The problems associated with sour gas in the oilfield industry and their solutions

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Abstract

Fossil fuels are still a necessary and important part of modern living, keeping cars running and houses heated for example. As demands have risen and reservoirs of oil and natural gas have depleted, it has become increasingly more important to tap in to fields that were once classified as undesirable. Sour fields, fields high in acidic gases such as hydrogen sulfide and carbon dioxide, are one such option. There are many difficulties and dangers associated with working sour fields, such as toxicity of the sour gases, hydrate formation and corrosion of equipment that have prevented these resources being used in the past. Many varied methods of overcoming these problems have been developed, from removing the sour components to inhibiting their effects. This review highlights the major issues raised by sour fields as well as a wide range of solutions in use today.

Contents

1 Natural gases: sweet and sour

Natural gas is an important fuel used in a range of applications. There is an increasing demand for natural gas, with consumption predicted to almost double between 2004 and 2030.[1] Many other fossil fuel stocks are waning and a desire for cleaner burning, low carbon fuels has also played a large part in the increased demand for natural gas.[1,2] Natural gas reserves can be generalized into two categories: sweet and sour. Sour gases contain significant amount of acid gas components. The acid gases are most commonly CO_2 and H_2S, though other sulfur containing compounds (mercaptans), can also be present. A gas may be referred to as sweet when the acidic components are below a certain threshold. This threshold varies depending on the company or country of origin; with pipeline transport specifications being between 3-15 ppm[3] and sales specifications at less than 4 ppm of H_2S.[4,5] The act of removing acid gases is called sweetening.

Gas is used in its sweetened state, for safety and efficiency reasons. When gas fields were in abundance, fields containing sour gas, were sealed off for later use, as the cost of sweetening the gas before use was not worth the smaller profits. Due to the increase in demand for natural gas and depletion of many sweet gas fields, use of sour fields are now a more economically viable undertaking, with the use of sour fields rising from 16 % of all natural gas produced in 1971 to 21 % in 2004 with a prediction that 26 % of all gas will be from sour reserves in 2030.[1]

In this review the dangers and problems associated with sour gas stores will be covered as well as the methods employed to overcome them.

2 Dangers and Problems

2.1 Toxicity

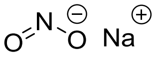
Beyond the risk of asphyxiation associated with a majority of gases, there are no particular health risks associated with CO_2. Unfortunately, the health risks from H_2S are more than adequate to make sour gas production a hazardous undertaking. Humans do have proteins capable of safely oxidizing or methylating H_2S in to excretable, safe compounds by use of *sulfite oxidase* and *s-methyltransferase*.[6] These proteins metabolize the small amounts of H_2S that are produced by the anaerobic processes of bacteria found in the intestines and liver. These proteins are not found in significant concentrations in the lungs and are not designed to cope with relatively large quantities of gas, greatly reducing their efficiency when dealing with toxicity from inhaled hydrogen sulfide.

The distinctive rotting egg smell of H_2S is detectable at around 0.05 ppm. The smell would be a good indication of its presence if not for at concentrations after 100 ppm it paralyses the olfactory nerve, killing the sense of smell and thus the awareness of danger. After 50 ppm the effects of sub-acute poisoning start to become apparent, gradually becoming more severe until 700 ppm when acute poisoning occurs.[6] Sub-acute poisoning has a range of symptoms.[6,7] In the 1930's "Gas eyes", or conjunctivitis, was usually taken as a routine hazard of the trade when working sour gas fields.[8] Symptoms often include sore eyes, swelling of the eyes, blurred vision, light sensitivity and the feeling that the eyelids are rough. Similar inflammations can occur in the nose and throat, such as rhinitis, pharyngitis, laryngitis and bronchitis. Mild exposure causes dryness of the nose, painful cough and the feeling of something being stuck in the throat. Moderate exposure can give a feeling of tightness and rawness in the chest, along with the build-up of mucous in the bronchia. More severe exposure results in a build-up of liquid in the airways and irregular bleeding or pus deposits.

Acute poisoning results very quickly in death. It is generally taken that only two breaths over 1000 ppm H_2S result in a loss of consciousness and the heart stops beating after 5-10 minutes.[6,7] Within these few minutes, rescue and treatment can be successful, though lasting neurological damage is possible. The extremely short time between exposure and collapse is referred to as a 'knockdown' effect.

