



Norwegian University of  
Science and Technology

# H<sub>2</sub>S removal technologies for maturing oil fields with sea water injection

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Master of Science in Mechanical Engineering

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**MASTER THESIS**

for

Student Lars Eirik Birkeland

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*H<sub>2</sub>S removal technologies for maturing oil fields with sea water injection**H<sub>2</sub>S-fjerning for aldrende olje-felter med sjøvannsinjeksjon***Background and objective**

Components such as water, H<sub>2</sub>S, CO<sub>2</sub> and heavy hydrocarbons need to be removed to an acceptable level before gas and oil is sent to further processing.

On the Norwegian Continental Shelf (NCS) the H<sub>2</sub>S levels in reservoirs using sea water injection for pressure maintenance shows a tendency to increase with time. For such fields, an H<sub>2</sub>S removal process needs to be implemented to control the H<sub>2</sub>S in the export gas.

The focus on this work will be to review technologies for H<sub>2</sub>S removal. A typical field on the NCS will be selected, and a technology assessment will be done. If needed, the evaluation of the appropriate technology (-ies) will be split in early and late life of the field.

**The following tasks are to be considered:**

1. Review of technologies for H<sub>2</sub>S removal from gas, oil and multiphase streams
2. Evaluation of technologies for H<sub>2</sub>S removal for a typical oil field on the NCS
3. Development of process simulation models for H<sub>2</sub>S removal in HYSYS
4. Development of process design for H<sub>2</sub>S removal technologies and mechanical design

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 Field work

Department of Energy and Process Engineering, 15. January 2018



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## Sammendrag

Forbedret olje- og gassutvinning utføres ofte med injeksjon av sjøvann i brønnen som trykkkompenserende virkemiddel. Med det følger potensielle utfordringer. Mikrobiologisk forsurening er vurdert som en betydelig kilde til den økende akkumuleringen av  $H_2S$  i den produserte væsken av hydrokarboner. Sjøvann er ofte rik på elektron akseptorer (sulfater/tiosulfater) som normalt er mangelvare nedstrøm reservoaret. Disse elektron akseptorene er ganske enkelt redusert av sulfat reduserende bakterier (SRB) til sulfid ( $S^{2-}$ ). Dermed ligger alt til rette for generering av  $H_2S$ . Opphav, vekst og overlevelse av SRB vil bli videre studert.

For typiske forhold på den norske kontinental sokkel (NCS), med lav konsentrasjon av  $H_2S$ , blir vanligvis scavenger teknologi eller fast adsorpsjon anlegg installert. Regenerativ amine anlegg er for det meste benyttet for store volumstrømmer av gass og lavt partialtrykk av surgass. Bulkfjerning av større mengder  $H_2S$  gjøres ofte med regenerativt fysisk løsemiddel eller membran teknologi som ofte har en større kapasitet.

Et typisk tre trinns offshore separasjon og stabiliseringsanlegg er blitt designet med fokus på  $H_2S$  behandlings teknologier; scavenger injisering og amin anlegg.

En reell komposisjon av reservoarstrømmen sammen med produksjons profiler for fremtidige år er kjent. Disse profilene sammen med prosessanlegget og amin anlegget vil bli grunnleggende for simuleringen. Simulering av reservoaret gjøres ved miksing av hydrokarbon multifase strømmen, den injiserte vannmengden,  $H_2S$  og en tilbakeført mengde av prosessert olje og gass.

En estimering av scavenger forbruk og kostnader er utført basert på omtrentlige tall for scavenger kjemikalie kost per liter og scavenger absorpsjonskapasitet. En estimering av størrelse, vekt, strøm forbruk og kost (høy usikkerhet) for ett amin anlegg er gjennomført basert på tall fra Hysys.

Forskjellige injeksjonspunkter eller en kombinasjon av to injeksjonspunkter i separasjonsanlegget er blitt simulert. Injeksjon etter første trinns kompresjon ble funnet til å være det billigste alternativet, men virker å være sårbart for korrosjon. Med kun en liten økning i kjemikaliekost og en betydelig reduksjon i potensial for korrosjon fremstår injeksjon etter første separator og mikser (gass fra 2. og 3. olje separator) som en bedre løsning. Undervannsinjeksjon ble observert til og ha en dramatisk økning i kjemikalie kost, men er muligens helt nødvendig for enkelte gamle anlegg der det ikke er benyttet korrosjon resistent material som følge av at feltet opprinnelig var sweet.

Validering av Hysys modellen beviste at en betydelig usikkerhet må forventes og det vil sannsynligvis være betraktelig lavere  $H_2S$  konsentrasjon i gas fasen for situasjoner i virkeligheten.

Scavenger teknologi virker og være den foretrukne prosessen basert på mange faktorer som inkluderer enkelthet og fleksibilitet, ett høyt potensial for stort fotavtrykk og investeringskost relatert med amine installasjon, generelt mer egnet for den spesifikke gass raten og  $H_2S$  nivået som ble observert, valideringen av Hysys modellen og grunnet en årlig strømkost for kokeren i amin anlegget som sannsynligvis ikke er langt unna kostnaden for scavenger kjemikalie (billigste alternativet).

## Abstract

Enhanced oil and gas recovery is often performed with seawater injection in the well as pressure compensating mean. With it, potential challenges arise. Microbiological souring is considered a major contributor to the increased mass of  $H_2S$  found in the produced hydrocarbon fluids. Seawater is often rich in electron acceptors (sulphate/thiosulphate), which are normally found in short supply downstream reservoir. These electron acceptors are easily reduced by sulphate reducing bacteria (SRB) to sulphide ( $S^{2-}$ ) and then the generation of  $H_2S$  is initiated. The origin, growth and survival of SRB are studied.

For typical NCS conditions, with low concentrations of  $H_2S$ , scavenger chemical injection or solid bed adsorption is usually installed to remove the toxic and corrosive gas. Regenerative amine plant is mostly applied for large volume, low acid gas partial pressure hydrocarbon streams. For bulk removal of larger amounts of  $H_2S$ , regenerative physical solvent or membrane technology are usually selected based on the generally higher absorption capacity for such processes.

A typical three stage offshore separation and stabilization plant is designed with focus on two  $H_2S$  sweetening technologies; scavenger injection and amine plant.

A real fluid composition and production profiles as well as  $H_2S$  production profiles for future years are known and will be the basis for the simulation. The reservoir is simulated by mixing the multiphase hydrocarbon stream, the injected seawater,  $H_2S$  and a returned amount of processed oil and gas

An estimation of the scavenger consumption and costs have been performed based on approximately numbers for scavenger chemical cost per liter and scavenger absorption capacity. Estimations of sizes, weight, power consumption and cost (high uncertainty) for the amine plant is done based on numbers from Hysys.

Different injection points or a combination of two injection points in the separation plant have been simulated. Injection after first stage compression was found to be cheapest but is vulnerable towards corrosion. With only a minor increase in chemical cost and a significant reduction in corrosion potential, injection after first separator and mixer (gas from 2. and 3. oil separator) may be a better solution. Subsea injection was observed to have a dramatic increase in chemical cost but may be necessary for old facilities without sour service installation, which is typically a result of the originally sweet reservoir.

The validation of the Hysys model proved that a significant uncertainty for the  $H_2S$  distribution must be expected, and we will probably find a considerable lower  $H_2S$  concentration in the gas phase for real scenario operations.

Scavenger technology seems to be the preferred process based on many factors including simplicity and flexibility, a high potential for a large footprint and CAPEX related with amine installation, generally more suited for this particular gas rate and  $H_2S$  level observed, the validation of the Hysys model and a yearly reboiler (amine) electricity cost that is possibly not far from the yearly scavenger cost (cheapest option).



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## Nomenclature

$H_2S$	Hydrogen sulfide
$CO_2$	Carbon dioxide
NRB	Nitrate reducing bacteria
SRB	Sulfate reducing bacteria
SRP	Sulfate reducing prokaryotes
t-SRB	Thermophilic SRB
m-SRB	Mesophilic SRB
h-SRB	Hyperthermophilic SRB
NCS	Norwegian continental shelf
CAPEX	Capital expenditures
ppm	Parts per million (mol)
TVS	Thermal viability shell
VFA	Volatile fatty acids
h-NRB	Heterotrophic nitrate -reducing bacteria
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
DIPA	Diisopropanolamine
DEA	Diethanolamine
DGA	Diglycolamine
TEA	Triethanolamine
DMPEG	Dimethyl ether of polyethylene glycol
LPG	Liquified petroleum gas
TEG	Tri ethylene glycol
MEG	Mono ethylene glycol
MEA-triazine	1,3,5-tris(2-hydroxyethyl)-hexahydro-S-triazine
MMA-triazine	1,3,5-trimethyl-hexahydro-S-triazine

## 1. Introduction

The high focus on environmental friendly emission and the levels of sulfur in gas and crude oil, has led to a rising attention towards different sour gas treating processes.

$H_2S$  is a foul, rotten egg smelling sour gas which is extremely toxic. Both emitting the gas into the atmosphere and exposure towards the gas can be harmful and extremely dangerous. Exposure of workers to the toxic gas can be fatal within short time. Hydrogen sulphide exposure is one of the most common sorts of inhalation death, second behind carbon monoxide poisoning [2]. The removal of hydrogen sulphide is not only necessary due to a health and safety standpoint, but the acid gas is also corrosive. Gas, oil and multiphase streams has traditionally been transported over long distances in high pressure pipelines.  $H_2S$  can cause cracking and pitting of high strength steel. The corrosion will typically appear more locally and can cause catastrophic failure to the steel/iron material. Stress Orientated Hydrogen Induced Cracking (SOHIC), Hydrogen Embrittlement (HE), Sulphide Stress Corrosion Cracking (SSCC), Hydrogen Induced Cracking (HIC) are some of the severe failures that can occur [3]. To protect pipelines and process facilities,  $H_2S$  must be reduced to an adequate level. Corrosion in general, is estimated to cost the oil and gas industry about 1.4 billion USD annually, only in US alone. The number is remarkable [2].

Maintaining pressure and increasing yield in oil and gas reservoirs is usually done with either gas, seawater, water or produced water injection in the well. As a result, oil and gas are easily transported through the production wells and the pressure is maintained at a desirable level. An increasing generation of  $H_2S$  in the produced fluids after years of production has been observed in many reservoirs with seawater injection. For some situations, the  $H_2S$  concentration is almost exponentially increased, from a few ppm to hundreds of ppm. Seawater or produced water is often rich in nutrients, which will support the growth of sulphate reducing bacteria (SRB). SRB is documented to have a major impact in the increased level of  $H_2S$  in both reservoir and produced fluids. Although microbiological souring (SRB) is considered the main contributor to  $H_2S$  accumulation, less is known about the different non-microbiological souring theories.

Today several different sweetening processes have been developed to meet the increasing demand for both large and small scale  $H_2S$  removal facilities. A number of factors should be evaluated when deciding which technology is the best suitable for the operation. Many different technologies will be discussed and evaluated.

Reservoirs on the Norwegian Continental Shelf are mostly sweet. That means a quite low amount of acid gas concentration in the produced fluid.  $H_2S$  in the sales gas must typically be brought down to a level around 3 ppm. To remove small amounts of  $H_2S$ , non regenerable scavenger chemicals or solid beds are usually used. For larger gas/oil streams or streams with high  $H_2S$  content, a regenerative process facility installation is in favor, as scavengers or solid beds might not be economic beneficial or capable of handle the large amounts of  $H_2S$ . Amine plants have a large variety of characteristics to handle different types of acid gas streams. The amine process has showed to be both reliable and efficient and is also the preferred regenerative process on NCS.



The purpose for this thesis is to understand the mechanisms of souring in a reservoir due to seawater injection. A lot of research and work have been done related with the topic, but still a lot of the souring behavior and theories are unclear and needs to be proven.

Several sweetening processes are hereby reviewed and evaluated. Selected processes based on typical NCS reservoir conditions are further evaluated in more detail.

A simulation of a typical 3 stage separation and stabilization plant is carried out. Oil, gas and water should be separated according to a specific production profile given. The objective is to find the best suitable removal technology between scavenger injection or installation of an amine plant. Because of the increase in  $H_2S$  due to seawater injection, a  $H_2S$  prediction overview has been given as basis and different future years will be simulated according to the predicted  $H_2S$  production in the well stream. Different scavenger injection points are also simulated.

## 2. Reservoir souring and seawater breakthrough

### 2.1. Introduction to reservoir Souring

The phenomenon “Reservoir souring” can be stated as “increasing mass of hydrogen sulfide ( $H_2S$ ) per unit mass of produced fluids” and is a result of water flooding. This situation is usually observed after some years of secondary oil recovery initiated by water breakthrough. Reservoir souring is suggested to be divided into microbiological and non-microbiological souring mechanisms. Today there is a wide agreement that the main contributor to the  $H_2S$  production is microbiological and the activity of the sulfate reducing prokaryotes (SRP).

The unexpected increase in  $H_2S$  concentration in oil/gas produced from reservoirs is a significant problem for many reservoirs around the world. The economic cost associated with reservoir souring is estimated to increase by 2% of total cost, due to sour service materials at the design stage of the project. For large projects exceeding 1 billion USD, this cost is quite significant [2]. For project where the estimation of souring potential has failed or not been accounted for, the cost of souring can be even higher. This is due to an unexpected cost of equipment such as sweetening units, internally coated pipes, or chemically injectors for corrosion inhibition. This substitution of equipment is not always possible because of both space limitations and costs, but also when complex situations makes it impossible.

Many North Sea oilfields have experienced an increase in  $H_2S$  production due to seawater flooding. The attention was led towards the Sulphur -reducing bacteria (SRB). A typical  $H_2S$  production profile for a well, after years of seawater injection, is showed in figure 2-1 [4]. The  $H_2S$  production during the first years is almost non-existent, before increasing almost exponentially during later life of production.

The problem is usually studied in context with water injection as mentioned before. When water is injected, the environment in the water swept regions of the reservoir will change. The availability of nutrients, such as sulphate, are likely to change. The cooling effect towards the hot well region, when the cold seawater is injected may create a beneficial environment for SRB and increase the bacteria population dramatically. At the same time, a more tolerant group of the bacteria/archaea (t-SRB and h-SRA) can increasing the potential for souring.

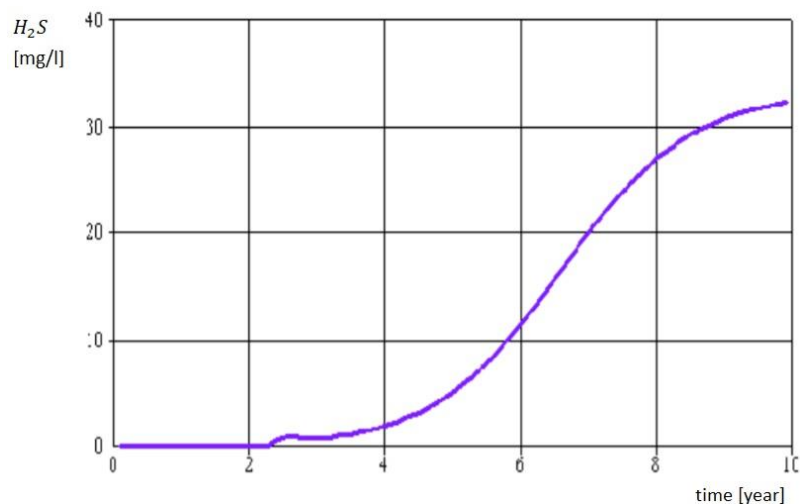


Figure 2-1: Typical production profile for  $H_2S$  when seawater injection is performed [4]

## 2.2. Non-microbiological souring

The complex physical environments for petroleum reservoirs can contribute to other mechanisms of souring than SRB. The phenomenon of geochemical souring or non-microbiological souring has been suggested. Very little is understood about it. For most situations, they are neglected. These theories are also believed to have a greater impact on the levels of  $H_2S$  in the reservoir originally, than on the reservoir souring [3].

The different non-microbiological souring mechanisms can be divided into:

- Thermochemical sulphate reduction; Direct reduction of sulphate by hydrocarbons, then generation of hydrogen sulphide [3].
- Thermal decomposition of organic Sulphur compounds (denaturation); Decomposition of sulphur compounds under high temperature [3].
- Dissolution of pyritic material; Reaction between pyrite from reservoir rock and the environment [3].
- Redox reactions involving bisulphite oxygen scavengers; Oxygen scavenger is rich in sulfite that can be directly converted to  $H_2S$  [3].

## 2.3. Microbiological souring

As mentioned earlier in the text, microbiological souring is considered to be the main contribution factor to the souring problem. It is also the only phenomena that we know for sure is related with souring.

SRB grow in the absence of oxygen. The microorganisms will in that case “breathe” sulphate rather than oxygen, which is known as a form of anaerobic respiration. SRB respiration involves the consumption of sulphate and an organic carbon source. The waste products become  $H_2S$  and  $CO_2$ .  $H_2S$  is only accumulated under anaerobic conditions. In the presence of air, it is rapidly and spontaneously oxidized to elemental sulfur [5]. We generally speak about *sulphate-reducing bacteria* and *sulphate-reducing archaea*, which we collectively refer to as *sulphate-reducing prokaryotes*.

From figure 2-2, the canonical dissimilatory sulphate reduction pathway on a molecule level is shown. Sulphate is converted to adenosine phosphosulfate (APS), then to sulfite and finally to sulfide, which is irreversible. [2]

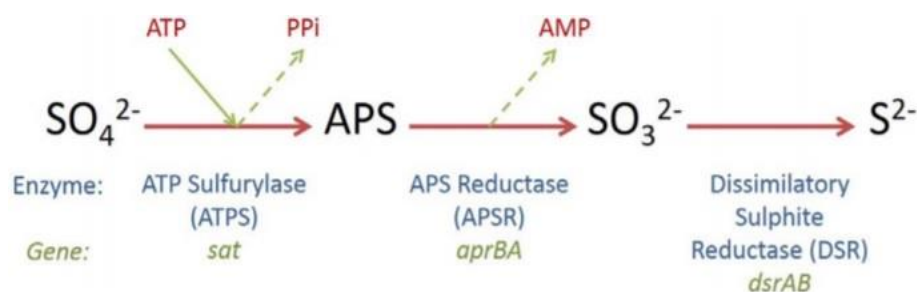


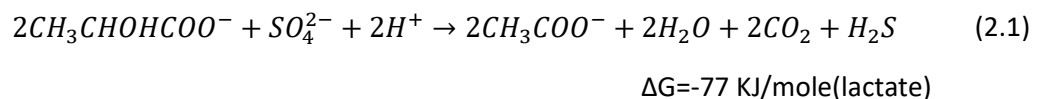
Figure 2-2: Sulphate reduction pathway [2]

SRBs are found naturally in sub surface reservoir. Oil reservoirs represent complex microbial ecosystems and have a large number of different groups of anaerobes. These reduced environments

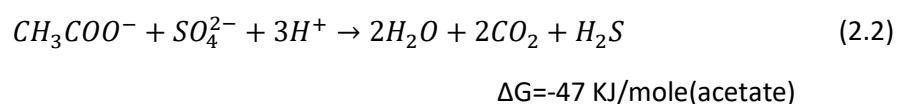
are usually rich in electron donors, but the relatively low number of terminal electron acceptors contribute to low  $H_2S$  production. Injecting seawater/sulfate-rich produced water into the well, might increase the microbial activity dramatically by introducing oxidants, particular sulphate ( $SO_4^{2-}$ ). Thiosulphate may be another, less dominant oxidant. The terminal electron acceptor sulphate is brought into vicinity of various electron donors in the organic -rich petroleum environment and the generation of  $H_2S$  is initiated. SRB's wide range of metabolic mechanisms will allow sulphate reduction to take place under many different reservoir conditions. Organic acids (e.g. VFA), alcohols and hydrogen are often the electron donors for sulfate acceptor. These may be biproducts of fermentative degradation of complex organic compounds. Petroleum hydrocarbons are other potential electron donors [6].

The volatile fatty acids (VFA) within carbon sources are considered as the most important electron donor and the main source for sulphate reduction. VFA is common in both formation water and in the mixing of formation water with injected seawater. However, there is a rising attention towards other oil components as carbon sources. It has been demonstrated that the aromatics toluene, ethylbenzene and alkanes were degraded by SRP, resulting in acetate. The toluene degradation has been further investigated in studies, concluding with a realistic role as an electron donor for sulphate reduction [2]. Other potential electron donors could be lactate, propionate, butyrate, benzoate, benzene, phenol, naphtenic and n-alkanes [7].

Acetate is common in many formation waters and is found in high concentrations. Acetate could be quite easy oxidized by SRB. But for some types of SRB, it is impossible. Oxidation of lactate to acetate could be a possibility for these types of SRB [7].



The oxidation of acetate by SRB:



Hydrogen can also be a source to electron donors, but only some SRBs are able to use it.



#### 2.4. Sulphate -Reducing Prokaryotes (SRP)

Sulphate -reducing bacteria is usually divided into two groups, *Desulfovibrio* and *Desulfotomaculum*. Other groups of the bacteria are known (e.g. *Desulfonauticus*). The two genera are better known,

according to their maximum temperature tolerance, respectively, as mesophilic (m-SRB), thermophiles (t-SRB) and sometime halophilic (both). Mesophilic prefers a moderate temperature range and will normally not grow at temperatures above 45 °C. Halophilic prefers saline conditions. Thermophiles are more robust and can tolerate temperature up to 70 °C (this can vary quite a lot, dependent on conditions). There have been reports claiming to have isolated the bacteria at a much higher temperature. *Desulfovibrio* was found at a maximum growth temperature of 85 °C. It seems to be a wide agreement that the SRB can tolerate a higher pressure and temperature in deep oil reservoir than first stated [3].

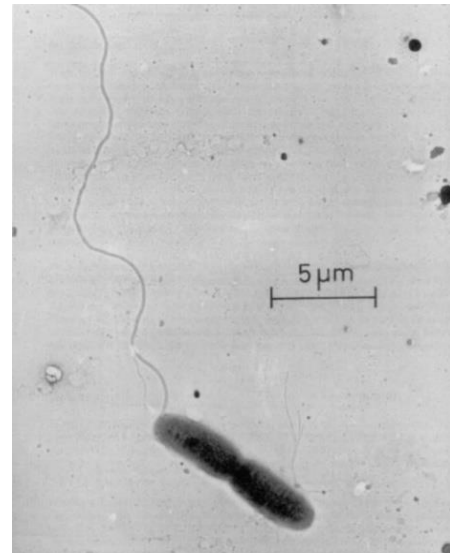


Figure 2-3: t-SRB recovered from a North Sea oil field [3]

The Archaeobacteria referred to as *Archaeoglobus fulgidus*, have been suspected to be responsible for souring in high temperature reservoirs. It is active at temperature above 80 °C. This is more known under “hyperthermophilic” behavior. Anaerobic reduction of sulphate by hydrocarbons is an energy consuming reaction and has proven to be hard for bacteria to accomplish [3]. Nadia Khelifi [8] showed that these hyperthermophilic bacteria were capable of metabolizing saturated hydrocarbons (C<sub>10</sub>– C<sub>21</sub>) as a carbon source, with either thiosulphate or sulphate as terminal electron acceptor at 70 °C.

M-SRB are considered to be the first sulphate reducing organisms to establish colony in the formation. Their concentration in the seawater are typically low, below 10 organisms per mL. However, the large quantum of seawater injected, can allow them to make their way into the well in large quantities and establish large colonies of bacteria downhole. As mention previously, these low tolerant bacteria are preferring a growth temperature between 8 °C - 45 °C. M-SRB are therefore only able to enable colonies in sufficient numbers, close to the injector [3].

The more robust thermophilic SRB are more resistant to higher temperatures, and will grow in temperature ranging from 45 °C - 80 °C. The pre-existence of m-SRB population may be beneficial for the establishment of t-SRB. The main cause of souring is evaluated to be t-SRB [3].

In figure 2-4, the growing and survival of t-SRB is shown for

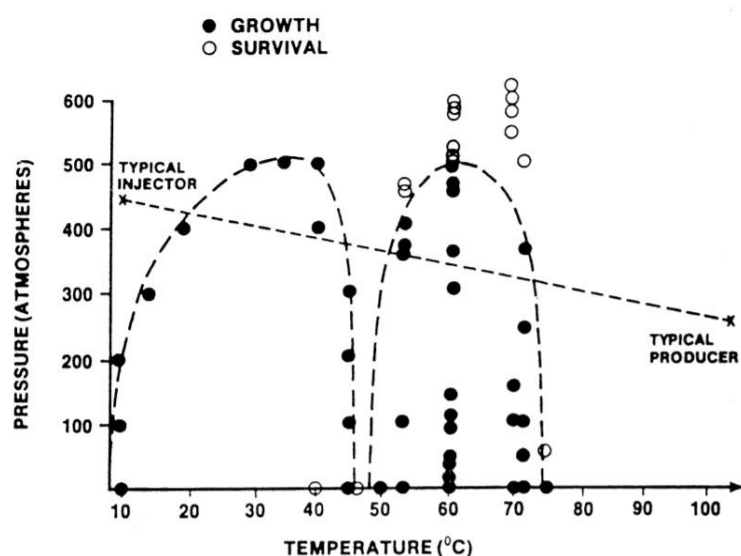


Figure 2-4: Growing and survival of t-SRB for different pressure/temperature levels at a North Sea oilfield [3]

different pressure/temperature levels. It has been developed through surveys/experiments/measurements from the Thistle oilfield in the North Sea [3].

## 2.5. Factors for ideal souring

There is evidence that SRB activity and  $H_2S$  generation have correlations with various environmental conditions. The most dominating factors include pressure, temperature, salinity, viable SRP community, water source, concentration of sulphate, carbon sources, nutrients availability (N and P) and trace metals [2].

In terms of salinity, for high concentrations of total dissolved solids (TDS) the microbial activity could be reduced or even become inactive. Reports have been suggested TDS values in freshwater up to 150,000 mg/l and in some rare situations, 200,000 mg/l [2].

Sulphate is mentioned earlier in the text, as an important electron acceptor. Usually low concentrations of sulfate are found in formation water, but there are high amounts in the seawater. Thereby the effect of souring, when introducing seawater in the well [2].

Carbon sources is also an important factor, as noted earlier. VFA is usually used as carbon source, but selected bacteria can utilize other organic compounds [2].

The range of pH 4.5 to 11.0 is usually a decent interval for SRB activity. The optimum growth pH is estimated to be around pH7. pH values found in oil field waters are between pH 6 and pH 8.6, which includes the optimal value of pH 7 [2].

Sulfide concentration is another feature that can limit the activity of SRBs. Sulfide has a toxic mechanism that can hinder the microbial activity when exposed to higher concentrations. The upper growth limit for SRB has been estimated to around 250 mg/l (sulfide), but there are observations that supports some higher amounts [2].

Temperature profile for the reservoir may have a major impact on the activity for the different types of bacteria as mentioned before. Especially in the injection zone, this can be decisive [2].

Pressure varies with depth in the reservoir. For pressure levels exceeding 15,000 psi, the  $H_2S$  production have been found to be poor and SRB activity nonexistent [2]. Evans [9] reported a maximum level of around 9,000 and 8,800 psi, based on laboratory data.

For souring prediction and modelling, other parameters like water flow path, extent of water breakthrough, reservoir data (geometry, geochemical, geology, rock properties, mineralogy), design of surface facility, gas lift operation etc. should also be evaluated [2].

## 2.6. Mineral adsorption and transport

An important factor when modeling the  $H_2S$  generation is the capability of the rock formation surface to adsorb, react and retain some of the newly formed  $H_2S$ . The most important minerals involving scavenging is iron-containing compounds, which typically includes iron oxides (e.g. Hematite ( $Fe_2O_3$ ), magnetite ( $Fe_3O_4$ ), goethite ( $FeO(OH)$ ), limonite), iron clays (e.g. beidellite), iron carbonates (siderite ( $FeCO_3$ )) and different types of chlorite (e.g. nimite ( $(Ni_5Al)(AlSi_3)O_{10}(OH)_8$ ), chamosite ( $(Fe_5Al)(AlSi_3)O_{10}(OH)_8$ )). As mentioned before, the reaction products are often sulfide

phase products, e.g. pyrite ( $FeS_2$ ), mackinawite (FeS). In addition to the availability of the minerals, solubility is also impacting the adsorption rate. Further, pH, temperature and pressure will all have a direct impact towards the solubility [2].

Typical factors that can prevent the scavenging rate is significant fracturing or flow channelization. Residence time for the injected fluid could be reduced due to the short-cut of the flow path following the flow channelization [2].

High permeability in the reservoir rock may also contribute to migration of SRB into the mineral pores, and more  $H_2S$  will be generated deep in the reservoir. For low permeability, the SRB will be restricted to an area near the well bore [2].

Evans [9] described some retardation factors; water transit time, mineral scavenging and partitioning of  $H_2S$  into residual oil. These factors can make the  $H_2S$  production insignificant, even though the  $H_2S$  accumulation is substantial. The  $H_2S$  is normally produced within the water phase and then distributed to the oil, gas and water phase in the reservoir. Typical factors influencing the partition coefficient are pH, pressure, temperature and dissolved solid concentration in the water phase. If the  $H_2S$  is mixed with the residual oil behind the flood front, the  $H_2S$  will be obstructed during its movement through the reservoir. The water transit time will depend on the fracture distribution, water velocity and well spacing. A typical long water transit time, from the injector to producer, will reduce the souring [9].

## 2.7. Seawater injection and SRB activity

For seawater flooding a large area of rock is cooled. This will create a large area downhole for microbiological activity. The cooling effect of the deaerated seawater can provide a number of opportunities for the microbiological generation of  $H_2S$ . A suitable condition is created for the reducible sulphur source to be supplied with the high availability of sulphate. The pH of the seawater/formation water mix is brought to good conditions for microbial activity (pH 6-9). The high flow ensures an increasing mixing zone with the formation water where growth is accomplished [3].

This cooled volume will generally increase over field life, reducing reservoir temperature. For low temperature reservoirs, this may be crucial.

Eden [3] noted that the efficiency of the microbiological reduction of sulphate to sulfide is low. For a decent growth environment for different types of SRB, the sulphate conversion factor is typical only up to 5%. Formation water can supply SRB with a suitable carbon source, etc. acetate (up to 1000 mg/l). The formation water will however often lack of important nitrogen or phosphorous sources. Injected water or reservoir treatments can provide the missing elements for a dramatic increase in  $H_2S$  production. Typical sources can be phosphorus containing scale treatments or nitrogen containing oxygen scavenger (ammonium bisulphite). A raise in the nutritional supply downhole from 2% to 5% can provide a 150 % boost of  $H_2S$  production.

### 3. Gas purification technologies for $H_2S$ Removal

#### 3.1. Acid gas removal technologies

Gas sweetening processes, also more commonly known as acid gas removal processes are used to remove the acid components (e.g.  $H_2S$ ,  $CO_2$ ) from the hydrocarbon fluid (purify the gas/oil). The processes are designed with purpose of capacity, optimizing capital cost and operating cost, to meet oil/gas quality and for environmental purposes.

#### 3.2. Absorption processes

Absorption involves a process where a component of a gas stream is contacted with a liquid in which the solubility is preferable high. Figure 3-1 shows a typical absorption process. Lean liquid enters at the top of the column and flows downwards, either by sprays or trays, due to gravity. Contaminated gas is introduced in the bottom of the column and is pushed upwards. The liquid is capable of capture the contaminants and rich liquid exits at the bottom, while clean gas flows out in the top of the column. This is known as a countercurrent tower (column). Contact surface area (height and diameter) is crucial for the efficiency (for which degree the acid gas concentration is reduced) when designing the column. The height is decided by the number of stages, either trays or packing, introduced with sprays or other internals.

The choice of solvent is equally important. Characteristics typically involves high solvent selectivity, high volatility, high gas solubility, low effects on product and environment, low cost and high availability, high chemical stability, non-corrosivity, low freezing point, low viscosity, non-flammability and low foaming tendency [10].

Absorption is normally classified based on whether *physical solution* or *chemical solution* is used, which can involve both reversible or irreversible reaction. For physical solvents, the acid gas component is more soluble in the liquid than the rest of the gas stream. The partial pressure in the gas phase is a strong function of the equilibrium concentration of the absorbate in the liquid phase. For chemical solvents, a chemical reaction takes place. The acid gas component and the solvent of the liquid phase reacts and form a loosely bonded product (reversible reaction). Irreversible reaction involves the same chemical reaction, but the reaction products can not readily be decomposed to release the absorbate [11].

#### 3.3. Alkanolamine based processes

The alkanolamine based processes are considered one of the most important among the sweetening processes, being widely used in the industry with a high acceptance. Their high reactivity together with availability at generally low operational cost makes them highly suitable for absorption operations. Their main limitations involve corrosion and footprint.

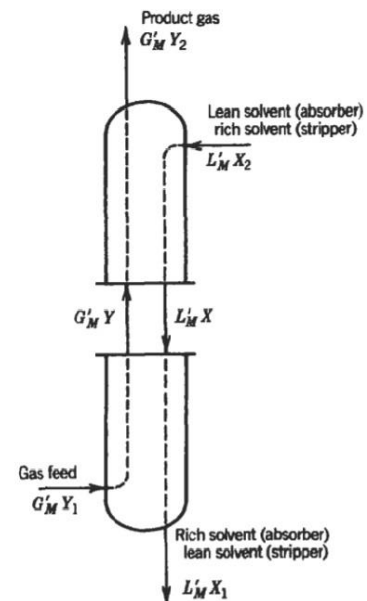


Figure 3-1: Material balance for countercurrent contactor [11]



### 3.3.1. Chemistry alkanolamines

The alkanolamines are composed of one amino group and at least one hydroxyl group. Basic structures of some common used alkanolamines are listed in figure 3-2. The amino group serves as the absorption factor while the hydroxyl group increases water solubility and brings down the vapor pressure. Primary amines, like monoethanolamine (MEA) and 2-(2-aminoethoxy) ethanol or diglycolamine (DGA), have two hydrogen atoms together with a nitrogen atom. Those are considered the most reactive. Secondary amines are the Diethanolamine (DEA) and Diisopropanolamine (DIPA) and have only one hydrogen atom bonded with the nitrogen atom. The tertiary amines have no hydrogen atoms attached to nitrogen atom and can be represented as completely substituted ammonia molecules. Triethanolamine (TEA) and Methyldiethanolamine (MDEA) are common tertiary amines. Absorption of  $H_2S$  (primary amine, MEA) [11]:

*Ionization of water:*



*Ionization of dissolved  $H_2S$ :*



*Protonation of Alkanolamin:*



*Dissociation of bisulfide ion:*



*Solution of hydrogen sulfide:*

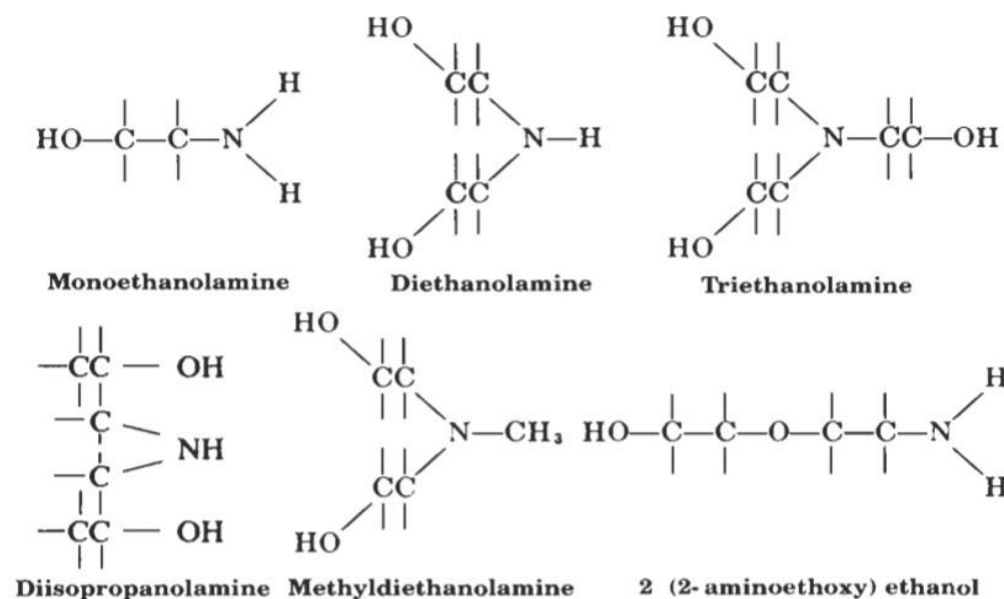


Figure 3-2: Structural formulas for common alkanolamines [11]

### 3.3.2. Monoethanolamine (MEA)

MEA is the strongest base of the amines, has the highest alkalinity of them all and the lowest molecular weight. That means a quite low amount of the chemical is required, a relatively low circulation rate and large carrying capacity. A high percent of removal is achieved (efficiency), and acid components can be removed up to a high percent. However, MEA reacts irreversibly with carbonyl sulfide and carbon disulfide ( $CO_S$  and  $CS_2$ ). Accumulation of reacted solids and solution losses is a big problem, especially if the concentration of  $CO_S$  and  $CS_2$  in the gas is significant. A higher vapor pressure than the others can cause significant solution vaporization losses, especially for low-pressure facilities. Treatments of the purified gas with water wash can overcome this problem. A high corrosion rate (highest of the amines) for the acidic solutions is also causing problems, especially if the amine concentration exceeds 20 wt%. These problems/advantages will favor a gas stream with low acid gas concentrations and limit high acid gas partial pressure streams, which will demand high loading of amines. MEA will also have a quite large heat of reaction with  $H_2S$  and about 30 % higher than DEA. The stripping system will therefore consume considerable more energy [11].

### 3.3.3. Diglycolamine (DGA)

DGA is a primary amine, same as MEA, and possess some of the same characteristics. However, DGA has some major advantages that makes it preferable. The chemical solvent has high reactivity, low equilibrium partial pressure, low vapor pressure, low circulation rate and low steam consumption. Because of the low vapor pressure, a much higher concentration of DGA in the solution can be allowed. Thereby lower stream consumption and circulation rate is achieved. For large volumes of low pressure gas, DGA can be very effective. This is mainly because it can operate efficient at high ambient temperature and moderate pressure. Such conditions are typical for the Middle East and DGA is widely used in these areas. DGA can experience both capital and operating saving costs in addition to improved operation, compared to MEA [11].

### 3.3.4. Diethanolamine (DEA)

DEA can be especially desirable for streams with high amount of  $CO_S$  and  $CS_2$  because of the poor reactivity with these two compounds. DEA has small vaporization losses as a result of low vapor pressure. Some disadvantages with the process can be the requirement of vacuum distillation for recovery of the amine and the forming of corrosive degradation products with  $CO_2$ . Anyway, regeneration will typically provide a cleaner solution than MEA. DEA has a wide range of treating high pressure natural gas streams with high  $H_2S$  content. Even though DEA is not capable of achieving the low  $H_2S$  level than MEA, pipeline specifications can be met quite easy if the regeneration solution can have a certain degree of purity (low acid gas level). The corrosivity of the solution is also noticeable lower than MEA [11].

### 3.3.5. Methyldiethanolamine (MDEA)

This aqueous solution is relatively new and has since its arrival replaced many of the primary and secondary amines. It possesses some great advantages. Low specific heat and heat of reaction with  $H_2S$  results in low energy consumption for regeneration. Even though it is not as reactive as MEA, its low vapor pressure can allow concentration of up to 60 wt% in an aqueous solution without

significant evaporation losses. MDEA is an excellent corrosion inhibitor and corrosion problems are normally nonexistent. The solvent has a high resistance to degradation, both chemical and thermal. However, its high popularity is much because of its unique selectivity for  $H_2S$  in the presence of  $CO_2$ . Some reports have showed with decent design, that this selective solvent can reduce  $H_2S$  concentrations down to acceptable levels and allow a large amount of  $CO_2$  to flow through unabsorbed [11].

### 3.3.6. Flow process solution

Determining amine concentrations can vary and is usually performed based on the operating conditions. Table 3-1 lists some typical levels.

As mentioned before, increasing the amine concentrations can reduce circulation rate and the following energy costs. This potential favorable effect will however mostly be reversed due to higher acid gas vapor pressure for a more concentrated solution [11].

