at a high system pressure (70atm).
- The ability to absorb the corrosive gas decreases as the original H$_2$S concentration increases and this proves to be true for all water cuts and system pressures.
- For both system pressures, the poorest absorption ratio is always found when the solvent is pure petroleum and the original H$_2$S concentration is the highest.
- The 300-meter loop tests demonstrated that having a flow increases the gas absorption ratio since the gas is fully entrapped within the liquid. A 100% absorption ratio was achieved when the liquids were in a slug regime flow.
APPENDIX A. AUTOCLAVE SYSTEM OPERATION CHECKLIST
A. Safety Revision
1. Make sure there is no pressure in System
2. Make sure all valves are closed

B. Fluids Input
1. Open valve 4
2. Open Regulator 3
3. Open valve 1
4. Input Liquids
5. Close valve 1
6. Close valve 4
7. Close Regulator 3
8. Make sure Regulator 1 is closed
9. Open valve 2
10. Open H2S Tank
11. Open Regulator 1
12. Input H2S until desired pressure has being reached in the Autoclave
13. Close Regulator 1
14. Close H2S Tank
15. Close valve 2

C. H2S Concentration Reading
1. Allow five minutes to pass
2. Make sure Regulator 3 is closed
3. Open valve 4
4. Open Regulator 3 until 2 PSI is being delivered to H2S monitor 1
5. Acquire Concentration reading from monitor
6. Close valve 4
7. Close Regulator 3
8. Attach outlet hose from Regulator 3 to Vacuum Subsystem
9. Vent H2S Monitor 1

D. De-Emulsifier Injection
1. Make sure valve 6 and 8 are closed
2. Open valve 7
3. Inject the de-emulsifier
4. Close valve 7
5. Make sure valve 9 is closed
6. Open valve 8
7. Make sure valve 7 is closed

E. HPSC Filling
1. Open valve 5
2. Open valve 6
3. Allow Fluids to go to HPSC
4. Close valve 8
5. Close valve 5
6. Close valve 6
7. Allow the de-emulsifier to take effect

**F. LPSC Fluids Filling**

1. Connect LPSC to Autoclave system
2. Make sure valve 11 is closed
3. Open valve 10
4. Very Slowly open 9 (keep in mind 70atm difference between sample collectors)
5. Allow water to go to the LPSC
6. Close valve 9 as soon as Oil flows into LPSC
7. Close valve 10
8. Connect H₂S monitor 2 to LPSC
9. Open valve 11
10. Acquire H₂S concentration reading
11. Close valve 11
12. Unhook LPSC from Autoclave system
13. Connect LPSC to vacuum sub-system
14. Open valve 10
15. Allow gases to be sucked by vacuum sub-system
16. Discharge water from LPSC
17. Close valve 10
18. Connect LPSC to Autoclave system
19. Make sure valve 11 is closed
20. Open valve 10
21. Very Slowly open 9 (keep in mind 70atm difference between sample collectors)
22. Allow oil to go to the LPSC
23. Close valve 9 as soon as gases flow into LPSC
24. Close valve 10
25. Open valve 11
26. Acquire H₂S concentration reading
27. Close valve 11
28. Unhook LPSC from Autoclave system
29. Connect LPSC to vacuum sub-system
30. Open valve 10
31. Allow gases to be sucked by vacuum sub-system
32. Discharge oil from LPSC
33. Close valve 10
34. Connect LPSC to Autoclave system
35. Make sure valve 11 is closed
36. Open valve 10
37. Very Slowly open 9 (keep in mind 70atm difference between sample collectors)
38. Allow gases to go to the LPSC
39. Close valve 9 when pressure becomes homogeneous
40. Close valve 10
41. Open valve 11  
42. Acquire H₂S concentration reading  
43. Close valve 11  
44. Unhook LPSC from Autoclave system  
45. Connect LPSC to vacuum sub-system  
46. Open valve 10  
47. Allow gases to be sucked by vacuum sub-system  

**G. System Bleeding**  
1. Disconnect H₂S monitor 1 from Autoclave system  
2. Connect recently disconnected hose from H₂S monitor 1 to Vacuum Subsystem  
3. Make sure Regulator 3 is closed  
4. Open valve 4  
5. Open Regulator 3 until delivering 15 PSI  
6. When the pressure in the Autoclave system has reached zero  
7. Close Regulator 3  
8. Close valve 4  
9. Open Valve 3  
10. Make sure Regulator 2 is closed  
11. Open N₂ Tank  
12. Deliver N₂ until 50~60psi has been reached within the System  
13. Close Regulator 2  
14. Close N₂ Tank  
15. Close Valve 3  
16. Make sure valve 9 is closed  
17. Place disposal container underneath valve 9  
18. Make sure valve 7 is closed  
19. Open valve 1  
20. Open valve 5  
21. Open valve 6  
22. Open valve 8  
23. Open valve 9  
24. When all liquids are out of Autoclave system  
25. Close valve 1  
26. Close valve 5  
27. Close valve 6  
28. Close valve 8  
29. Close valve 9  