H_2S reacts with and deactivates a range of proteins, by either reacting with sulfide bridges, or coordinating to metals. One major concern is its ability to inhibit cytochrome oxidase, more effectively, but by a similar method to hydrogen cyanide.[9–12] Hydrogen sulfide binds to the iron(III) centers of cytochrome oxidase, preventing transport and use of oxygen on a cellular level. This is one of the suggested ways that death occurs. H_2S also binds to the iron in haemoglobin, preventing oxygen transport through the blood. Often the cause of death is taken to be asphyxiation. There is evidence of selective uptake of H_2S in the brainstem and significant damage to the respiratory centers in the brain. This results in a cessation of breathing that is swiftly followed by death.[11]

There are no hard and fast regulations on how to treat acute H_2S poisoning, though commonly similarities with cyanide poisoning result in use of the cyanide kit. The chemicals used are 3 % sodium nitrite (**1**) and amyl nitrite (**2**). These promote the production of methemoglobin, Fe^{3+} haemoglobin, which has a much higher affinity for H_2S than cytochrome oxidase or standard ferrous haemoglobin. The removal is a competitive mechanism with the methemoglobin and cytochrome oxidase competing for H_2S and requires more nitrite being administered every half hour until the patient is in the clear.[8,10,12,13]



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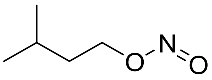


(2)

Hydrogen sulfide does not show any conclusive signs of chronic toxicity. Long term exposure to low concentrations does not build up, though damage can occur to the central nervous system. Analysis of communities living down-wind of sources of H_2S, e.g. paper mills, sweetening facilities and swine farms, showed abnormalities in tests designed to assess memory, balance and reaction time.[14] There is no evidence that these symptoms become worse with exposure time and these symptoms are also present in cases where people have recovered from acute poisoning, suggesting that this is not a chronic effect.

Hydrogen sulfide is as dangerous to other animals as it is to humans and has been described as "a menace to all aerobic organisms" by Bagarinao in a review on the toxicity and environmental impacts of sulfide on aquatic life.[15] No H_2S resistant cytochrome c oxidase has evolved, leaving all creatures relying on aerobic respiration at risk from H_2S poisoning, though occasional creatures do find ways of surviving in relatively sour environments. As seafloor hydrothermal vents produce a significant amount of hydrogen sulfide, deep sea creatures that live around these vents developed methods of protecting themselves from H_2S at a normally toxic concentration. One such solution is to form symbiotic relationships with sulfur oxidizing bacteria, which oxidize the H_2S to much less harmful compounds, such as elemental sulfur. Another is the production of sulfur binding proteins to prevent H_2S from reaching their cytochrome c oxidase, similar to the mode of action taking in treating H_2S poisoning by forming methemoglobin.[15] Effective as these methods are, even organisms adapted to a H_2S rich environment with perish if the concentration was increased and the H_2S successfully started to bind to cytochrome c oxidase.

Plants are also adversely affected by H_2S becoming visibly less healthy as they lose foliage or parts begin to blacken and die. There is evidence that plants can even be more susceptible to the effects of H_2S than humans, with health issues beginning at lower concentrations.[16] When released into the atmosphere hydrogen sulfide contributes heavily to acid rain by photooxidising to sulfuric acid. Acid rain is very damaging to plant life and rock formations, as well as contaminating water supplies and soil.[17] In general H_2S is a very potent and dangerous pollutant and great care should be not to allow release of significant quantities in the environment.

2.2 Gas Clathrate Hydrates

Clathrate hydrates are a well-established problem in the oilfield industry, and sour gas components can significantly promote their formation. Cages of hydrogen bonded water molecules form around small molecules, for example methane found in natural gas, in favorable conditions of low temperatures and high pressures, such as those in undersea pipe lines. When grown to a large enough size, these clathrates can form plugs that block pipes causing large delays that are costly and hazardous. Pipe rupturing and the flammable nature of the clathrates are a significant concern.[18]