Table 3-1: Amine molar specifications [12]

	Wt%	Solution S.G (15 C)	MW, kg/kmol	Mol. Frac. amine	Kg amine/m <sup>3</sup> solution	Kmol/m <sup>3</sup> solution
MEA	15	1.008	61.08	0.049	151.2	2.48
DEA	35	1.044	105.14	0.084	366	3.48
DGA	60	1.062	105.14	0.204	652	6.20
MDEA	50	1.048	119.17	0.131	524	4.40

A simple schematic presentation of an amine process operation can be seen in figure 3-3. Sour gas enters bottom of the absorber at high pressure and flows upwards while being contacted by an aqueous alkanolamine solution, which is introduced at the top of the column. The cleaned gas flows out in the top of the contactor. Rich amine exits at the bottom and is transported to an intermediate

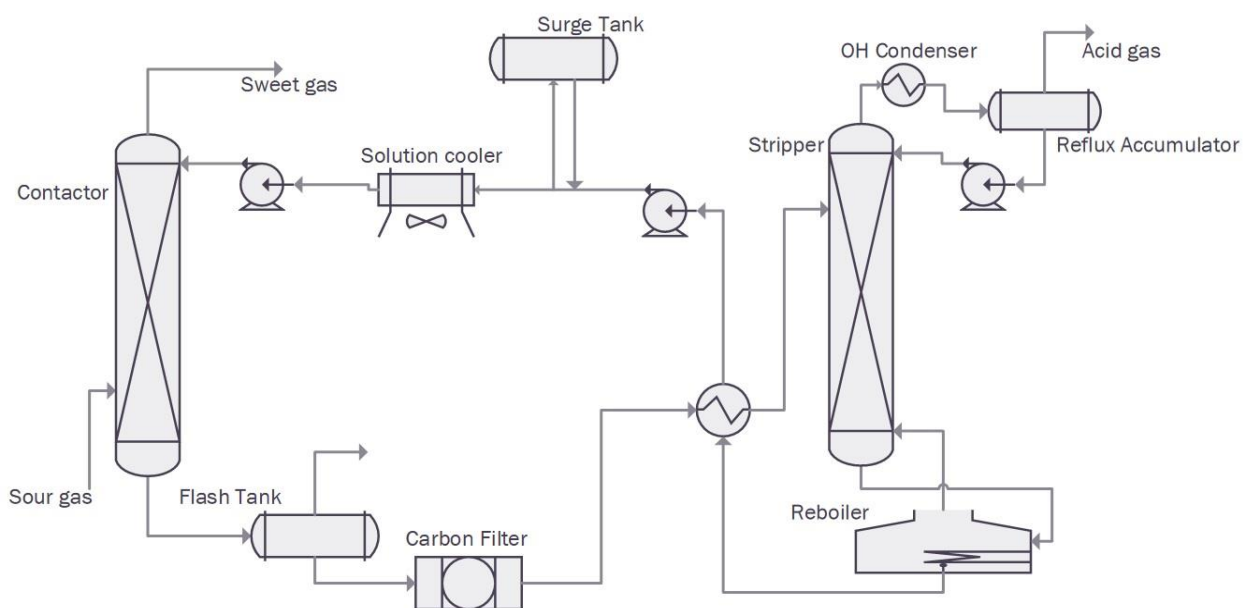


Figure 3-3: Standard amine gas treating unit [12]

pressure flash drum. This is necessary for high pressure feed gas streams. Here liquid hydrocarbons and dissolved gases, condensed in the absorber, are flashed off. Flash gas is often used as fuel [12].

The rich solution is further transported via heat exchange with the hot lean amine solution, before the heated solution enters the stripper at the top. The regeneration is done by countercurrent contact with steam at high temperature and low pressure. The steam strips the acid compounds from the solution. The acid gas and the steam then exit at the top and enters a condenser. Here, a large part of the steam is condensed and cooled. Further the steam/acid gas is separated in the reflux accumulator and sent to flare or processing. Condensed steam returns at the top of the stripper as reflux [12].

Lean alkanolamine solution is brought back to absorber and cooled in two stages, first via the amines heat exchanger, before cooling down to desired temperature (around 30 °C - 40 °C). Cooling down to required temperature is important because large amine vaporization losses occurs at higher temperatures. In addition, higher temperatures will lower the acid gas carrying capacity in the solution. Lean, cooled solution enters the top of the absorber [12].

### 3.3.7. Process improvements

A lot of improvements to reduce equipment and energy costs have been suggested.

For large, high-pressure feed gases, utilizing the large pressure loss can save a lot of energy. When the feed gas is brought into the absorber, the pressure reduction for the rich solution is significant. Installing power recovery turbine can collect some of the energy lost. Some large plants are using it successfully [11].

Other modifications are; use of several amine feed points, side cooler, water wash and split flow design. In the absorption contactor, bulk removal of acid gas is usually done in the middle of the tower, so that less solvent is required at top. Many feed points can optimize this distribution. By reducing temperature inside absorber, the absorption rate is increased. The circulation rate and energy costs are reduced. Installation of a side cooler to cool the solution have been done with success [11].

Water wash can be a simple improvement. The water wash is placed at the top of the absorber and is used to reduce amine losses. Condensate from reflux drum can be used for this purpose. Other process solutions are the use of recirculating water wash with water wash pump [11].

A popular modification for large plants and high acid gas concentration feed streams is the split-stream cycle. The amine stream is split into two different solutions and is feed at different points into the absorber. One of the amine streams is treated to lean level, while the other stream is just treated to semi-lean level. The semi-lean solution is introduced in the middle, where acid gas concentrations is the largest and bulk acid gas removal is desirable. The lean solution enters the top of the absorber, where acid gas concentration is low and will require a lean solution if the sales gas specifications should be reached. This split -solution can save considerable amounts of steam costs. However, the stripper and absorber are often needed to have a more complex design with more trays/nozzles [11].

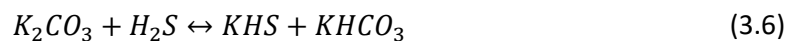
### 3.3.8. Flexsorb SE

Flexsorb SE is capable of an even higher degree of selectivity towards  $H_2S$  than MDEA and can be a better option, especially to treat low  $H_2S$  concentration gas streams (NCS conditions). The different types of Flexsorb processes use sterically hindered amines in aqueous solution. Steric hindrance adjusts the formation of carbamates. The amount of carbamates present is generally an indication of the speed of  $CO_2$  absorption.  $CO_2$  reacts normally fast with the amine to first form carbamate and then the bicarbonate  $HCO_3^-$ . Different degrees of hindrance will lead to desirable absorption purposes. Flexsorb SE uses severely hindered amines, which will make it highly selective towards  $H_2S$ . Moderately hindered is used to increase capacity for  $CO_2$  and absorption rate. Steric hindrance also seems to reduce degradation, mainly because the nitrogen in the amine is not involved in carbamate formation [11].

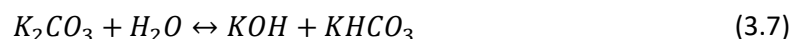
Exxon developed the Flexsorb SE considering treatment of gas streams with low pressure and low  $H_2S$  concentration. Flexsorb SE has a severely hindered N-group in which it hinders the carbamate formation and almost no carbamate is produced. The absorbed  $CO_2$  is hindered with about 1:10 to 1:20. Flexsorb SE can be highly suitable for NCS because of its excellent ability to treat low acid gas partial pressure streams. Typical very low  $H_2S$  concentration gas streams with partial pressure only around 0.069 - 0.138 bar can be reduced to about 1 – 2 ppmv  $H_2S$ . This is achieved with only half of the circulation rate, compared with MDEA. The corresponding reboiler power consumption and tower diameter are further reduced. Higher partial pressure will reduce these advantages and MDEA will be more competitive. Sterically hindered solvent is reported to be more expensive as well [12], [13].

### 3.4. Carbonate Process

This is a relatively old process. It is quite similar to the alkanolamine process, but it has one essential difference, that the hot potassium carbonate system operates at high temperature. Considerable amount of heating equipment will be saved. A high temperature leads to an increasing solubility of potassium bicarbonate. A low circulation rate, high carrying capacity and increased concentration of potassium solution is achieved. The process is especially applicable for high acid gas partial pressure and high amounts of heavier hydrocarbons. High to medium acid gas content is desirable. The main reaction is [12]:



This reaction is normally done in two stages. First hydrolysis of the potassium carbonate and then reaction of potassium hydroxide with  $H_2S$ :



A simplified flow sheet can be found in figure 3-4. From the figure, the process is operating at high temperature, so no heating/cooling in-between contactor and stripper is necessary. Instead, heat exchange between sour gas and sweetened gas is occurring before/after contactor. The contactor is

countercurrent and operating normally around 110 °C. The sweet gas out of contactor can contain high amount of water. Some is condensed in the gas-to-gas heat exchanger, but a scrubber is often needed for dehydration to product gas specification. The stripper operates around 0.15 – 0.70 bar. Rich solution will flash off a large portion of acid gas in the top tray due to the sudden pressure reduction. The partially stripped solution continues down the stripper for the final release of steam generated in reboiler. From the top of the stripper, humid acid gas enters a condenser and steam and acid gas are separated in the reflux accumulator. Water from reflux accumulator is brought back to stripper. The bottom part of the stripper operates normally at 116 – 121 °C. The lean solution from the bottom is then pumped back to the absorption column [12].

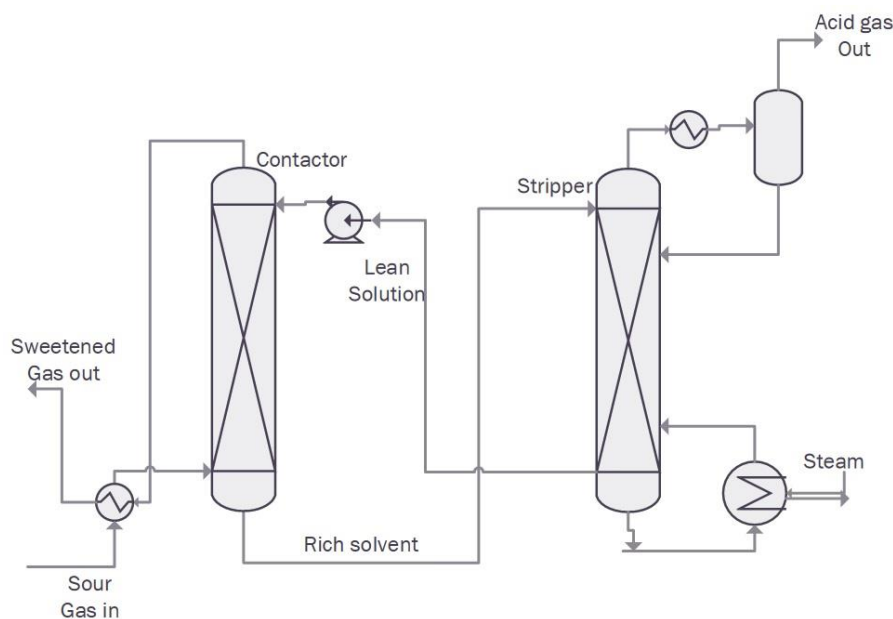


Figure 3-4: Basic hot carbonate process [12]

### 3.5. Physical Absorption Methods

A physical solvent can have some great benefits compared to a chemical solvent. Physical solvents are nonreactive, meaning they only interact physically with the dissolved gas. The interaction is weak. High content of acid gas can require large amount of energy (heat) to regenerate the solvent. Physical solvents can easily be stripped without the need for large energy supply. Heat, pressure reduction or a combination is normal for regeneration purposes. As noted before, the process favors high acid gas partial pressure and low temperature, which means a generally higher absorption capacity is observed than with the use of chemical solvents. Low acid gas partial pressure, high number of heavier hydrocarbons and low outlet pressure discourage the use of physical solvents. It may also have a lower circulation rate than for chemical solvent, particularly when partial pressure is high. Since the interaction is only physical, the solubility of the acid gas in the solvent is very important. Solubility for acid gas components in some solvent are showed in table 3-2. As you can see, the solubility of  $H_2S$  compared to  $CO_2$  is much higher. That makes physical solvent a good option for  $H_2S$  absorption and a high rate of selectivity can be achieved [11] [10].

Table 3-2: Solubility of some physical solvents [11]

Solubility, Mol% at 1atm and 298K

Solvent	$CO_2$		$H_2S$	
	Calc.	Exp.	Calc.	Exp.
<i>Dimethyl-2-pyrrolidone</i>	2.31	1.99	22.7	21.1
<i>n-Methyl-2-piperidone</i>	2.39	1.68	24.0	22.5
<i>n-methyl-caprolactam</i>	1.88	1.62	21.3	21.7
<i>n-Methyl-4-piperidone</i>	2.83	2.25	24.6	24.4
<i>n-Ethyl-pyrrolidone</i>	1.91	1.30	21.2	15.6
<i>Selexol Solvent</i>	3.39	3.56	29.6	22.4

For a simple process design, only an absorber, an atmospheric flash vessel and a recycle pump is required. Pressure reduction is used for regeneration of the solvent, and no heat or steam is necessary. After flashing off the acid gas at atmospheric pressure from the rich solution, the lean solution has some amount of acid gas, which correspond to equilibrium at 1 atm acid gas partial pressure. This amount represents the theoretical minimum partial pressure of acid gas in the cleaned gas stream. A higher form of purification is done with the use of either vacuum, inert gas stripping or heating the solvent. Prevent loss of valuable gas components and maintaining the temperature relatively low, are other process modifications. The absorption steps are more or less the same as with chemical/carbonate processes. The design of the process builds on the liquid/vapor equilibrium data for the components [11].

Adjusting the flow rate can be a useful tool for obtaining a high selectivity. By allowing just enough flow rate, the absorbed  $H_2S$  will be significant higher than of  $CO_2$ , because the solvent will be quickly used before it can react with  $CO_2$ . If a larger flow rate is introduced, generally all  $CO_2$  and  $H_2S$  in addition to the lightest hydrocarbon components will be absorbed. For a smaller flow rate, the components with the lowest solubility will be left out. However, the absorption is never perfect, and the spent solution will always contain some unwanted components like  $CO_2$  and hydrocarbons from C1 to C5. It is all about finding the ideal flow rate [12].

The Selexol process has showed capability of wide use in commercial application. It uses *dimethyl ether of polyethylene glycol* (DMPEG). The acid gas solubility in DMPEG is proportional to the acid gas partial pressure, as noted before. Selexol solvent has significantly greater solubility for  $H_2S$  than for  $CO_2$ . Selectivity is easily achieved. A general process scheme is showed in figure 3-5. For this particular case, the high  $H_2S$  to  $CO_2$  ratio gas stream is sweetened from 127 ppmv  $H_2S$  down to 4 ppmv  $H_2S$ , while the  $CO_2$  content is only reduced from 3.5% to 3%. Dehydrated sour gas is contacted with the DMPEG solvent at high pressure (about 69 bar) and ambient temperature in a countercurrent contactor. Rich solvent in the bottom is taken through 3 stages of flashing. In the high-pressure flash (21 bar), the flashed vapor has a large portion of methane. This vapor/methane is reinjected into the absorber, through a compressor. For the intermediate flash (12 bar), the flash gas is used as fuel gas. In the last low-pressure flash (1 bar), most of  $CO_2$  and  $H_2S$  are flashed off. Semi

lean solvent is pumped back, first cooled, then injected into the absorber for contact with rich acid gas. Rich solvents are heat exchanged with the lean solvents before entering the stripper for regeneration. From the stripper, lean solvent is pumped to the absorber to handle the last stage of sweetening before the gas specification is reached [12].

The three flashes are important for separating out hydrocarbons, but the heavier hydrocarbons are also more soluble in the solvent than the lighter hydrocarbons. Intermediate flash is therefore required for separating the solvent/heavier hydrocarbons [12].

Sulfinol is another process licensed by Shell. Here a mixture of chemical and physical solvent is used. Sulfinol-D has a mixture of sulfolane, water and DIPA (diisopropanolamine). Sulfinol-M has a mixture of sulfolane, water and MDEA (methyldiethanolamine). The solvent represents both chemical and physical absorption behavior. The equilibrium relationships become very complex. Advantages for a hybrid compared to amine involves reduced corrosion, lower sweet gas water content, low energy consumption, low foaming tendency. Somewhat higher co-absorption of heavier hydrocarbons can occur [12].

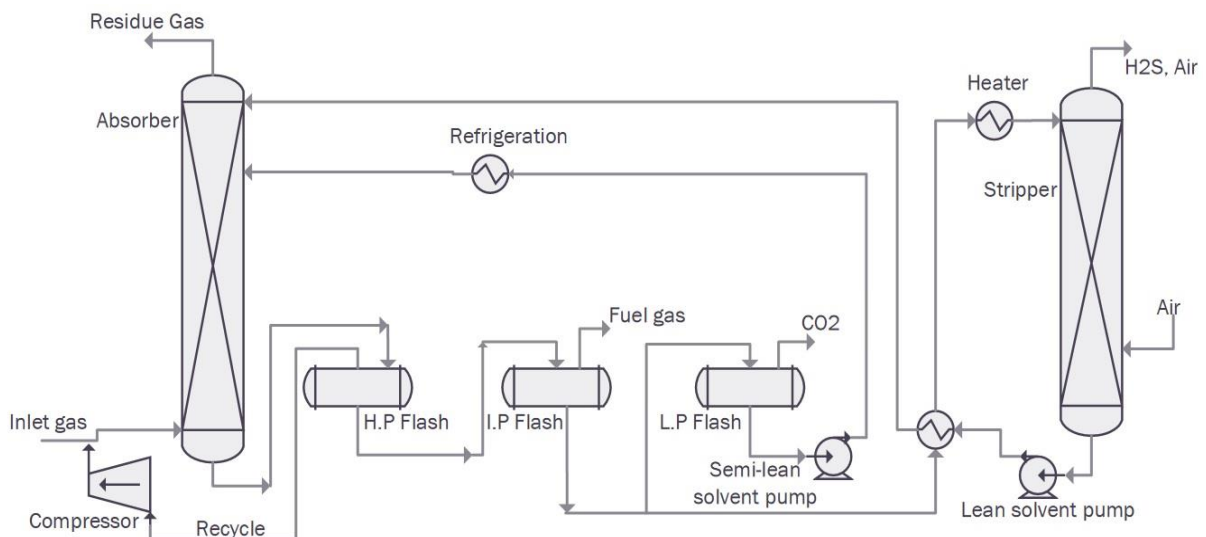


Figure 3-5: Selective Selexol process with low CO<sub>2</sub> to H<sub>2</sub>S ratio [12]

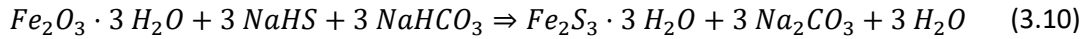
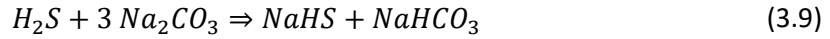
### 3.6. Oxidation processes

#### 3.6.1. General oxidation principle

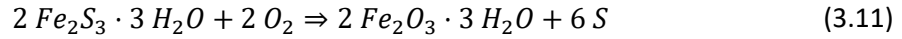
These processes are based on absorption and oxidation of hydrogen sulfide to elemental sulfur in liquid systems. A large advantage with oxidation processes is the general selectivity of H<sub>2</sub>S over CO<sub>2</sub>. However, these types of processes can result in large liquid flow rates. Sometimes the separation of the precipitated sulfur from liquid mixtures can be challenging.

The chemistry in liquid oxidation processes is typically based on H<sub>2</sub>S reacting with an alkaline component, normally either sodium carbonate or ammonia. Further, a reaction between the reacted hydrogen sulfide and added iron oxide, to iron sulfide is observed. The regeneration is done by contacting the solution with air. Then, the iron sulfide is converted to elemental sulfur and iron oxide. The main reactions taking place are the following [11]:





Regeneration:



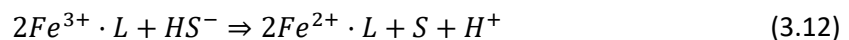
### 3.6.2. Chelated iron solution

Iron-chelated solution have reached a wide acceptance in the industry lately. The technology is based on a chelating agent and ferrous iron ions that is oxidized/reduced in an aqueous solution. The chelating agent is not impacting the reaction but is necessary for keeping the iron ions stable in the solution. Neither  $Fe^{3+}$  or  $Fe^{2+}$  are very soluble and stable in aqueous solution. Normally, the iron ions will precipitate as either ferric hydroxide ( $Fe(OH)_3$ ) or ferrous sulfide ( $FeS$ ) when the concentration is low. The chelating agents are organic substances and have the ability to “wrap” around the iron ions and hinder them from forming precipitates. The non-hazardous scrubbing solution makes the process highly applicable and in favor over other oxidation processes. There are primarily two processes that have been commercialized and reached a wide acceptance. LO-CAT and SulFerox are quite comparable (chemically), but there are technological differences. Typical differences are the iron concentration in the solution, oxidized vessel design, chemical composition of the solution and plant operating conditions. Economically factors are chemical losses, power requirement (pump, air blower) and equipment costs [11] [14].

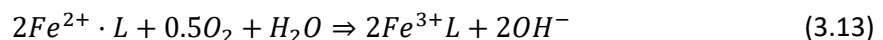
### 3.6.3. LO-CAT

Both LO-CAT and Sulerox processes have been installed in large numbers (Sulferox over 30 and LO-CAT over 100) and is highly applicable for offshore operations [15] [14] .

This solution is basically water and ferric iron, with a chelating agent holding the iron ion stable in the solution. The process is suitable for removing intermediate amounts of  $H_2S$ , typically ranges of 0.5 ton/day to 25 ton/day or potentially higher. LO-CAT possesses some great advantages, they are non-toxic, they operate at ambient temperature; no heating or cooling is necessary, and a great removal efficiency can be reached, up to 99.99%. The basic chemistry (“L” is the chelating agent) is given below [14]:



Regeneration:



A flow scheme is presented in figure 3-6. The LO-CAT solution enters at the top of the absorber.  $H_2S$  ions are absorbed from the acid gas and oxidized by the ferric ion. Elemental sulfur is generated from  $H_2S$  ions and ferric ion is reduced to ferrous state. Spent ferrous solution are transported for

regeneration, where it is oxidized in presence of air. Regenerated solution is pumped back to the absorber. Sulfur slurry exits in the bottom of the oxidizer vessel and is pumped through a filter. Here elemental sulfur is filtered out and ferric solution is returned to the oxidizer vessel for maximum ferric iron solution recovery. The filter cake that is removed, containing approximately 65 wt% sulfur and 35 wt% diluted LO-CAT solution [11] [14].

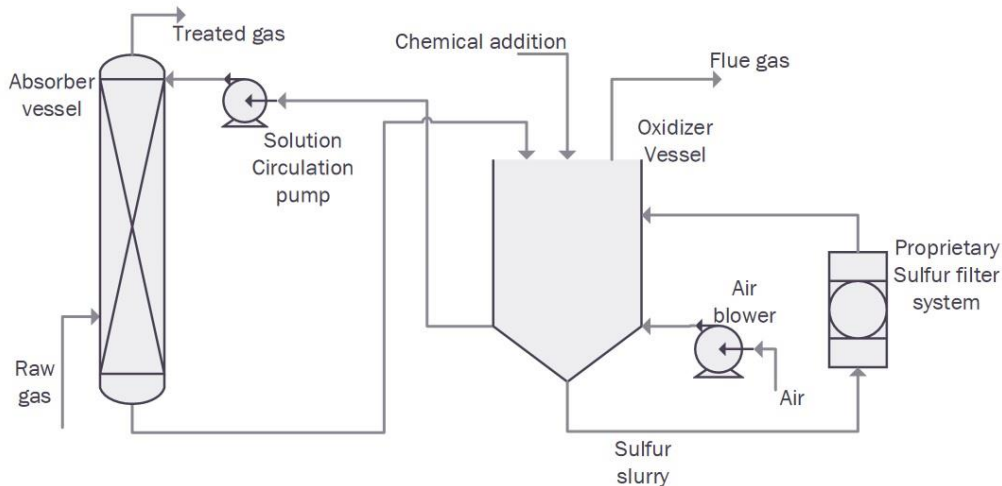
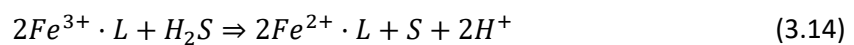


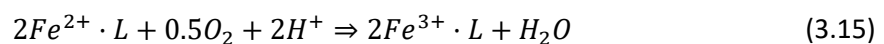
Figure 3-6: LO-CAT DirectTreat processing configuration [14]

#### 3.6.4. SulFerox

This process uses a high iron concentration solution together with chelating agents for redox  $H_2S$  removal. The iron content can vary between 1 to 3 wt%, which is quite high. This high concentration can be beneficial in form of accelerated kinetics and is not depending on a high pH for efficient  $H_2S$  removal. The unwanted biproduct thiosulfate is also claimed to be neglected, because the lifetime of  $H_2S$ ,  $HS^-$  and  $S^{2-}$  are reduced. High concentration will also reduce circulation rate and maintain high absorption rate. Pump and equipment costs are reduced. Typical challenges involving keeping the chelate degradation rate low and further chemical costs low. Basic characteristics associated with the process is low circulation rate, high removal rate, low chemical losses and simple/compact design. Chemistry absorption [11]:



Regeneration:



A basic flowchart is presented in figure 3-7. The process is quite similar to LO-CAT, with the same steps for absorption, regeneration with oxidation, filter and regeneration of the filtrate (ferric iron solution) [15].

Shells SulFerox process can handle gas streams with sulfur production of 0.1 to 20 ton/day. The high iron concentration allows a small liquid flow. This system has some advantages over a conventional system. It is especially flexible for treating gas streams with varying hydrogen sulfide content and gas

volumes with large fluctuations. Capital expenditures and operating cost can be improved. The process can handle low and high-pressure gas streams with medium to low concentration of hydrogen sulfide, which is desirable for NCS. The produced sulfur is non-toxic. The process can be especially applicable for offshore operation because of low weight and small footprints [15].

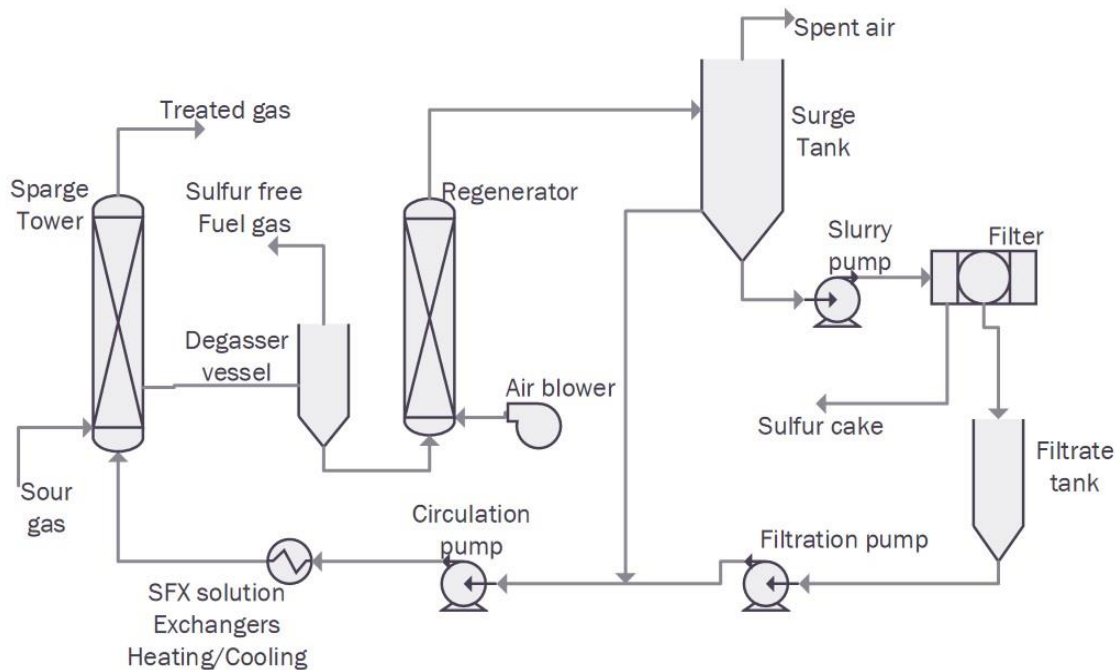


Figure 3-7: SulFerox process [15]

### 3.7. Scavenger processes

#### 3.7.1. General principle

For removal of small amounts of  $H_2S$ , non-regenerable scavenger chemicals is commonly used. Scavenger is used for small quantities, either by low volume gas or low amount of  $H_2S$  in the gas stream. This is a commonly used process on NCS and simplicity of operation together with generally low  $H_2S$  concentration are often the main reasons for the popularity. The method is typically continuous operation. The material is used to capture and retain sulfur components. The capacity is not finite, and the chemical (scavenger together with absorbed acid gas) needs to be removed and replaced with fresh chemical. When choosing the scavenger chemical, the waste product is an important factor. An environmental acceptable waste product is often required. Some reasons in favor of scavenger are listed in table 3-3. The different scavenger types are listed in table 3-4 [11].

Table 3-3: Reasons for considering Scavengers [12]

- |  |
|--|
| <ol style="list-style-type: none"> <li>1. If there is say &lt; 50 – 100 – 200 Kg/d sulfur in gas.</li> <li>2. Uncertainty of amount of <math>H_2S</math> from a drill-stem test, delay investment that may be unnecessary.</li> <li>3. Handle short term overload on a contactor.</li> <li>4. Temporary measure to handle progressive souring of a reservoir due to water-flooding.</li> </ol> |
|--|

Table 3-4: Categorization of sulfur scavenging processes [11]

<b>Liquid phase absorption processes:</b>	
1.	<i>Iron oxide slurries.</i> Chemistry same as dry iron oxide. Ease of removing/replacing reactants.
2.	<i>Zinc oxide slurries.</i> More reactive, more expensive than iron oxide.
3.	<i>Oxidizing solutions.</i> Oxidizing agents, e.g. nitrite, chlorite, oxygen, peroxide.
4.	<i>Aldehydes.</i> E.g. formaldehyde. Reacts rapidly, strong odor of final product.
5.	<i>Alkylamine/aldehyde condensation products.</i> Form liquid product. Strong odor. May have corrosive inhibition properties.
6.	<i>Triazine.</i> Form water soluble liquid byproducts. Corrosion inhibition properties of byproducts.
7.	<i>Alkaline solution.</i> Water solution of sodium hydroxide. Selectivity is possible.

Sour gas and scavenger chemicals are contacted in different methods. Bubble towers (single or lead/lag), in-line injection, down-hole or subsea injection are all suitable contacting methods. Desirable properties are typically low or non-toxic, stable in storage, selective to  $H_2S$ , low odor, unaffected by ambient or contact temperature, minimum disposal costs when consumed, no solid reactions products produced, reactive and low cost. Scavengers are normally quite cheap and can be brought into operation quickly. Sometimes disposal cost exceeds the cost of scavenger chemicals. A common problem is when the reaction between  $H_2S$  and some chemical will form  $H_2O$ . All the hydrogen sulphide will be converted into water. Considerable dehydration of the treated gas is required. Some issues concerning scavenger are listed in table 3-5 [12].

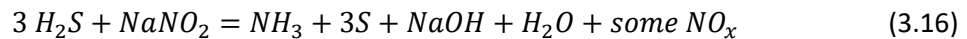
Amine -based scavenger is by far, the most used non-regenerable scavenger chemical. Mainly triazine has been the standard scavenger for oil/gas industry. This is a product of an amine and an aldehyde reaction. The very few problems related with the chemical (excellent corrosion inhibitor) and the high absorption capacity and low cost have made the chemical very popular.

Table 3-5: Scavenger issues [12]

1.	Configuration <ul style="list-style-type: none"> <li>- Lead/lag, line injection, etc.</li> </ul>
2.	Water <ul style="list-style-type: none"> <li>- Wet vs. dry – avoid repeating dehydration</li> </ul>
3.	Temperature <ul style="list-style-type: none"> <li>- If too low the reaction may be slow</li> <li>- If too high, there may be volatile problems</li> </ul>
4.	Selectivity <ul style="list-style-type: none"> <li>- Selectivity for <math>H_2S</math> only or does the process involve reactions with both <math>H_2S</math> and <math>CO_2</math></li> </ul>
5.	Residue/Impurities <ul style="list-style-type: none"> <li>- Is residual oxygen in the treated gas acceptable?</li> <li>- Possible formations of <math>NO_x</math> or <math>NH_3</math></li> <li>- Gums and deposits</li> </ul>
6.	Flexibility/turndown <ul style="list-style-type: none"> <li>- Flexibility/operability at reduced rates and short-term overload</li> </ul>
7.	Clean-out and disposal <ul style="list-style-type: none"> <li>- Disposal of spent chemicals, costs</li> <li>- Hazardous/non-hazardous; fully spent and partially spent</li> </ul>
8.	Co-Adsorption

### 3.7.2. Sulfa-Check

Sulfa-Check is based on sodium nitrite,  $Na_2NO_2$  in a buffered aqueous solution. This solution absorbs  $H_2S$  and is gradually transformed into a slurry containing both particles of elemental sulfur and other precipitated solids. When the initial nitrite is consumed, the contaminated slurry is discharged and replaced with fresh solution. The contact is usually done in a bubble tower. A simplified reaction equation can be noted as:



The process is quite popular, and a number of processes are currently in operation. Benefits include the spent slurry to be nonhazardous in addition to noncorrosive to mild steel, simple changeouts of spent solution and equipment is cheap and simple. The simple scrubbing vessel has only a mist eliminator at top and a gas sparger at the bottom. The technology can handle large fluctuations in gas volume with variable  $H_2S$  content and have small footprints with limited headroom [16] [11].

### 3.7.3. Triazine chemical

Triazine is the preferred scavenger chemical around the world. Its high popularity comes with a lot of advantages. High selectivity over  $CO_2$ , high absorption capacity, reaction products are water-soluble (or oil soluble) and generally low corrosion problems. Both in line injection and bubble towers can be used, generally dependent on sulfur amount. Drawbacks are potential solid deposit, potential environmental unacceptable, toxicity and potential hazardous spent solution. For the environmental factor, the spent triazine can be dumped in the ocean, but the long-term effect of doing so is unclear.

Despite being very effective in removing  $H_2S$ , the triazine-based scavenger has an undesired effect to raise the pH in the system it is injected, increasing the scaling deposition in the system. The solubility of e.g.  $CaCO_3$  tend to decrease with higher pH. Iron carbonate, magnesium carbonate and calcium carbonate are type of scales observed within different levels of pressures, temperatures and carbonate concentrations [17].

However, triazine can have a great impact towards the TEG dehydration system. Wilson [18] described a situation for a North Sea platform, that the required pH correction additive that needs to be added to maintain TEG system around pH level 8 can be reduced or almost eliminated because of the effect triazine has on pH. It should be noticed that the spent scavenger is usually removed from the gas before the TEG dehydration unit and for that matter, the scavenger will have no impact on the dehydration unit.

Carbonate is often present in produced water. If the triazine chemical is contacted with produced water, scaling can occur as a result of increased pH. The scavenger is however often injected directly into the gas stream, after a separator. The contact between produced water and scavenger is minimized but scaling in the injection system has been reported in some cases. However, the spent chemical is sometimes transported through the production facility for disposal into a subsurface

reservoir. Fouling and corrosion of downstream equipment can be a potential problem. Scaling in the reservoir and injectivity impairment are other issues [17]. Overboard disposal can eliminate these types of problems, but that can have a negative environmental impact. Scaling and the forming of carbamate with produced water is an important reason that triazine is not suited for subsea injection.

Operating at temperatures higher than 130 °C will cause triazine to break down to thermally unstable amines. As a result, the triazines decomposes to low molecular weight, low flash point amines. A potential corrosion problem in the pipelines may occur [19].

### 3.7.4. MEA-triazine and MMA-triazine

MEA or 1,3,5-tris(2-hydroxyethyl)-hexahydro-S-triazine is by far the most applied triazine scavenger in the oil and gas industry with more than 90 % of the applications. MMA-triazine or 1,3,5-trimethyl-hexahydro-S-triazine is another form of triazine scavenger but is not as prevalent as MEA and represents less than the 10% [20].

The reaction with  $H_2S$  for MEA and MMA are showed in figure 3-8, respectively. The two scavengers react with two molecules of  $H_2S$  to first form the thiadiazine (III) and (IV). Second, the dithiazine (V) and (VI). The unwanted and problematic solid byproduct amorphous dithiazine is formed from dithiazine (V) by polymerization. The forming of amorphous dithiazine solid is absent for MMA-triazine due to completely different molecular structure. This is a significant advantage. There are risks of solid deposit for MMA if significant overspend chemical injection occur, but this solid is just 5-methyl dithiazine and is easily removed with solvent or heating. Dithiazine solid is very difficult to remove. MMA-triazine is generally more expensive than MEA, but MEA benefit from the significant lower molecular weight (129 and 219 for MEA). This corresponds to slightly double number of moles in a given mass/volume solution with MMA vs. MEA. MEA experience however a double increase in reaction stoichiometry compared with MMA and is often picked based on this feature. But the lower molecular weight advantage will more or less counteract the 50 % decrease in stoichiometry for MMA. [20]

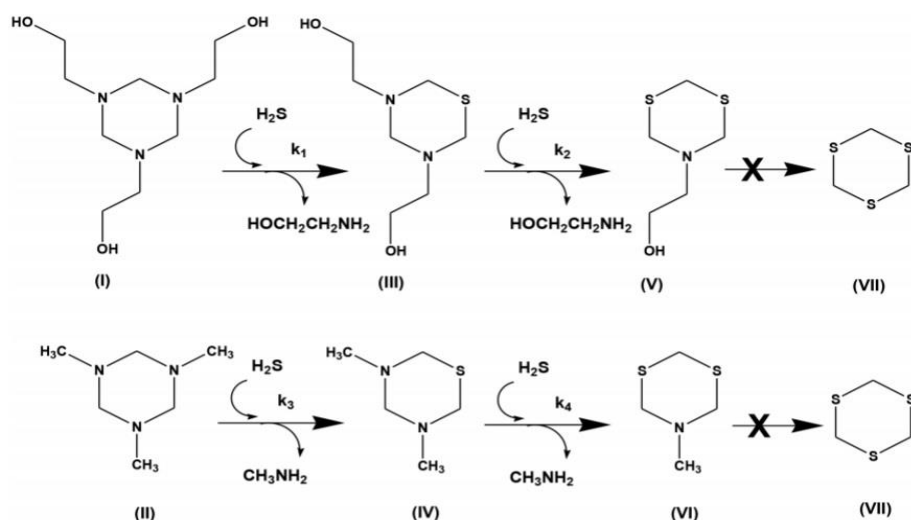


Figure 3-8: MEA and MMA reaction products [20]

### 3.8. Adsorption processes

#### 3.8.1. General adsorption phenomenon

Adsorption involves a materials ability to attract a liquid or a gas to its surface as a result of forces existing here. Surface area is important, as the quantity of material adsorbed has a direct function of the surface area available for adsorption. Adsorption processes is always designed with a very large surface area to weight ratio. Adsorbent particles are often irregular granules or performed shapes, e.g. tablets or spheres [11].

In operation, the sour gas is brought through a bed and the acid gas components is naturally attached to the material. When the bed material has reached its capacity and is fully loaded, the adsorbent material must be cleaned. The impurity is either discarded, removed for reclaiming, or regenerated in place. Regeneration is normally done with either increasing the temperature (steam), reducing total pressure, reducing partial pressure with stripping gas, displacing the adsorbate with a more strongly adsorbed species or a combination of these methods. For regeneration purposes, the plant has usually more than one bed (tower). Regeneration mode is applied for one of the bed, while the other(s) are running on cleaning mode. A higher adsorption rate will typically be seen. Common adsorption materials include silica, alumina, carbon (activated), silicates and molecular sieves [11].

#### 3.8.2. Molecular Sieve

Molecular sieve or crystalline sodium-calcium aluminosilicates. This synthetic molecular sieve is suitable for selective removal of  $H_2S$ . Separation is based on differences in molecular sizes. Its capability of rejecting large molecule and adsorb small molecule makes it applicable for many different sour gas treatments. In addition to its relatively large surface area, the material has a large advantage in the highly localized polar charge. That makes it a very strong adsorbent for unsaturated and polar-type compounds ( $H_2S$ ). The adsorption capacity is significant higher than other adsorbents, especially for low concentrations. As for other types of adsorbent materials, a very high purity is typically achieved [12].

The mechanisms of adsorption for molecular sieve is quite complex. A combination of “sieving action” and physical adsorption. The molecule is passed through the pore opening in the sieve before it is adsorbed on the active centers inside the crystal structure.

A simple molecular sieve process is presented in figure 3-9. The process can be operated in constant mode because of the two towers. The different valves can be adjusted dependent on which of the towers that operates at regeneration mode. Let us assume tower 2 is running at regeneration and cooling mode, while the sour gas is sweetened in tower 1. The sour gas is brought downwards and cleaned by the molecular sieve in tower 1. The gas exits at bottom before a small amount of the cleaned gas is brought to the regeneration gas heater. The heated regeneration stream is sent to tower 2, through the molecular sieve bed. With bed temperature increasing, adsorbed  $H_2S$  is easily removed into the regeneration stream, which is further sent to flare. The regeneration unit is in continuously operation until  $H_2S$  is removed completely. A regeneration gas loss of about 1 – 2 percent in the flare and heater is normal [12].