**H. System Cleaning**  
1. Make sure all valves are closed  
2. Open valve 4  
3. Open Regulator 3  
4. Open valve 1  
5. Input 1L of Kerosene and 1L of Water  
6. Close valve 1
7. Close valve 4
8. Close Regulator 3
9. Open valve 5
10. Open valve 12
11. Open valve 13
12. Turn on Haskel pump at 40psi for 2 minutes
13. Turn Haskel Pump off
14. Close valve 12
15. Close valve 13
16. Close valve 5
17. Make sure Regulator 2 is closed
18. Open valve 3
19. Open N₂ Tank
20. Deliver 3atm
21. Close N₂ Tank
22. Close Regulator 2
23. Close valve 3
24. Make sure valve 7 is closed
25. Make sure disposal container is under valve 9
26. Open valve 5
27. Open valve 6
28. Open valve 8
29. Open valve 9
30. After all Kerosene and N₂ is out
31. Close valve 5
32. Close valve 6
33. Close valve 8
34. Close valve 9
35. Open valve 1
36. Allow pressure in Autoclave to reach zero
37. Close valve 1
For safety purposes the whole Autoclave system was put inside a cabinet. Every junction of this cabinet was doubly sealed with vinyl sealant and duct tape. The cabinet has an explosion-proof polymer window that can be opened and closed at will in order to manipulate the valves and set the experiments before running them. It also has four ports that are used by the vacuum subsystem.

This subsystem is the main mechanism for assuring an appropriate management of any H₂S there might be in the cabinet due to a leak. The gas may come from an improper tank connection or an escape from a fitting (due to failures in the system). This vacuum sucks all the air in the cabinet twice per minute and then directs it towards a 10%W NaOH solution, through where the gas is bubbled.

The purpose of this procedure is to obligate any remaining Hydrogen sulfide react with the Sodium Hydroxide and thus convert it in a non-harmful compound. With the objective of having full redundancy, two vacuums (each with its NaOH canister) are used. The first one vacuums the air at head-height since this is the location where most of the tubing and fittings are located. The second vacuum sucks the air from a lower level, near where the Hydrogen sulfide tank is. The position where the second vacuum is placed is ground level due to the fact that H₂S is heavier than air, then in case a leak exists Hydrogen sulfide will tend to go down to the bottom. Sodium Hydroxide is used for scrubbing H₂S out of air but cannot be used to remove this compound from oil since that
reaction is highly reversible: if the waterflood’s pH changes Hydrogen sulfide reappears [13].

The Autoclave System’s operators wear ©3M 6100 series Respirator masks. They have ©3M 6002 Gas mask cartridges, designed for escaping from environments with Hydrogen sulfide concentrations up to 200ppm.