The size of the guest molecule determines the structure of clathrate that is formed.[19,20] The structures shown below in Figure 1 are the most commonly formed clathrates, the cubic structure I and structure II and the hexagonal structure H.[21] It is possible to form more exotic structures with certain guests, for example dimethyl ether promotes the formation of a trigonal structure T. In pipe lines it is usually structure I and structure II that occur. The smaller components such as methane, CO_2 and H_2S form structure I clathrates whilst larger components like ethane form structure II clathrates.[22]

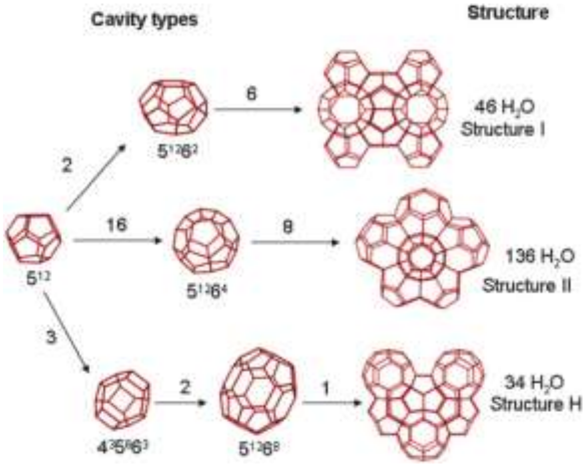


Figure 1. The structures of the most common types of clathrate hydrate (reproduced with permission from ref. 15).

It was originally thought that clathrate hydrates are metastable crystal structures and that favorable interactions with a guest increased the stability. Rodger[23] simulated the formation of clathrates to test the validity of the assumptions made in the cell theory by van der Waals and Platteeuw.[24] Van der Waals and Platteeuw created a statistical thermodynamic model based on the assumptions that the free energy of the clathrate lattice is unaffected by the guest molecule, cavities only have one guest, guest-guest interactions do not occur and quantum effects can be ignored. Rodger used these assumptions to run a molecular dynamics simulation of clathrate formation and found that the free energy of the water crystal is significantly affected by the guest, thus the assumption that the free energy is not affected is not appropriate. He further concluded that clathrate hydrates are not in fact metastable, but will collapse to an ice phase, Ih, or liquid water upon removal of the guest, depending which is the more thermodynamically stable state under the conditions used. His calculations suggest that it is not the favorable interaction between cage and guest that give the hydrates their stability, but the hydrophobic interaction between an aliphatic guest and the water, that keeps the cage open, agreeing with the observation of Jeffrey in 1984[25] that molecules with either many or strong hydrogen bonding groups do not readily form clathrates. Looking at the temperature of decomposition for hydrates of propane, ethane thiol and ethanol, ethanol shows by far the least stable structure. The ethanol hydrate decomposes at -73 °C compared to ethane thiol at 3 °C and propane at 6 °C.[26] The OH of the ethanol hydrogen bonds with the water, introducing defects into crystal structure, decreasing the stability. This further evidences the theory that repulsive interactions stabilize the clathrates. Adding polar species, such as ethanol and methanol, destabilize the clathrate enough to act as inhibitors.

Hydrogen sulfide forms hydrates at the lowest partial pressure of all the components in sour gas. This seemingly contradicts the theory that more polar molecules make less stable clathrate hydrates as H_2S is more polar than methane.[26] One theory of the unexpected low clathrate formation pressure of H_2S is that the presence of H_2S changes the polarity of the system and increases the level of moisture in the gas.[27] The more water there is in the system, the higher the likelihood of it crystallizing and hydrates forming. It has also been proposed that favorable size could more readily form clathrates.[28] Addition of H_2S to a mixture of cyclohexane and water actually promotes formation of a cyclohexane clathrate hydrate.[29] Normally cyclohexane is too big to be a suitable guest in a structure II type cage, but H_2S fills the smaller cavities in the structure stabilizing the clathrate, smaller molecules stabilizing clathrates that wouldn't normally form are referred to as help gases.[30] In methane/H_2S clathrates H_2S fills the smaller cavities of the structure I clathrate whilst methane fills the larger cavities.[31]

The favorability of H_2S clathrate formation brings added danger to the system as hydrates formed in a sour system are rich in H_2S.[28,32] In a mixture of methane and H_2S with 1 % H_2S, the resulting clathrate will on average contain 12 % H_2S as a guest.[31] As well as the health hazard associated with the formation of clathrate hydrates, such as flammability and pipe blockage, these H_2S rich clathrates also bring all the troubles associated with H_2S toxicity.