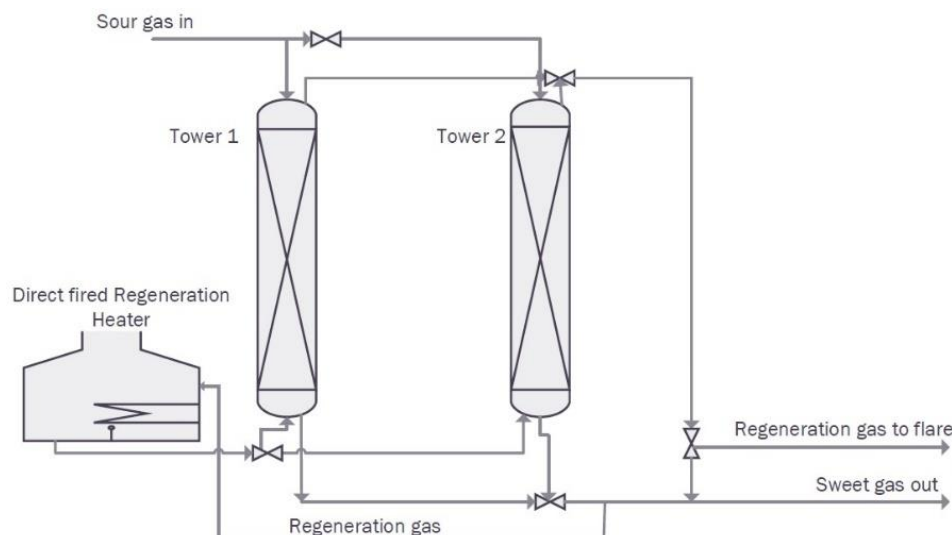
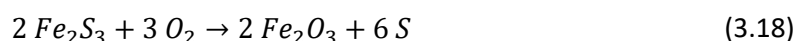
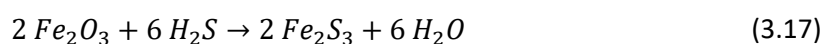


Figure 3-9: Simple molecular sieve adsorption process [12]

### 3.8.3. Iron oxide (sprong) process

One of the oldest method of removing sulfur compounds from gas streams. The chemical reactions are as follow [12]:



As seen from the equations, the acid gas stream is contacted with *hydrated ferric oxide*. It reacts to form *ferric sulfide*. The *ferric sulfide* is easily transformed to elemental *sulfur* and *ferric oxide*, by oxygen exposure. The newly formed *ferric oxide* is used again to react with the sour gas. This reaction-regeneration cycle can be repeated many times.

The regeneration of the process can be done very effectively. Small amounts of oxygen or air is constantly added to the sour gas stream. In-situ regeneration allows large savings in labor costs for loading and unloading the adsorbent in the vessel. Higher sulfur recovery per pound of adsorbent can also be achieved. Regeneration can also be done with the removal of the fouled bed, and then expose it to oxygen/air for regeneration [12].

### 3.8.4. Sulfatreat

Sulfatreat is a commercialized technology that uses iron oxide on a ceramic support. This fixed bed of granular is installed in simple pressure vessels. The process can be compared to the iron sprong process, but the proprietary material is different and much more effective. Sulfatreat has replaced iron sprong in large numbers and the improvements have been significant. The iron oxide is represented as either  $Fe_2O_3$  or  $Fe_3O_4$ . Hydrogen sulfide reacts with both forms to generate a mixture of iron sulfides. High selectivity is achieved together with low investment cost (batch type) [11].



Konczvald [16] reported of an installation of sulfatreat offshore. The field had experienced rising levels of  $H_2S$  in the gas after years of water reinjection. After exceeding 28 ppm the initial liquid injection  $H_2S$  removal technology was not capable of maintaining the 3 ppm specification for the sales gas. The Sulfatreat process was introduced, with a series of 2 beds. This process was generally picked considering a number of factors including, no toxic gases are generated, no oral or dermal reactions, non-hazardous material (flammability, reactivity, ignitability, corrosivity) and it does not foam. The material cost less than iron sponge and is not affected by liquid hydrocarbon poisoning.

### 3.8.5. Zinc Oxide bed

Zinc oxide (particularly Puraspec) is a well-established adsorbent used for  $H_2S$  operations on North Sea platforms. Originally, the zinc oxide process was based on high temperatures, because the performance is generally dependent on temperature. A general reaction between the hydrogen sulfide and zinc is expressed as [12]:

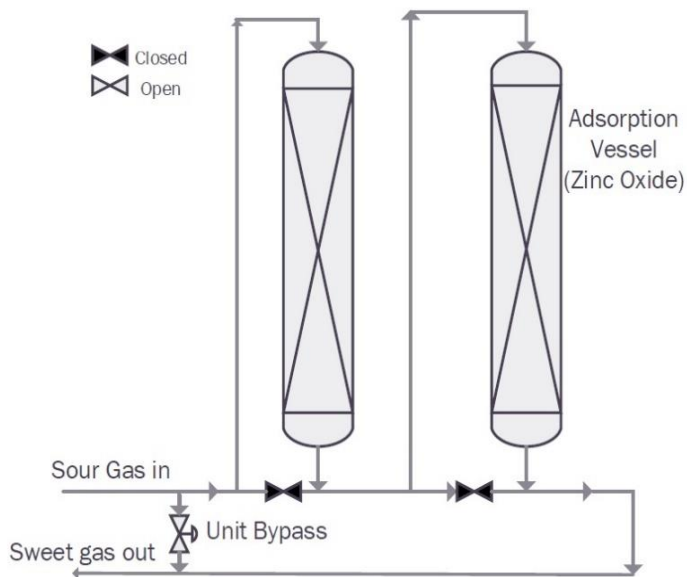


Figure 3-10: Zinc oxide bed, South Morecambe [12]

A more efficient bed is developed to meet low-temperature gas streams. This bed-material has an increased porosity and surface area, and a little reduction in density. For improved performance, an installation downstream from a compressor is often implemented. This is due to the utilization of the heat generated in the compressor. Even though it is based on low temperature streams, higher temperature will be in favor for the efficiency. A schematic of a typical zinc-oxide installation on a North Sea platform is showed in figure 3-10. For this particular example (South Morecambe), the feed gas has just 5 ppmv  $H_2S$  in the gas. Thus, only a portion of the sour gas stream is sent through the zinc bed. The bed cleans the gas down to 0 ppm before it is blended with the rich gas from the unit bypass valve. The final gas stream exits at 3 ppm  $H_2S$ . The installation consists of two beds in series, with interconnecting piping to allow either reactor to be operated in the lead position. Changing contaminated bed can easily be done without interrupting the production. The spent bed material is usually reprocessed for metal recovery by sending them to metal refineries.

Contaminated bed material can sometimes contain up to 20 wt% sulfur. The bed is typically discharged with gravity flow. No added heat is required, and it is claimed to be effective down to 0 °C. The process can handle over 6.7 MNm<sup>3</sup>/h of natural gas to pipeline specifications and streams of up to 50 ppmv or 100-200 kg per day of sulfur in large scale processes. This process can handle liquids (LPG) as well and is often being related with great predictability [12].

### 3.8.6. Carbon-based Adsorbents

Activated carbon is applicable for  $H_2S$  removal, e.g. iodine-impregnated carbon solid bed. A constant small flow of air is added for conversion of  $H_2S$  to elemental Sulphur at 40 – 50 °C. Cleaning efficiency of 1 ppm  $H_2S$  is possible. Many installations of this type have treated gas streams with  $H_2S$  content of 310 ppm and gas flows up to 240 000 Nm<sup>3</sup>/h, which is quite high for an adsorption process [12].

## 3.9. Membrane Permeation Technology

### 3.9.1. Membrane mechanisms

The membrane technology builds on differences in rates of permeation for the gas components over a thin membrane barrier. The function of permeation relates with the gas compounds solubility in the membrane material. The characteristics of membrane material and gas components will affect the total rate of permeation. The separation of the gas components is performed based on two principles, the difference in the rates of permeation and difference in partial pressure. For the stream to be able to flow through the membrane, a driving force is needed. A limited partial pressure difference will function as the driving force. The partial pressure difference will keep a small portion of the permeating component (acid gas) in the residue gas. Therefore, hundred percent efficiency will never be reached. Bulk removal of  $H_2S$  is often the purpose. However, multiple stages and recycle systems can result in a relatively clean gas stream, with high purity. This is also obtained from hybrid systems, which uses membranes for bulk removal, before another technology is used for final cleanup [11].

Table 3-6: Factors for choosing/rejecting membranes [11]

<b><u>Advantages:</u></b>	<b><u>Disadvantages:</u></b>
<ul style="list-style-type: none"> <li>- Low capital investment</li> <li>- Ease of operation. Process can be operated unattended</li> <li>- Good weight and space ratio.</li> <li>- Ease of scale up (improved capacity). However, expensive.</li> <li>- Minimal associated hardware</li> <li>- No moving parts</li> <li>- Ease of installation</li> <li>- Flexibility</li> <li>- Minimal utility requirements</li> <li>- Low environmental impact</li> <li>- Reliability</li> <li>- Ease of incorporation of new membrane developments</li> </ul>	<ul style="list-style-type: none"> <li>- A clean feed is required. Particulates, and in most cases entrained liquids, must be removed. Filtration to remove particles down to one micron in size is preferred.</li> <li>- Costly to improve capacity.</li> <li>- Because membranes use pressure as driving force of the process, there may be a considerable energy requirement for gas compression.</li> </ul>

Kohl [11] described some costs related with the process when sales gas specifications should be reached. The capital costs for a hybrid solution was found to be around the same as for a conventional process, but with significant lower energy consumption. A single membrane process was found to be almost twice the costs as conventional type process.

There have been some problems with condensation of liquid hydrocarbons across the membrane. Typically, the gas stream will become “heavier”, resulting in increased concentration of heavier components ( $C_3+$  hydrocarbons) through the membrane. Together with the decrease in temperature, condensation of some liquid hydrocarbons can occur. This causes problems like forming barrier to permeation because of the wetted membrane or gas leakage. Eventually the performance will suffer from such problems, even though the membrane can physically tolerate it. Membrane life is about 3 – 7 years before it is replaced [11].

The transport mechanisms can be described by a solution- diffusion phenomena. The different steps: (1) adsorption of the gas at one surface of the membrane, (2) solution of the gas into the membrane, (3) diffusion of the gas through the membrane, (4) release of the gas from solution at the opposite surface, and (5) desorption of the gas from the surface [11].

A basic overall equation can be noted as [12]:

$$Q_i = P_i A (pp_{i,HP} - pp_{i,LP}) \quad (3.20)$$

Q= Volume (flow rate) permeating through the membrane surface  
i= the individual components such as  $H_2S$   
 $P_i$ = permeation coefficient for component i in the membrane material  
A= Membrane surface area  
 $pp_{i,HP}$ = partial pressure for component i on the high-pressure side  
 $pp_{i,LP}$ = partial pressure of component i on the low-pressure side

### 3.9.2. Membrane types

Two main types and most popular module configurations are the *spiral-wound* and *hollow-fiber*. The two types can be seen in figure 3-11 and figure 3-12.

Spiral-wound consists of several envelopes, which is formed with two membrane sheets divided by a porous support material. The support material protects against pressure and forms the permeate flow channel. From figure 3-12 the rich gas enters one side of the module and exits at the other side as residue flow.

Permeable gases migrate through the membranes and flows in a spiral path inward within the envelope, through the channel spacer, before entering the perforated collection tube and exits as permeate.

For the hollow-fiber arrangement, thousands of hollow fiber packages in bundles are mounted in a pressure vessel, just like a shell and tube heat exchanger. The feed gas enters at the shell side. The faster permeating gases (figure 3-11) moves through and into the fiber bore side and is brought out via the open end of the bundle. For lower pressure configuration, the diameter of the fibers is more

or about two times than that of the high-pressure configuration. For this setting, the rich gas is instead brought into the fiber bore side, and the permeate exits through the shell side. This will govern the pressure drop on inlet gas side.

The hollow-fiber and the spiral-wound will each have advantages. Hollow-fiber has a packing-density significant higher than spiral-wound. However, a general higher permeation rate for the material will make them more or less similar in performance. For future developments, the hollow-fiber can be in favor, if a more effective thin film is created [11].

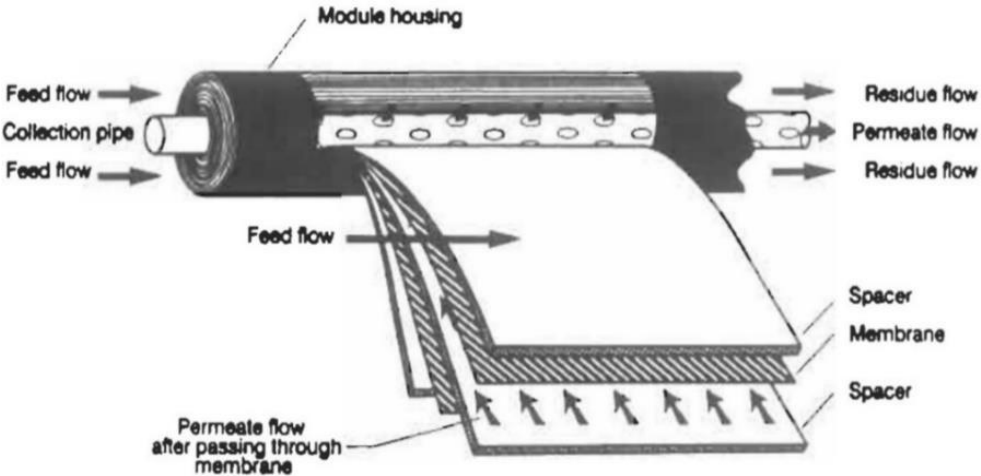


Figure 3-12: Spiral-wound membrane vessel [11]

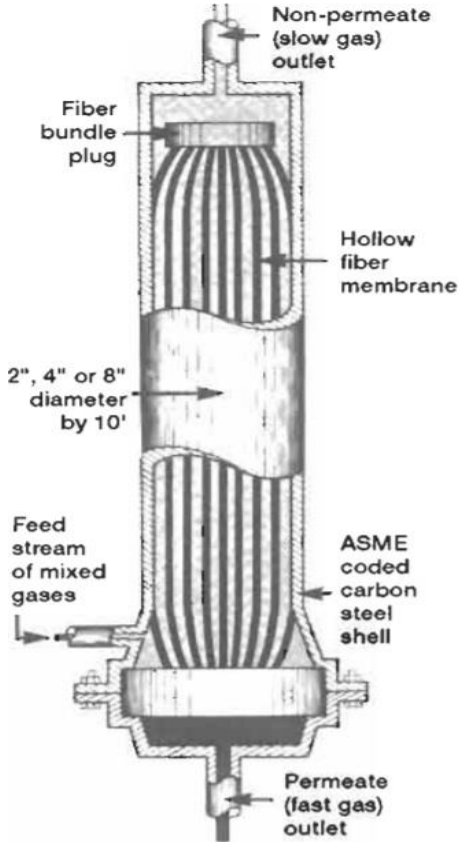


Figure 3-11: Hollow-fiber membrane vessel [11]

## 4. $H_2S$ sweetening processes for NCS

### 4.1. Process selection

Throughout the text, we have seen that  $H_2S$  can be treated with several different processes. But each process has different characteristics and the environment and situation for the oil/gas will be crucial whether the process will be suitable or not. An overview of processes that should be selected based on partial pressure, plant size and sulphur capacity are listed in table 4-1. Figure 4-1 shows a chart of applicable processes based on  $H_2S$  concentration and gas volume flow. It should be noted that, even for very low  $H_2S$  concentrations, liquid oxidation, amine and mixed amine/physical solvent are the best suited processes for larger volumes of gas. However, for large gas rate, Sulferox should be considered for tail gas treatment. For larger  $H_2S$  content, Claus process would be more desirable.

Table 4-1: Rough guidelines for process selection [11]

#### GUIDELINES FOR SELECTION OF $H_2S$ REMOVAL PROCESSES

TYPE OF PROCESS	$H_2S$	Plant Size	Partial Pressure	Sulphur Capacity
ABSORPTION IN ALKALINE SOLUTION	A	H	L	H
PHYSICAL ABSORPTION	A	H	H	H
ABSORPTION/OXIDATION	A	H	L	L
DRY SORPTION/REACTION	A	L	L	L
MEMBRANE PERMEATION	A	L	H	L
ADSORPTION	A	L	L	L
METHANATION	-	L	L	L

A= Applicable, H=High, L=Low; dividing lines between high and low is roughly 20 MMscfd for plant size, 100 psia for partial pressure and 20 tons/day for Sulphur capacity. (20 MMscfd = 0.565 MSm<sup>3</sup>/d. 100psi = 6.89 bar)

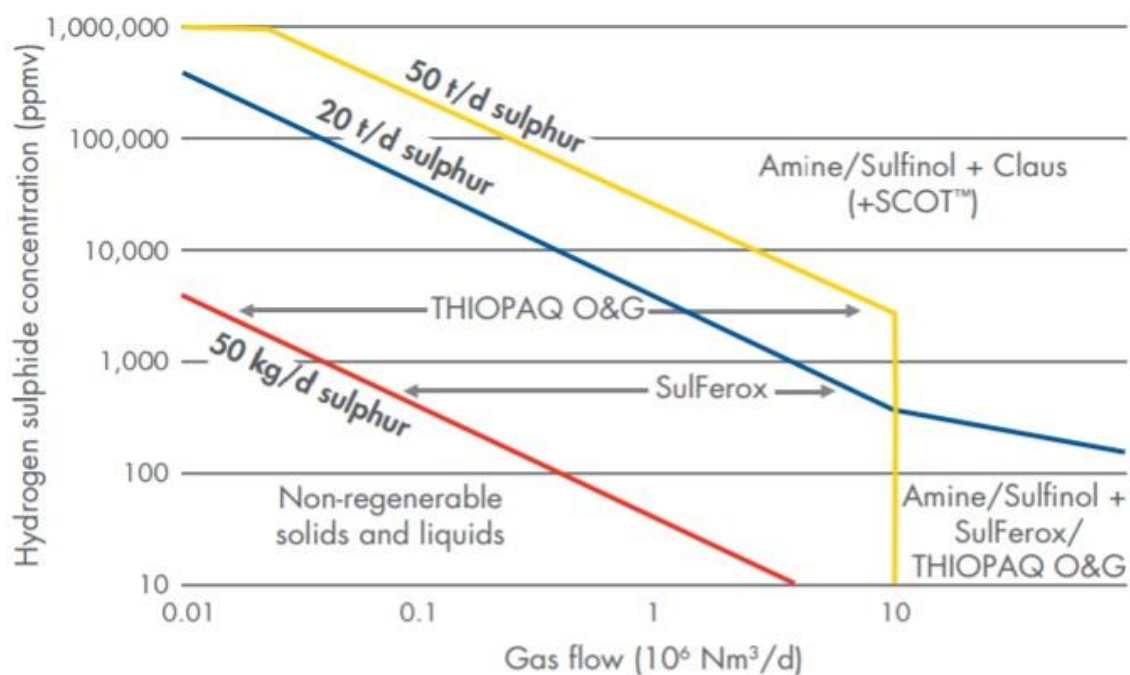


Figure 4-1: Selection map for some processes patented by Shell [15]

From the table, both absorption in alkaline solution and physical absorption is applicable for treating high-volume gas streams containing hydrogen sulphide. But there is a difference for the partial pressure. Absorption using alkaline solution is much more economical when the acid gas partial pressure is low. Physical solvent is a strong function of partial pressure and will have a higher capacity than alkaline solution.

The platform topside will always have limited space. A compact, well fitted design, with high contact-surface area to weight ratio will be crucial. Table 4-2 lists some dominant factors that needs to be evaluated.

Table 4-2: Some factors influencing the process selection [16]

<b>Method Selection</b>	
<b>Process Issues:</b>	<b>Platform Characteristics:</b>
$H_2S$ (ppm): Max. m <sup>3</sup> /day Safety vs. BACT (Best available control technology): Desulf. Criteria Contaminants, Mercaptans Cost of Permitting: Emission Controls Energy demand	Available deck footprints Max. load/footprints/future expansion On-deck storage of: Raw chemicals Elemental sulfur Disposal: Distance to shore
<b>Process selection:</b>	<b>Gas Line Criteria:</b>
Regenerative or spent? Toxic waste disposal Chemical usage/day? Process poisoning; acid gas tolerance; absorber/contactactor P&T etc. Recycle vs. Reinject	Gas line capacity: BTU/SCM Slippage; Dew points: Min. P/T, precipitates, corrosion, water temp. Maintenance: Pigging/repairs

For platforms with limited storage space, a practical solution can be to inject spent absorbent/sulfur slurry into the oil emulsion line and send it to shore for processing and separation. A regeneration plant will also be suitable but will cover more valuable space on platform. If platform is close to shore, a non-regenerative batch operation can be in favor economically, because of the short distance, and simple off/on loading of spent/new chemical.

#### 4.2. Evaluation of technologies based on NCS conditions

A typical oilfield on the Norwegian continental shelf will be relatively sweet but may experience reservoir souring as we have discussed previously in the text.

Alkanolamines has a high acceptance on NCS for treating larger gas streams/amounts of  $H_2S$  when regeneration is more expedient. Today MEA solvent is rapidly being replaced with mainly MDEA, but also DIPA/sulfinol, Flexsorb, DGA etc. MEA is affected by large corrosion problems, solution vaporization losses and high energy consumption. DGA can be operated at high ambient temperature

and low to moderate total pressure. This will not suit NCS conditions (prevalent in Middle-East). MDEA will likely be one of the best suited solvent for NCS usage. As noted before, non-corrosive, selective, low amine losses, low partial pressure and high amine concentration, low heat of reaction corresponding to low energy (heat) consumption in the reboiler are the main benefits.

Physical solvent will not be suitable for typical NCS conditions with low acid gas partial pressure.

Membrane should be rejected as well. This process is suitable for bulk removal of acid gas, and requires a higher partial pressure, like physical solvent. Removing hydrogen sulfide to low concentration is however difficult without a large increase in costs. A hybrid process will be necessary. Membrane is also more suitable for handling  $CO_2$ , than for  $H_2S$ . For larger gas streams, membrane will have a significant increase in equipment costs.

Direct oxidation can be suitable for small/medium gas streams or smaller acid gas concentration. Both dry sorption and liquid oxidation has proven to be good options for treating sour gas offshore. Sulferox and LO-CAT have been installed on both platforms and FPSOs. These processes have however not received much attention on NCS and there has been minor experience with them.

Adsorption can be an excellent choice for handling small concentrations of  $H_2S$ . Puraspec (zinc oxide bed) has been installed in some numbers at NCS. This is normally for reservoirs that are initially sweet (few ppm  $H_2S$ ) and not experiencing reservoir souring. Solid bed/adsorption is very vulnerable against higher concentrations of  $H_2S$ . The need for changeouts (of bed material) will increase dramatically. For the case we are looking into, with reservoir souring occurring, adsorption will not be sustainable for future  $H_2S$  levels. Problems can be many, including expensive changeouts, labor and chemical costs, hazards associated with opening and cleaning the vessel, logistics and costs for returning the spent bed to shore for reprocessing, variable life period. Wilson [18] described a successful zinc oxide replacement with triazine scavenger for an offshore facility. The  $H_2S$  content had exceeded 150 ppm  $H_2S$ , which is a significant level to process for a solid bed. The triazine represented a huge improvement towards the production, costs and  $H_2S$  removal system.

Scavenger chemicals, preferably triazine will always be a great choice for NCS conditions and is normally the best non-regenerable operation for handling  $H_2S$ . Triazine represents great absorption capacity, can handle rising  $H_2S$  concentrations to a certain level, corrosion inhibitor, flexibility and simple operation are only some of the advantages.

## 5. Offshore process simulation

### 5.1. Hydrocarbon separation and stabilization plant design

#### 5.1.1. General description

The offshore oil-gas treating plant was designed based on a 3-stage separation of the reservoir fluid. The Hysys model is shown in appendix F and figure 5-1. The multiphase reservoir stream enters a first stage separator, where wet gas is sent upstream for further separation of gas and liquids. The gas is cooled for more liquid knockout, then treated for water and acid gas before it is compressed in two stages, ready for transport. The oil/condensate is sent from the first separator to a second separator for more water knockout. Further, partly pressure reduction and separation in two stages is performed to take out more water and gas components. Finally, the oil is pumped in pipeline to shore after third separator. Table 5-4 lists some key features for the model (mainly temperatures and pressure levels).

#### 5.1.2. Reservoir conditions

The reservoir fluid composition is shown in table 5-1. The reservoir is simulated by mixing injected seawater,  $H_2S$ , the reservoir stream and produced gas and oil. The reservoir pressure and temperature are set to 195.7 bar and 82.5 °C. The multiphase reservoir stream is first sent to a mixer and blended with the liquid that is extracted after first compression in the gas compression train (figure 4-2). The mixed stream enters the first separator at 16 bar and 70 °C. Some temperature and a large pressure loss from the reservoir were accounted for.

#### 5.1.3. Oil conditioning train

From the first separator, most of the water, heavy hydrocarbons (oil) and the light hydrocarbons (gas) are separated. The heavier hydrocarbons are initially pressure reduced to 9.5 bar before it is mixed with liquids from the first gas separator in the gas compression train. The mixed liquid is heated to 80 °C and enters the second separator at 8 bar, after experiencing some pressure loss in pipeline and heat exchanger. More water and gas are separated from the oil. The oil/condensate is further pressure reduced to 2.56 bar and mixed with more liquids from the intermediate separation unit upstream. The mixed fluid enters the third separator for final separation of gas and oil. Finally, the oil is pumped up to a pressure of 13 bar and sent to shore in pipeline.

#### 5.1.4. Intermediate separation/compression train

Gas from second and third separator are sent to an intermediate separation/compression train.

The gas leaving third oil separator is cooled from around 73 °C to 30 °C before entering a separator for more liquid knockout. A pressure loss of 0.3 bar in the heat exchanger was accounted for. The following gas is compressed to 8 bar again, mixed with gas from second separator, then cooled from around 83 °C to 30 °C, before entering a separator for more hydrocarbon separation. The heat exchanger pressure loss was set to about 0.5 bar. The separated gas is further compressed to 16 bar and then mixed with the gas from the first separator. The mixed gas stream then enters the gas compression train.



The liquids from the two separators are pressure reduced/raised from 7.5 bar and 2.26 bar respectively, to 2.56 bar and mixed. The mixed liquid stream is again mixed with the oil/condensate before entering third stage separation.

#### 5.1.5. Gas compression train

The inlet gas stream is first cooled from around 70 °C to 30 °C, before entering the separator. The liquid from the separator is pressure reduce to 9.5 bar and mixed with the same pressure reduced liquid from first oil separator. The gas from the separator is compressed to 55.7 bar, then cooled to around 30 °C, before entering a three-phase separator for more water separation. The oil/condensate are sent downstream and mixed with the multiphase stream from the reservoir. The gas is sent for final compression to 170.5 bar and cooled to 30 °C. A pressure loss from first stage compression to second stage compression was set to 7.7 bar because of dehydration unit and scavenger injection/amine unit. This may not be entirely representative.

Table 5-1: Reservoir fluid composition

<b>Name</b>	<b>Formula</b>	<b>Mol%</b>
<b>Methane</b>	$CH_4$	0.1679
<b>Ethane</b>	$C_2H_6$	0.0505
<b>Propane</b>	$C_3H_8$	0.0649
<b>Nitrogen</b>	$N_2$	0.0057
<b>Carbon dioxide</b>	$CO_2$	0.0009
<b>i-Butane</b>	$C_4H_{10}$	0.0150
<b>n-Butane</b>	$C_4H_{10}$	0.0346
<b>i-Pentane</b>	$C_5H_{12}$	0.0158
<b>n-Pentane</b>	$C_5H_{12}$	0.0199
<b>C6*</b>	-	0.0281
<b>C7*</b>	-	0.0433
<b>C8*</b>	-	0.0470
<b>C9*</b>	-	0.0340
<b>C10-C12*</b>	-	0.0885
<b>C13-C15*</b>	-	0.0845
<b>C16-C18*</b>	-	0.0637
<b>C19-C22*</b>	-	0.0582
<b>C23-C27*</b>	-	0.0460
<b>C28-C34*</b>	-	0.0452
<b>C35-C43*</b>	-	0.0497
<b>C44-C55*</b>	-	0.0262
<b>C56*+</b>	-	0.0105
<b>Total</b>		1.0000

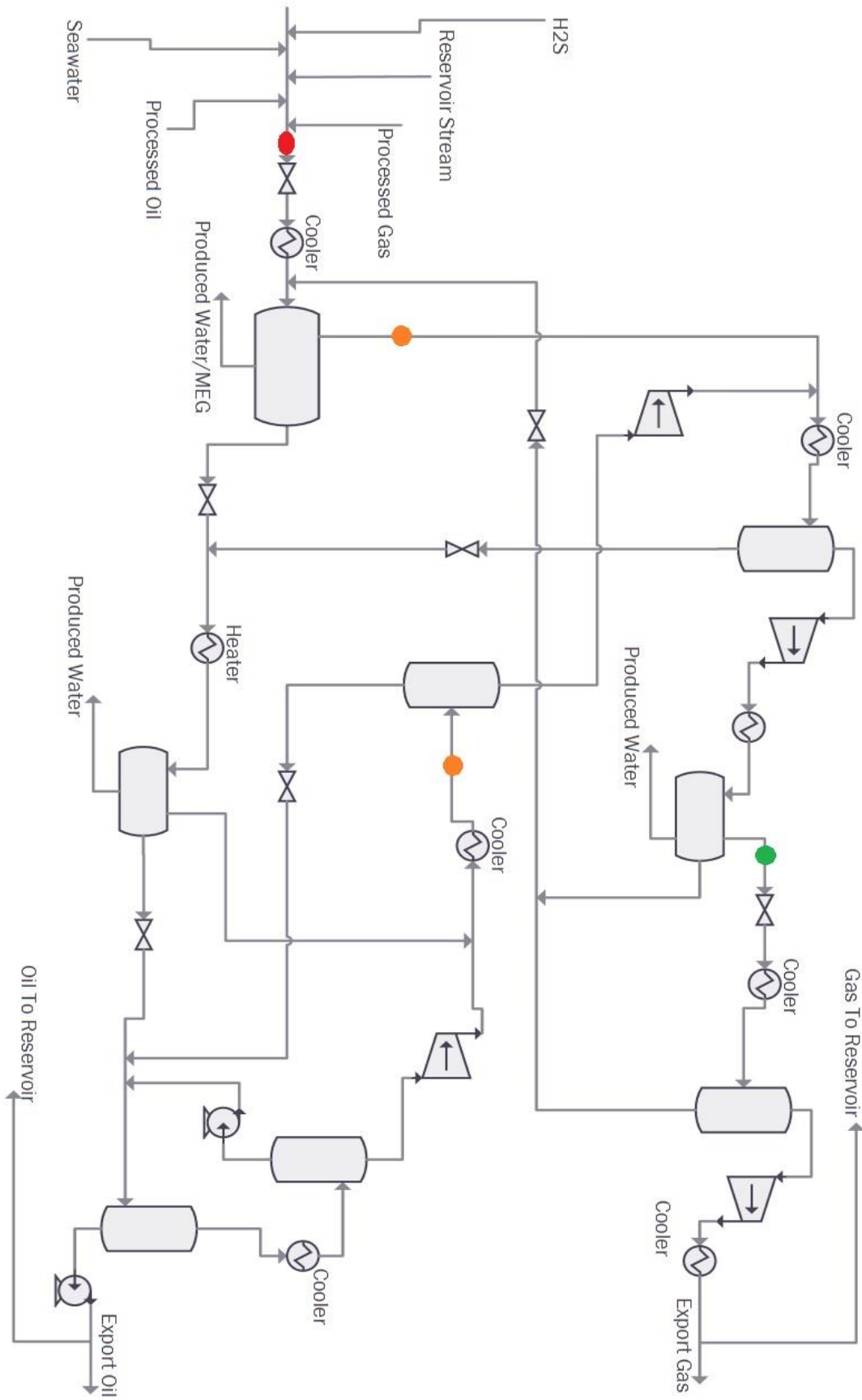


Figure 4-2: Offshore separation and stabilization plant in hysys

Table 5-2: Production profile for phase 1

Year	$H_2S$ expected* [Kg/d]	$H_2S$ high* [Kg/d]	Water rate [Sm <sup>3</sup> /d]	Oil rate [Sm <sup>3</sup> /d]	Gas rate [Sm <sup>3</sup> /d]
2019	-	0	0	14200	577421
2020	-	0	0	56289	2244732
2021	-	0	0	56289	2242023
2022	-	0	0	98814	3578311
2023	-	0	40	98814	3574000
2024	-	0	40	98814	3523730
2025	-	8	2096	98814	3513479
2026	-	19	5101	98814	3518859
2027	-	230	55899	98818	3490990
2028	-	459	87134	98814	3423499
2029	-	695	107769	64630	2625706
2030	-	859	115108	51443	1879764
2031	-	940	116592	39360	1435201
2032	-	1028	115730	30651	1115045
2033	-	1101	115628	24946	906172
2034	-	1176	115058	21024	762305
2035	-	1240	115628	18059	653940
2036	-	1289	116036	15548	563649
2037	-	1346	115557	13715	495926
2038	-	1571	116311	12168	440466
2039	-	1478	119222	11008	398163
2040	-	1489	119980	10479	377755
2041	-	1492	118973	9588	345133
2042	-	1538	117857	10041	367518
2043	-	1550	118176	8897	326801
2044	-	1578	115289	8281	304508
2045	-	1383	105291	7710	284328
2046	-	1253	95591	7014	255502
2047	-	1092	83668	6774	245849
2048	-	1167	88467	4813	173896
2049	-	860	78136	6281	225378
2050	-	1072	83239	5983	215124
2051	-	1104	86726	5049	186053
2052	-	958	77137	4675	167973
2053	-	993	77030	4403	159287
2054	-	947	60957	4757	170439

Table 5-3: Production profile for phase 2

Year	$H_2S$ expected* [Kg/d]	$H_2S$ high* [Kg/d]	Water rate [Sm <sup>3</sup> /d]	Oil rate [Sm <sup>3</sup> /d]	Gas rate [Sm <sup>3</sup> /d]
2019	0	0	0	0	0
2020	0	0	0	0	0
2021	0	0	0	0	0
2022	0	0	0	3450	0
2023	0	0	0	11755	231037
2024	0	0	0	12330	495272
2025	0	0	0	22807	769820
2026	0	0	0	31288	971436
2027	5	7	2272	31811	1217239
2028	40	56	8258	32282	1126910
2029	70	98	17424	31579	1901414
2030	103	144	23602	21812	2002177
2031	143	200	28336	16262	1990918
2032	172	241	29557	13247	1930888
2033	193	270	29078	10599	1796795
2034	215	301	29293	8252	1658509
2035	236	330	29738	7009	1567997
2036	253	354	30645	6465	1509990
2037	282	395	31094	5744	1490879
2038	314	440	31520	5174	1456132
2039	334	468	32203	4635	1448445
2040	385	539	33400	4109	1441798
2045	446	624	33000	2872	1454257
2050	525	735	34000	2012	1468789
2055	625	875	34500	1616	1589186

Table 5-4: Plant design values

Parameter	Symbol	Value
Reservoir temperature [C°]	T <sub>R</sub>	82.5
Reservoir Pressure [bar]	P <sub>R</sub>	195.7
First stage separation temperature, oil [C°]	T <sub>O1</sub>	70.0
First stage separation pressure, oil [bar]	P <sub>O1</sub>	16.0
Second stage separation temperature, oil [C°]	T <sub>O2</sub>	80.0
Second stage separation pressure, oil [bar]	P <sub>O2</sub>	8.00
Third stage separation temperature, oil [C°]	T <sub>O3</sub>	71.9
Third stage separation pressure, oil [bar]	P <sub>O3</sub>	2.56
Oil export temperature [C°]	T <sub>Eo</sub>	72.1
Oil export pressure [bar]	P <sub>Eo</sub>	13.0
First stage separation temperature, gas [C°]	T <sub>G1</sub>	30.0
First stage separation pressure, gas [bar]	P <sub>G1</sub>	16.0
Second stage separation temperature, gas [C°]	T <sub>G2</sub>	30.0
Second stage separation pressure, gas [bar]	P <sub>G2</sub>	55.7
Third stage separation temperature, gas [C°]	T <sub>G3</sub>	30.0
Third stage separation pressure, gas [bar]	P <sub>G3</sub>	48.0

<b>Oil export temperature [C°]</b>	$T_{EG}$	60.0
<b>Oil export pressure [bar]</b>	$P_{EG}$	170.5
<b>Compressor adiabatic efficiency</b>	$E_A$	0.750
<b>Compressor polytropic efficiency</b>	$E_P$	0.774

## 5.2. Simulation

The main objective with the simulation was to get an overview of the  $H_2S$  distribution in the gas, oil and water phase. Later in the text, a simulation of an amine plant and scavenger injection based on the process plant will be carried out. From table 5-2 and 5-3, two real production profiles for a known North Sea reservoir are given. The simulation is based on these data and carried out for future years. It is important to notice that the produced  $H_2S$  is estimated based on worst case souring scenario. Some of the produced oil and gas are sent back to the reservoir to get the right amount of production.

Apart from the main separation part of the process, the model had to include some tools to handle the produced hydrocarbons that is returned to the reservoir. In hysys an adjuster was used to get the right amount of oil and gas production, while a virtual stream was added for the oil/gas to be sent back to the reservoir without any error.

## 6. Scavenger injection simulation

### 6.1. Simulation

For oilfields that experience reservoir souring, like this in particular, there may be a risk of a dramatic increase in scavenger chemical costs for future years. To evaluate whether scavenger chemical can be a desirable process, several simulations in Hysys has been performed. The scavenger simulation was conducted with a component splitter in Hysys, which separates out the  $H_2S$ . The final sales gas specification was set to 3 ppm  $H_2S$ . There has been simulated four situations for injection points, subsea scavenger, separator after first stage compression, after inlet separator and mixer and partly subsea injection combined with injection after first stage compression. 15 liters of scavenger chemical per 1 kg of  $H_2S$  absorbed was used for gas absorption (triazine) and 7 liters per 1 kg  $H_2S$  for scavenger injection into multiphase stream (subsea, non-triazine). 330 days per year are used. It is important to notice that the oil can contain up to 0.3 wt% sulfur (as  $H_2S$  in this case) in final export oil. For this simulation, the final  $H_2S$  content in the oil is closer to 0 wt% than 0.3 wt% for all years. In appendix E, the results are listed in tables. In appendix F, the Hysys models for different injection points are presented. From figure 5-1 the different injection points are marked:

- Red point, subsea injection.
- Orange points, injection after inlet separator and mixer
- Green point, injection after first stage compression.

### 6.2. Results

#### 6.2.1. Separator after 1. stage compression

The  $H_2S$  is removed only after first stage compression to reach a sales gas specification of 3 ppm.