<table>
<thead>
<tr>
<th>HAZARD</th>
<th>PRIMARY</th>
<th>SECURİTY MEASURES</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2S</td>
<td>Leak from tank Hydrogen sulfide tanks placed inside the cabinet if there would be a leak it would stay inside the cabinet and sucked by the vacuum system into the NaOH bucket.</td>
<td>The cabinet is double-sealed first with a sealant and then with hermetic closing tape on all vertices. In case the vacuum system would fail there is a secondary one working simultaneously.</td>
</tr>
<tr>
<td></td>
<td>Leakage from system There are two H2S environmental sensors monitoring the cabinet’s interior. Also, the vacuum systems would come into play if this scenario would come to be.</td>
<td>One of the H2S environmental sensors is at head-height and another one aiming to the bottom, since Hydrogen Sulfide is heavier than air. There is also the vacuum redundancy mentioned above.</td>
</tr>
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<td></td>
<td>Corrosion All parts (tubing, valves, flanges, plugs, regulators, sensors, adaptors, etc.) are made of Carbon Steel or 316 Stainless Steel. All flexible hoses are made of Teflon.</td>
<td>The Hydrogen Sulfide concentrations being worked with, as the expect lifetime of the stop inside the primary measures more than satisfactory.</td>
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<tr>
<td></td>
<td>Fire Due to H2S’ ability to ignite by spark or flame in concentrations between 4 and 44% in air, no electrical equipment is installed inside the cabinet. Nonetheless, the highest percentage used is 0.03%</td>
<td>Having the cabinet sealed-closed, as it is assures that in case of a fire inside the cabinet it would not propagate to outside the cabinet due to the lack of oxygen to conduct the combustion. There are also several Fire Extinguishers in the vicinity.</td>
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<td>NaOH</td>
<td>During Handing Security gloves, garments and protective lenses are utilized.</td>
<td>The NaOH is set on the lower side of the cabinet in case there is a spill it would not fall on any person. It is also in a tray that can contain corrosive liquids.</td>
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<td>While Running Experiments The NaOH buckets of the vacuum systems have a filter that assures that only gases will come out due to the bubbling being related to the vacuum.</td>
<td>This NaOH buckets are inside a spill tray and covered with plastic.</td>
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<td>High Pressure Tubing The Carbon Steel pipe used is rated at 1220°f @ 7500 psi.</td>
<td>The primary measure is sufficient for the actual pressures that will be worked with.</td>
</tr>
<tr>
<td></td>
<td>Valves, Tees, etc. All parts are rated for pressures beyond the ones being worked on.</td>
<td>The primary measure is sufficient for the actual pressures that will be worked with.</td>
</tr>
<tr>
<td></td>
<td>Hosing Teflon hoses are rated for over 1550 psi.</td>
<td>The primary measure is sufficient for the actual pressures that will be worked with.</td>
</tr>
<tr>
<td></td>
<td>Autoclave The Autoclave has a pressure relief valve that blows into the cabinet. Additionally, an aluminium shield has been placed around the O-Ring, which is likely the first place where there would be a leak in case of an explosive failure.</td>
<td>The Autoclave has a pressure relief valve that blows into the cabinet. Additionally, an aluminium shield has been placed around the O-Ring, which is likely the first place where there would be a leak in case of an explosive failure.</td>
</tr>
</tbody>
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APPENDIX C. HENRY’S CONSTANT FOR H₂S IN DIFFERENT WATER CUTS
Henry’s Law states that

*At a constant temperature, the amount of a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.* [12]

This can be written as

\[ e^p = e^{kc} \]  \hspace{1cm} (23)

where \( e \) is Euler’s number, \( p \) is the partial pressure of the solute above the solution, \( k \) is Henry’s Law constant and \( c \) is the concentration of the solute in the solution in any of its units. This can also be written as

\[ p = kc \]

Henry’s Law’s constants are defined in the limit

\[ k_c = \lim_{{c \to 0}} \frac{P_{H_2S}}{c_{H_2S,absorbed}} \]  \hspace{1cm} (24)

In the case of this investigation the concentration of the solution in the solute \( c \) will be given in mass units (per two liters of solvent volume), when

\[ k_m = \lim_{{m \to 0}} \frac{P_{H_2S}}{m_{H_2S,absorbed}} \]  \hspace{1cm} (25)

This is done due to the fact that petroleum’s molecular mass can only be acquired as a guesstimate (it is a highly complex mixture of chemical compounds that can entail hundreds of different species) and this can affect the reliability of the results. In the same
manner, maintaining all calculations in molar solubility units \( \left( \frac{\text{mol}}{m^3} \right) \) permits the results of this investigation to be utilized on a broader range of types of crude oil.

Henry’s law is in reality only an approximate law [11]. Solutions that obey Henry’s Law are called ideal dilute solutions. It is the intention of this thesis to find the Henry’s Law’s constant for Hydrogen sulfide as the solvent changes from a 0%WC to a 100%WC mixture. Based on the results of the tests and the previously mentioned equations the real \( k_m \) is obtained. In the following graphs \( k_m \) is indicated on the vertical axis as \( k \). Also, on the bottom right of each graph an equation is found, this is the mathematical expression of \( k_m \).

0% Water Cut
After extrapolating as previously mentioned the real \( k_m \) values were found. For each water cut two values were identified, one for each pressure. It was found that pressure has indeed an important role in this phenomenon. At 20atm \( k_m \approx 660 \frac{\text{KPa}}{\text{kg}} \) where as at a higher pressure (70atm) \( k_m \approx 840 \frac{\text{KPa}}{\text{kg}} \).
Figure 29: Petroleum - 20atm

Figure 30: Petroleum - 70atm

33% Water Cut

The same trend as the one found for the 0% WC is observed when the solvent is changed to 33%. Moving from an original H₂S concentration of 50ppm to 100ppm there is a decrease. After that, a stronger sloped increase is noticeable. At 20atm \( k_m \approx 725 \frac{KPa}{Kg} \)

where as at a higher pressure (70atm) \( k_m \approx 620 \frac{KPa}{Kg} \).
**66% Water Cut**

The polynomial to the second order regression can be seen as the dotted gray line. Identifying the intercept between this line and the $y$ axis permits to find the value of $k$ for this state in particular. At 20atm $k_m \approx 840 \frac{KPa}{kg}$ where as at a higher pressure (70atm) $k_m \approx 445 \frac{KPa}{kg}$. 
As water cut increases the curve tends to flatten out. The effect of this phenomenon on the value of $k$ is to decrease it. At 20atm $k_m \approx 480 \frac{KPa}{kg}$ where as at a higher pressure (70atm) $k_m \approx 600 \frac{KPa}{kg}$. 