2.3 Corrosion

Neither CO_2 nor H_2S are corrosive on their own, but when dissolved in water, they create corrosive solutions. Corrosion leads to a thinning of pipes and embrittlement of the metal. This eventually leads to the pipe rupturing and in more severe cases could lead to explosions when the thinning metal is no longer strong enough to support the high pressures present in an operational pipeline.

When corrosion is caused by the presence of CO_2, CO_2 dissolves in water to create carbonic acid, H_2CO_3. Carbonic acid reacts with the iron in the pipe by reaction (1).

$$Fe + H_2CO_3 \longrightarrow FeCO_3 + H_2 \tag{1}$$

Carbon dioxide corrosion mainly proceeds by pitting. Localized areas of corrosion form instead of an even coating across the whole pipe. The resulting $FeCO_3$ can form a protective scale layer, coating the pipe, preventing further corrosion to the metal. This protective layer can start to chip away and the exposed metal begins corroding again. This is called mesa corrosion and results in deep, sharp edges pits in the pipe, named after the mesa type mountains found in the Americas.[33,34] The term mesa corrosion is only used with respect to corrosion by CO_2.

Hydrogen sulfide corrosion of the form shown in reaction (2), resulting in hydrogen radicals[4,35] that further weaken the metal by stress cracking.

$$H_2S + Fe + H_2O \longrightarrow FeS + 2H^{\bullet} + H_2O \tag{2}$$

The corrosion can take the form of pitting, uniform corrosion or stepwise cracking. Though often all three contribute to the eventual breakdown of the pipeline.[36] Pitting is a more general form of mesa corrosion as shown in Figure 2. Corrosion occurs at certain spots causing pits in the surface whilst leaving other parts practically unscathed. Uniform corrosion involves corrosion of the whole surface at an even rate, leading to a thinning of the pipe.

Figure 2. Severe pitting on a section of well tubing.[34]

Stepwise cracking is a weakening of the metal by absorbed small molecules. Stepwise cracking can also in this instance be called sulfide stress cracking, which is a specific and more rapid form of hydrogen induced cracking.[37] A high hydrogen sulfide content greatly increases the rate of corrosion by this mechanism.[38] Iron, and many alloys of iron, have a body-centered cubic packing structure that does not give much slip capability or flexibility. Welding, or some alloying processes, result in areas in the metal that are richer in atomic hydrogen, this causes defects in the packing structure that results in small voids called blisters. Hydrogen radicals produced in the H_2S corrosion process can diffuse into the metal, joining up the hydrogen-blisters that are already present. This causes the metal to crack. Then this crack can become joined with the next blister widening the crack in a stepwise fashion, the effects of which are shown in Figure 3.

Figure 3. Pipeline after failure due to stress cracking (reproduced with permission from ref. 27).

3 Sweetening

The process in which acid gases are removed from a natural gas stream is called sweetening. Sour gases are required to be sweetened before commercial use, for example, it is not desirable for fatal concentrations of H_2S to be mixed in with cooking gas. A lot of sweetening facilities can be quite large so the sweetening occurs after transport. Inhibitors must then be used to prevent hydrate formation and corrosion. More compact facilities have been designed to allow sweetening before pipe transport. There are several methods of sweetening in current use and further processes have been suggested or are in development. Each has advantages and disadvantages with the nature of the gas field often determining which method is most suitable and if it is possible to sweeten before transport.

Many methods are effective at removing one acidic component, but not others. This results in many plants having two removal columns, to remove the H_2S and CO_2 separately. In cases where both are removed at once, it may become necessary to separate them for disposal or reuse. For applications where higher purity is needed, another polishing column is added to further decrease the amount of acid components remaining in the sweetened gas.

3.1 Physical solvents

Solvents are a key component in the many sweetening processes and may be divided into two categories: physical and chemical. Chemical solvents remove acid gases by chemically reacting with the impurity. Physical solvents on the other hand, absorb the gases without any reaction taking place.

Physicals solvents work on the premise that the acid gases have different solubility than the desired hydrocarbons. The sour gas is flowed through a solvent with higher affinity for the sour components at high pressure, resulting in an acid gas rich solvent and a sweetened natural gas stream. To regenerate the solvent the pressure is dropped and the gases can desorb. This is often followed by a flushing with a stripping gas, such as air, steam or nitrogen, to remove any remaining acid gas.