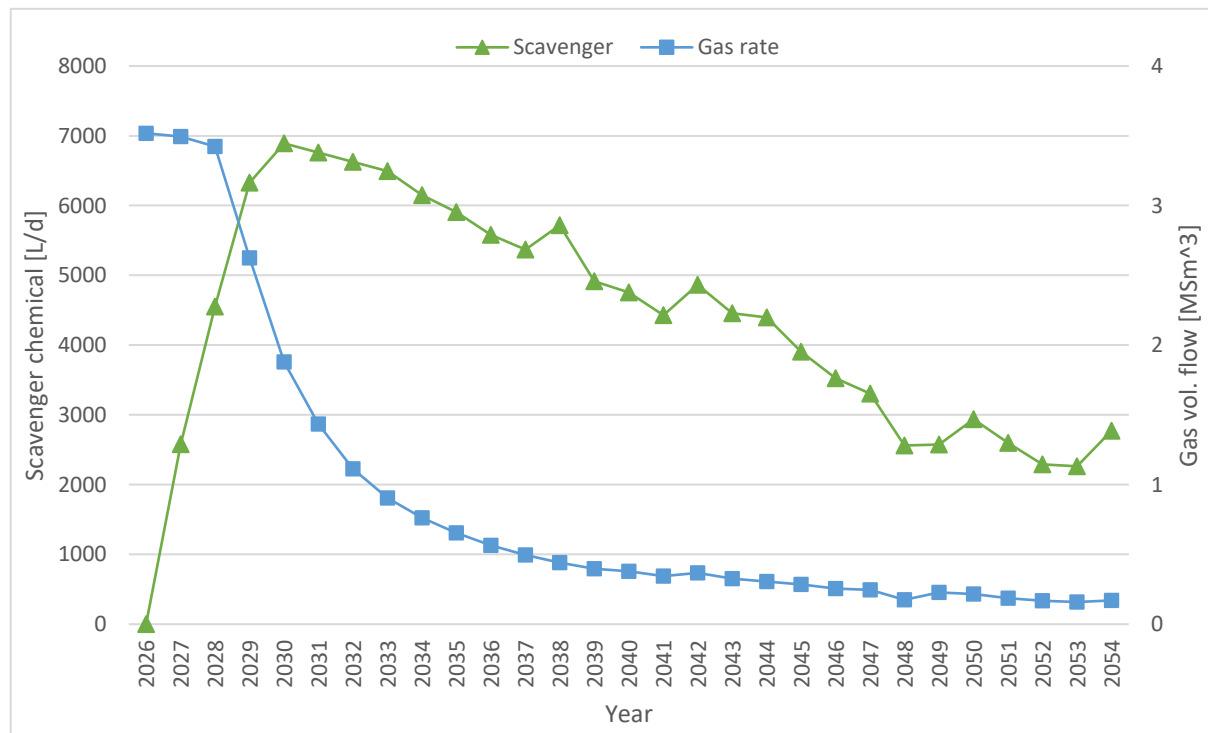


Figure 6-1: Scavenger chemical consumption with injection after compression. Phase 1

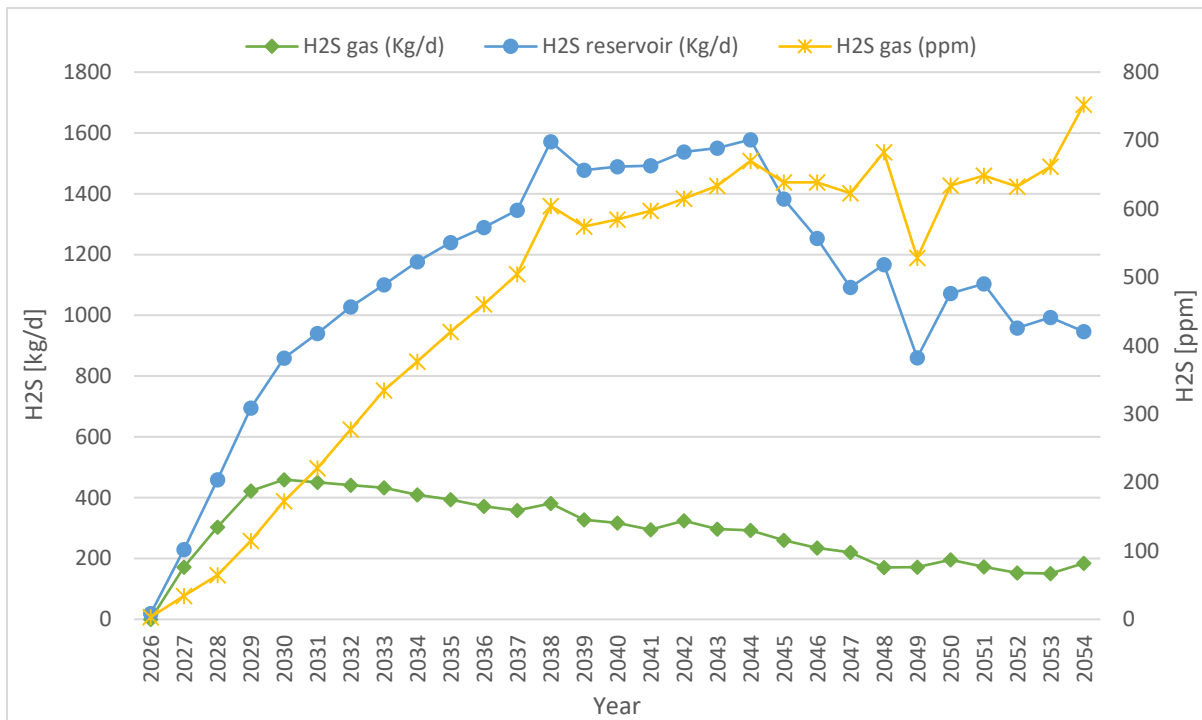


Figure 6-2: H<sub>2</sub>S removed in gas to reach sales gas quality compared with H<sub>2</sub>S production in reservoir. Phase 1

The scavenger consumption for different years are shown in figure 6-1 together with sales gas rate. From figure 6-2, H<sub>2</sub>S (kg/d) absorbed in the gas and H<sub>2</sub>S (kg/d) production in the reservoir are given from first vertical axis. The second vertical axis shows the H<sub>2</sub>S (ppm) content in gas to be treated. The scavenger consumption is proportional to the absorbed H<sub>2</sub>S and we see a high consume of chemical the first years but will rapidly fall continuously for later years.

The H<sub>2</sub>S chart shows something important. The H<sub>2</sub>S that must be removed to reach sales gas quality is significantly lower than the production of H<sub>2</sub>S in the reservoir. From the simulation we see that a large proportion of the H<sub>2</sub>S follows the water after inlet separator. The rest ends up in the oil and gas. Even though the H<sub>2</sub>S production in the reservoir is increasing through the production period, the H<sub>2</sub>S that is required to be removed in the gas, is decreasing. This is explained by an increasing water injection rate corresponding to a significant water-cut ratio (99 % for most years), a high decline in sales gas production and a high oil to gas production ratio. The water especially will take a bigger part of the multiphase reservoir stream and more H<sub>2</sub>S will end up here accordingly. The oil to gas ratio will only have a minor impact towards the H<sub>2</sub>S distribution and the oil is observed to contain about maximum 58 kg/d H<sub>2</sub>S, when the oil production rate (oil) is at its highest. The large water-cut ratio is by far the dominating factor here.

For the charts involving phase 2, the H<sub>2</sub>S distribution is rather different than observed from phase 1. The sales gas production rate from figure 6-3 is pretty constant through the period. The oil production and water injection rate are considerably lower than for phase 1. As a result, more H<sub>2</sub>S ends up in the gas and further removed. But even if a larger proportion of the H<sub>2</sub>S ends up in the gas, we can see from the chart that some H<sub>2</sub>S eventually ends up in the water. This is enhanced especially towards the end of the period, when we have the largest water injection rate. Therefore,

we get rising  $H_2S$  levels in the gas corresponding to a rising scavenger consumption. The need for scavenger chemical will only increase for later life of production.

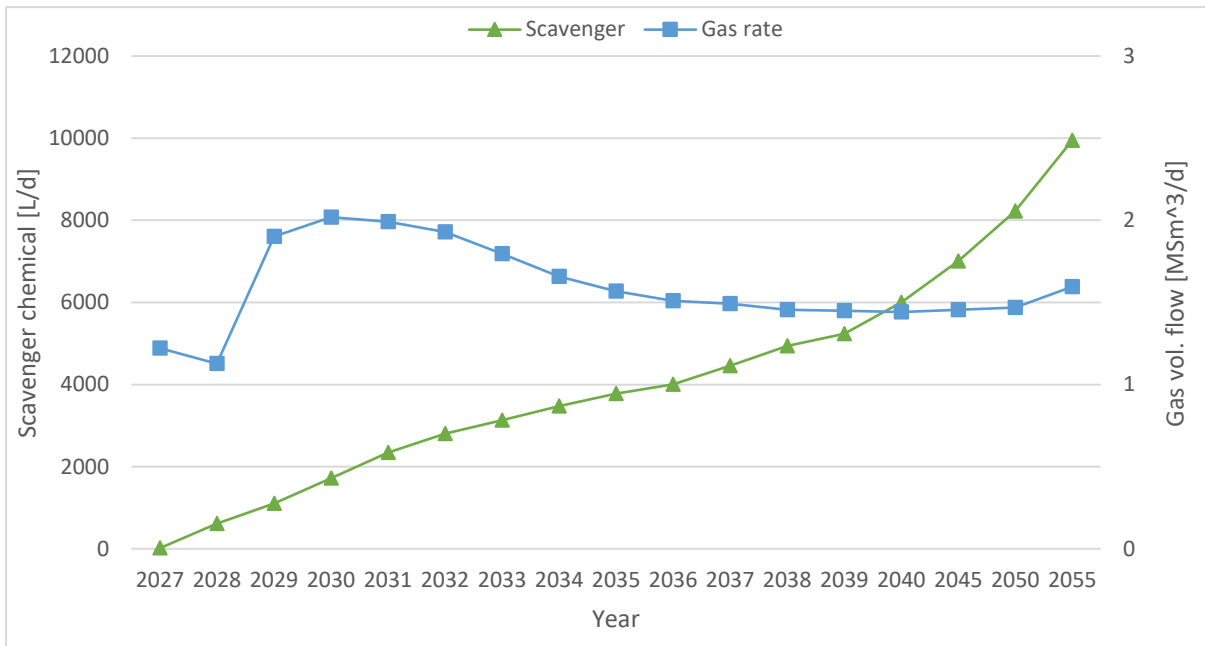


Figure 6-3: Scavenger chemical consumption with injection after compression. Phase 2

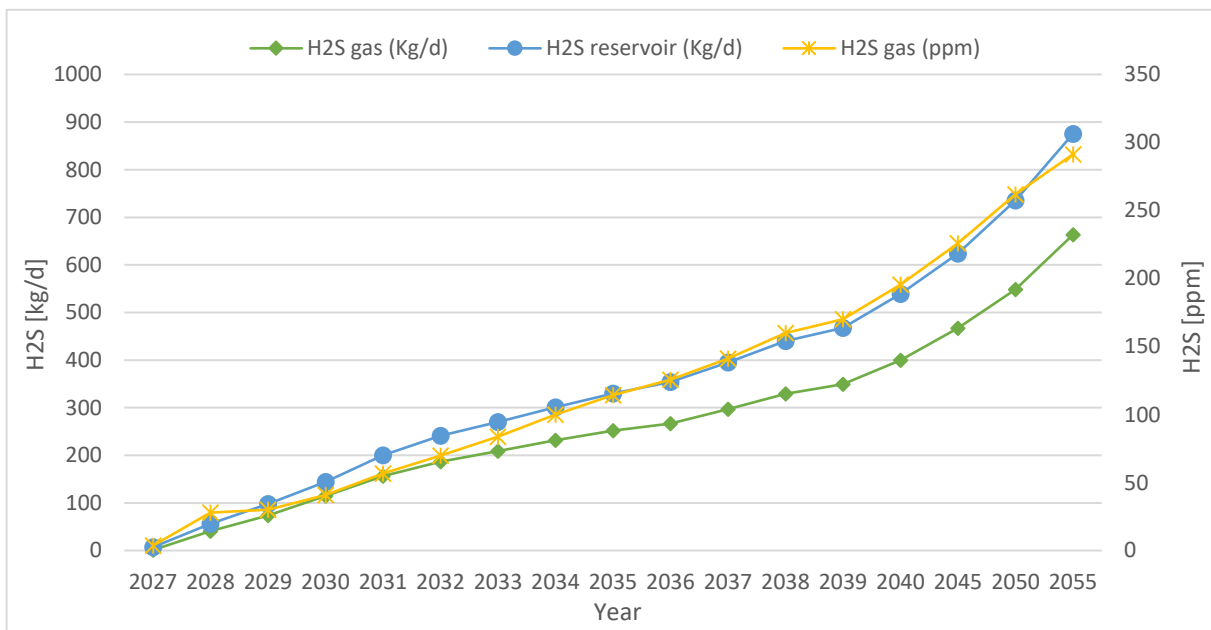


Figure 6-4: H2S removed in gas to reach sales gas quality compared with H2S production in reservoir. Phase 2

### 6.2.2. After inlet separator and mixer

The injection was performed after inlet separator and after a mixer that contains gas from second and third separator (showed in figure 5-1). Injection after only first and second oil separator would have allowed a higher  $H_2S$  concentration (ppm) in the sales gas than acceptable. The gas was treated to a specification of 3 ppm after 1. separator. The rest of the  $H_2S$  was removed after mixer, to reach sales gas specification of 3 ppm.



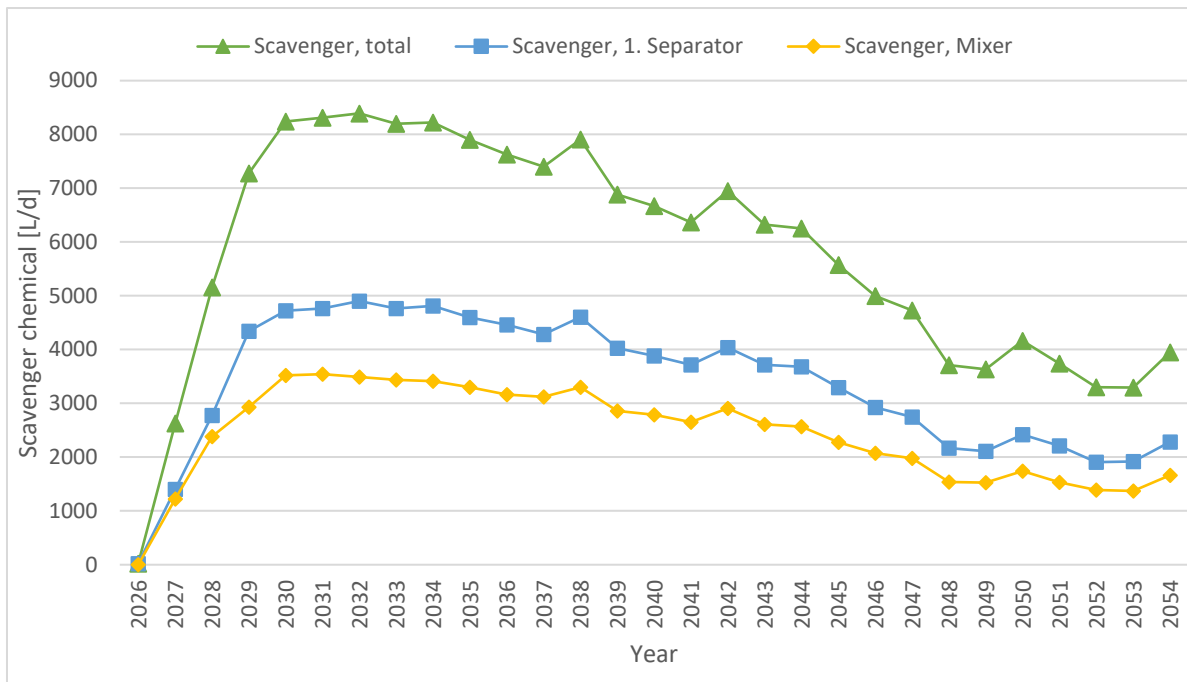


Figure 6-5: Scavenger chemical consumption for scavenger injection after 1. stage separation and mixer. Phase 1

Results for phase 1 shows slightly higher total scavenger consumption than injection after compression. Some of the gas that is treated after first separator or after mixer will be separated out and end up in the oil. In this way, the oil will probably contain less  $H_2S$  (probably not noticeable). From figure 6-5, the scavenger chemical consumption is higher after first separator compared to injection after mixer. This can be explained by the higher gas rate after first stage separation than the total gas rate after second and third stage separation. A higher gas rate represents a higher amount of  $H_2S$  in the following gas stream (figure 6-6).

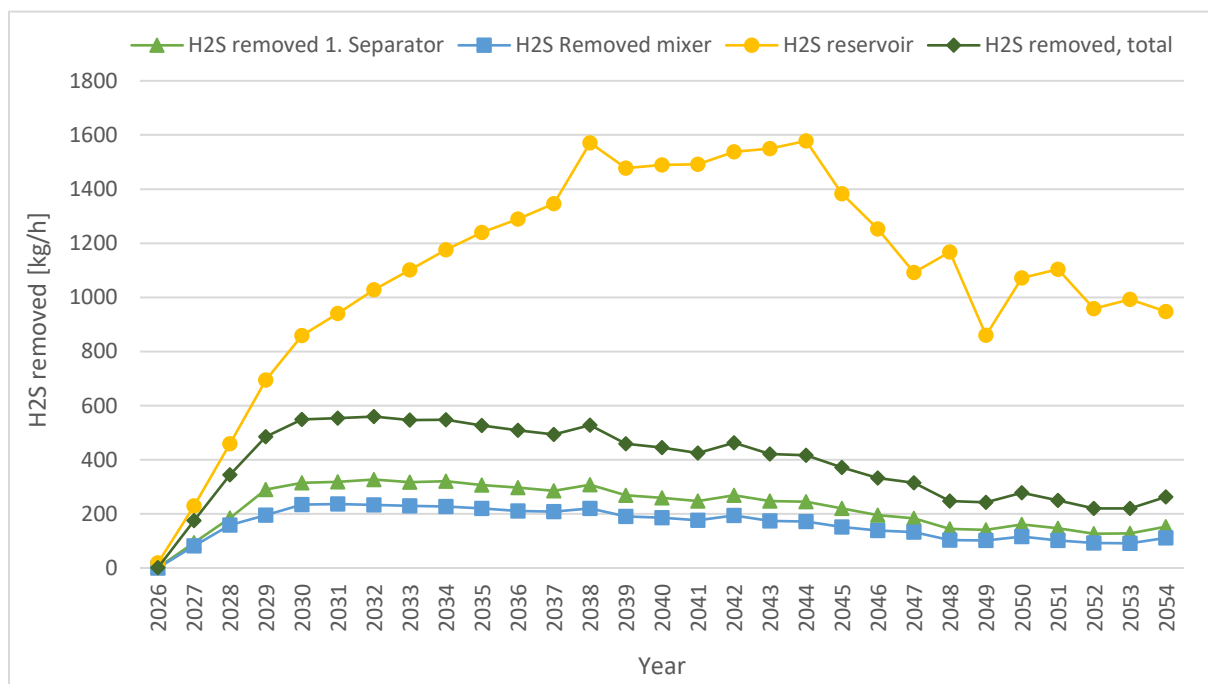


Figure 6-6: H2S removed in gas two places to reach sales gas quality compared with H2S production in reservoir. Phase 1

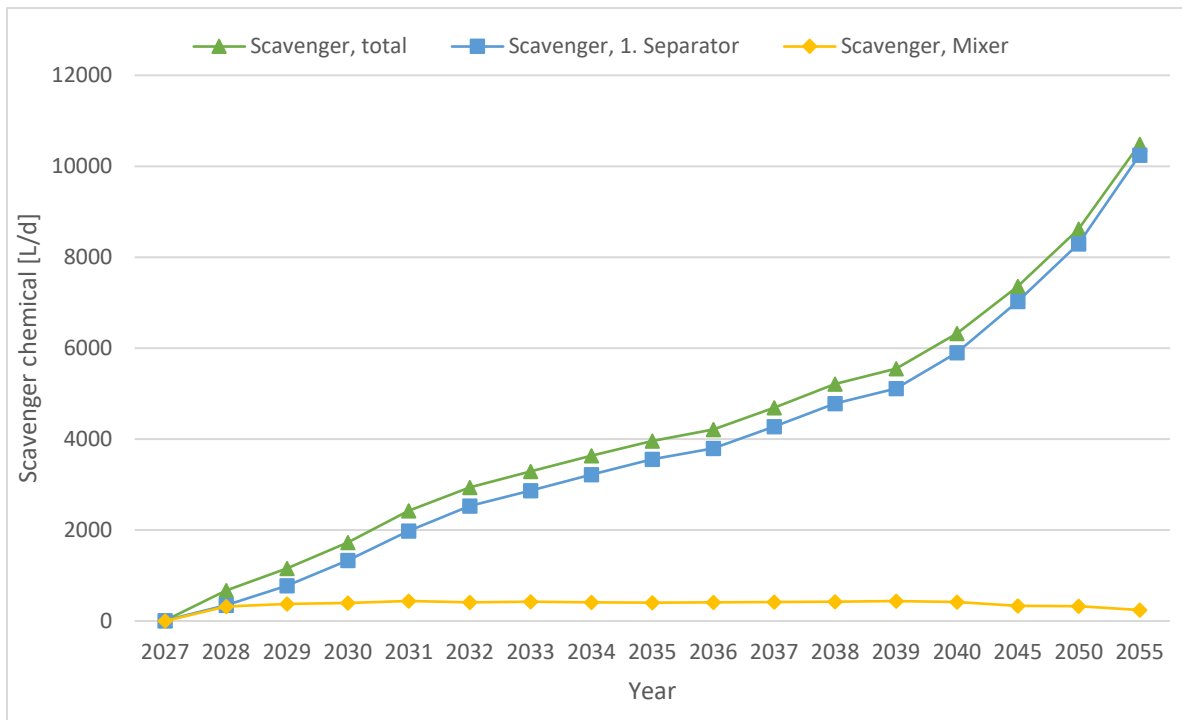


Figure 6-7: Scavenger chemical use with injection after 1. stage separation and mixer. Phase 2

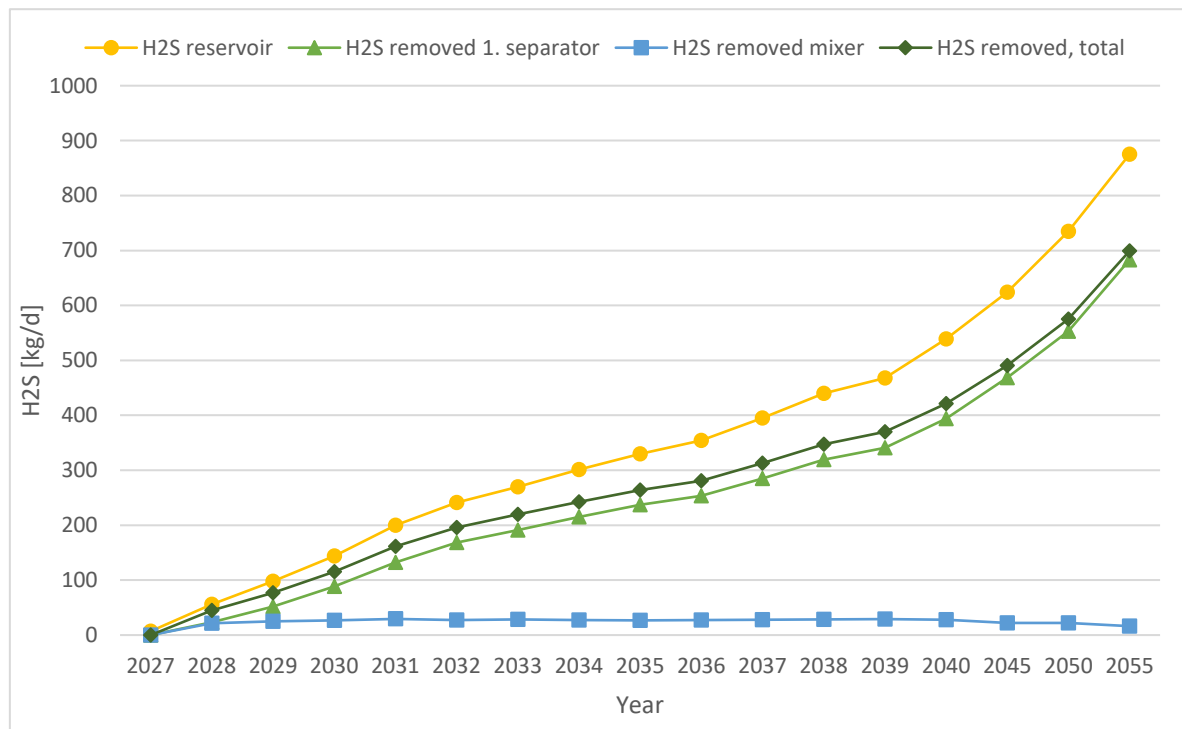


Figure 6-8: H2S removed in gas two places to reach sales gas quality compared with H2S production in reservoir. Phase 2

The higher total scavenger consumption (compared to injection after compression) is also observed for phase 2, but the increase in scavenger chemical consumption for these injection points are lower than the increase we observe for phase 1. A significant higher oil production for phase 1 seems to be the impacting factor here.

As seen from figure 6-6, phase 1 will only experience some difference in  $H_2S$  amount in the gas and the corresponding scavenger injection rate for injection point 1 (after inlet separator), compared to injection point two (after mixer). The situation will however be totally different for phase 2. From figure 6-8, the scavenger chemical rate injected after first separator versus the consumption after the mixer is significantly higher. For phase 2, almost all  $H_2S$  is removed after first Separator and only an insignificant amount of  $H_2S$  is removed after the mixer.

This seems reasonable because of the oil and gas production (distribution of oil and gas in the offshore facility). For phase 1 the oil production is significantly higher than for phase 2. This higher oil production represents a higher amount of hydrocarbons in second and third separator and thereby a higher amount of  $H_2S$  in the corresponding streams. At the same time, the gas production for phase 2 is higher than phase 1 (not in the beginning, but totally). This together with a lower oil production (than phase 1) results in less oil to be treated and less waste of chemicals. For phase 2 we have a low oil to gas production ratio which corresponds to a low rate of gas from the second and third separator and thereby a low injection rate is required here.

**6.2.3. Subsea scavenger**

The multiphase stream was treated with multiphase scavenger chemical subsea (non-triazine). The scavenger consumption was dependent on a sales gas specification of 3 ppm. As noted before, the scavenger capacity is 7 liters per kg  $H_2S$ .

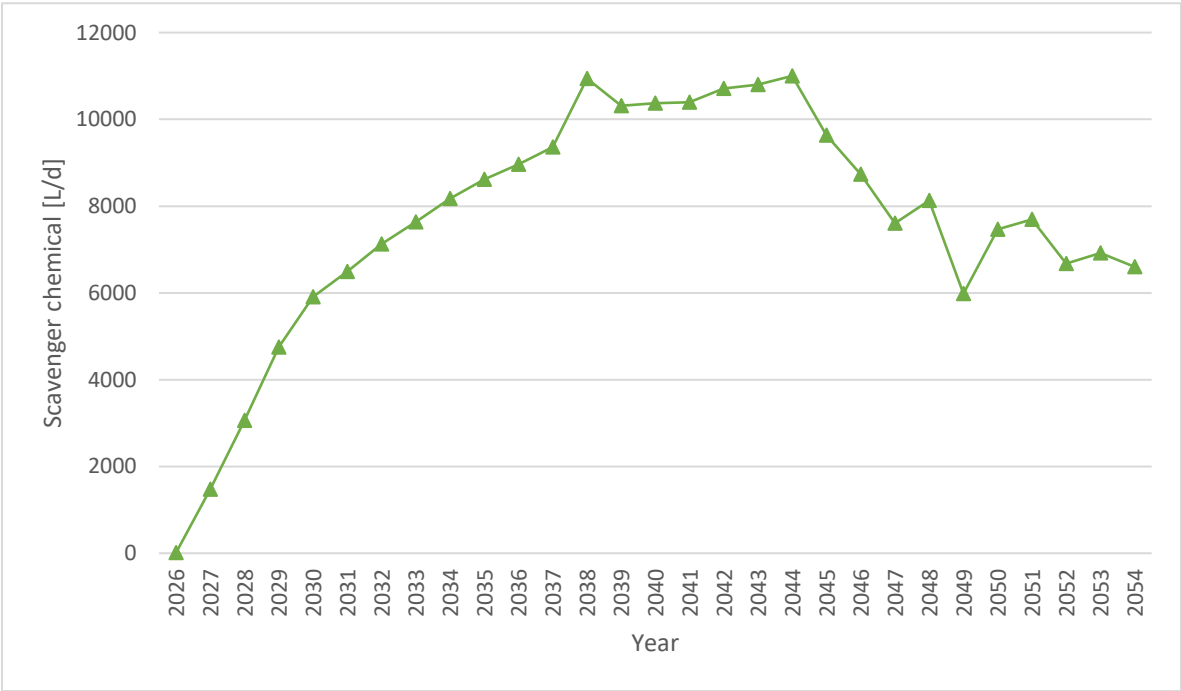


Figure 6-9: Subsea scavenger consumption. Phase 1

From the charts involving phase 1, the  $H_2S$  removed (figure 6-10) is almost the same as the  $H_2S$  production in the reservoir. The difference varies with some kg/d  $H_2S$  (some  $H_2S$  is allowed in the oil and gas). This corresponds to an increase in scavenger chemical consumption (and later revealed, a dramatic increase in costs) even though the scavenger capacity is considerably higher. Both the oil,

water and gas will be treated and become free from  $H_2S$  (except from the 3 ppm). Because of the oil to gas ratio and a significant water injection rate (water-cut ratio) explained previously, the  $H_2S$  absorbed subsea is considerable compared to what we remove topside to reach sales gas quality.

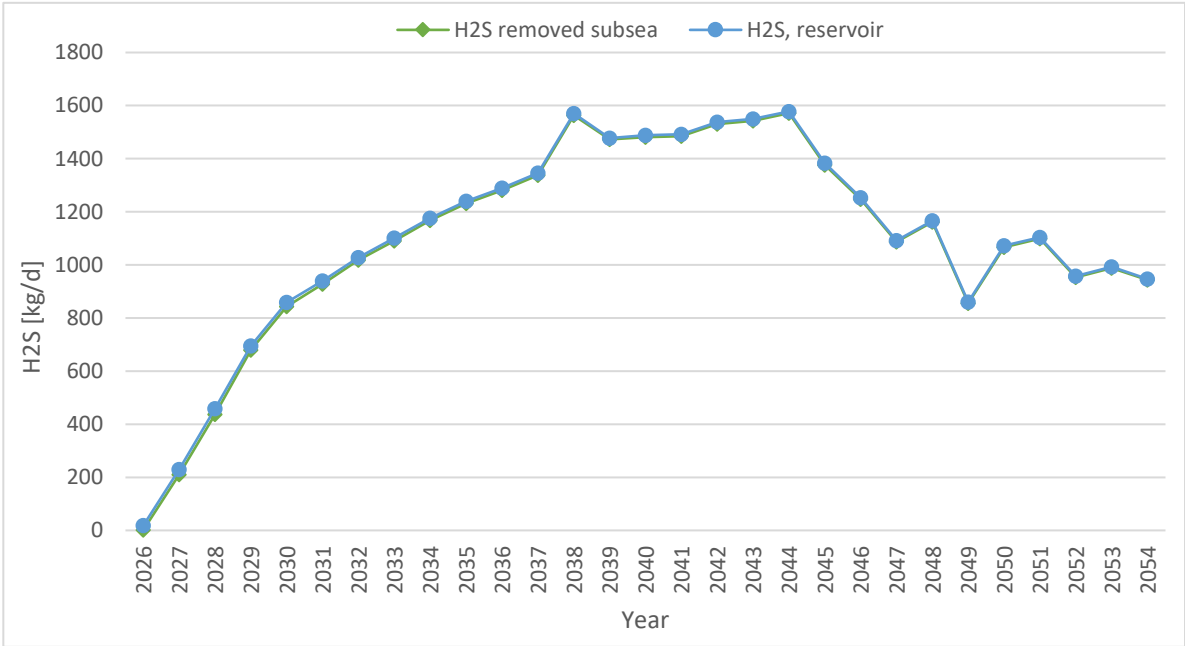


Figure 6-10: H2S removed subsea compared with H2S production in reservoir. Phase 1

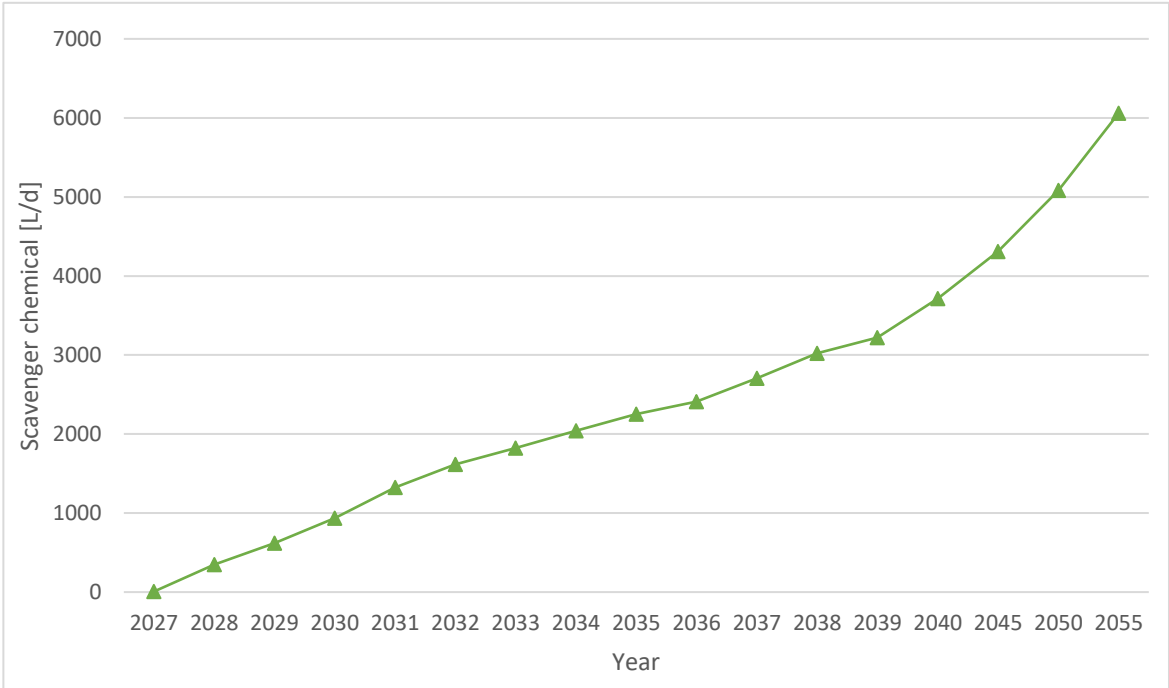


Figure 6-11: Subsea scavenger consumption. Phase 2

The lower oil to gas ratio and water injection rate observed for phase 2 result in a smaller difference in  $H_2S$  removed subsea compared to topside, as to what the case is for phase 1. Less scavenger chemical is “wasted” on oil and water. Subsea scavenger seems to be more appropriate for phase 2

than for phase 1. The larger capacity for multiphase scavenger causes a large decrease in scavenger consumption for subsea injection than for the two other injection options.

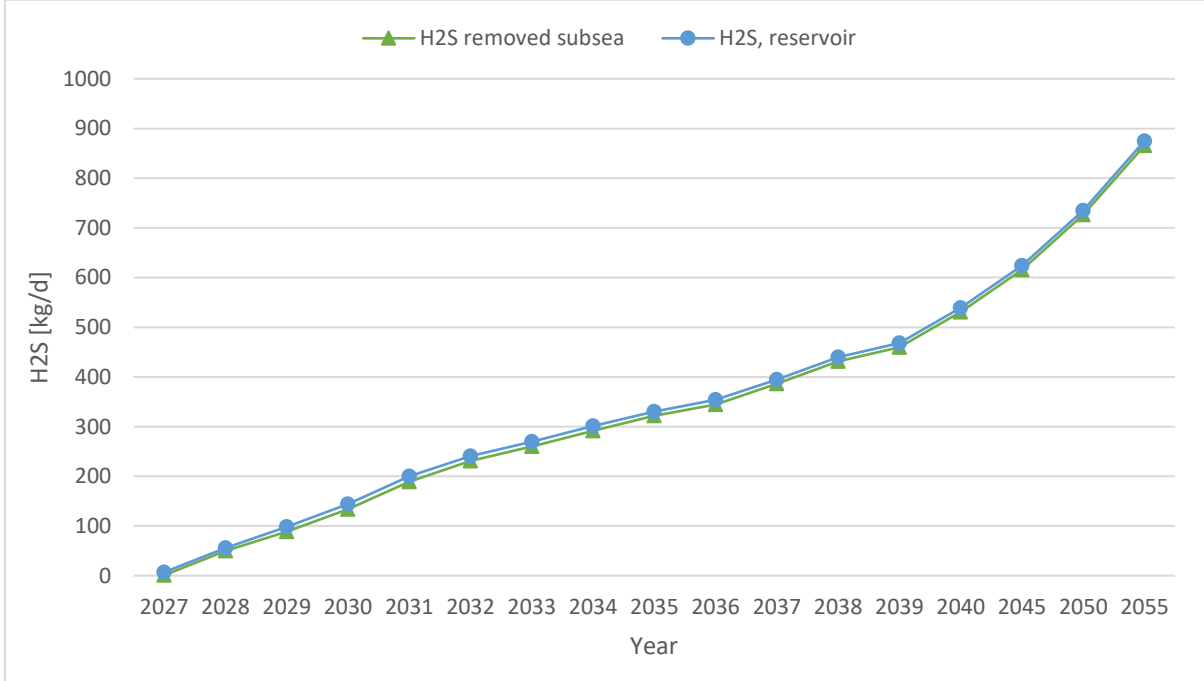


Figure 6-12: H2S removed subsea compared with H2S production in reservoir. Phase 2

**6.2.4. Scavenger injection after compressor combined with partly subsea injection**  
 Subsea scavenger is applied in combination with injection after compressor. 25%, 50% and 75% of the  $H_2S$  is removed subsea and the rest after compression to get a sales gas specification of 3 ppm

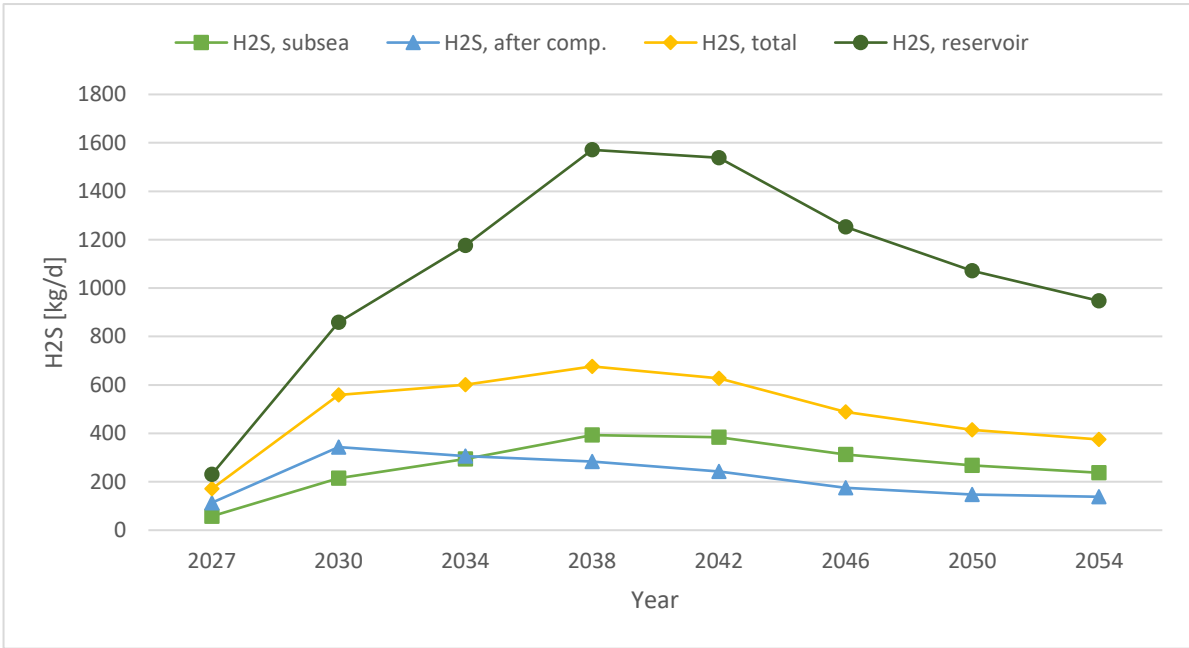


Figure 6-13: 25% H2S removed subsea. Rest of H2S removed after compression. Phase 1.

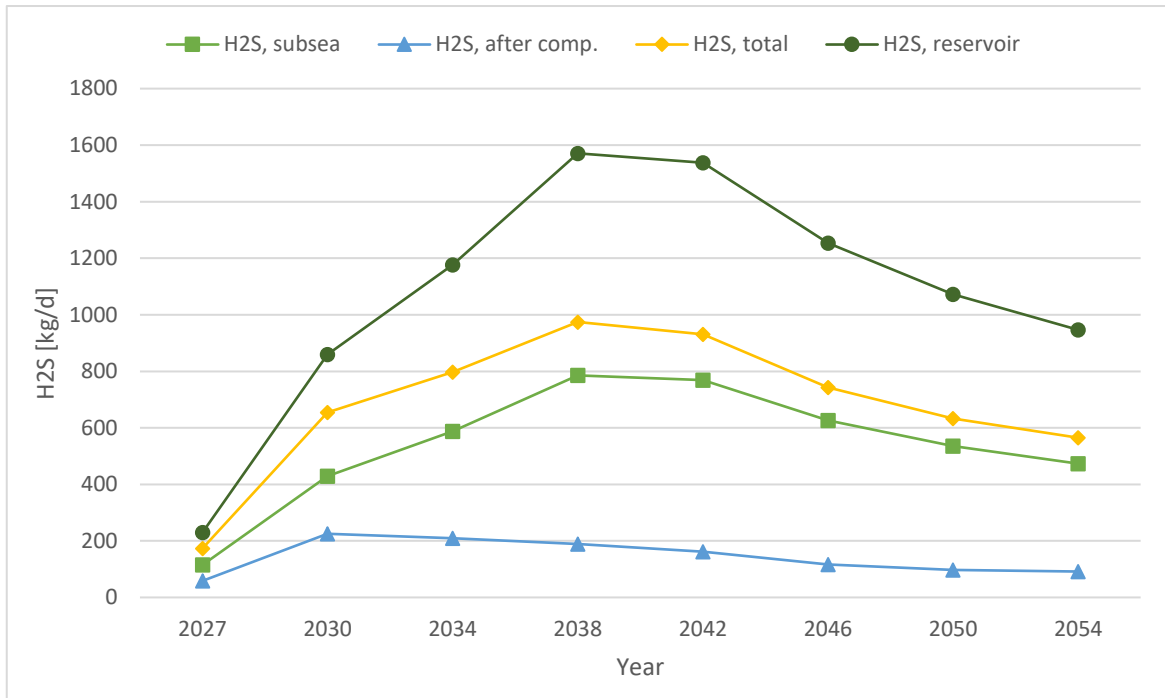


Figure 6-14: 50% H<sub>2</sub>S removed subsea. Rest of H<sub>2</sub>S removed after compression. Phase 1.