100% Water Cut
When segregating all the data by the original pressure (20atm or 70atm) the following figures can be plotted:
Figure 37: Results at 20atm - Comparison of $k$ as a function of H$_2$S concentration

In Figure 24 it can be seen that as the original H$_2$S concentration increases, the separation between each solvent becomes clearer. The highest value pertains to the lowest water cut (i.e. pure petroleum – light blue curve) whereas the lowest value is that of the highest water cut (pure brine – brown curve). All of the curves have a minimum approximately 100ppm.

Figure 38: Results at 70atm - Comparison of $k$ as a function of H$_2$S concentration
The same kind of comparison plot is repeated for the results of the tests at 70atm. Again, as the original H$_2$S concentration increases, the separation between each solvent becomes clearer. The highest value pertains to the lowest water cut (i.e. pure petroleum – light blue curve) whereas the lowest value is that of the highest water cut (pure brine – brown curve). Nevertheless, all of these curves per se have little importance, what is of utter significance is the value that can be found from them which is their intercept with the y axis. Table 2 summarizes the encountered values.

**Table 6: Values of $k_{ma}$**

<table>
<thead>
<tr>
<th>%WC</th>
<th>P(atm)</th>
<th>$k$(KPa/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20</td>
<td>664</td>
</tr>
<tr>
<td>0</td>
<td>70</td>
<td>841</td>
</tr>
<tr>
<td>33</td>
<td>20</td>
<td>725</td>
</tr>
<tr>
<td>33</td>
<td>70</td>
<td>621</td>
</tr>
<tr>
<td>66</td>
<td>20</td>
<td>842</td>
</tr>
<tr>
<td>66</td>
<td>70</td>
<td>447</td>
</tr>
<tr>
<td>100</td>
<td>20</td>
<td>478</td>
</tr>
<tr>
<td>100</td>
<td>70</td>
<td>602</td>
</tr>
</tbody>
</table>

The oil industry can take advantage of these values when they are exploring a new well: when the first fluid samples are taken, the water cut and reservoir pressure can be easily identified; with that information the corresponding $k$ can be chosen and the expected amount of H$_2$S to be liberated by the liquids during the fluid decompression can then be estimated. Obtaining a reading of the H$_2$S concentration when the fluids reach the platform would not give the explorers enough data for them to predict how much of the gas to expect at different points of the piping. The reason is that the H$_2$S that reaches the platform is mainly in the gaseous state, but in the reservoir part of it was in the aqueous phase and was liberated during the decompression process of flowing up through the pipe. Since H$_2$S is a corrosive gas, a Hydrogen sulfide scavenger is injected at different
points of the pipe to attack the unwanted gas. For doing this in an appropriate manner the best would be to know exactly what the concentration is at the distinct locations of the pipe (in order to inject exactly the required quantity of scavenger at each of these points). It is for this reason that knowing the values of $k$ is of immense consequence.

Analyzing the values of $k$ (from table 2) at different total pressures permitted to observe different behaviors. During the simulation of the reservoir at low pressure, an increasing and almost linear conduct between 0 and 66%WC is notorious followed by a drop between 66 and 100%WC.

![Figure 39: Results of $k$ as a function of %WC at 20atm](image)

An almost mirror image is found when plotting the data for the 70atm tests. An almost linear trend is found between 0 and 66%WC, but this time it is a negative slope. As the brine/petroleum ratio increases above 66% an increase is found on the $k$ curve. Then, 66%WC is a minimum for the low pressure scenario and a maximum for the high pressure.
Finally, in order to appreciate the role of the pressure in the reservoir on the value of $k$ the following chart was plotted:

Here, it is noticeable that the pure fluids (petroleum-light blue and brine-brown) have a positive slope, meaning that its value of $k$ increases with pressure, while the mixtures have a negative slope. It is seen that the most pressure-sensitive solvent is 66%WC: in the conducted tests it yielded both, the highest (842kPa/kg) and lowest (447KPa/Kg) values of $k$ (low pressure and high pressure, respectively).
LIST OF REFERENCES