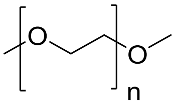
A physical solvent requires a high affinity for components that need removing and a low affinity for the gas that is to be recovered. It is also highly desirable for the solvent to have a low vapor pressure and a low viscosity.[39] The low vapor pressure minimizes solvent loss from evaporation and cuts down the number of recovery steps needed to reclaim the lost solvent, which can be costly in in resources and energy. Many recovery steps involve washing the solvent out of the gas stream using water. The solvent often then requires drying and any removal of water from the natural gas stream is effectively undone. When the viscosity of the solvent gets too high, the flow rate of the gas through the solvent is greatly decreased, this only gets worse as the processes are preferably run at low temperatures to increase gas solubility in the solvent. Once the mass transfer becomes too slow, the process no longer remains cost effective.

Selecting a solvent is a compromise between the vapor pressure and viscosity, efficiency and speed. Many different solvents have been tested and patented over the years, with many solvents used in a range of registered processes. A few of the major solvents and their advantages and disadvantages are discussed below.

A commonly used solvent is the dimethyl ether of polyethylene glycol (DEPG) (**3**).[39,40] The process involves a two-step removal. The first column removes H_2S due to the solvent's higher affinity for H_2S over CO_2 or methane. The rich solvent from this column is stripped using steam and fed back into the column for reuse. The second column is for the removal of CO_2 as the solvent is selective for CO_2 over methane. The solvent from the second column is then regenerated by stripping with either air of nitrogen. DEPG has a very low vapor pressure and does not require any steps to recover lost solvent from the gas. It also removes water from the gas stream further reducing the chances of corrosion or hydrate formation. The downside to DEPG is its high viscosity that requires a slow flow rate and relatively high operating temperature.

In systems with low concentrations of H_2S, propylene carbonate (PC) (**4**) can be used.[39,41,42] PC has a high affinity for CO_2 but is not particularly effective at removing H_2S. It has a very low affinity for light hydrocarbons, greatly decreasing the loss of product by product dissolution. PC also has a very low vapor pressure and the viscosity does not greatly increase with cooling, allowing for effective removal of CO_2. The main disadvantage of PC is it's intolerance to water, it reacts slowly, but irreversibly, with water, so is not appropriate for use in particularly wet conditions.

N-methyl pyrrolidone (NMP) (**5**) is a readily available physical solvent produced by a range of companies.[39,42] NMP has a higher vapor pressure than DEPG. This leads to the requirement of either washing the gas thoroughly with water, or keeping the column at a low enough temperature that the vapor pressure is greatly reduced. NMP is highly selective for H_2S so very desirable for applications where CO_2 removal is not wanted, such as splitting a waste stream of CO_2 and H_2S for disposal.



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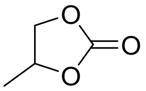

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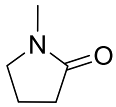

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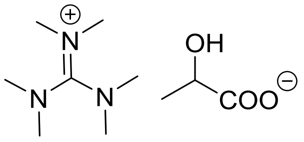
Multiple processes have been designed using methanol as a physical solvent, Rectisol and Ifpexol® being two of the more common.[39,43] Methanol has a very high affinity for sour components, with a higher affinity for H_2S than CO_2. The high vapor pressure of methanol means the process must be kept at a very low temperature, but the low viscosity leads to no loss of rate. Even at low temperatures the resulting gases need to be washed with water to collect the solvent vapor that has escaped. Even with the added cost of recovery and cooling, the high absorption, especially at low temperatures, and the relatively cheap cost of methanol make it a viable option for sweetening.