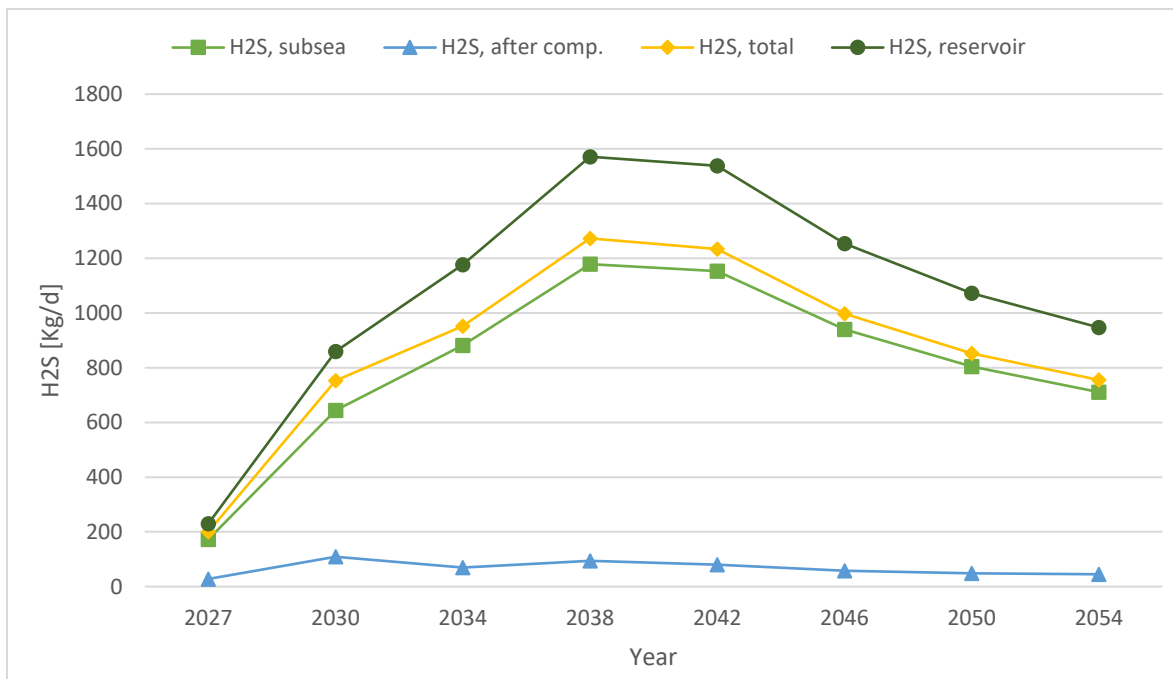


Figure 6-15: 75% H<sub>2</sub>S removed subsea. Rest of H<sub>2</sub>S removed after compression. Phase 1.

The results are as expected. 75% H<sub>2</sub>S subsea removal has the highest consumption (figure 6-16), followed by 50% and then 25%. The scavenger consumption is also higher than the injection after compression, but for 25% of injection subsea, the scavenger consumption is lower than the injection after inlet separator and mixer.

From figure 6-15, the 75% injection subsea will have the highest number of  $H_2S$  removed to reach sales gas specification, which is rather obvious. In comparison with all injection points options, the amount of  $H_2S$  removed lies in-between injection after first separator and mixer and subsea injection, with 25% subsea injection lying just above injection after first separator and mixer.

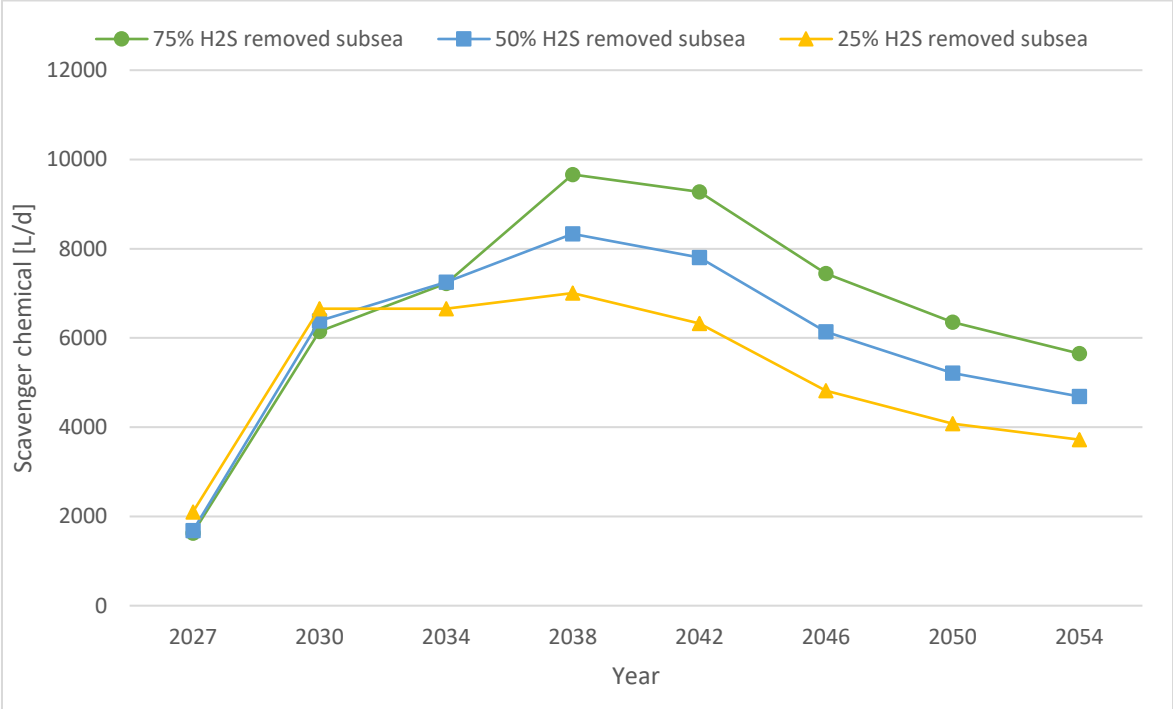


Figure 6-16: Scavenger consumption for the three options. Phase 1.

For the scavenger consumption and figure 6-16, 75% subsea injection has the lowest consumption rate in the beginning of the period. A higher absorption capacity for the multiphase scavenger chemical (7 L/kg  $H_2S$ ) results in a low subsea scavenger consumption. Even though the multiphase scavenger absorption capacity is twice the gas scavenger, the large amount of  $H_2S$  absorbed subsea will make 75% subsea injection the most scavenger consuming option.

When we observe the scavenger consumption in comparison to the other injection points, we actually have a lower scavenger consumption in the beginning for the 25% removal subsea compared to removing everything after compression. But the increasing  $H_2S$  accumulation in the reservoir and higher water injection rate tend to make injection after compression a lower scavenger consuming option, even though the absorption capacity is much lower for gas scavenger.

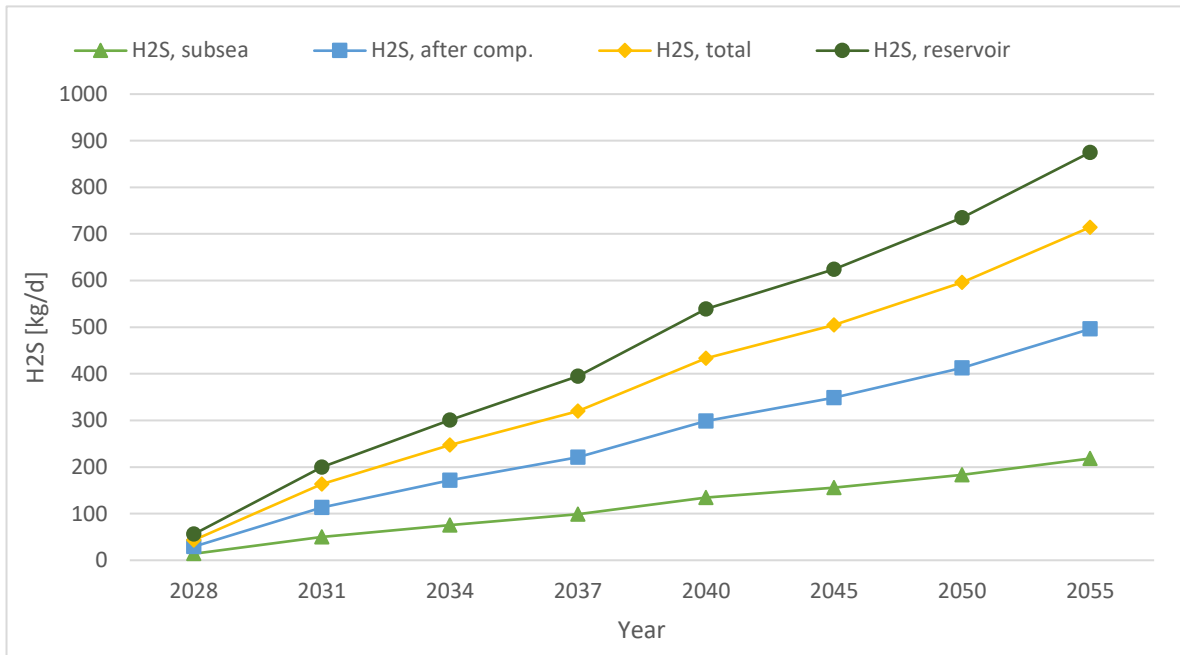


Figure 6-17: 25% H2S removed subsea. Rest of H2S removed after compression. Phase 2.

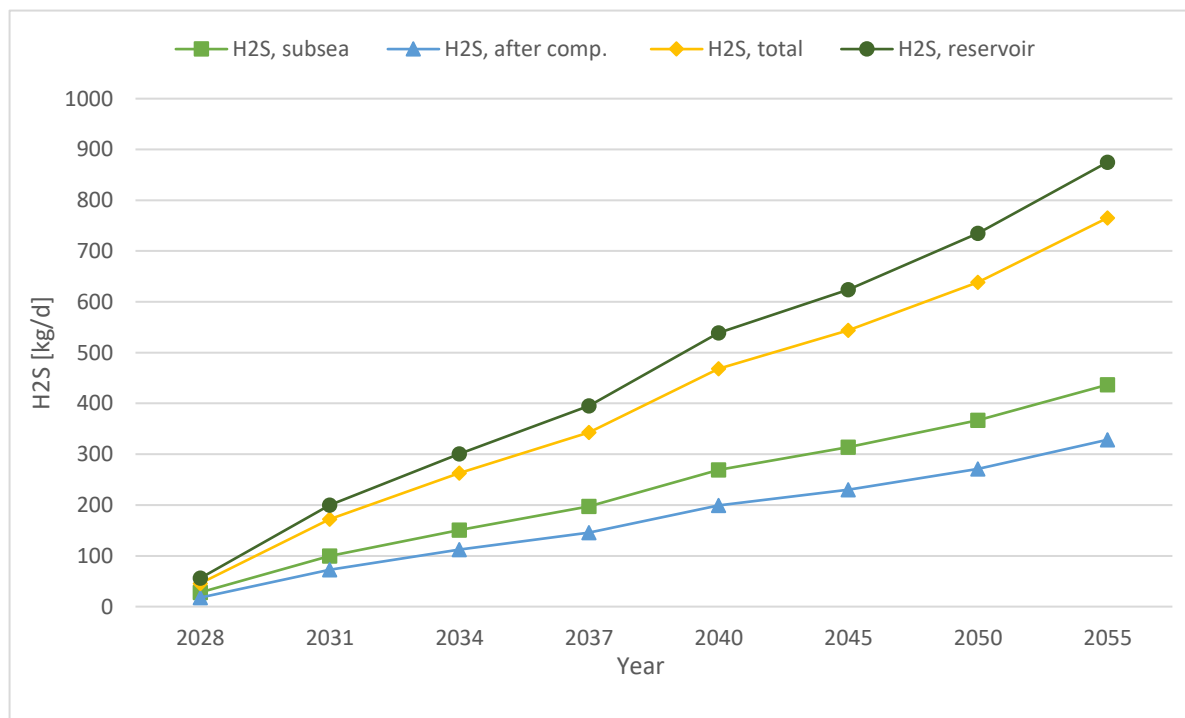


Figure 6-18: 50% H2S removed subsea. Rest of H2S removed after compression. Phase 2.

For the figures including phase 2, we have a similar behavior as for the subsea scavenger. From figure 6-20, 75% subsea injection has the smallest chemical injection rate among the three options, and the consumptions for all three each are smaller than injection after compression and injection after first separator and mixer. This is explained in the subsea injection part. From figure 6-17 to 6-19, the total  $H_2S$  absorbed is highest for 75 % subsea injection, as expected.



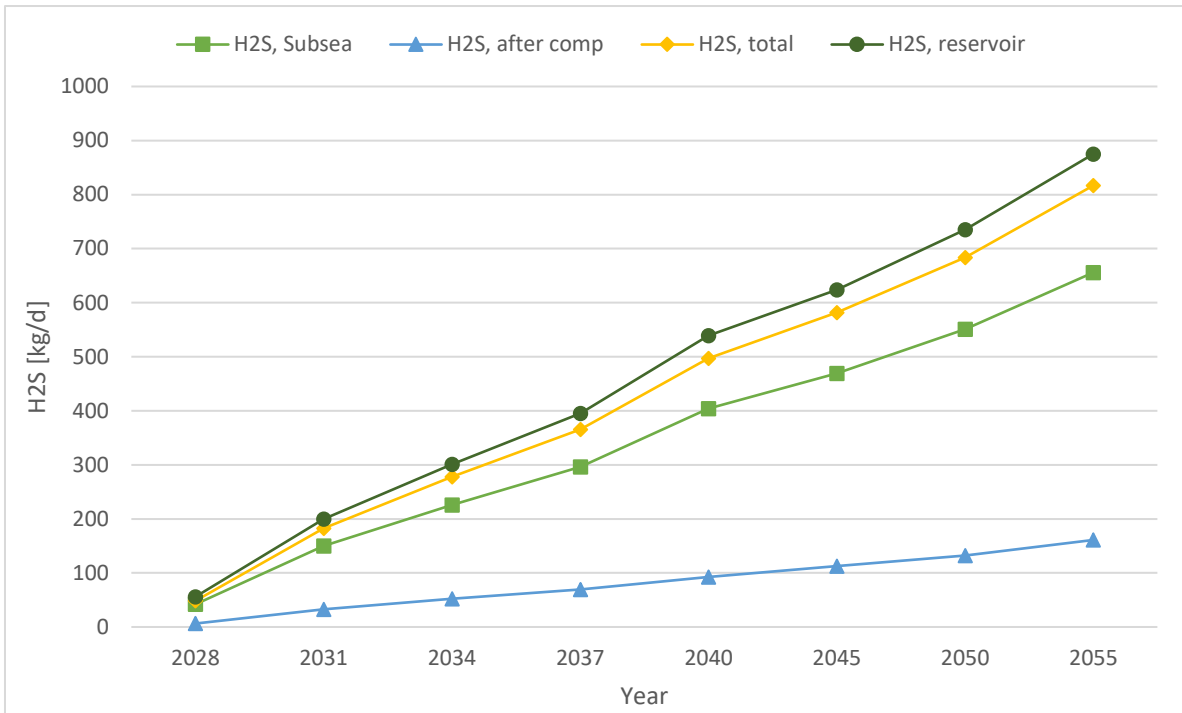


Figure 6-19: 75% H<sub>2</sub>S removed subsea. Rest of H<sub>2</sub>S removed after compression. Phase 2.

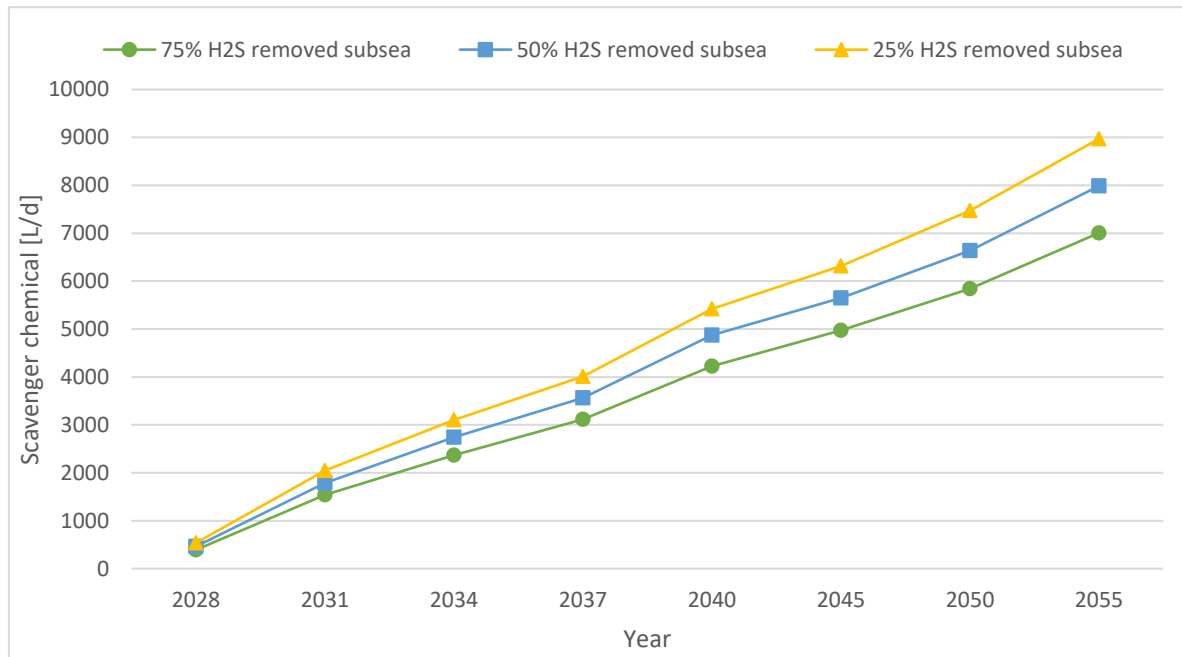


Figure 6-20: Scavenger consumption for the three options. Phase 2.

### 6.2.5. H<sub>2</sub>S distribution in produced water

A large proportion of the produced H<sub>2</sub>S in the reservoir fluid ends up in the produced water after inlet separator (except for subsea injection). This is the main reason and dominating factor for the large difference in absorbed H<sub>2</sub>S for injection after compression compared to subsea injection. Only an insignificant amount of H<sub>2</sub>S ends up in the produced water from other separators (less than 0,1 kg/d). The distribution of H<sub>2</sub>S in the water is studied further in Chapter 10 and Appendix C.

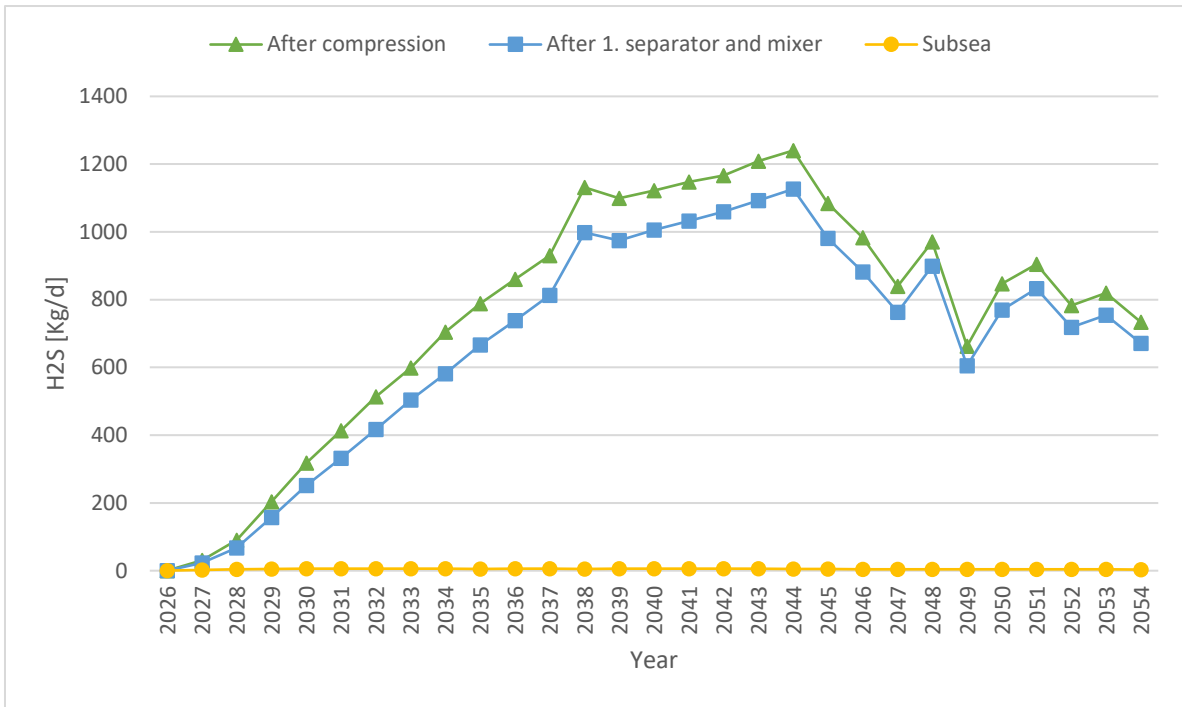


Figure 6-21: H2S in produced water after inlet separator. Phase 1

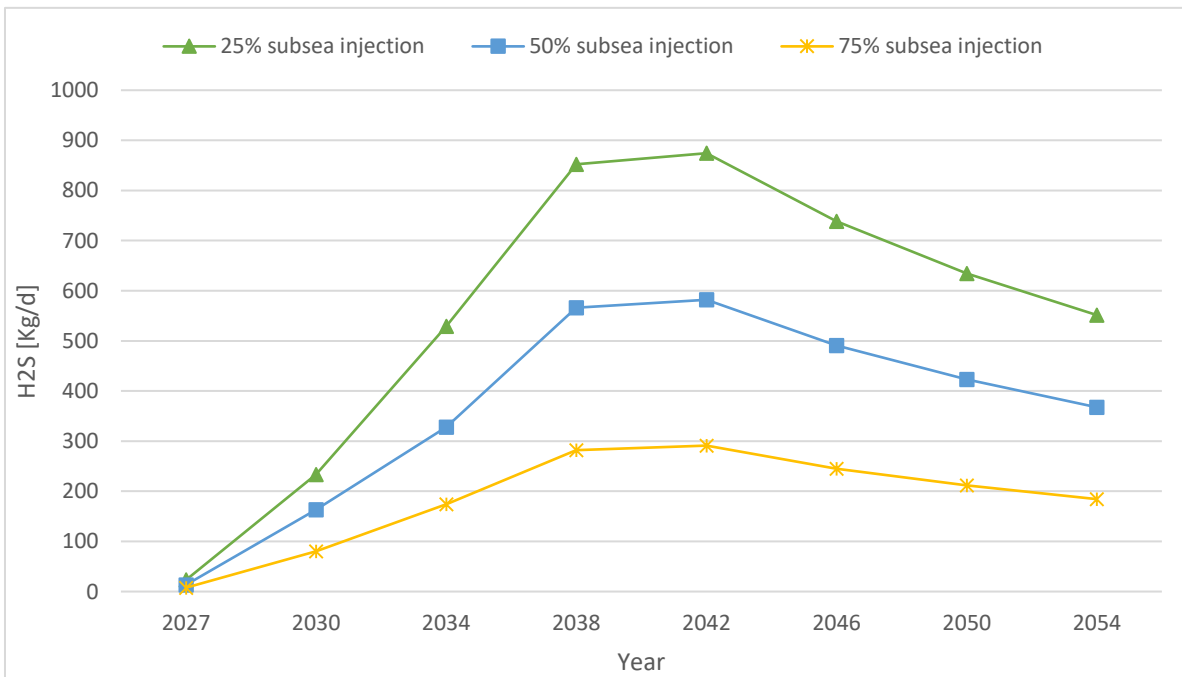


Figure 6-22: H2S in produced water after inlet separator for partly subsea injection. Phase 1

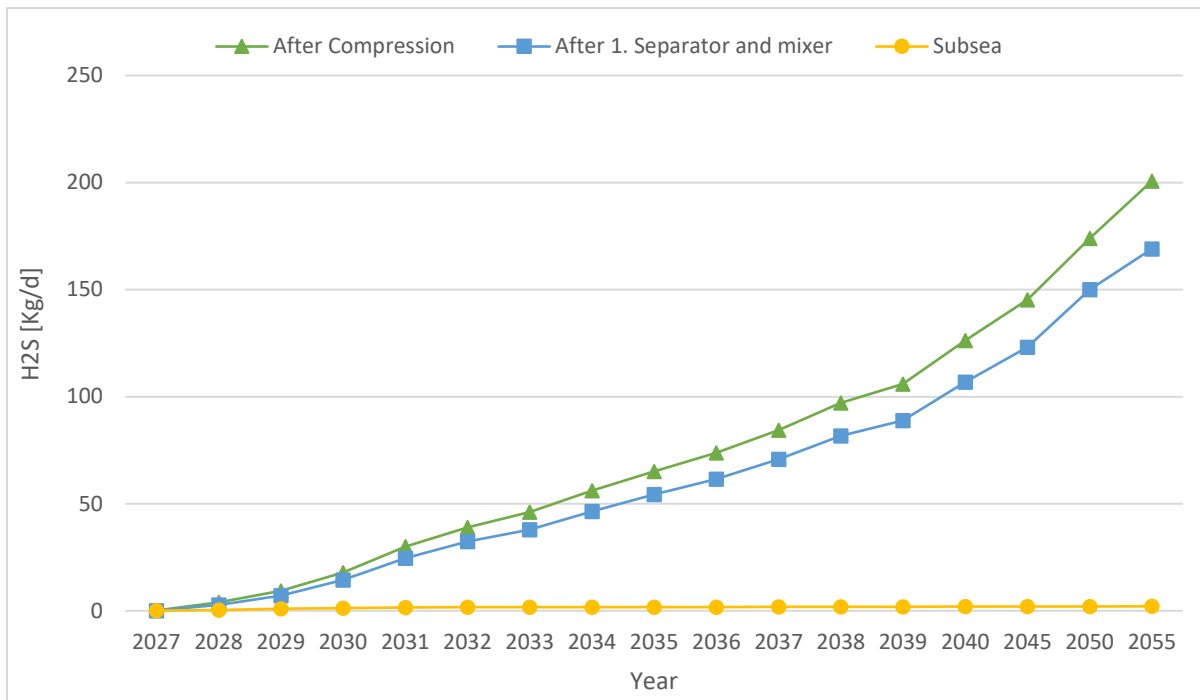


Figure 6-23: H2S in produced water after inlet separator. Phase 2

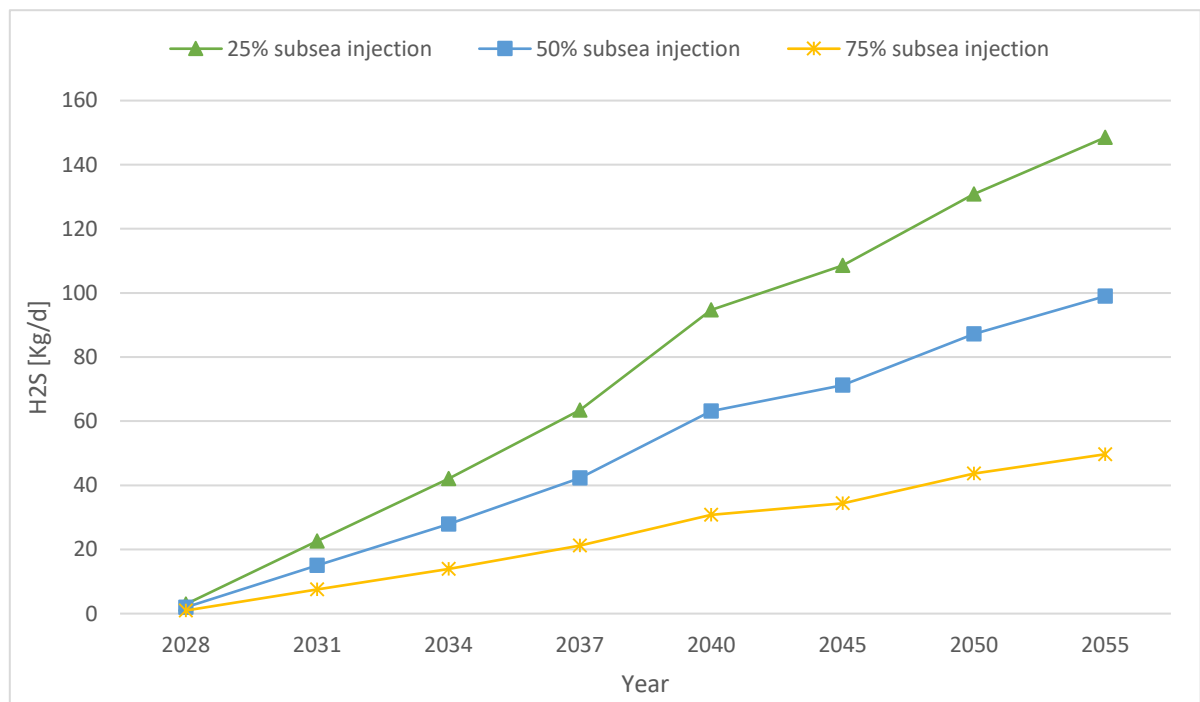


Figure 6-24: H2S in produced water after inlet separator for partly subsea injection. Phase 2

## 7. Amine plant simulation

### 7.1. Design

The design in hysys was based on a standard, simple amine configuration explained previously in the text. The sour gas is contacted with a mixture of 50 wt% MDEA amine and 50 wt% water in the absorber. The rich mixture exits at the bottom of the absorber. The pressure is then reduced to 15 bar, and some of the hydrocarbons are flashed in the flash tank. Further, the rich mixture is heat exchanged with the hot lean amine flow from the stripper. The pressure is reduced again to 1.2 bar before entering the stripper. The amine mixture is boiled at a temperature around 110 °C. The hot mixture of acid gas and amine is condensed at around 25 °C in the top of the stripper. The acid gas is easily separated from the amine and is sent for further treatment. The cooled amine-water mixture is sent back to stripper for regeneration. The hot lean amine is sent back to the absorber, first cooled in two stages, then pumped up to 55.7 bar. Some water and an insignificant amount of MDEA amine are added in the makeup vessel to reach an amine concentration of 50 wt%. The mixture is now ready for absorption operation. Some important parameters for the design are listed in table 7-1. A flow scheme of the amine plant is shown in figure 7-1.

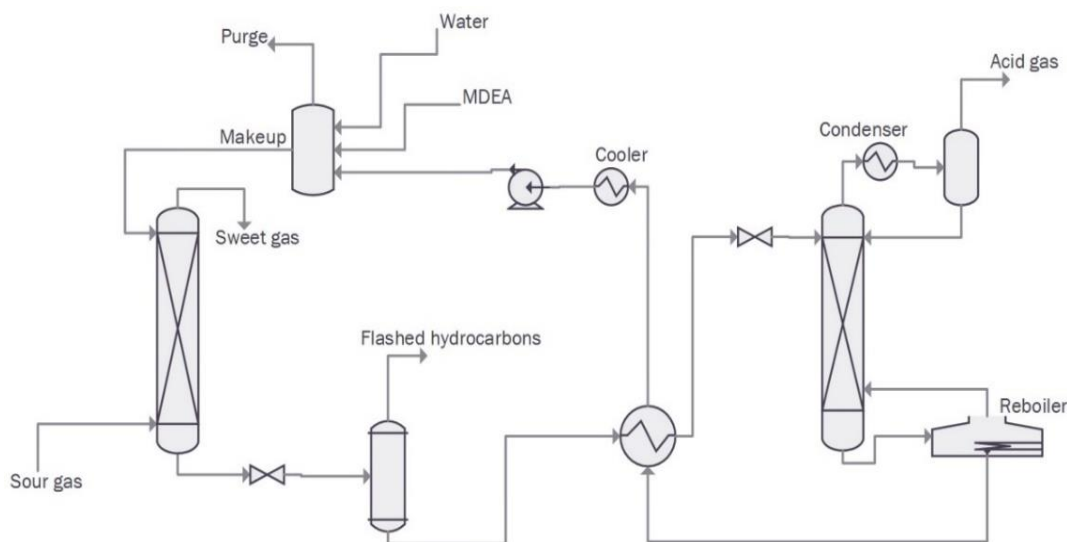


Figure 7-1: Amine plant design in hysys

Table 7-1: Amine plant key values

Parameter	Value
Gas inlet temperature [C°]	27.5
Absorber pressure [bar]	55.7
Absorber stages	4
Lean gas temperature [C°]	28.4
Flash pressure [bar]	15.0
Lean amine temperature [C°]	30.8
MDEA amine concentration [%wt]	50
Stripper stages	4+2

Stripper pressure [bar]	1.2
Stripper amine inlet temperature [C°]	98.0
Stripper temperature [C°]	110.0
Reboiler temperature [C°]	110.0
Condenser temperature [C°]	25.0

## 7.2. Simulation

The simulation was performed with the acid gas package in Hysys. The amine plant is placed after first stage compression to utilize the higher pressure. In Hysys a stream splitter was used to switch from SRK package to acid gas package. A virtual stream was used to get the right composition, pressure and temperature. Connecting the ordinary stream to the amine plant proved to make the simulation much more complicated and slow. This will presumably lead to more uncertainties in the simulation. Modified hysys-sim out was used for calculations in the absorber/stripper. The amine flow rate was adjusted to get a sales gas specification of around 3 ppm. High gas flow or high  $H_2S$  concentration should result in a high amine flow rate.

## 7.3. Results

### 7.3.1. Phase 1

From figure 7-2 the amine volume flow rate is shown in correlation with the gas volume rate. Like the scavenger injection, the amine liquid volume flow is high in the early stage of souring due to a high gas production rate. From the scavenger simulation we know that for year 2026, the  $H_2S$  level will exceed the sales gas quality of 3 ppm, but only with 0.2 ppm. We assume that the amine plant will be running from year 2027 (not profitable to run the amine plant from year 2026). As for the scavenger injection, the amine flow rate will not decline at the same rate as for the gas production rate because of the increasing mass of hydrogen sulfide in the produced fluid.

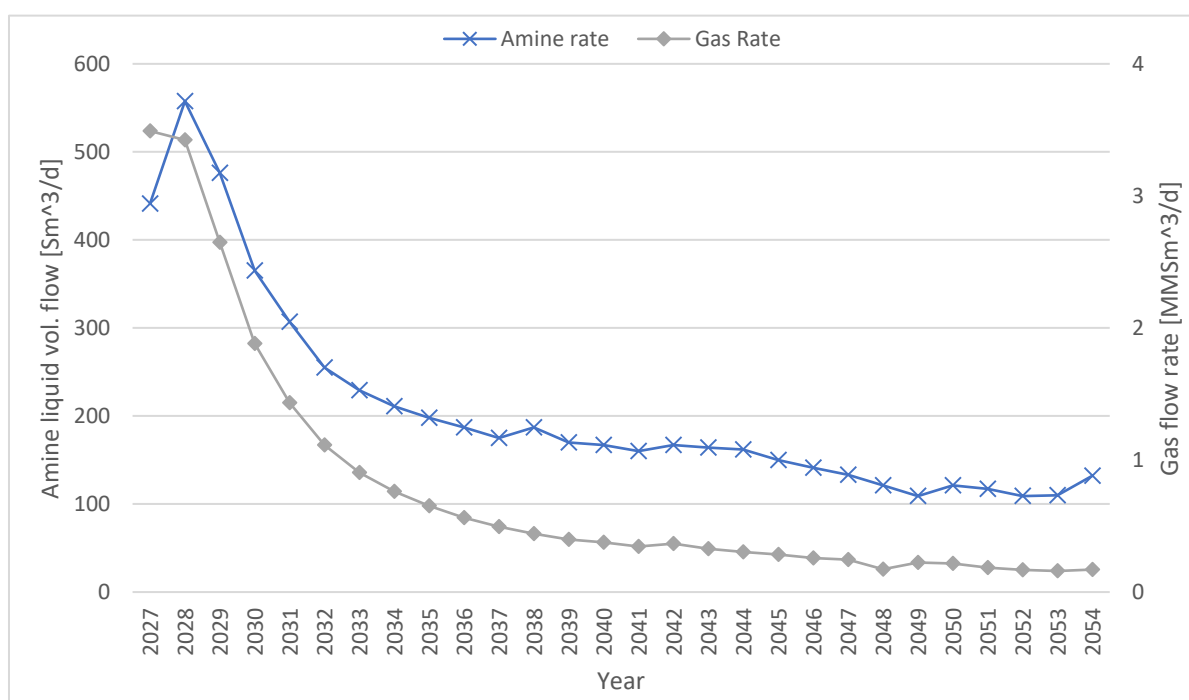


Figure 7-2: Amine flow rate and gas flow rate. Phase 1

The power consumption for the reboiler is shown in terms of the first vertical axis in figure 7-3. For the second vertical axis, the mass of  $H_2S$  in the gas to be treated is plotted. The power consumption (figure 7-3) has a direct correspondence to the amine flow rate and more energy (heat) is required to boil off a higher amine flow rate.

The power consumption and the corresponding amine flow rate are not entirely dependent on mass of  $H_2S$  in the gas. The export gas rate is also an important parameter. From the figure we observe that the highest power consumption is found in year 2028, but the  $H_2S$  amount in the gas is not particularly large. When we have the highest  $H_2S$  amount in the gas, which is seen in year 2031, the power consumption is significantly lower compared to year 2028. This is due to the large decline in gas production rate.

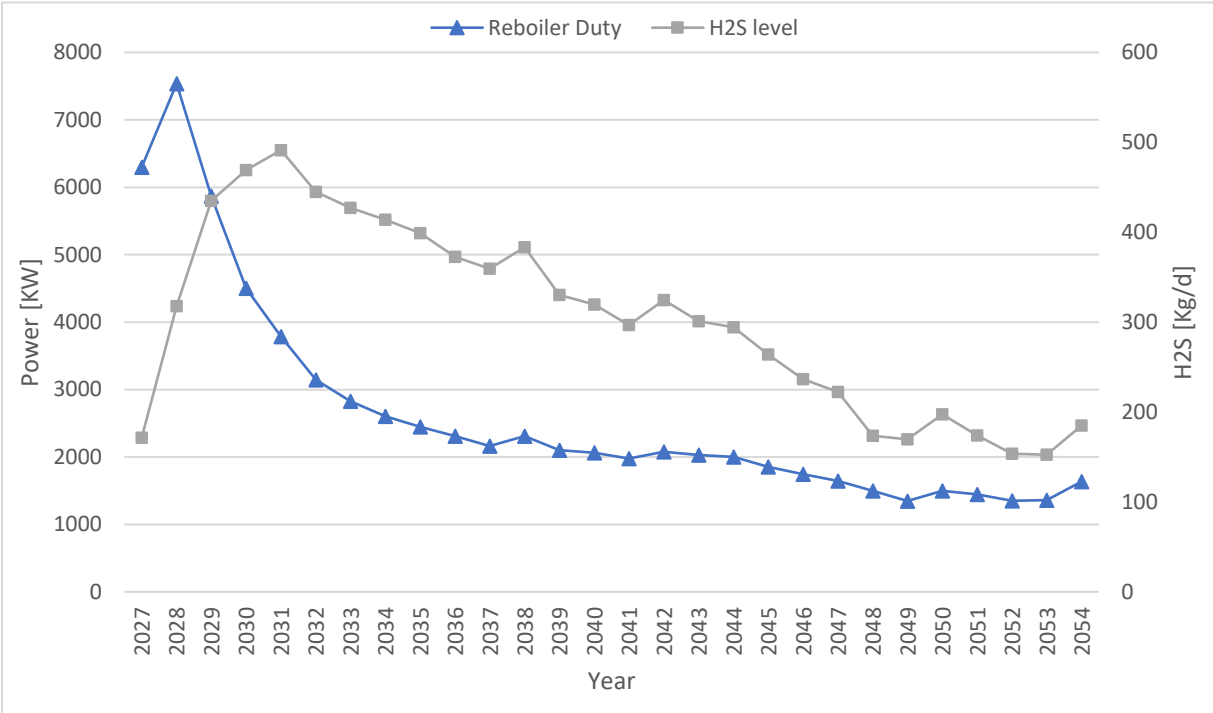


Figure 7-3: Reboiler power consumption and H2S in gas to be treated. Phase 1

7.3.2. Phase 2

A similar behavior as for scavenger injection simulation and the amine simulation results from phase 1, is observed in figure 7-4 and 7-5. The sales gas production rate is only reduced with about 0.5 MMSm<sup>3</sup> throughout the period. The production of  $H_2S$  in the reservoir will only increase during the period. The amine flow rate must be increased to maintain sales gas quality. With only a minor decrease in gas production rate and a large increase in mass of  $H_2S$  in the gas, a significant increase in amine flow rate and the following power consumption is required.

Both maximum amine flow rate and maximum power demand are higher for phase 1. The total power consumption for the period is higher for phase 2.

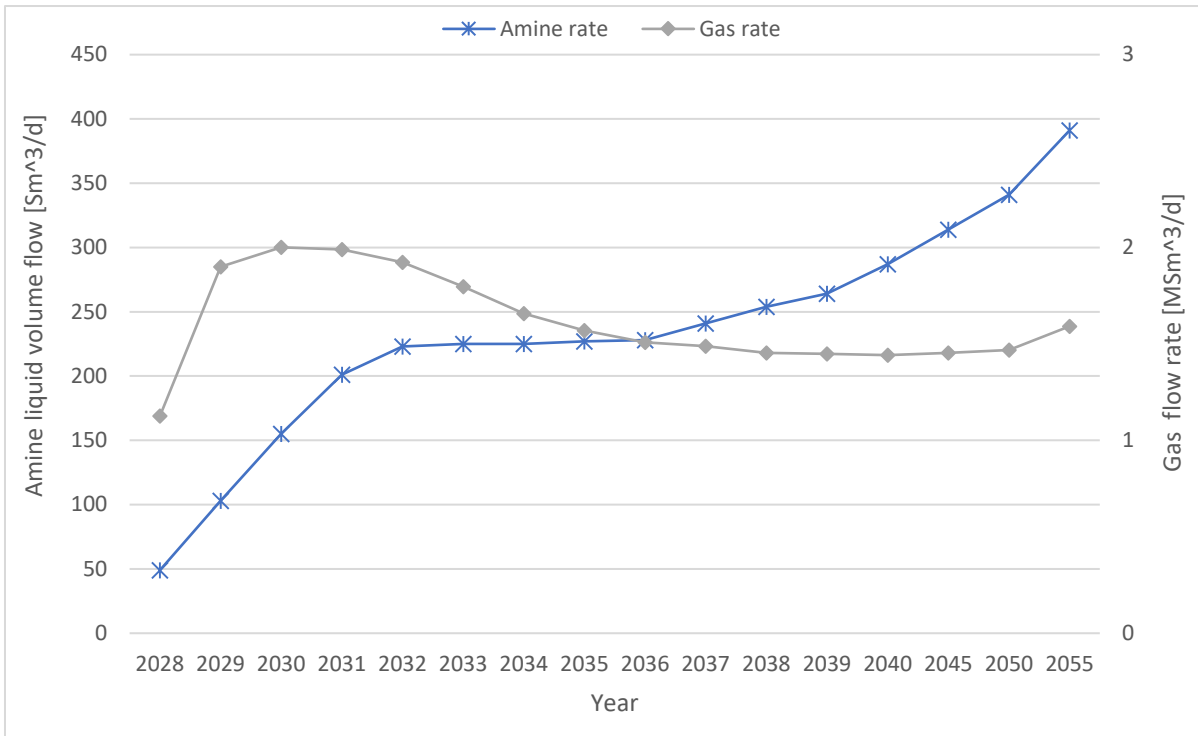


Figure 7-4: Amine flow rate and gas flow rate. Phase 2

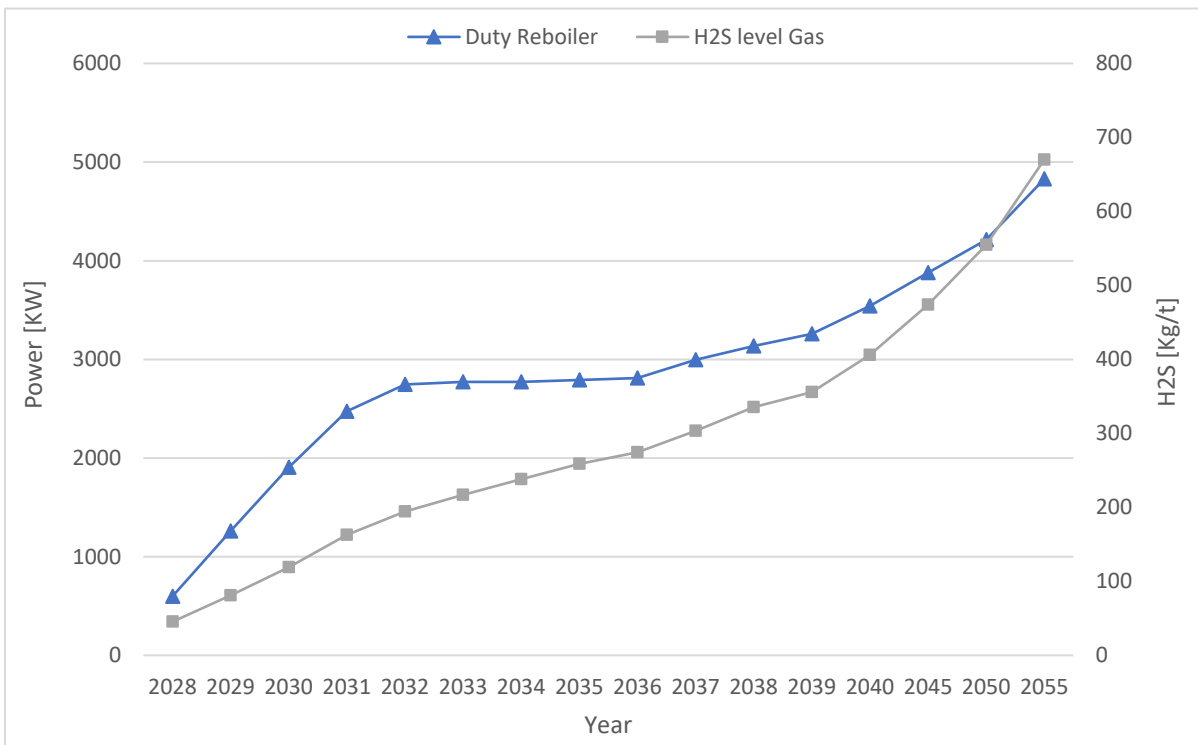


Figure 7-5: Reboiler power consumption and H2S in gas to be treated. Phase 2

## 8. Cost and size estimation

### 8.1. Scavenger chemical cost estimation

The scavenger cost is proportional to the scavenger consumption and therefore we have similar graphs. The price was set 1.1 Euro per liter gas scavenger and 2.2 Euro per liter multiphase (subsea) scavenger. 330 days for one year are used same as before. A tremendous difference in cost between subsea scavenger and injection after compression is shown in figure 8-1. The scavenger cost for the whole period was found to be 442 MNOK for injection after compression, 591 MNOK for injection after first separator and mixer and 1560 MNOK for subsea injection.

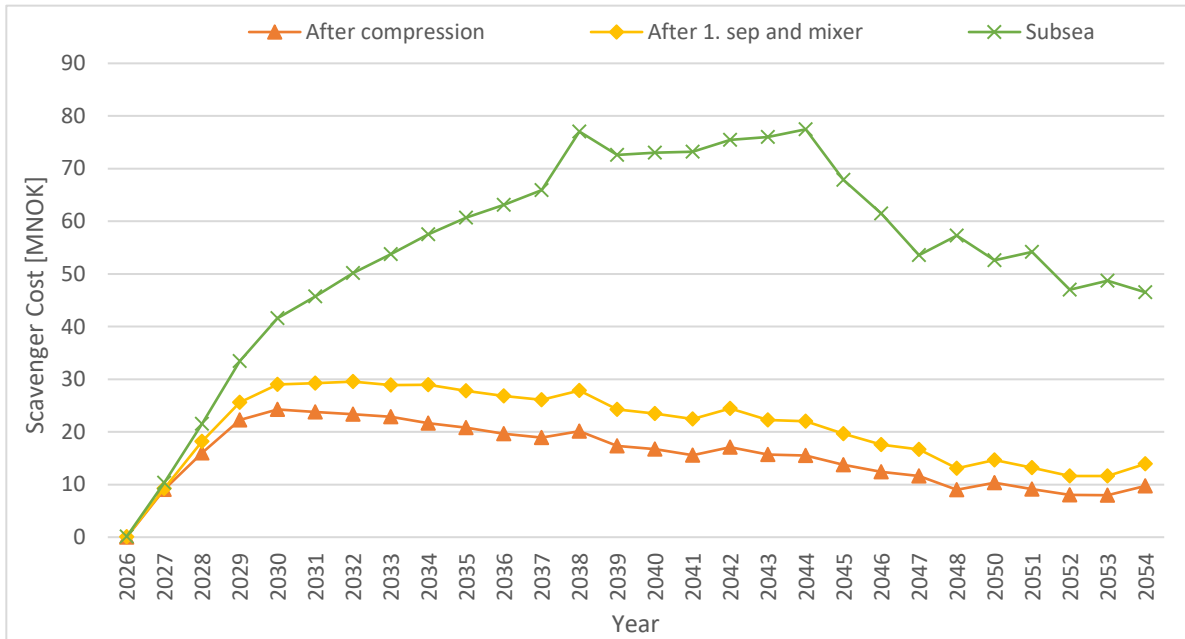


Figure 8-1: Scavenger chemical cost. Phase 1

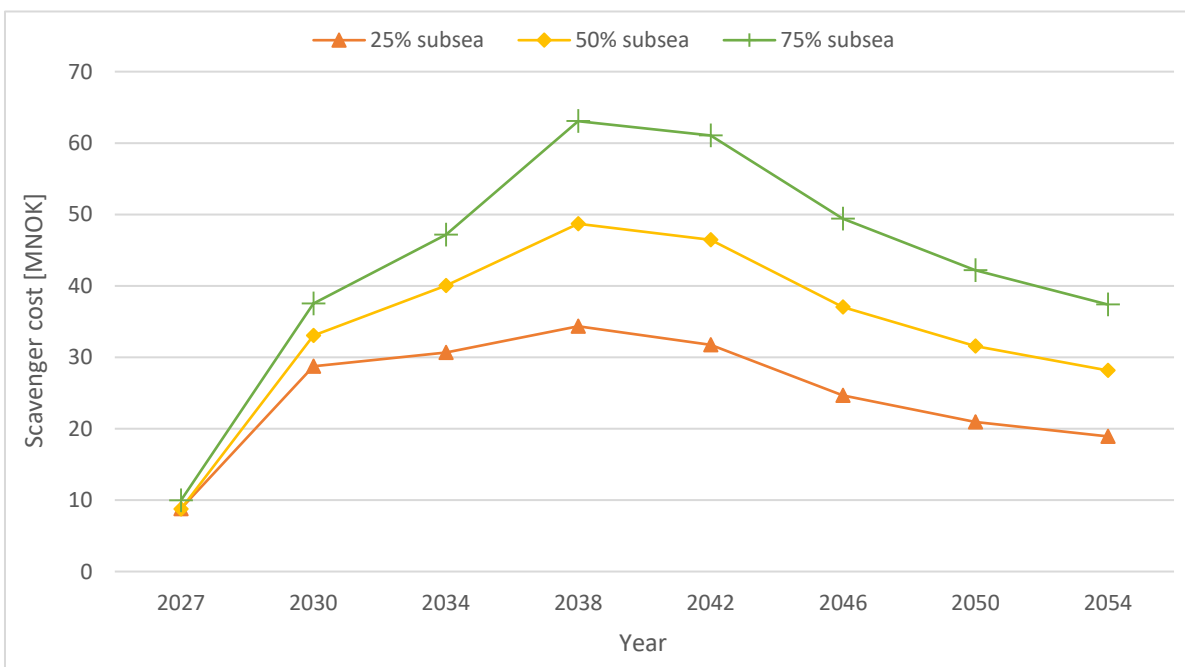


Figure 8-2: Scavenger chemical cost for partly subsea injection. Phase 1.



The costs for partly subsea injection are as expected. It is placed between injection after separator and mixer and injection subsea. The total costs for the three options were estimated to be 735 MNOK, 1019 MNOK and 1296 MNOK for 25%, 50% and 75% subsea scavenger injection, respectively. Not all years were simulated as seen from the figure. The missing years were estimated based on the average between the previous year and coming year.



Figure 8-3: Scavenger chemical cost. Phase 2

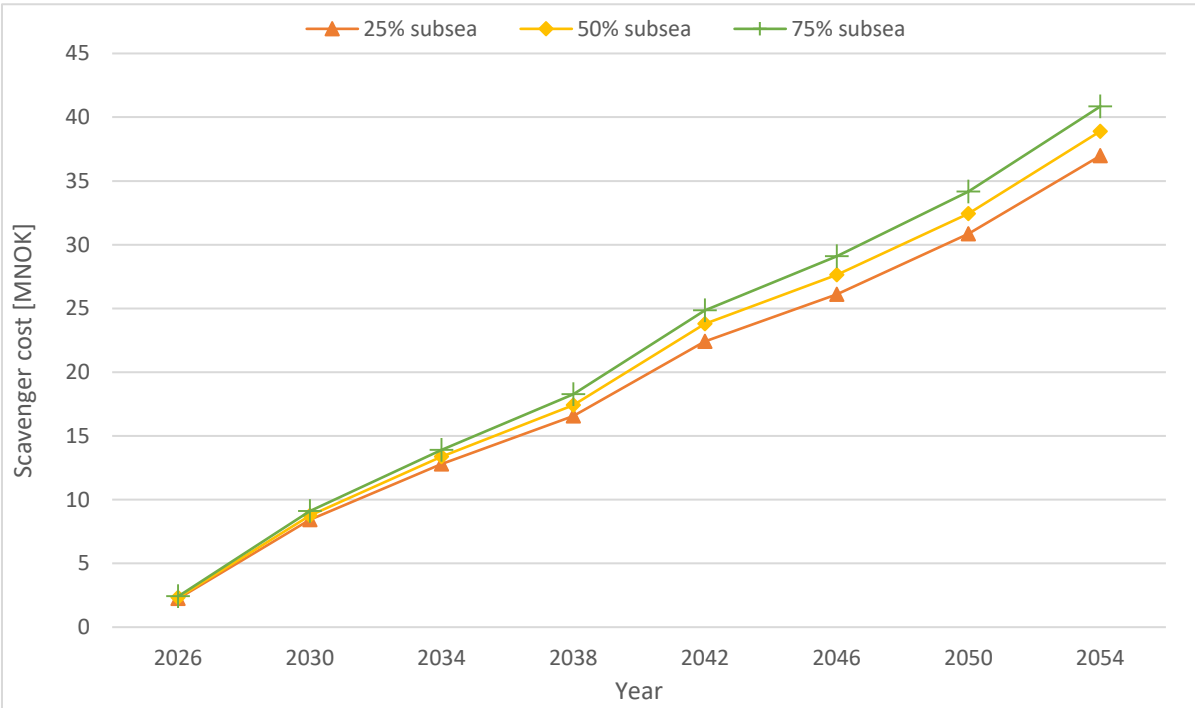


Figure 8-4: Scavenger chemical cost for partly subsea injection. Phase 2

The scavenger costs for phase 2 are shown in figure 8-3. The difference in costs between subsea scavenger and the two other options is not so large compared to phase 1. The costs for the three situations were estimated to 568 MNOK, 598 MNOK and 695 MNOK for injection after compression, injection after 1. Separator and mixer and subsea injection, respectively. The same estimation method as for partly subsea injection is used, with the average between the previous year and coming year multiplied with the numbers of years in-between.

From figure 8-4, partly subsea injection for phase 2 is shown. This is as expected, with 75% injection being the highest. The plotted costs for the three injection options are placed between subsea scavenger and the two other injection options, as for phase 1. The estimated cost for the three situations were 602 MNOK, 635 MNOK and 666 MNOK for 25%, 50% and 75% respectively. Notice 25% injection subsea is not far from the costs of injecting after first separation and mixer. The difference between the three is not as great compared to phase 1.

## 8.2. Amine sizing

Size and weight estimations are obtained from Hysys. Sieve trays are used. Most of the sizes are held at a constant level for the different years during the period, but the stripper sizes and weight are automatically adjusted according to amine flow rate. From table 8-1 to table 8-3, the stripper, reboiler and condenser size estimates correspond to year 2028 and 2054 for phase 1. Further work is required to calculate an appropriate size for both stripper and absorber design, able to handle the large fluctuations in both gas flow rate and  $H_2S$  levels that is observed throughout the production period.

Table 8-1: Selected weight estimations in Hysys for amine plant

	Absorber	Flash Tank	Stripper	Reboiler	Condenser	Heat exchanger	Cooler	Pump
<b>Equipment Weight [Kg]</b>	6486	1814	5625 - 2631	3810 - 1043	23768 - 4853	16375	2132	1497
<b>Total Installed Weight [Kg]</b>	12792	5023	16675 - 10182	13797 - 6124	37436 - 12962	29017	6901	3245
<b>Total Weigth Amine Plant [Kg]</b>	36831 - 55882							
<b>Total Installed Weigth Amine Plant [Kg]</b>	86246 - 124886							

Table 8-2: Stripper and absorber sizing

	Absorber	Stripper
<b>Diameter Bottom section [m]</b>	0,9144	1,6764 – 0,9144
<b>Bottom tangent to tangent height [m]</b>	6,096	6,096
<b>Bottom Tray spacing [m]</b>	0,6096	0,6096

Table 8-3: Flash tank design for amine plant

	Flash Tank
Liquid volume [m3]	3,27
Vessel diameter [m]	1,07
Vessel tangent to tangent height [m]	3,66

### 8.3. Amine energy and scavenger cost comparison

A rough estimation of the energy costs has been made. Only the power demand for the reboiler is accounted for. Seawater is usually utilized for the condenser and cooler. The pump power has little impact on the total power consumption (at least in this case). 0.5 NOK Kwh is used. This number is based on the current power price (0.45 kr per Kwh), but the grid rent is not accounted for. One can assume that an individual contract is made and for that reason will be cheaper than regular pricing (why the grid rent is not accounted for). We know that the platforms will be fully electrified with electricity from shore.

Phase 1 is chosen here because space has been set aside for an amine plant to be installed on the existing platform. If an amine plant were to be installed, a reasonable solution would be to connect the gas stream from both phase 1 and 2 for treatment. It is unclear if the infrastructure would allow it.

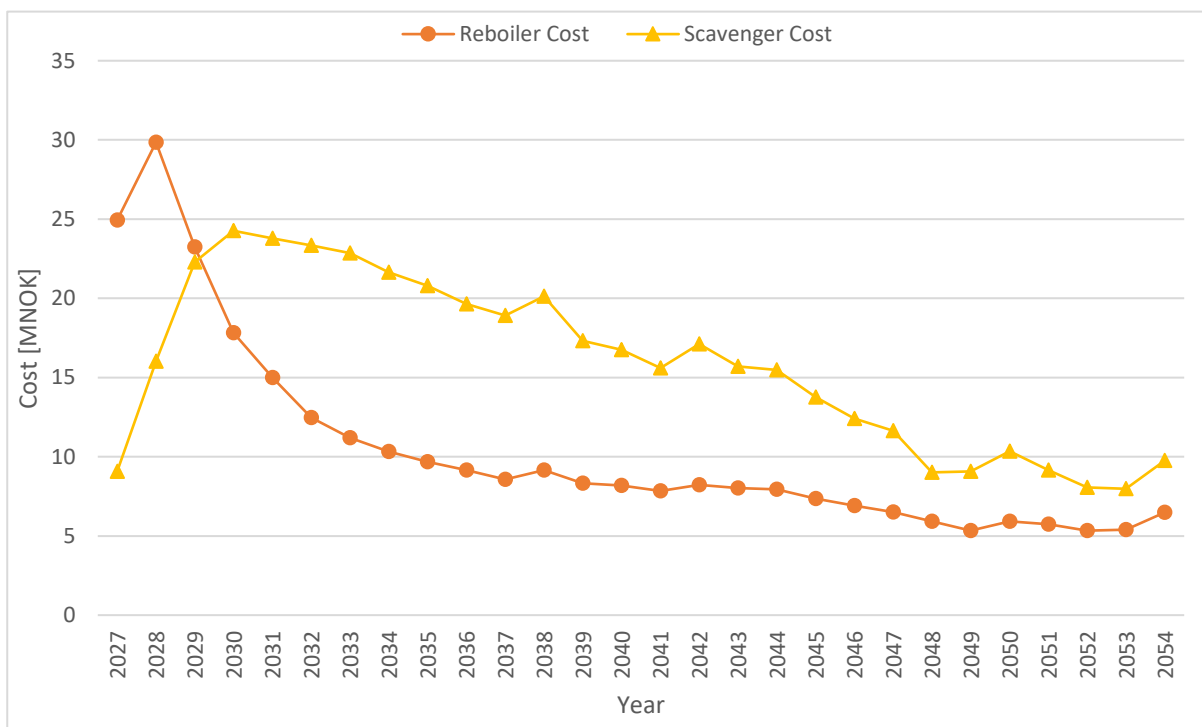


Figure 8-5: Rough cost estimate for scavenger chemical and electricity. Phase 1

## 9. Selection map comparison

From Chapter 5 and figure 5-1, a selection map is presented for some of the processes discussed previously in the text. For the current technologies, which include amine plant and scavenger injection, a comparison diagram is made based on results from the injection after first stage compression simulation.

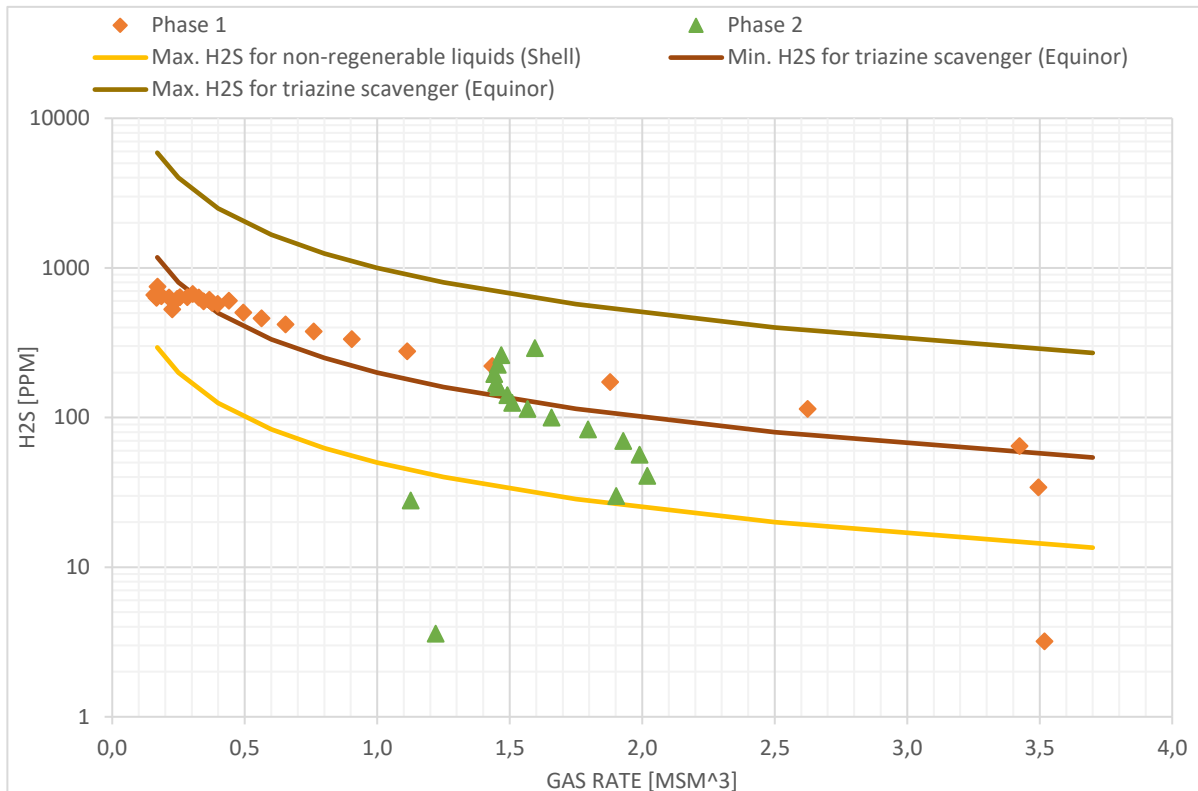


Figure 9-1: Phase 1 and 2 expressed in terms of  $H_2S$  content [ppm] and gas rate [ $MSm^3$ ]. The different lines are the recommended lower/upper limit for  $H_2S$  concentration/gas rate for non-regenerable liquids/triazine liquid

A correlation between  $H_2S$  concentration and gas rate for the two phases (phase 1 and 2) are plotted in figure 9-1 together with lines that represent a recommended minimum and maximum standard for sulfur amount in the gas when non-regenerable liquids/triazine scavenger should be used. These values are 50 Kg/d, 200 kg/d and 1 T/d obtained from Shell and Equinor.

The same plots for phase 1 and 2 are shown in figure 9-2 together with a recommended minimum line for sulfur amount in the gas that represents amine technology according to Shell.

The simulation results for both phase 1 and 2, implemented in figure 9-1, will exceed the maximum line for non-regenerable liquid scavenger given by Shell. The lines obtained from Equinor will however be highly representative. Considering Equinor is the operator for the oilfield, triazine scavenger technology seems to be a suitable process.

From figure 9-2 we see a large gap between the simulation results plotted and the minimum line for amine installation given by Shell. The gas flow rate for an amine installation should be rather large (10  $MSm^3/d$ ) for low  $H_2S$  concentration (in the beginning of production for phase 1 and 2). Gas

rates in this range are not seen for this oil field. For lower gas rates, the  $H_2S$  concentration should exceed 100000 ppm to defend an amine plant installation. Such numbers are not even close compared to  $H_2S$  concentration in the gas found in this oilfield.

The figures shows a much greater gap between minimum line for amine installation and the results obtained from Hysys, than between non-regenerable liquids/triazine scavenger lines and the same results plotted.

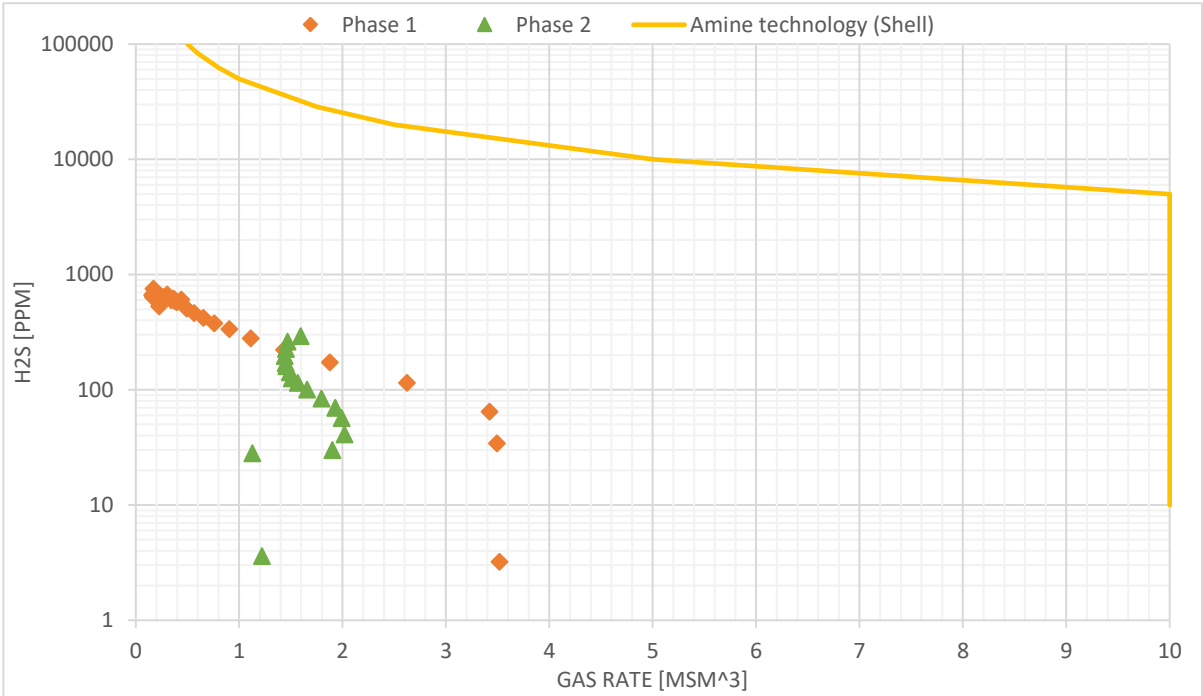


Figure 9-2: Phase 1 and 2 expressed in terms of H<sub>2</sub>S content [ppm] and gas rate [MSm<sup>3</sup>]. Amine technology line is the recommended minimum limit for H<sub>2</sub>S concentration/gas rate according to Shell.

## 10. Validation of the $H_2S$ partitioning to the oil, gas and water

The  $H_2S$  partitioning in the system is crucial with respect to the  $H_2S$  concentration in the gas phase. To evaluate whether the  $H_2S$  distribution for the model in Hysys is credible, a comparison with a theoretical  $H_2S$  partitioning model is performed. Appendix C describes a model based on three parameters;  $H_2S$  solubility in water, salting-out effect and ionization. A Henry's law approach is used to calculate the molecular fractions for the aqueous phase and Peng -Robinson equation of state is applied for the non-aqueous phase. Results (coefficients) from the model were also compared with other real scenario measurements for  $H_2S$  partitioning. The coefficients for the model and the measurements showed to be rather similar and the model can be stated as quite accurate.

From Appendix C, it is known that pH can have a large impact on  $H_2S$  partitioning to the gas phase because of the ionic strength and salting-out phenomena (figure C-2 to figure C-5). It is also claimed to have an influence on the partitioning of  $H_2S$  in gas for different water cut rates (figure C-1). Hysys is however unable to calculate pH and to evaluate the corresponding effect caused by dissociation, ionic strength and salting-out. A large uncertainty for the  $H_2S$  distribution will possibly follow.

For low pH (about pH3) it is known that about all  $H_2S$  is in molecular form and the partitioning to the gas is only a function of the water-cut ratio, regardless of the ionic strength. For higher pH (about pH7) the ionic species dominated over molecular form and dissociation, salting-out and ionic strength all impact the final gas phase  $H_2S$  concentration. These phenomena will result in a lower  $H_2S$  concentration in the gas phase than what is observed in Hysys. Scavenger technology will be in favor.

Figure C-5 shows the  $H_2S$  distribution in an oilfield system for two pH values and for different water cut rates. For pH7 and a 90% water cut ratio, 94% of the  $H_2S$  is leaving the separator in the liquid phases. This is a significant amount compared to the results found here, notably because the water-cut ratio in Hysys is over 90 percent for the majority of time illustrated.

Different values for mole fractions were taken from Hysys (table 10-1 and 10-2) and compared to results from the partitioning model (Appendix C). The reservoir stream for the oil in Hysys was estimated to have an API of 37.2. The pressure and temperature were obtained to 16 bar (232 psi) and 63 °C in Hysys. For the partitioning model, an API of 34 and a 50 % water cut rate were used. The results list some  $H_2S$  concentrations for different years and the corresponding water cut rates. The calculated partitioning coefficients are listed in table 10-3.

Table 10-1: H2S concentrations [ppm] for some years. Phase 1

Year	H2S gas [ppm]	H2S oil [ppm]	H2S Water [ppm]	Water cut ratio
2026	2,49	0,89	0,03	0,393
2027	27,08	9,30	0,29	0,875
2028	51,10	17,35	0,55	0,925
2034	309,00	102,10	3,24	0,985
2044	520,70	171,30	5,44	0,994
2054	611,10	201,00	6,38	0,994

Table 10-2: H2S concentrations [ppm] for some years. Phase 2

Year	H2S gas [ppm]	H2S oil [ppm]	H2S Water [ppm]	Water cut ratio
2027	2,92	1,05	0,03	0,466
2028	21,66	7,62	0,24	0,761
2029	25,60	8,85	0,28	0,871
2036	120,40	40,25	1,28	0,983
2039	165,00	55,08	1,75	0,988
2055	287,20	95,37	3,03	0,990

Table 10-3: H2S partition coefficients for the different years, respectively. K[1] and K[2] are for phase 1 and phase 2.

Year	K <sub>ow</sub> [1]	K <sub>gw</sub> [1]	K <sub>go</sub> [1]	Year	K <sub>ow</sub> [2]	K <sub>gw</sub> [2]	K <sub>go</sub> [2]
2026	31,8	88,5	2,8	2027	31,8	88,2	2,8
2027	31,7	92,3	2,9	2028	31,8	90,3	2,8
2028	31,6	93,1	2,9	2029	31,7	91,7	2,9
2034	31,5	95,3	3,0	2036	31,6	94,4	3,0
2044	31,5	95,7	3,0	2039	31,5	94,5	3,0
2054	31,5	95,7	3,0	2055	31,5	94,9	3,0

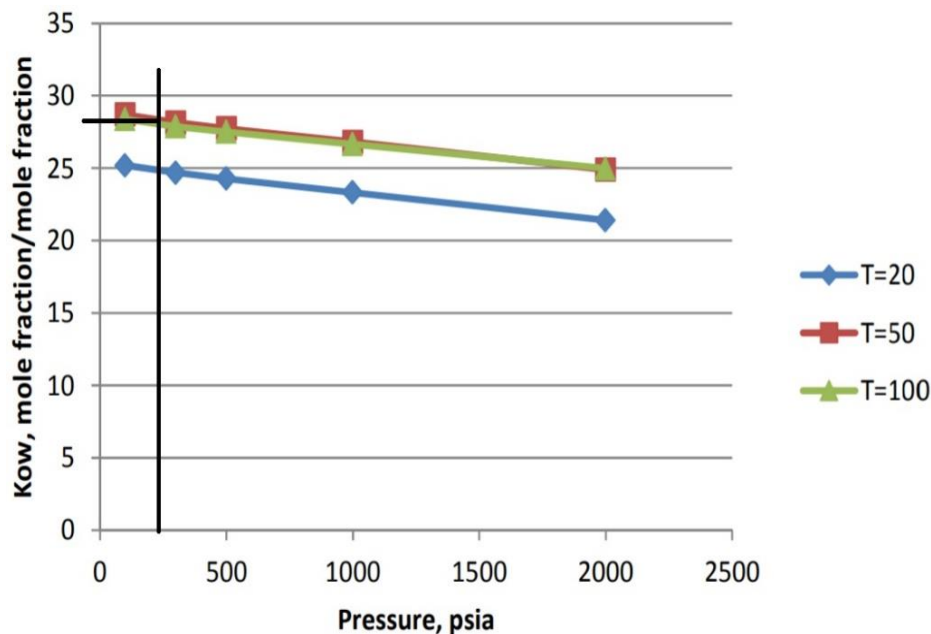


Figure 10-1: K<sub>ow</sub> calculated from the H2S partitioning model in terms of different pressure and temperatures. The interception of the black lines represents the K<sub>ow</sub> -value as a function of existing temperature (63 °C) and pressure (16 bar =223 psi) obtained from Hysys [25]

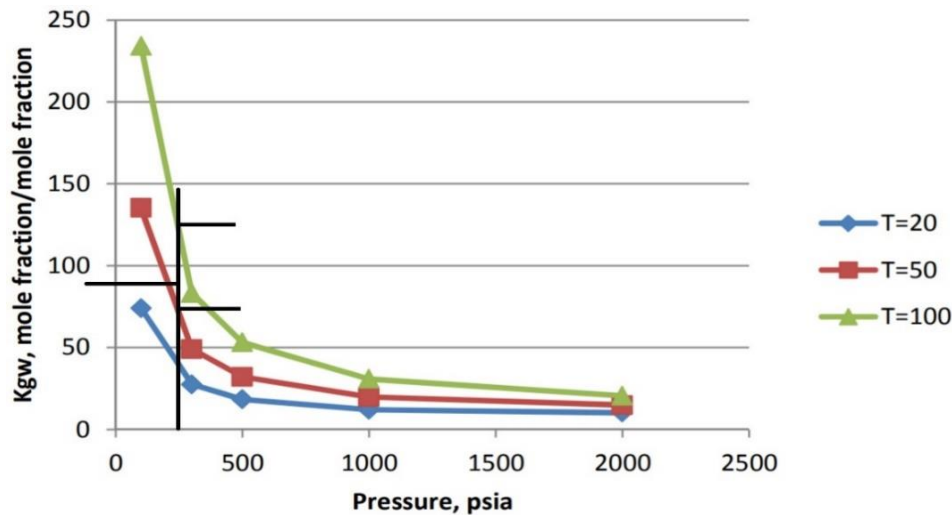


Figure 10-2:  $K_{gw}$  calculated from the H<sub>2</sub>S partitioning model in terms of different pressure and temperatures. The interception of the black lines represents the  $K_{gw}$  -value as a function of existing temperature (63 °C) and pressure (16 bar =223 psi) obtained from Hysys [25]

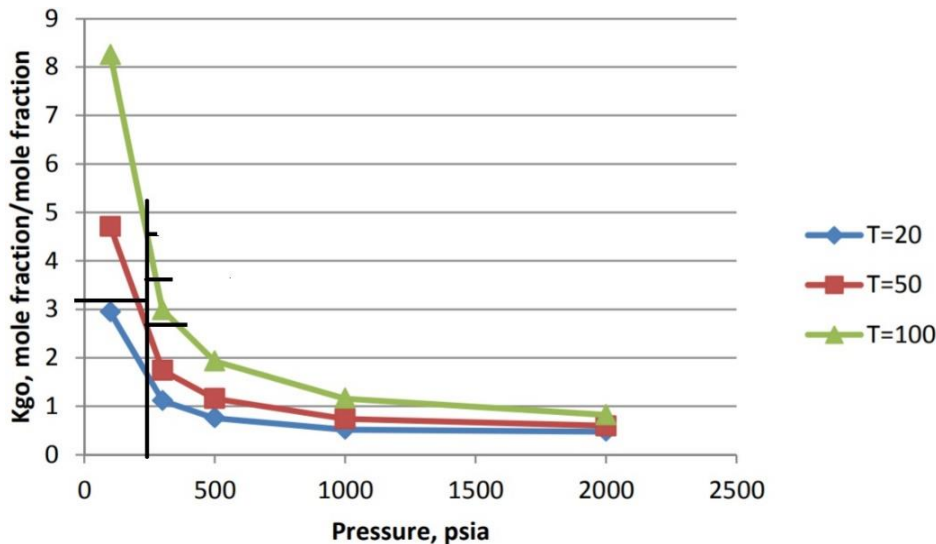


Figure 10-3:  $K_{go}$  calculated from the H<sub>2</sub>S partitioning model in terms of different pressure and temperatures. The interception of the black lines represents the  $K_{go}$  -value as a function of existing temperature (63 °C) and pressure (16 bar =223 psi) obtained from Hysys [25]

The different coefficients (K-values) for the existing pressure and temperature from Hysys (16 bar and 63 °C) are marked with black lines in figure 10-1 to figure 10-3. Table 10-3 shows some variations for the coefficients for different water cut rates. The  $K_{ow}$  is approximately constant for all water-cut ratios.

$K_{ow}$  was estimated to about 31.6 for all the years and both phases. From figure 10-1 we observe a value of about 28, which differs some compared to  $K_{ow}$  found in Hysys.  $K_{gw}$  was in Hysys found between 88 and 95, which is rather representative for the value found in figure 10-2 (about 88).  $K_{go}$  was estimated between 2.8 and 3 while figure 10-3 shows a value of around 3.15.



Although the difference between the coefficients are quite small, the Hysys model is likely to be inaccurate. From the theory (Appendix C) we know that the impact of pH, ionic strength and salting-out will typically represent a decrease of  $H_2S$  concentration in the gas phase and an increase in the water. From the figures and the corresponding pressure and temperature (black line), this behavior seems to have some relevance.  $K_{gw}$  was calculated to about 95 for a water cut ratio of 99 percent, which represents an increase in  $K_{gw}$  when we in reality should have noticed a decrease because of a significant lower concentration of  $H_2S$  in the gas phase and a higher amount in the water.

The same observation is made for  $K_{ow}$ . A higher amount of  $H_2S$  in the water will correspond to a lower  $K_{ow}$ , but for the values obtained from Hysys, a higher  $K_{ow}$  (31.5) than  $K_{ow}$  (28) from the partitioning model is observed, even though the water cut ratio is almost twice as for the partitioning model.

The water-cut ratio is significant for both phase 1 and 2 and is found to be close to 99 percent for most years. One should expect that a large proportion of the  $H_2S$  would end up in the produced water, with respect to the partitioning model. As seen from chapter 6.2.5, there seems to be some large differences here. The figures involving phase 1 (figure 6-30 and 6-31) shows that a large proportion ends up in the water, but this proportion is not even close when comparing to the proportion that follows the water for the partitioning model and figure C-4. As stated before, 94 percent of the  $H_2S$  ends up in the liquid phase for a pH equal to 7, API of 23.8 and a 90 percent water-cut ratio. An equivalent water-cut ratio from phase 1 (2028) would result in only 34 percent of the  $H_2S$  in the liquid phase, which is a significant difference. This difference is especially enhanced for phase 2, where we observe from the results in chapter 6 that most of the  $H_2S$  will follow the gas phase for the whole period even though the water-cut ratio is significant. For an equivalent water-cut ratio (90 %, 2029), only 24.5 percent of the  $H_2S$  ends up in the liquid phase.

The different pressure for the Hysys model (16 bar) and figure C-4 (about 1 bar) may represent another significant uncertainty. From figure 10-2 the gas-water coefficient ( $K_{gw}$ ) is shown for different pressure and temperatures. For increasing pressure, the coefficient is observed to fall, especially for pressure levels in the range of 0.5 bar – 20 bar. The higher pressure tends to decrease the  $H_2S$  partitioning to the gas phase. There are reasons to suspect that an even higher percentage than the 94 %  $H_2S$  will be seen for this particular Oilfield in real life, because of the higher pressure (16 bar).

One should notice that these numbers may not be entirely comparable because a lot of parameters will typically have an impact at the same time. In this case, fluid composition (different API), probably pH and pressure (same temperature) are all different. The pH will probably be closer to pH 7 than pH 3 because a typical minimum pH observed for a North Sea oil system is about pH 5.5. Some of the arguments discussed may be hypothetical. But a certain correlation is reasonable. We should suspect a large uncertainty in the Hysys model, disregarded of the last arguments discussed, but because of Hysys and its lack of understanding pH, dissociation, ionic strength and salting-out effects.

## 11. Discussion results

Amine plant installation and scavenger injection (triazine chemical) were further evaluated for a known North Sea oilfield. The simulation concludes a large difference in both scavenger consumption and the corresponding scavenger costs found for the different injection points.

*Scavenger injection after first stage compression* was found to be the cheapest and less scavenger consuming option. This is previously explained, mainly due to the large proportion that follows the water after inlet separator, but also because less heavier hydrocarbons are treated, which in this case represents a “waste” of chemicals. In real life, the higher pressure will also have a certain benefit towards the absorption efficiency and capacity. A higher partial pressure will typically increase the scavenger absorption rate. At the same time, one should evaluate whether the  $H_2S$  will cause a corrosion problem towards the piping and the equipment. Because the  $H_2S$  is removed almost at the end of the gas separation and compression train, the solution will be vulnerable for corrosion.

*Scavenger injection after first separator and mixer* experienced some increase in scavenger chemical. In particular for phase 1 with at higher oil-to-gas production ratio corresponding to a higher amount of heavier hydrocarbons treated. Despite the higher costs observed, scavenger injection at two places can be both a more flexible and possibly a necessary solution. Because of the large masses of hydrogen sulfide, injection at only one point can increase the risk of accumulation of  $H_2S$  in the gas after treatment and failure to reach sales gas quality. Injection of scavenger chemical after inlet separator is also a common way of treating the gas, mainly due to the normally high-pressure level. For this particular oil field, the inlet pressure level is of no benefit. However, the potential corrosion problems seem to be reduced considerably.

*Subsea scavenger injection* is by far the most expensive option, particularly for phase 1. In this case the cost is more than double of injection after compression. The multiphase scavenger type’s capacity is more than double of the gas scavenger type’s capacity, but the chemical typically costs twice, meaning the benefit is reversed. Although subsea injection potential corrosion problems will be non-existent. Treating both the water and oil, if not necessary, would result in a high chemical consumption and a corresponding high cost. This solution seems to be of an expensive character. However, some oilfields with typically old, sweet service installations where reservoir souring was unexpected, it could turn out to be completely necessary.

*Partly subsea injection* can be a necessity and a flexible way of reducing the total sulfur content in the hydrocarbon fluid before it enters piping and equipment and further reduce the exposure of  $H_2S$  towards the steel.

The results from the amine plant show a high energy consumption for a couple of years. For phase 1 we have a high gas flow rate in the early stage of production corresponding to a high amine flow rate and a high steam consumption. For phase 2 we see the opposite, a more constant gas flow rate, but a high rate of souring towards the end of production. An installation of an amine plant is a big investment and if this investment were to be made, a connection of the gas flow from phase 1 and phase 2 would be desirable if the infrastructure and distances would allow it. This correlation, with

high and low amine flow rate in the beginning of production, for phase 1 and 2 respectively (and opposite at the end of production), may be an excellent basis for amine plant design, with a more constant amine flow rate and a size that is easier to design properly.

There should be extensive reasons to invest in an amine plant with a high capital expenditure cost that may exceed 1 Billion NOK. From the production estimates we know it is a large potential for souring and generation of  $H_2S$  in the produced fluids. However, figure 6-21 – 6-24 show that there is a large potential for the  $H_2S$  to follow the water after inlet separator, especially when the seawater injection rate is high. From Chapter 10, this amount is probably significantly higher in real life, which results in a quite large advantage for scavenger injection.

A comparison between scavenger costs and reboiler electricity costs is shown in figure 8-5. This is a rough estimate, but shows that in addition to the investment cost, an electricity cost would follow. From the figure, the scavenger cost per year is not far from the electricity cost (for some years, more). It is reasonable to believe that this difference in cost is increased in favor of amine plant, if we multiply the scavenger costs for both phase 1 and 2 compared to connecting phase 1 and 2 gas stream to treatment in an amine plant. The scavenger costs are more or less doubled while the power consumption will not necessarily double but increase some. Nevertheless, a huge investment in addition to a yearly electricity cost seems to make the scavenger solution a more competitive alternative. The results are based on estimates for worst case souring scenario, which will be in favor of scavenger (the souring may be less than estimated).

Table 5-1 and figure 5-1 show some typical key numbers and dividing lines for selecting the most suitable process. It should be noticed that these diagrams/tables give an indication in terms of what technology can be suitable and may not be entirely representative. There should be made no definitive decision based on such approximately numbers.

From table 5-1, the dividing line for absorption in alkaline solution between large and small capacity is set to  $0,565 \text{ MSm}^3/d$ , which is in the lower part of the range for this situation. However, the sulfur capacity is set to 20 t/day, which will never be experienced here.

From chapter 9 it seems to be a wide agreement that scavenger technology is a more suitable process than the amine plant. However, for the standard suggested by Shell, neither of them would be entirely suited according to the figure, and another technology(ies) seems to be the favorable process.

It is clear that Sulferox technology fits the specifications for  $H_2S$  and gas rate well (0.1 t/d – 20 t/d). LO-CAT, a similar technology will also be suitable (0.5 t/d – 25 t/d). From previously (chapter 3), Sulferox was especially highlighted to handle large fluctuations in  $H_2S$  content or gas rate, which is typical for this oil field. Low weight and small footprint is another great advantage in relations to offshore operations.

## 12. Uncertainty

In the work of this thesis it has been discovered a large range of uncertainties. The production profiles for gas rate, water rate, oil rate and  $H_2S$  production in the reservoir are only estimates and may not be entirely representative. The  $H_2S$  production is a worst-case scenario and therefore a lower  $H_2S$  production may be seen.

Most of the results are found from simulations in Hysys, which again are based on these production estimates. Hysys is among the best simulation programs that exists and has a wide acceptance in the oil and gas industry. Soave-Redlick Kwong is used as the equation of state. SRK together with Peng Robinsons are considered to be the best Eor for oil and gas processing. Although both Hysys and SRK represents a high degree of accurate, there will always be uncertainties related to the programs. In this thesis notably, the amount of  $H_2S$  that ends up in the produced water after inlet separator will be crucial and have a big impact on the results. The  $H_2S$  amount in the gas phase found from the program is likely to be significantly lower in real life due to the effect of pH discussed earlier and in Appendix C.

The amine plant was simulated with the acid gas package, which is meant for simulation with absorption of acid gas ( $CO_2$ ,  $H_2S$ ) in alkaline/physical solution.

Scavenger consumptions and costs are only based on approximate numbers and an uncertainty will follow. While the cost is more or less representative, the scavenging consumption factor depends on a lot of other factors. Elmawgoud [21] reported that the scavenging process is not only dependent on the scavenger efficiency, but also on other parameters such as scavenger injection rate, pipe length, pipe diameter and gas flow rate. With an increased pipe length, the contact time is increased and the final  $H_2S$  level is reduced. The opposite was observed when the pipe diameter was increased following a drop in both gas velocity and turbulence corresponding to a lack of good mixing between the scavenger and gas. Increasing the gas flow rate, meaning an increase in velocity and turbulence at constant pipe diameter, would ensure good mixing between the reactants.

### 13. Conclusion

In the thesis we have looked upon the consequences  $H_2S$  and reservoir souring can have as well as in terms of catastrophic failures, and a dramatic increase in costs. It is known that the problem arises due to waterflooding and the stimulation of SRB.

For NCS conditions and a known North Sea Oil field, a number of technologies were rejected based on their characteristics. Physical solvent demands a high partial pressure to be efficient. Membrane is similar and most convenient for bulk removal. Adsorption is not capable of handling the  $H_2S$  levels observed for this oilfield, without heavily changeouts of bed material (or regeneration of bed material). Scavenger chemical injection (triazine) and absorption in alkanolamine solution (MDEA, amine plant technology) were picked for further evaluation and simulation.

*Scavenger injection after compression* was found to be the cheapest alternative.

*Scavenger injection after inlet separator and mixer* was found to be a more expensive option.

*Subsea scavenger injection* was found to have a dramatic increase in chemical costs.

*Partly subsea injection* was found to have chemical costs in-between *Subsea scavenger injection* and *Scavenger injection after inlet separator and mixer*.

*Amine plant installation* was found to be a less attractive alternative than scavenger injection. For an amine plant to be profitable, a significant higher gas flow rate and a higher amount of  $H_2S$  should be seen to defend the large investment and electricity cost. This will also represent a dramatic increase in scavenger chemical consumption and costs, making scavenger less attractive.

The simulation results show great differences in the costs for the corresponding injection points. One may assume that the cheapest option would be the most convenient, but for this situation, a significant increase in costs for sour service material would most likely follow. Sour service installation is reported to have five times rise in costs, which increase the expenses dramatically. Particularly because the  $H_2S$  is removed almost at the end of the processing facility, meaning a larger part of the facility would require sour service installation. Taken this into account, one could argue that injection after inlet separator and mixer could be an advantageous solution with only a minor increase in chemical costs. More work should follow, before a conclusion is suggested.

The installation of an amine plant may offer another challenge. A quite extensive facility is required to treat the acid gas from the stripper before it can be released. This treating facility is reported to have approximately the same size as the amine plant. This installation is likely to have a large CAPEX as well as causing a significant space problem on the platform.

The validation of the  $H_2S$  distribution in Hysys proved that a large uncertainty in the Hysys model should be expected. A lower  $H_2S$  concentration in the gas phase will probably be observed in real life, which will govern scavenger technology.

Even though scavenger technology seems to be the favorable choice among the two of them, another process may be an excellent solution as well. Scavenger should be selected based on low

$H_2S$  levels. SulFerox and LO-CAT have been reviewed previously in the text and they are a great process for medium  $H_2S$  levels observed for this particular oil field.

## 14. Suggestions for further work

Based on the results and selection map, the scavenger technology was not necessarily the best suited process for this particular oil field. SulFerox technology has shown to be an efficient process for removing medium amount of  $H_2S$ . It has also a wide acceptance for offshore operations with quite low footprints. LO-CAT is a similar process. There is however minor experience with LO-CAT and SulFerox on NCS, but both technologies should be further evaluated. Investment costs and electricity/power costs are the crucial parameters.

For the amine plant simulation, MDEA solvent is used. Even though MDEA is considered to be among the best solvents, it has been shown previously in the text that there could be a better option, particularly for selective  $H_2S$  absorption. Flexsorb SE is especially applicable for low pressure/partial pressure that is observed for this oilfield. The solvent has been reported to achieve half of the circulation rate and energy consumption that MDEA solvent are capable of [13]. Amine plant was found to be a less attractive option than others, but is another solvent able to make it more competitive?

Corrosion challenges were discussed in the conclusion part. More work should follow to estimate the costs of the different injection points when we account for the potential increase/decrease in sour service material.

A lot of uncertainties have been mentioned with the model. In-situ investigations, field tests or lab work could be options that can give a more credible estimate for a real-situation scenario.

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## Appendix A: Equation of state (EOR)

In thermodynamics or physics, we could express physical variables like pressure, temperature, volume or internal energy in a mathematical relation. It describes the state of matter. EOR is very useful when we need properties of mixtures of fluids and gases at e.g. different pressures and temperatures. There are several Eor, but Peng-Robinson and Soave-Redlich-Kwong are among the most famous and trusted Eor.

The model was simulated based on SRK as the equation of state (Eor). This model was first introduced by Redlich and Kwong in 1949 but was modified by Soave in 1972. The modification involved the suggestion of a two-variable dependency for the energy parameter “a”.

$$a = a(T, \omega) \quad (\text{A.1})$$

Now it is a function of not only the temperature, T, but also as a function of the shape (sphericity) of the molecule. This correction was done to get better calculation results of multicomponent vapor-liquid equilibrium [22]. The SRK equation of state is given by:

$$P = \frac{RT}{V_m - b} - \frac{\alpha a}{V_m(V_m + b)} \quad (\text{A.2})$$

Where,

$$\alpha = [1 + (0.48508 + 1.55171\omega - 0.15613\omega^2)(1 - \sqrt{Tr})]^2 \quad (\text{A.3})$$

$$a = 0.427480 \frac{R^2 T_c^2}{P_c} \quad (\text{A.4})$$

$$b = 0.086640 \frac{RT_c}{P_c} \quad (\text{A.5})$$

The different parameters are given by the critical pressure and temperature,  $T_c$  and  $P_c$ , the acentric factor,  $\omega$ , the gas constant, R and the molar volume,  $V_m$ . From the equation, a is stated as the energy factor and is explained as a pressure reduction in the system caused by the gas, because of the attractive forces between the molecules. Parameter b represent the volume occupied by the gas molecules [23].

## Appendix B: Absorber/stripper design

This appendix section is based on the book “Air pollution control equipment” by Theodore [24]. The main types of absorbers (most common) are packed columns, which is a continuous operation and plate columns, which is a staged operation. The packed column is the most used in absorption of gaseous pollutants.

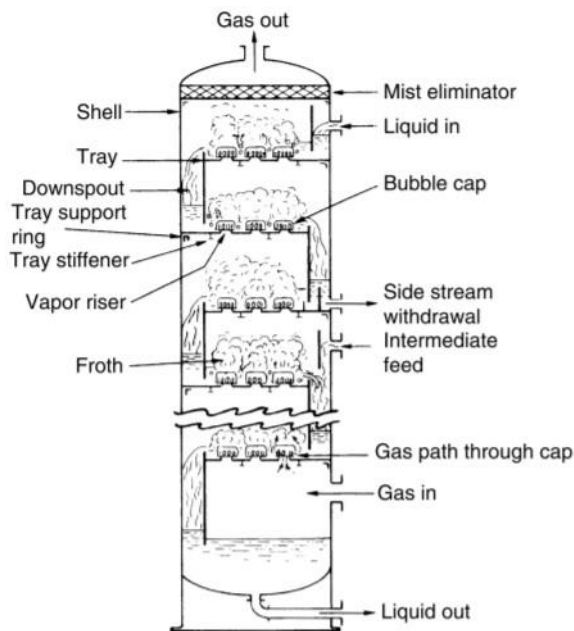


Figure B-1: Plate column [24]

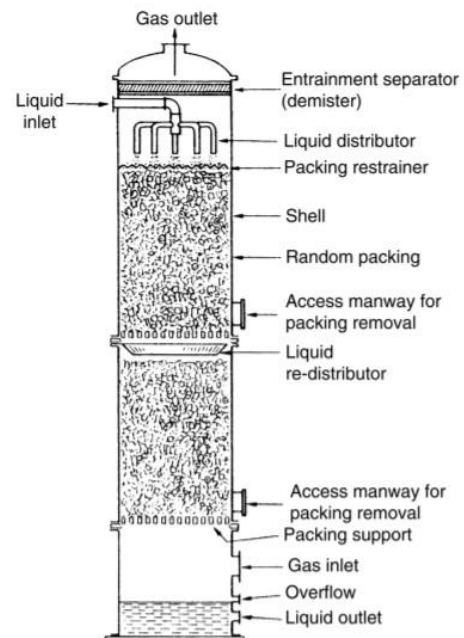


Figure B-2: Packed column [24]

The absorption operation is based on the equilibrium between the absorbing liquid (solvent) and solute gas (pollutants, H<sub>2</sub>S in this situation). Usually we speak about a correlation of  $x$ , the mole fraction of solute in the liquid, against  $y$ , the mole fraction in the vapor in equilibrium with  $x$ . Henry's law is usually applicable, with Henry's law constant  $m$ . Then we have:

$$y = mx \quad (\text{B.1})$$

Further, a mass balance around the column is performed. Total moles in = Total moles out.

$$G_{m1} + L_{m2} = G_{m2} + L_{m1} \quad (\text{B.2})$$

$G$  and  $L$  represent the molar flow rates of gas and liquid, respectively. The mole balance (from figure B-3):

$$G_{m1}y_{A1} + L_{m2}x_{A2} = G_{m2}y_{A2} + L_{m1}x_{A1} \quad (\text{B.3})$$

We assume  $G_{m1}=G_{m2}$  and  $L_{m1}=L_{m2}$ . Then we have:

$$G_{m}y_{A1} + L_{m}x_{A2} = G_{m}y_{A2} + L_{m}x_{A1} \quad (\text{B.4})$$

Rearranging gives an equation for a straight line, known as the operating line. It describes the operation conditions in the column.

$$\frac{L_m}{G_m} = \frac{y_{A1} - y_{A2}}{x_{A1} - x_{A2}} \quad (\text{B.5})$$

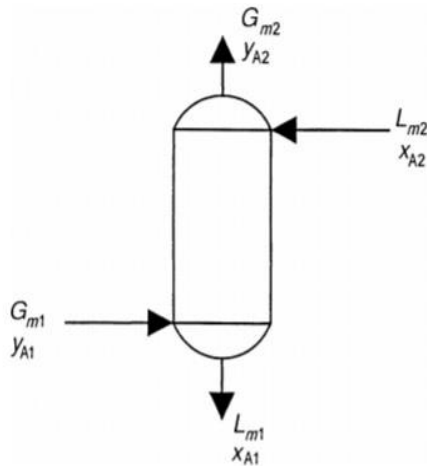


Figure B-3: Absorber column balance [24]

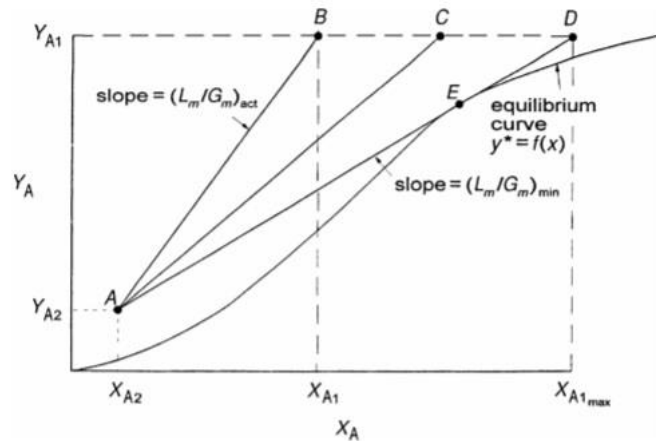


Figure B-4: Equilibrium curve and operating line for both actual conditions and minimum conditions.

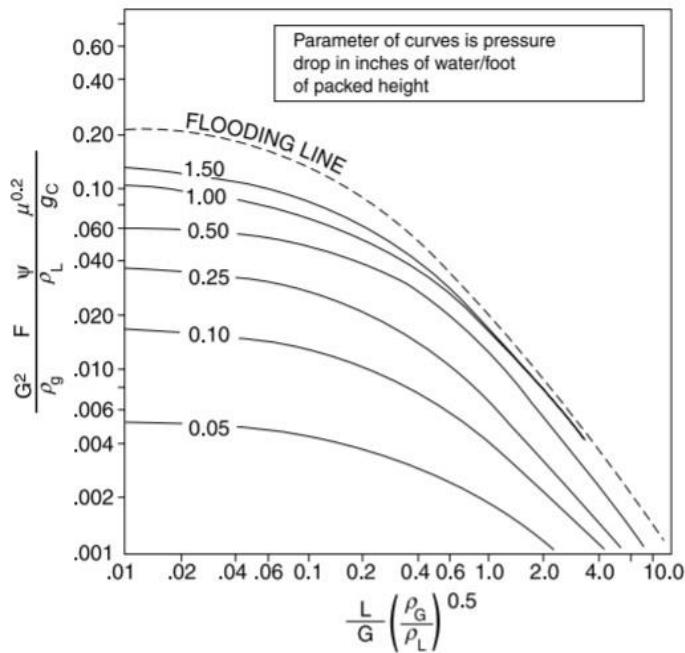
From figure B-4, the curve has the slope  $\frac{L_m}{G_m}$  and passes through the coordinates  $(x_{A1}, x_{A2})$  and  $(y_{A1}, y_{A2})$ .

For most designs (and in this case) the rate of gas to be treated, the concentrations of  $y_{A1}$  and  $y_{A2}$  and the composition of the entering liquid  $x_{A2}$  are normally fixed by process requirements and are known. The liquid rate is usually varied, dependent on how clean the gas should become.

From the figure we can see that we have a slope for actual liquid-to-gas ratio and a slope for minimum liquid-to-gas ratio. The actual liquid-to-gas ratio is always higher than minimum. That is to ensure that we have a sufficient contacting time and sufficient mass transfer between the liquid and gas flow. In real situations there will always be some losses and the mass transfer will not necessarily be so smooth than calculated.

### Packed column

The diameter of a packed column is often design based on the *flooding velocity*. This is the superficial velocity (velocity if the column is empty) when flooding occurs. Flooding is described as a situation when the gas flow is increasing and due to this, the liquid flow is forced back because of the drag force on the liquid. The liquid is prevented from flowing freely down the column. This lead to accumulation of liquid and blocking of the cross-section area. The usual operating range is typically 50 – 75% of flooding rate. Figure B-5 shows a correlation for the pressure drop, developed by U.S. Stoneware.



$L, G = \text{lb}/\text{ft}^2 \cdot \text{s}$   
 $\rho_L, \rho_G = \text{lb}/\text{ft}^3$   
 $F = \text{packing factor, dimensionless}$   
 $\Phi = \text{ratio of water density to liquid density, dimensionless}$   
 $g_c = 32.2 \text{ ft} \cdot \text{lb}/\text{lb}_f \cdot \text{s}^2$   
 $\mu_L = \text{viscosity of liquid, cP}$

Figure B-5: Generalized pressure drop correlation to estimate column diameter [24]

After the term for both the x-axis and y-axis have been calculated, the cross-sectional area  $S$  could be estimated, based on the fraction  $f$  of flooding velocity chosen for operation:

$$S = \frac{\dot{m}}{fG} \tag{A.6}$$

Where  $\dot{m} = \text{lb}/\text{s}$  of gas and  $S = \text{area, ft}^2$ .

The diameter is then calculated based on the cross-sectional area of a cylinder:

$$D = 1.13\sqrt{S} \tag{B.7}$$

The column height is given by:

$$Z = N_{OG}H_{OG} \tag{B.8}$$

Where  $N_{OG}$  is the number of overall transfer units, dimensionless.  $H_{OG}$  is the height of overall transfer units, ft.  $Z$  is the height of packing, ft.

To determine the number of overall transfer units,  $N_{OG}$ , many different equations can be used dependent on the specific conditions. If the pollutants to be absorbed is very dilute:

$$N_{OG} = \int \frac{dy}{(y - y^*)} \tag{B.9}$$

If the operating line and equilibrium line are both parallel and straight:

$$N_{OG} = \frac{(y_1 - y_2)}{(y - y^*)} \quad (\text{B.10})$$

If the operating line and equilibrium line are just straight:

$$N_{OG} = \frac{(y_1 - y_2)}{(y - y^*)_{ln}} \quad (\text{B.11})$$

If Henry's law applies (operating line and equilibrium line straight), the number of transfer units are commonly calculated by:

$$N_{OG} = \frac{\ln\left[\frac{(y_1 - mx_2)}{(y_2 - mx_2)}\right] \left(1 - \frac{1}{A}\right) + \frac{1}{A}}{1 - \frac{1}{A}} \quad (\text{B.12})$$

And

$$A = \frac{L}{mG} \quad (\text{B.13})$$

m is the slope of the equilibrium curve. This equation could be applied if the gas is highly soluble or if the absorbate (pollutant) reacts with the liquid.  $N_{OG}$  could also be found graphically from figure B-6.

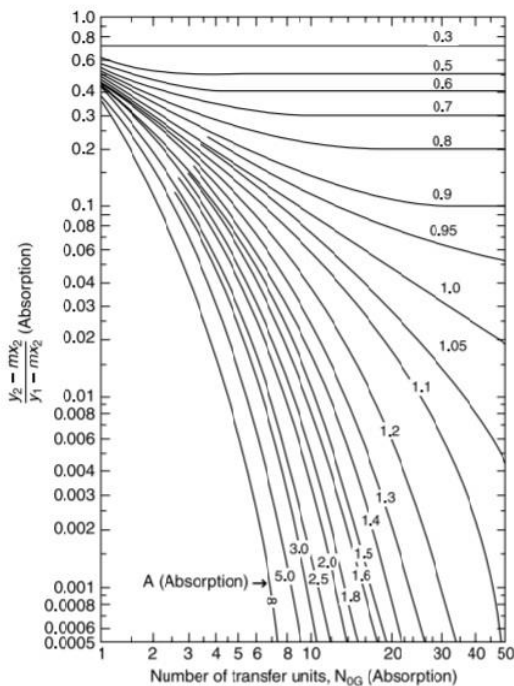


Figure B-6: Number of transfer units for packed column with constant absorption factor, A [24]

### Plate columns

As for packed columns, plate column diameter is often based on the superficial velocity and the prevention of flooding. This superficial gas velocity for a given type of plate at flooding is given by:

$$V_F = C_F \sqrt{\frac{\rho_L - \rho_G}{\rho_G}} \quad (\text{B.14})$$

$\rho_L$  and  $\rho_G$  are liquid and gas densities, lb/ft<sup>3</sup>.  $V_F$  is the gas volumetric flowrate through the net column cross-sectional area for gas flow, ft<sup>3</sup>/s\*ft<sup>2</sup>.  $C_F$  is an empirical coefficient that depends on the type of plate and operating conditions. The net cross-section area is the difference between the column cross-section and the area taken up by downcomers

The column height is calculated based on actual plates and the plate spacing chosen. Actual plates are determined by the theoretical plates divided by the overall plate efficiency.

For dilute gases and liquid solutions where Henry's law can be applicable. Here, both the operating line and the equilibrium curve is considered straight. In this case, the Kremser-Brown-Souders equation can be used for calculating theoretical stages (plates), N:

$$N = \frac{\log\left[\frac{(y_{N+1} - mx_0)(1 - \frac{1}{A}) + \frac{1}{A}}{(y_1 - mx_0)(1 - \frac{1}{A}) + \frac{1}{A}}\right]}{\log A} \quad (\text{B.15})$$

$mx_0$  is the gas composition in equilibrium with the entering liquid.  $y_{N+1}$  and  $y_1$  represent inlet and outlet concentration of solute in gas stream. L and G are the total mole rate of liquid and gas flow per unit time per unit column cross-sectional area, respectively.

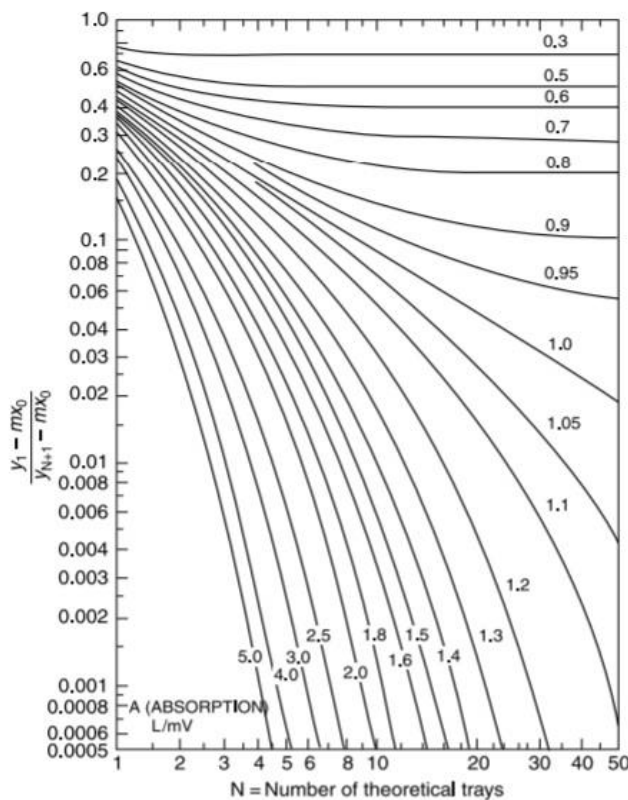


Figure B-7: Number of theoretical stages for countercurrent plate columns [24]

$N_{act}$  is determined based on the mechanical design and the conditions of operation. For the same conditions as mentioned before, straight operating and equilibrium line/curve,  $E_0$  can be expressed:

$$E_0 = \frac{\text{equilibrium trays}}{\text{actual trays}} = \frac{\log[1 + E_{MGE}] \left(\frac{1}{A} - 1\right)}{\log\left(\frac{1}{A}\right)} \quad (\text{B.16})$$

$E_{MGE}$  = Murphree efficiency corrected for entrainment (values available in the literature). Empirical data for standard tray design can be seen in figure B-8. This figure shows accurate data for bubble-cap trays but can be used for rough estimates for sieve and valve trays.

Then we have:

$$N_{act} = \frac{N}{E_0} \quad (\text{B.17})$$

The tower height  $Z$  is then:

$$Z = N_{act}(h) \quad (\text{B.18})$$

Where  $h$  is the height between plates. This is usually in the 12 – 36-inch range. 24-inch is most common.

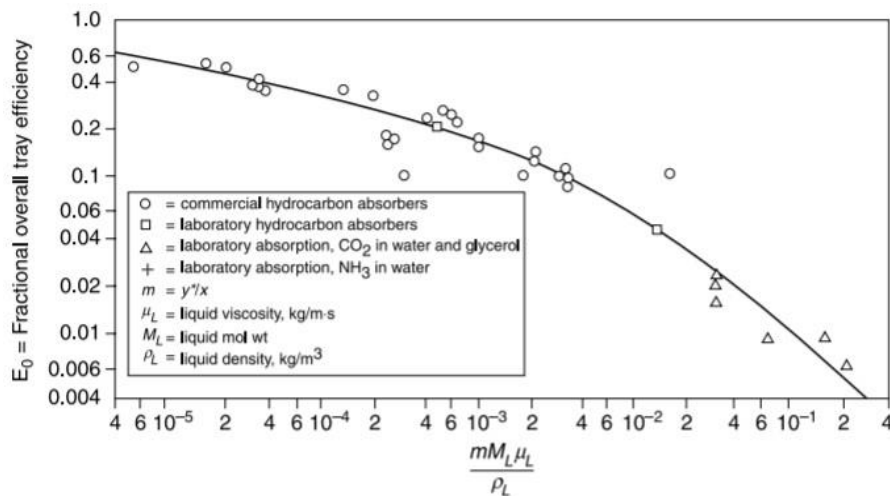


Figure B-8: Overall tray efficiencies of bubble-cap tray absorbers [24]

### Strippers

For strippers, the absorbate is transferred from the liquid to gas. The calculations are mainly the same except for some equations, which have some changes (mainly opposite of absorption). The height of packed tower:

$$Z = (H_{OL})(N_{OL}) \quad (\text{B.19})$$

Number of transfer units for packed column,  $N_{OL}$ :



$$N_{OL} = \frac{\ln\left[\frac{(x_2 - y_1/m)}{(x_1 - y_1/m)}\right](1 - A) + A}{1 - A} \quad (\text{B.20})$$

$$A = \frac{L}{mG} \quad (\text{B.21})$$

$$S = \frac{1}{A} = \frac{mG}{L} \quad (\text{B.22})$$

For stripping in plate columns:

$$N = \frac{\log\left[\frac{(x_0 - y_{N+1}/m)}{(x_N - y_{N+1}/m)}\left(1 - \frac{1}{S}\right) + \frac{1}{S}\right]}{\log(S)} \quad (\text{B.23})$$

## Appendix C: $H_2S$ equilibrium model for oilfield system

Burger, Jenneman and Carroll [25], developed a valid equilibrium model that describes the partitioning of  $H_2S$  and the distribution of  $H_2S$  in oil, water and vapor in an oilfield system.

Partitioning of  $H_2S$  in an oilfield system is dependent on many variables and is based on a thermodynamic process. Variables includes temperature, pressure, fluids composition, ionic strength and water pH. Especially pH is important for water cut system. At neutral or basic pH levels, the dissociation of  $H_2S$  into  $HS^-$  and  $S^{=}$  ions are considerable. These ions will only remain dissolved in the water phase and will not follow the oil and gas.

The developed model includes a Henry's law approach for the aqueous phase and the Peng-Robinson equation of state for the non-aqueous phase to calculate mole fractions for the various components. The effect of water pH and ionic strength on dissociation of  $H_2S$  are implemented in the model as well. From the text, the relative solubility of  $H_2S$  in crude and water within the reservoir was observed to have a function of the crude molar density, meaning that lighter crudes (higher molar densities) are capable of dissolve more  $H_2S$  relative to water.

### **Solubility in water**

As written before, a Henry's law approach was applied for the solubility of gases in liquids and for this situation, water. At low pressure, the relation could be noted as:

$$m_{H_2S} H = y_{H_2S} P \quad (C.1)$$

Where,

$m_{H_2S}$  = The molarity of  $H_2S$  in the aqueous phase. Moles of solute per kg of solvent (mol/kg).

$H$  = Henry's constant for solute  $H_2S$  in water, kPa\*kg/mol.

$P$  = Total pressure.

$y_{H_2S}$  = mole fraction of  $H_2S$  in the gas.

The relation is described with a Henry's law statement, "The solubility is directly proportional to the partial pressure ( $y_{H_2S} P$ )". Henry's constant is a function of the temperature and the solute-solvent pair.

For high pressure and high solute concentration, Henry's law is normally considered to be inaccurate and not useable. A modified version of the relation that accounts for non-idealities in both aqueous vapor and liquid can be stated as:

$$\gamma_{H_2S} m_{H_2S} H \exp \left[ \int_{P_w^0}^P \left( \frac{\bar{v}_{H_2S}}{RT} \right) dp \right] = y_{H_2S} P \hat{\Phi}_{H_2S}^V \quad (C.2)$$

Where,

$\gamma_{H_2S}$  = Activity coefficient for  $H_2S$

$\bar{v}_{H_2S}^\infty$  = Partial molar volume of  $H_2S$  in water at infinite dilution,  $m^3/kmol$

R = Universal gas constant, 8.314 KJ/kmol\*K

T = Absolute temperature, K

$\hat{\Phi}_{H_2S}^V$  = fugacity coefficient for component i in the vapor, unitless

This equation is well suited for calculating the  $H_2S$  distribution in aqueous phase and hydrocarbon-rich liquid. Here the fugacities in the liquid phase are implemented and are calculated with an equation of state.

The equation can be modified further for situations where the molar volume at infinite dilution is independent of the pressure. From the equation, the pointing correction (effect of pressure on the reference fugacity, here the Henry's constant) is given as the exponential term. This can now be simplified as:

$$\left[ \int_{P_w^0}^P \left( \frac{\bar{v}_{H_2S}^\infty}{RT} \right) dp \right] \approx \frac{\bar{v}_{H_2S}^\infty (P - P_w^0)}{RT} \quad (C.3)$$

Where,

$P_w^0$  = vapor pressure of water, kPa

The partial molar volume at infinite dilution in water is stated to be about  $35 \text{ cm}^3/\text{mol}$ . The fugacity is calculated with an equation of state (SRK, Peng-Robinson e.g.).

### Salting out effect

The salting out effect is explained by the mechanisms that for most gases, the solubility is lower in a salt solution than pure water. The ionic salts are observed to drive out the dissolved gases. This effect was studied by Sechenov and an equation for this effect was noted as:

$$\log \left( \frac{m_{water}}{m_{electrolyte}} \right) = k I_{electrolyte} \quad (C.4)$$

Where,

$I_{electrolyte}$  = Concentration of the electrolyte, molality

k = salting-out coefficient, unitless

$m_{water}$  = solubility in pure water, molality

$m_{electrolyte}$  = solubility in the electrolyte solution, molality

The salting out coefficient for sodium chlorite is reported to be around 0.0721. For Natrium chlorite (NaCl) it is nearly a constant.

### Ionization

When the  $H_2S$  is dissolved in the water, a series of chemical reactions takes place:



These reactions are described as (1) the dissociation of  $H_2S$  to form bisulfide ion, (2) the dissociation of the bisulfide ion to sulfide ion and (3) the self-ionization of water.

Further, each of the reactions are expressed in an equilibrium relation ("mass action" relation):

$$K_1 = \frac{a_{H_{(aq)}^+} a_{HS_{(aq)}^-}}{a_{H_2S_{(aq)}}} = \frac{\gamma_{H_{(aq)}^+} \gamma_{HS_{(aq)}^-} m_{H_{(aq)}^+} m_{HS_{(aq)}^-}}{\gamma_{H_2S_{(aq)}} m_{H_2S_{(aq)}}} \quad (C.8)$$

$$K_2 = \frac{a_{S_{(aq)}^{2-}} a_{H_{(aq)}^+}}{a_{HS_{(aq)}^-}} = \frac{\gamma_{S_{(aq)}^{2-}} \gamma_{H_{(aq)}^+} m_{S_{(aq)}^{2-}} m_{H_{(aq)}^+}}{\gamma_{HS_{(aq)}^-} m_{HS_{(aq)}^-}} \quad (C.9)$$

$$K_W = \frac{a_{H_{(aq)}^+} a_{OH_{(aq)}^-}}{a_{H_2O}} = \frac{\gamma_{H_{(aq)}^+} \gamma_{OH_{(aq)}^-} m_{H_{(aq)}^+} m_{OH_{(aq)}^-}}{\gamma_{H_2O} x_{H_2O}} \quad (C.10)$$

The equilibrium constants are known and available from other literature. The activity coefficient is unity, when the solution is very dilute. For low ionic species concentration, the activity coefficient can be calculated using Debye-Hückel limiting law:

$$\ln \gamma_i = A |z_i| \sqrt{I} \quad (C.11)$$

Where,

$z_i$  = charge of the ion, unitless

A = Debye-Hückel constant, molality

I = ionic strength, molality

And I is given as:

$$I = \frac{1}{2} \sum m_i z_i^2 \quad (C.12)$$

Now we can summarize the concentrations of the different sulfide species to get the total hydrogen sulfide in the aqueous solution:

$$t_{H_2S(aq)} = m_{HS(aq)} + m_{S(aq)} + m_{H_2S(aq)} \quad (C.13)$$

To obtain electroneutrality we have:

$$m_{H(aq)} = m_{HS(aq)} + 2 m_{S(aq)} + m_{OH(aq)} \quad (C.14)$$

For base or acid solution, additional ions must be implemented in this equation. E.g. sodium hydroxide, sodium ion must be implemented left hand side of equation. Hydrochloric acid, chloride ion implemented right side of equation.

The definition of pH is required. The pH needs to be known together with ionic strength to estimate the ionic species. For infinite dilution, as noted earlier in the chapter, the activity coefficient is assumed to be unity and we only need the pH of the water. For solution more dilute, the Debye-Hückel limiting or extended law as described before are used.

$$pH = -\log(a_{H(aq)}) \approx -\log(m_{H(aq)}) \quad (C.15)$$

The activity coefficient is neglected here (common to do).

### Algorithm for oilfield system

Now the previous relations are implemented into an equilibrium model for calculating the distribution of  $H_2S$  between oil, gas and water in an oilfield system.

To calculate the mole fraction of the various components (water,  $H_2S$  and the hydrocarbons fractions) in the three phases, Peng-Robinson is used for non-aqueous phases and the Henry's law approach is used for aqueous phase noted earlier in the chapter. The Henry's law constant for  $H_2S$  is given as:

$$\ln H_{H_2S_w} = 315.722 + 0.05303T - \frac{12224.4}{T} - 49.7825 \ln T \quad (C.16)$$

The  $H_2S$  partitioning coefficients (K-values) are essential for the equilibrium of  $H_2S$  in each phase and are given as a relation of their mole fraction:

$$K_{ow} = \frac{\text{mole fraction } H_2S \text{ in the oil phase}}{\text{mole fraction } H_2S \text{ in the aqueous phase}} \quad (C.17)$$

$$K_{gw} = \frac{\text{mole fraction } H_2S \text{ in the vapor phase}}{\text{mole fraction } H_2S \text{ in the aqueous phase}} \quad (C.18)$$

$$K_{go} = \frac{\text{mole fraction } H_2S \text{ in the vapor phase}}{\text{mole fraction } H_2S \text{ in the oil phase}} \quad (\text{C.19})$$

Knowing the molecular weights, masses of each of the three phases, the partitioning coefficient and the  $H_2S$  concentration in one phase, we can calculate the amount of molecular  $H_2S$  in each phase.

Further the salting-out and ionization effect must be determined. We know from previous that ionization adds  $HS^-$  and  $S^{-2}$  to the water, while salting-out reduces the amount of molecular  $H_2S$  in the water. When we have all three phenomena that influence in the partitioning (distribution of molecular  $H_2S$ , salting-out and ionization) we can get the final  $H_2S-HS^- - S^{-2}$  system equilibrium.

### Oilfield example

The earlier discussed model from Burger, Jenneman and Carroll [25] was applied with various scenarios to determine the impact of  $H_2S$  partitioning between oil, gas and water as a function of temperature, pressure, water chemistry and hydrocarbon composition. Some of the results are taken from the text and presented here. The selected results are picked based on chapter 10 earlier in the text.

In figure C-1 we observe a large impact on  $H_2S$  concentration in the gas phase for different water cut rates, when pH is low (pH 3). For pH 7, water cut rates are not impacting on the system. This is due to the domination of ionic species over molecular form at higher pH and vice versa at low pH.

Figure C-2 and figure C-3 are great representations of the impact pH has on  $H_2S$  partitioning in the gas phase. At low pH (pH 3) the  $H_2S$  partitioning in the gas are constant, unaffected by the water ionic strength. The  $H_2S$  concentration in the gas is only a function of the water cut ratio (figure C-1) because all  $H_2S$  is in molecular form as discussed for figure C-1. For higher pH values (pH 7), dissociation, salting-out and ionic strength (Debye-Hückel) all have an impact on the final gas phase  $H_2S$  concentration, which is seen in figure C-2. In figure C-3 we observe the significant effect pH has on the partitioning to the gas for higher pH values (pH 6 and beyond).

Figure C-4 presents the  $H_2S$  distribution in gas, oil and water for different water cut rates and the two pH values discussed earlier (pH3 and pH7).

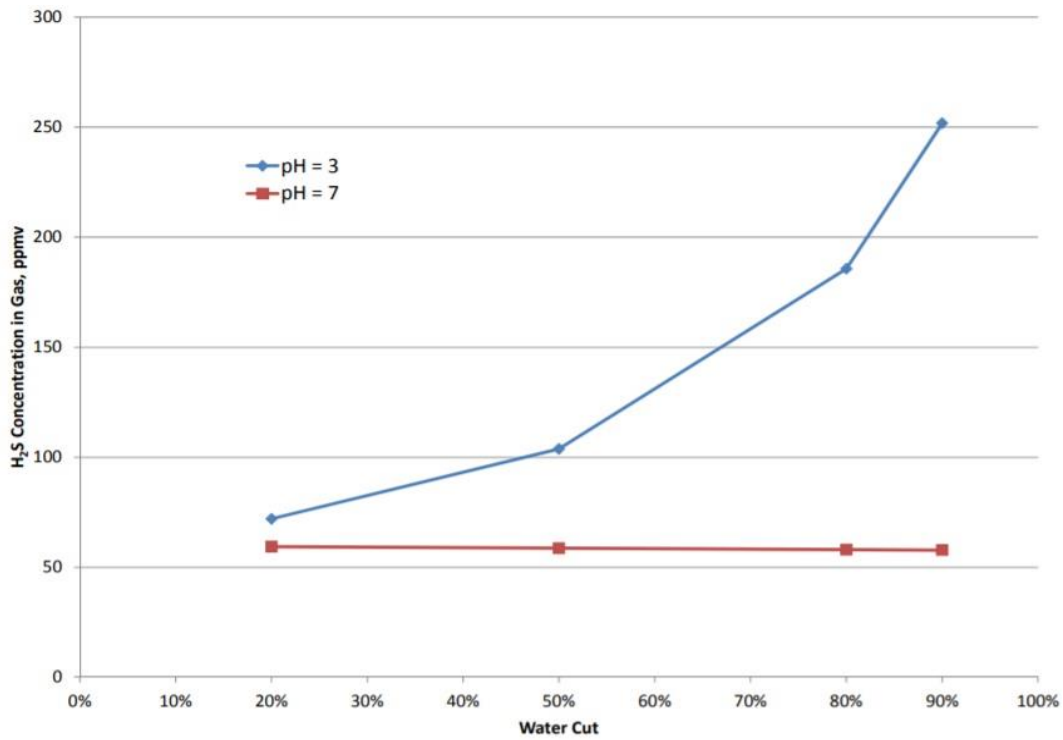


Figure C-1: Impact of water cut on the H<sub>2</sub>S partitioning to the gas phase for two pH values [25]

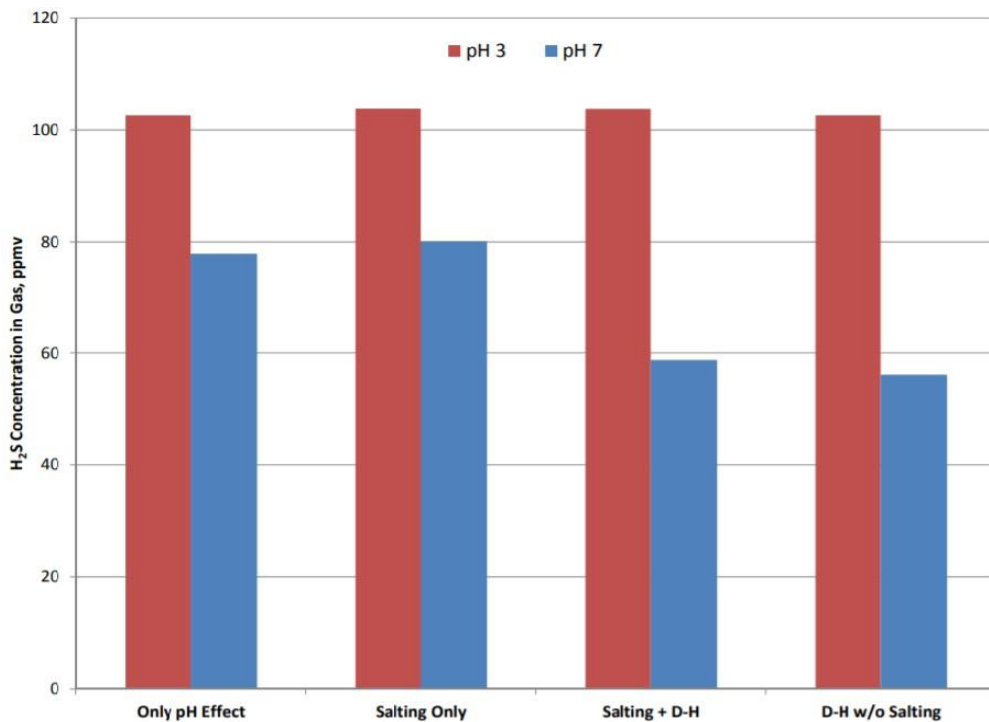


Figure C-2: H<sub>2</sub>S concentration in gas phase for two pH values given in terms of different parameters (pH, salting-out and ionic strength) impacting the H<sub>2</sub>S partitioning (D-H, Debye-Hückel extended limiting law). Water cut ratio is 50% [25]

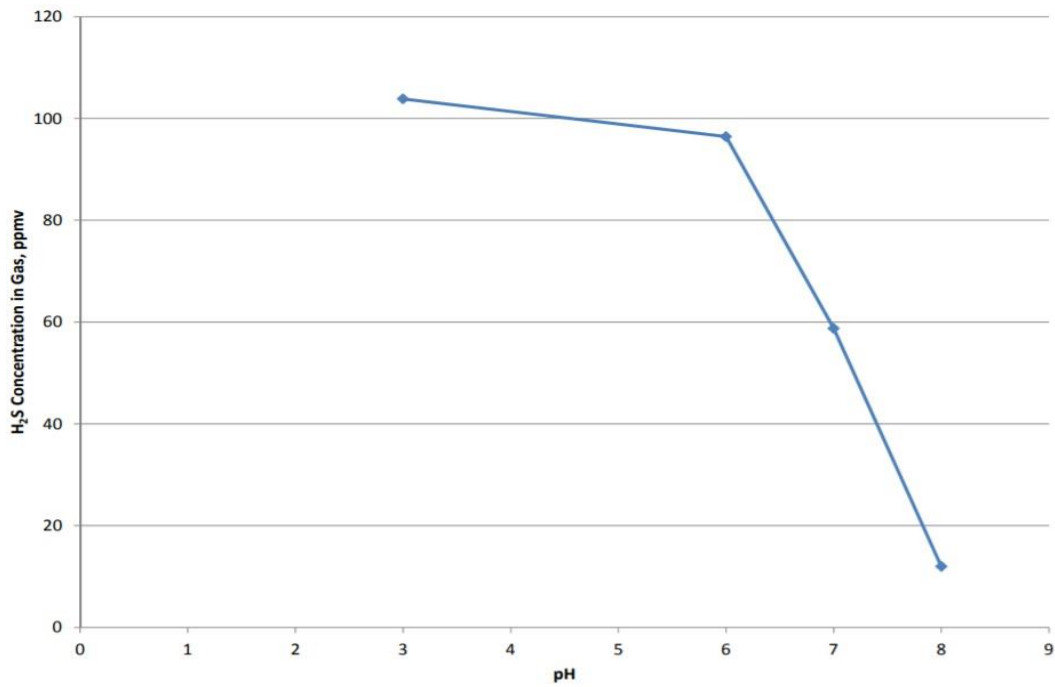


Figure C-3: Impact different pH values have on H<sub>2</sub>S concentration in the gas phase. Water cut ratio is 50% and ionic strength is 0.5 Eq/L [25]

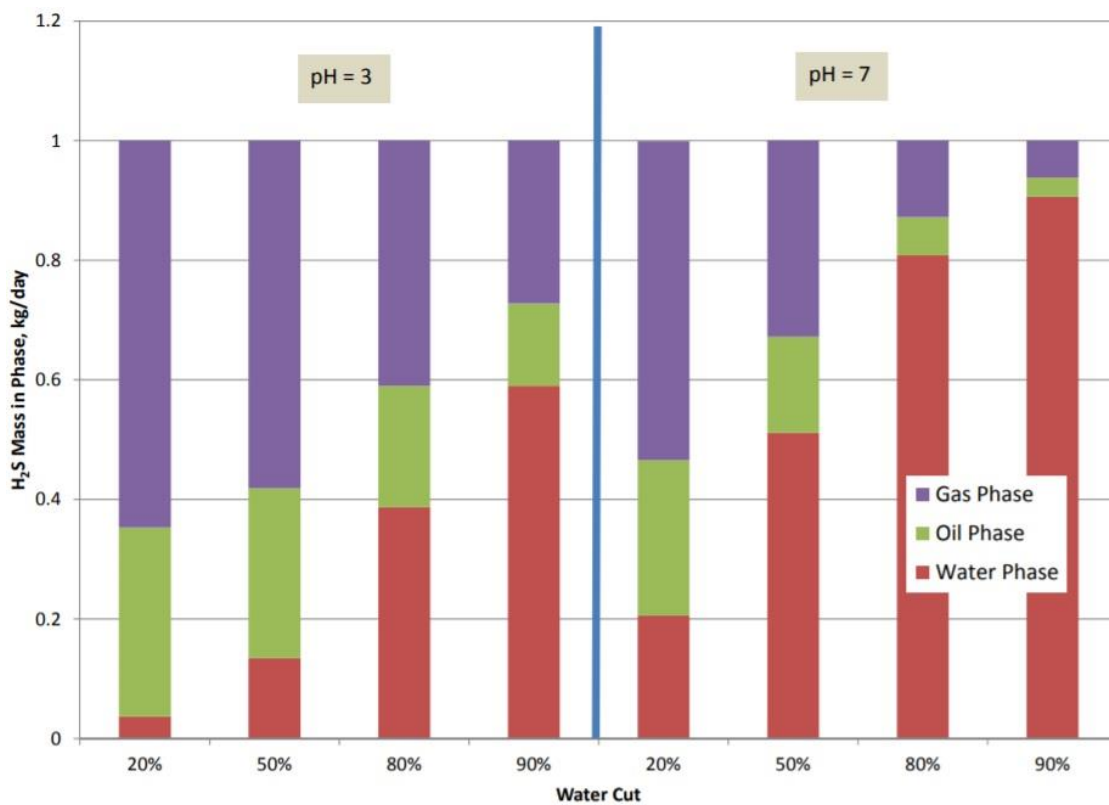


Figure C-4: H<sub>2</sub>S partitioning to the gas, oil and water phase as a function of pH and water cut ratio for a H<sub>2</sub>S rate of 1 kg/d. The pressure is 1 bar and a temperature of 60 °C. The API is equal to 23.8. [25]



## Appendix D: Simulation data

### Fluid composition:

Table D-1: Reservoir fluid composition

		Mole frac		
<b>Nitrogen</b>		0.0057	Nitrogen	0.0057
<b>CO2</b>		0.0009	CO2	0.0009
<b>Methane</b>		0.1679	Methane	0.1679
<b>Ethane</b>		0.0505	Ethane	0.0505
<b>Propane</b>		0.0649	Propane	0.0649
<b>i-Butane</b>		0.0150	i-Butane	0.0150
<b>n-Butane</b>		0.0346	n-Butane	0.0346
<b>i-</b>			i-Pentane	0.0158
<b>Pentane</b>		0.0158	n-Pentane	0.0199
<b>n-</b>			n-Hexane	0.0258
<b>Pentane</b>		0.0199	Cyclopentane	0.0022
<b>C6*</b>		0.0281	n-Heptane	0.0222
P	nC6	0.0258	Cyclohexane	0.0199
N	cyclo-C5	0.0022	Benzene	0.0012
A		0.0000	n-Octane	0.0186
<b>C7*</b>		0.0433	Cycloheptane	0.0224
P	nC7	0.0222	Toluene	0.0060
N	cyclo-C6	0.0199	n-Nonane	0.0157
A	benzene	0.0012	Cyclooctane	0.0083
<b>C8*</b>		0.0470	m-Xylene	0.0099
P	nC8	0.0186	1020*	0.0885
N	cyclo-C7	0.0224	1021*	0.0845
A	toluene	0.0060	1022*	0.0637
<b>C9*</b>		0.0340	1023*	0.0582
P	nC9	0.0157	1024*	0.0460
N	cyclo-C8	0.0083	1025*	0.0452
A	m-xylene	0.0099	1026*	0.0497
<b>C10-C12*</b>		0.0885	1027*	0.0262
<b>C13-C15*</b>		0.0845	1028*	0.0105
<b>C16-C18*</b>		0.0637		<b>1.000</b>
<b>C19-C22*</b>		0.0582		
<b>C23-C27*</b>		0.0460		
<b>C28-C34*</b>		0.0452		
<b>C35-C43*</b>		0.0497		
<b>C44-C55*</b>		0.0262		
<b>C56+*</b>		0.0105		
<b>H2O</b>		0.00		

Table D-2: Properties for the heavier hydrocarbons in the reservoir fluid

EOS	SRK									
Enthalpy	Property package EOS									
	NBP / C	MW	Liq dens	Tc / C	Pc / bar	Vc	Omega	Vc*1000	n	Cn
<b>C6*</b>	68.75	85.03	666.4	234.2	29.69	0.37	0.296	370	6	C6
<b>C7*</b>	91.95	93.06	725.5	255.6	32.26	0.4797	0.4593	479.7	7	
<b>C8*</b>	116.7	105.7	753.1	279	29.43	0.4974	0.4962	497.4	7	
<b>C9*</b>	142.2	119.6	773.5	301.1	26.71	0.5321	0.5359	532.1	8	
<b>C10-C12*</b>	187	143.2	807.1	335.5	23.85	0.6016	0.6039	601.6	10	C10
<b>C13-C15*</b>	247.6	181	855.8	382.6	21.44	0.726	0.7051	726	13	C13
<b>C16-C18*</b>	298.2	220.6	873.8	421.9	19.apr	0.9001	0.806	900.1	16	C16
<b>C19-C22*</b>	342.7	268.4	890.9	463.9	17.28	01.des	0.9184	1120	19	C19
<b>C23-C27*</b>	396	324.6	916.9	510.2	16.44	1.387	1.037	1387	23	C23
<b>C28-C34*</b>	452.5	395.7	944.1	564	15.91	1.745	1.165	1745	28	C28
<b>C35-C43*</b>	512.7	532.3	974.2	656.3	15.18	2.473	1.325	2473	38	C38
<b>C44-C55*</b>	579	678.2	1003	746.1	15.sep	3.274	1.362	3274	48	C48
<b>C56+*</b>	668.7	906.7	1037	880.4	15.31	apr.62	1.109	4620	65	C65

## Appendix E: Simulation result data

### Injection after 1. stage compression

Table E-1: Scavenger injection after compression, phase 1

Year	H2S to be removed [kg/d]	H2S in water after 1. separator	H2S concentration in gas to be treated [ppm]	Gas rate [Sm <sup>3</sup> /d]	Scavenger chemical consumption rate[L/d]	Scavenger chemical consumption rate[L/Y]
2025	0	-	-	3513479	0	0
2026	0.2	0.27	3.20	3518000	3	990
2027	172	30.9	34.1	3495000	2579	850905
2028	303	90.0	64.0	3424000	4551	1501830
2029	422	203	115	2625000	6330	2088999
2030	459	317	173	1879000	6891	2274080
2031	451	414	221	1435000	6758	2229975
2032	442	514	278	1114000	6627	2186910
2033	433	599	335	904900	6491	2142063
2034	410	704	377	761200	6149	2029302
2035	394	789	420	654600	5907	1949310
2036	372	860	461	563700	5579	1840905
2037	358	930	504	495200	5370	1772199
2038	381	1132	604	440500	5718	1886940
2039	328	1099	574	397900	4916	1622115
2040	317	1122	585	377900	4755	1569150
2041	295	1148	597	344600	4428	1461240
2042	324	1166	615	367400	4863	1604790
2043	297	1209	634	326800	4458	1471140
2044	293	1240	670	304600	4397	1450944
2045	260	1084	639	284000	3906	1288980
2046	235	983	639	256200	3525	1163250
2047	220	839	623	246200	3303	1089990
2048	171	971	683	174200	2562	845559
2049	172	662	529	226500	2577	850410
2050	196	847	634	215000	2936	968814
2051	173	905	649	185900	2597	856944
2052	153	783	633	168100	2290	755618
2053	151	819	662	159000	2265	747500
2054	185	733	753	170800	2771	914265
Total:					<b>125500</b>	

Table E-2: Scavenger injection after compression, phase 2

Year	H2S to be removed [kg/d]	H2S in water after 1. separator	H2S concentration in gas to be treated [ppm]	Sales gas rate [Sm <sup>3</sup> /d]	Scavenger chemical consumption rate [L/d]	Scavenger chemical consumption rate [L/Y]
2027	1	0,14	3,60	1221000	17	5495
2028	41	3,90	28,0	1127000	610	201168
2029	74	9,30	29,9	1902000	1104	364320
2030	115	17,8	40,9	2019000	1721	567765
2031	156	30,0	56,5	1991000	2346	774180
2032	187	38,9	69,7	1929000	2802	924660
2033	209	46,1	83,6	1796000	3129	1032570
2034	232	56,2	99,9	1658000	3476	1146915
2035	252	65,2	114,3	1568000	3779	1246905
2036	267	73,8	125,6	1510000	4001	1320165
2037	297	84,4	141,2	1492000	4457	1470645
2038	329	97,1	159,9	1456000	4937	1629045
2039	349	105,9	170,1	1449000	5235	1727550
2040	400	126,2	195,4	1442000	5999	1979505
2045	467	145,2	225,8	1455000	7007	2312145
2050	548	174,0	261,8	1469000	8222	2713145
2055	663	200,7	291,3	1596000	9947	3282395
2041 - 2044					26010	
2046 – 2049					30456	
2051 - 2054					36337	
Total:					<b>161586</b>	

### Injection after 1. separation and mixer

Table E-3: Scavenger injection after 1. stage separation and mixer, phase 1

Year	H2S in water after 1. separator	H2S to be removed, 1. stage separator [kg/d]	H2S to be removed, 2. stage separator [kg/d]	H2S to be removed, total [kg/d]	Gas rate [Sm <sup>3</sup> /d]	Scavenger chemical, 1. sep. [L/d]	Scavenger chemical, 2. sep. [L/d]	Scavenger chemical [L/d]
2025	0	0	0	0	-	0	0	0
2026	0	1,5	0	1	3519000	22	0	22
2027	23	94	81	175	3491000	1403	1222	2625
2028	67	185	159	344	3426000	2777	2382	5160
2029	157	289	196	485	2626000	4342	2933	7275
2030	252	315	235	549	1880000	4723	3518	8241
2031	332	318	236	554	1436000	4767	3543	8310
2032	417	327	233	559	1131000	4903	3489	8392
2033	504	318	229	547	906400	4763	3437	8200

2034	582	321	227	548	762400	4811	3411	8222
2035	667	307	220	527	653300	4599	3302	7901
2036	739	297	211	508	563300	4461	3164	7626
2037	813	285	208	494	495700	4282	3122	7403
2038	998	307	220	527	440000	4607	3302	7908
2039	974	268	191	459	398200	4025	2859	6884
2040	1006	259	186	445	377200	3882	2789	6671
2041	1032	248	177	424	344500	3714	2651	6365
2042	1060	269	194	463	367100	4037	2910	6947
2043	1092	248	174	422	326400	3717	2609	6326
2044	1126	246	171	417	304200	3683	2571	6254
2045	981	220	152	372	284300	3297	2276	5573
2046	882	195	138	333	255500	2924	2072	4995
2047	763	183	132	315	245400	2747	1982	4728
2048	899	145	103	247	173500	2168	1541	3708
2049	605	141	102	242	225400	2109	1527	3636
2050	770	161	116	278	215200	2421	1744	4165
2051	833	147	102	250	185400	2210	1533	3743
2052	719	127	93	220	167400	1907	1391	3298
2053	754	128	91	220	159600	1921	1372	3293
2054	671	152	111	263	170900	2285	1664	3949
								<b>167816</b>

Table E-4: Scavenger injection after 1. stage separation and mixer, phase 2

Year	H2S to be removed 1. stage separator [kg/d]	H2S to be removed 2. stage separator [kg/d]	H2S in water after 1. separator [kg/d]	H2S to be removed, total [kg/d]	Gas rate [Sm <sup>3</sup> /d]	Scavenger chemical, 1. Sep [L/d]	Scavenger chemical, 2. Sep [L/d]	Scavenger chemical [L/d]
2027	0,8	0	0,10	0,8	1230000	12	0	12
2028	23	22	3,00	45	1127000	347	323	670
2029	52	25	7,00	77	1910000	777	377	1154
2030	89	27	14,4	115	2001000	1330	400	1730
2031	132	29	25,0	162	1990000	1983	441	2423
2032	169	27	32,3	196	1930000	2529	407	2937
2033	191	28	38,0	219	1794000	2868	424	3292
2034	215	28	46,5	242	1659000	3221	414	3635
2035	237	27	54,4	264	1567000	3555	404	3959
2036	253	28	61,0	281	1519000	3798	413	4211
2037	285	28	71,0	313	1491000	4274	416	4691
2038	319	28	82,0	347	1457000	4785	423	5209
2039	341	29	89,0	370	1448000	5112	440	5552
2040	394	28	107	421	1442000	5904	418	6322

2045	468	22	123	491	1453000	7027	335	7362
2050	553	22	150	575	1469000	8294	328	8622
2055	683	16	169	699	1603000	10245	241	10486
2041 – 2044								27367
2046 – 2049								31968
2051 – 2054								38216
Total:								<b>169814</b>

## Injection, subsea

Table E-5: Scavenger injection subsea, phase 1

Year	H2S production from reservoir [kg/d]	H2S to be removed, Subsea scavenger [kg/d]	H2S in water after 1. separator	Multiphase stream rate to be treated [Sm <sup>3</sup> /d]	Gas rate [Sm <sup>3</sup> /d]	Scavenger chemical [L/d]	Scavenger chemical [L/Y]
2025	8	0		-	-	0	0
2026	19	2	0,3	19260000	3517000	14	4689
2027	230	210	2,4	85630000	3491000	1472	485793
2028	459	437	4,3	126700000	3424000	3058	1009285
2029	695	679	5,34	149800000	2625000	4753	1568328
2030	859	844	5,76	157400000	1879000	5907	1949455
2031	940	928	5,59	157800000	1435000	6494	2143056
2032	1028	1018	5,6	155500000	1115000	7124	2350772
2033	1101	1091	5,82	154600000	906300	7634	2519240
2034	1176	1167	5,72	153400000	763000	8170	2696232
2035	1240	1231	5,51	153800000	653300	8618	2844072
2036	1289	1280	5,7	154000000	563800	8963	2957863
2037	1346	1338	5,76	153100000	497900	9364	3090110
2038	1571	1563	5,48	153900000	440200	10939	3609999
2039	1478	1473	5,72	157600000	398100	10310	3402330
2040	1489	1481	5,84	158500000	377800	10370	3422034
2041	1492	1485	5,62	157100000	342900	10393	3429657
2042	1538	1530	5,69	155700000	367500	10713	3535409
2043	1550	1542	5,91	155900000	326900	10797	3562990
2044	1578	1572	5,21	152100000	304600	11001	3630304
2045	1383	1377	4,78	138900000	284200	9637	3180085
2046	1253	1248	4,2	126100000	255700	8733	2881771
2047	1092	1087	4,03	110500000	245900	7607	2510416
2048	1167	1162	4,13	116500000	174000	8132	2683458
2049	860	855	3,84	103100000	225200	5985	1975096
2050	1072	1067	3,96	109800000	215200	7469	2464724
2051	1104	1099	4,23	114200000	186200	7692	2538320
2052	958	953	3,7	101600000	168200	6674	2202516
2053	993	988	3,69	102000000	159400	6919	2283366
2054	947	943	2,87	80450000	170500	6603	2179023
Total:						<b>73110391</b>	

Table E-6: Scavenger injection subsea, phase 2

Year	H2S production in reservoir [kg/d]	H2S to be removed, Subsea scavenger [kg/d]	H2S in water after 1. separator	Multiphase stream rate to be treated [Sm <sup>3</sup> /d]	Gas rate [Sm <sup>3</sup> /d]	Scavenger chemical [L/d]	Scavenger chemical [L/Y]
2027	7	1,0	0,05	-	1211000	7	2310
2028	56	49,9	0,42	14930000	1137000	349	115269
2029	98	88,3	0,92	27640000	1900000	618	203973
2030	144	133,7	1,28	34930000	2001000	936	308824
2031	200	189,3	1,61	40600000	1991000	1325	437283
2032	241	230,8	1,64	41870000	1930000	1615	533079
2033	270	260,3	1,64	40880000	1819000	1822	601293
2034	301	291,7	1,73	40780000	1658000	2042	673919
2035	330	321,6	1,68	41170000	1567000	2251	742827
2036	354	344,1	1,76	42250000	1510000	2409	794963
2037	395	386,6	1,8	42750000	1490000	2706	893046
2038	440	431,6	1,82	43220000	1457000	3021	996904
2039	468	460,0	1,82	44060000	1450000	3220	1062508
2040	539	530,7	1,94	45570000	1442000	3715	1226009
2045	624	615,7	1,93	44940000	1454000	4310	1422290
2050	735	726,5	1,99	46190000	1468000	5085	1678169
2055	875	865,6	2,13	46930000	1590000	6059	1999536
2041 – 2044						5296599	
2046 – 2049						6200918	
2051 – 2054						7355410	
Total:						<b>32545128</b>	

**Partly subsea injection compared with injection after compression**

Table E-7: 25% H2S removal subsea. Rest removed after compressor. Phase 1.

Year	H2S production in reservoir [kg/day]	H2S to be removed, Subsea [kg/d]	H2S to be removed, after comp [kg/d]	H2S to be removed, Total [kg/d]	H2S in water after 1. separator [kg/d]	Sales gas rate [Sm <sup>3</sup> /d]	Scavenger chemical consumption rate[L/d]
2027	230	57,5	113	171	23	3493000	2101
2030	859	215	343	558	234	1879000	6655
2034	1176	294	306	600	529	762000	6654
2038	1571	393	284	676	852	426500	7005
2042	1538	385	242	627	874	366500	6325
2046	1253	313	175	488	738	254600	4817

2050	1072	268	147	415	634	215300	4077
2054	947	237	138	374	551	170200	3721
2028-2029							8756
2031-2033							19964
2035-2037							20489
2039-2041							19995
2043-2045							16712
2047-2049							13340
2051-2053							11696
Total:							<b>152307</b>

Table E-8: 50 % H2S removal subsea. Rest removed after compressor. Phase 1.

Year	H2S production in reservoir [kg/day]	H2S to be removed, Subsea [kg/d]	H2S to be removed, after comp [kg/d]	H2S to be removed, Total [kg/d]	H2S in water after 1. separator [kg/d]	Sales gas rate [Sm <sup>3</sup> /d]	Scavenger chemical consumption rate[L/d]
2027	230	115	59	174	13	3488000	1684
2030	859	430	225	655	163	1886000	6384
2034	1176	588	209	797	328	763400	7253
2038	1571	786	189	974	566	441100	8332
2042	1538	769	161	930	582	367200	7803
2046	1253	627	117	743	491	255200	6138
2050	1072	536	97	633	423	215100	5214
2054	947	474	91	565	368	170100	4686
2028-2029							12102
2031-2033							20454
2035-2027							23376
2039-2041							24201
2043-2045							20911
2047-2049							17027
2051-2053							14850
Total:							<b>180413</b>

Table E-9: 75 % H2S removal subsea. Rest removed after compressor. Phase 1.

Year	H2S production in reservoir [kg/day]	H2S to be removed, Subsea [kg/d]	H2S to be removed, after comp [kg/d]	H2S to be removed, Total [kg/d]	H2S in water after 1. separator [kg/d]	Sales gas rate [Sm <sup>3</sup> /d]	Scavenger chemical consumption rate[L/d]
2027	230	173	28	200	8	3488000	1626
2030	859	644	109	753	80	1879000	6144
2034	1176	882	70	952	174	761700	7221
2038	1571	1178	94	1273	282	440400	9663



2042	1538	1154	80	1233	291	367300	9272
2046	1253	940	58	998	245	255300	7448
2050	1072	804	48	852	211	214700	6351
2054	947	710	45	756	184	170100	5653
2026-2029							11654
2031-2033							20047
2035-2027							25325
2039-2041							28402
2043-2045							25080
2047-2049							20698
2051-2053							18006

Table E-10: 25 % H2S removal subsea. Rest removed after compressor. Phase 2.

Year	H2S production in reservoir [kg/day]	H2S to be removed, Subsea [kg/d]	H2S to be removed, after comp [kg/d]	H2S to be removed, Total [kg/d]	H2S in water after 1. separator [kg/d]	Sales gas rate [Sm <sup>3</sup> /d]	Scavenger chemical consumption rate[L/d]
2028	56	14	29	43	3	1126000	536
2031	200	50	113	163	23	1991000	2045
2034	301	75	172	247	42	1657000	3104
2037	395	99	221	320	63	1490000	4008
2040	539	135	298	433	95	1441000	5419
2045	624	156	349	505	109	1455000	6320
2050	735	183	413	596	131	1470000	7474
2055	875	218	496	714	149	1589000	8969
2029-2030							2581
2032-2033							5149
2035-2036							7112
2038-2039							9427
2041-2044							23477
2046-2049							27588
2051-2054							32887
Total:							<b>146095</b>

Table E-11: 50 % H2S removal subsea. Rest removed after compressor. Phase 2.

Year	H2S production in reservoir [kg/day]	H2S to be removed, Subsea [kg/d]	H2S to be removed, after comp [kg/d]	H2S to be removed, Total [kg/d]	H2S in water after 1. separator [kg/d]	Sales gas rate [Sm <sup>3</sup> /d]	Scavenger chemical consumption rate[L/d]
2028	56	28	18	46	2	1126000	463
2031	200	100	72	172	15	1990000	1786
2034	301	151	112	263	28	1660000	2740
2037	395	198	145	343	42	1489000	3564
2040	539	270	199	468	63	1441000	4871

2045	624	314	230	544	71	1454000	5649
2050	735	367	271	638	87	1468000	6638
2055	875	437	329	765	99	1589000	7986
2029-2030							2249
2032-2033							4526
2035-2036							6303
2038-2039							8435
2041-2044							21039
2046-2049							24573
2051-2054							29247
Total:							<b>130066</b>

Table E-12: 75 % H2S removal subsea. Rest removed after compressor. Phase 2.

Year	H2S production in reservoir [kg/day]	H2S to be removed, Subsea [kg/d]	H2S to be removed, after comp [kg/d]	H2S to be removed, Total [kg/d]	H2S in water after 1. separator [kg/d]	Sales gas rate [Sm <sup>3</sup> /d]	Scavenger chemical consumption rate[L/d]
2028	56	42	6,45	48	1	1129000	391
2031	200	150	32	182	8	1989000	1537
2034	301	226	52	278	14	1659000	2366
2037	395	296	69	366	21	1490000	3115
2040	539	404	93	497	31	1443000	4223
2045	624	469	113	582	34	1453000	4974
2050	735	551	132	683	44	1469000	5844
2055	875	656	161	817	50	1588000	7005
2029-2030							1928
2032-2033							3903
2035-2036							5481
2038-2039							7337
2041-2044							18393
2046-2049							21637
2051-2054							25699
Total:							<b>113832</b>

### Amine Plant

Table E-13: Selected results for amine plant, phase 1.

Year	H2S production in reservoir [kg/d]	H2S production in gas [kg/d]	H2S Gas [ppm]	Sales Gas rate [Sm <sup>3</sup> /d]	Amine flow rate [Sm <sup>3</sup> /d] (liquid vol flow, std cond.)	Stripper, Reboiler [KW]	Pump [KW]	Cooler [KW]	Stripper, Condenser [KW]
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2025	8	-	-	-	-	-	-	-	-
2026	19	-	-	-	-	-	-	-	-
2027	230	172	39	3491000	441	6298	37	158	7703
2028	459	318	64	3423000	558	7538	47	200	9430
2029	695	435	114	2647000	476	5869	40	172	6256
2030	859	469	187	1881000	365	4502	31	131	4808
2031	940	491	238	1433000	307	3788	26	112	4050
2032	1028	445	277	1114000	255	3147	22	93	3367
2033	1101	427	327	905400	229	2827	19	85	3025
2034	1176	414	377	762800	211	2606	18	78	2789
2035	1240	399	423	653300	198	2446	17	74	2618
2036	1289	373	459	562600	187	2311	16	70	2473
2037	1346	360	503	495800	175	2163	15	65	2316
2038	1571	383	602	441000	187	2312	16	70	2475
2039	1478	330	574	398700	170	2102	14	64	2249
2040	1489	320	587	377300	167	2065	14	63	2227
2041	1492	297	598	343900	160	1978	14	61	2117
2042	1538	325	612	367400	167	2077	14	63	2223
2043	1550	301	635	328300	164	2028	14	62	2170
2044	1578	294	671	303500	162	2003	14	62	2143
2045	1383	264	641	285100	150	1855	13	57	1985
2046	1253	237	639	256500	141	1744	12	54	1866
2047	1092	222	626	246000	133	1645	11	51	1760
2048	1167	173	692	173600	121	1497	10	47	1601
2049	860	170	526	223500	109	1348	9	41	1443
2050	1072	198	631	216800	121	1497	10	46	1602
2051	1104	174	648	185800	117	1448	10	45	1548
2052	958	154	633	168300	109	1349	9	42	1442
2053	993	153	662	159400	110	1361	9	43	1456
2054	947	185	752	170500	132	1638	11	53	1751

Table E-14: Selected results for amine plant, phase 2.

Year	H2S accumul ation in reservoir [kg/d]	H2S accumul ation in gas [kg/d]	H2S Gas [ppm]	Gas rate [Sm <sup>3</sup> /d]	Amine flow rate [Sm <sup>3</sup> /d] (liquid vol flow, std cond.)	Strippe r Reboile r [KW]	Pump [KW]	Coole r [KW]	Strippe r, Conden ser [KW]
2027	7	-	-	-	-	-	-	-	-
2028	56	45	28	1126000	49	598	4	18	638
2029	98	81	32	1900000	103	1261	9	38	1344
2030	144	119	41	2001000	155	1904	14	56	2029
2031	200	163	57	1989000	201	2473	17	73	2637
2032	241	194	70	1924000	223	2746	19	81	2929
2033	270	217	84	1798000	225	2772	19	82	2957
2034	301	238	100	1657000	225	2772	19	83	2958
2035	330	259	114	1569000	227	2792	19	83	2987

2036	354	274	126	1509000	228	2812	19	83	3001
2037	395	303	141	1489000	241	2997	21	88	3200
2038	440	335	160	1454000	254	3134	21	92	3346
2039	468	356	170	1448000	264	3258	22	96	3478
2040	539	406	195	1442000	287	3542	24	104	3783
2045	624	474	226	1454000	314	3877	26	114	4141
2050	735	555	262	1468000	341	4211	29	124	4499
2055	875	670	292	1591000	391	4829	33	142	5161

## Cost Estimation

Table E-15: Phase 1

Year	Cost[NOK/Y] after compression	Cost[NOK/Y] 1. sep. and mixer	Cost[NOK/Y] Subsea scavenger
2026	10563	78697	100070
2027	9079156	9241831	10366823
2028	16024526	18167292	21538146
2029	22289619	25616003	33468126
2030	24264428	29015801	41601374
2031	23793833	29260341	45732821
2032	23334330	29548191	50165464
2033	22855812	28873196	53760577
2034	21652652	28948724	57537591
2035	20799138	27818451	60692496
2036	19642456	26850324	63120788
2037	18909363	26068112	65942950
2038	20133650	27844859	77037372
2039	17307967	24237492	72605716
2040	16742831	23488554	73026206
2041	15591431	22413210	73188880
2042	17123109	24461434	75445624
2043	15697064	22274303	76034211
2044	15481572	22019727	77470679
2045	13753417	19621858	67863005
2046	12411878	17587895	61496997
2047	11630193	16647761	53572269
2048	9022115	13056239	57264987
2049	9073875	12802720	42148553
2050	10337245	14663973	52597206
2051	9143592	13179301	54167757
2052	8062439	11612764	47001685
2053	7975820	11593222	48727024
2054	9755208	13903415	46500351
<b>Total:</b>	<b>441899282</b>	<b>590895685</b>	<b>1560175748</b>

Table E-16: Partly subsea injection, phase 1

Year	Cost[NOK/Y] 25% Subsea scavenger/after compression	Cost[NOK/Y] 50% Subsea scavenger/after compression	Cost[NOK/Y] 75% Subsea scavenger/after compression
2027	8813313	8764018	9975452
2030	28733056	33064009	37511335
2034	30676880	40029625	47165135
2038	34346394	48696989	63063957
2042	31746238	46427464	61080170
2046	24682559	37054120	49386068
2050	20959348	31568774	42179257
2054	18936124	28171441	37410983
2028-2029	37546370	41828027	47486787
2031-2033	89114904	109640452	127014704
2035-2027	97534910	133089922	165343638
2039-2041	99138947	142686680	186216190
2043-2045	84643195	125222376	165699357
2047-2049	68462860	102934341	137347988
2051-2053	59843207	89610322	119385360
<b>Total:</b>	<b>735178303</b>	<b>1018788560</b>	<b>1296266381</b>

Table E-17: Phase 2

Year	Cost[NOK/Y] After compression	Cost[NOK/Y] 1. sep. and mixer	Cost[NOK/Y] Subsea scavenger
2027	58626	40669	49295
2028	2146463	2359313	2459840
2029	3887294	4064230	4352784
2030	6058053	6090271	6590302
2031	8260501	8533034	9331619
2032	9866122	10340414	11375899
2033	11017522	11590053	12831593
2034	12237583	12797438	14381440
2035	13304476	13938274	15851922
2036	14086161	14826120	16964519
2037	15691782	16516248	19057602
2038	17381910	18341058	21273923
2039	18432959	19547387	22673912
2040	21121318	22258986	26163041
2045	24670587	25922338	30351671
2050	28949252	30358924	35812122
2055	35023149	36921374	42670098

2041 - 2044	91583811	96362648	113029423
2046 - 2049	107239678	112562525	132327586
2051 - 2054	127944802	134560597	156964441
<b>Total:</b>	<b>568962049</b>	<b>597931899</b>	<b>694513032</b>

Table E-18: Partly subsea injection, phase 2

Year	Cost[NOK/Y] 25% Subsea scavenger/after compression	Cost[NOK/Y] 50% Subsea scavenger/after compression	Cost[NOK/Y] 75% Subsea scavenger/after compression
2026	2233434	2319349	2411073
2030	8433035	8753455	9109262
2034	12783354	13356589	13894965
2038	16546177	17415361	18269227
2042	22401942	23794009	24831677
2046	26096633	27624931	29085201
2050	30840012	32421162	34157945
2054	36960987	38885021	40829408
2029-2030	10666468	11072803	11520335
2032-2033	21216388	22110043	23004227
2035-2036	29329531	30771949	32164192
2038-2039	38948119	41209370	43100905
2041-2044	96997150	102837880	107833758
2046-2049	113873289	120092186	126486292
2051-2054	135601998	142612367	149974705
<b>Total:</b>	<b>602928516</b>	<b>635276475</b>	<b>666673173</b>

## Appendix F: Hysys models

### **Name/number system for streams and equipment:**

#### **Material streams:**

- 00 – Multiphase hydrocarbon stream
- 01 – Produced water
- 02 – Liquid (oil) from oil conditioning train
- 03 – Gas from gas compression train and first separator
- 04 – Gas from intermediate compression and separation train
- 05 – Liquid from gas compression train
- 06 – Liquid from intermediate compression and separation train
- 07 – Gas to be treated in amine plant
- 08 – Amine liquid flow
- 09 – Gas to be sent back to reservoir
- 10 – Oil to be sent back to reservoir

#### **Energy streams:**

- QC – Cold utility
- QH – Hot utility
- QP – Power

#### **Equipment:**

- E1 – Heater
- E2 – Cooler
- E3 – Heat exchanger for four streams.
- V1 – Valve
- S1 – Three phase separator
- S2 – Two phase separator
- S3 – Flash tank
- K1 – Compressor
- M1 – Mixer

X1 – Component splitter

O1 – Virtual stream

P1 – Pump

A1 – Adjuster

R1 – Recycle

T1 – Absorber tower

T2 – Stripper tower (distillation tower) with reboiler and condenser

**Models:**

Complete Hysys Model with Amine plant

Injection after first stage compression

Injection after first separator and two and three stage mixer

Subsea Injection

Partly subsea injection combined with injection after compression