Ionic liquids have also been investigated as potential physical solvents for sweetening sour gas. Advantages of ionic liquids are usually cited as low vapor pressure, potentially higher operating temperature and easy reuse, but they are expensive to manufacture so need to be significantly more effective to be worth using. A very extensive computational study has been performed on the sweeting ability of hexamethylguanidinium lactate (**6**).[44] Many ionic liquids, hexamethylguanidinium lactate included, have excluded space due to the large, diffuse ions being unable to pack well. Small molecules, such as CO_2 and H_2S, can diffuse into these gaps, as shown by the solvent expansion of around 17-20 % instead of over 50 % as is seen in conventional organic solvents. In hexamethylguanidinium lactate the gaps are smaller than the acid gas components, but the local structure of the ionic liquid rearranges to allow the acid gases to diffuse in, resulting in a solvent volume expansion of 21 %. This lack of expansion can reduce require space in absorption columns and the very low vapor pressure of ionic liquids will prevent solvent loss. Hexamethylguanidinium lactate shows much greater solvation for CO_2 and H_2S over methane, with CO_2 and H_2S having partial molar volumes in the solvent of 40.17 $cm^3 mol^{-1}$ and 32.85 $cm^3 mol^{-1}$ respectively and methane 155.02 $cm^3 mol^{-1}$. Though these numbers come from simulations containing only a single gas, the mixed gas systems tried gave comparable values, though no numbers were given for the full ternary system. There are a few papers[44,45] that suggest the use of ionic liquids, but there is no evidence that this method of sweetening has been implemented commercially.



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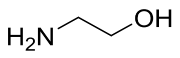
3.2 Chemical solvents

Unlike physical solvents, chemical solvents actually react with the acid gases. Most are mildly basic solutions, most often containing amines. Whereas physical solvents can be regenerated by simply dropping the pressure and flushing with another gas, chemical solvents require heating as well, to reverse the reactions that have taken place.

Acid gases are often selectively removed by using alkanolamines. Alkanolamines are a family of compounds containing both an amine and an alcohol group. Some of the most commonly used amines are monoethanolamine (MEA) (**7**), diethanolamine (DEA) (**8**), methyldiethanolamine (MDEA) (**9**) and sometimes what are referred to as activated alkanolamines, for example aMDEA.[46–52]



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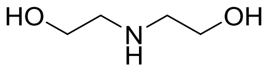

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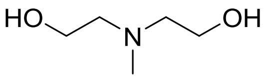

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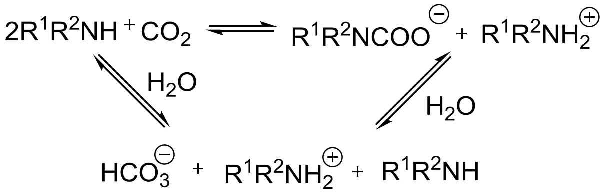
Primary and secondary amines, like MEA and DEA respectively, can react directly with the acid gas components. Reaction with H_2S involves just a single proton transfer so is much faster than the rate of mass transfer, making absorption the rate determining factor (Scheme 1).[53]

$$R^1R^2NH + H_2S \rightleftharpoons HS^{\ominus} + R^1R^2NH_2^{\oplus}$$

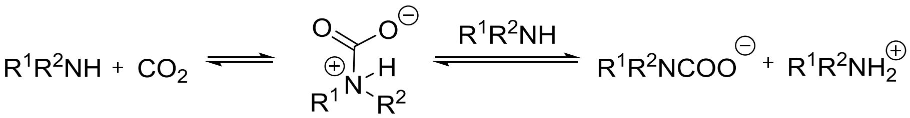
Scheme 1. Removal of H_2S by a primary or secondary amine where R^1 is an alkyl group and R^2 is an alkyl group or hydrogen.

Carbon dioxide reacts in a less direct fashion as shown in Scheme 2. In a system containing water the CO_2 can dissolve in the water to form carbonic acid, this can then be deprotonated by the amine. CO_2 can also react directly with two equivalents of amine to form a carbamate ion or directly with water to form a bicarbonate ion. The carbamate can convert, by addition of water to the bicarbonate.[53,54]



Scheme 2. Removal of CO_2 by a primary or secondary amine where R^1 is an alkyl group and R^2 is an alkyl group or hydrogen.

Much study has gone into the question of whether the formation of the carbamate proceeds via a zwitterionic intermediate or a neutral mechanism. Previous kinetic studies have included the zwitterion in their calculations[55] and the most recent theoretical studies into the mechanism suggest the zwitterion is formed and is the rate determining step (Scheme 3).[53,56,57]



Scheme 3. Formation of the zwitterion intermediate where R^1 is an alkyl group and R^2 is an alkyl group or hydrogen.

The efficiency of a chemical solvent is reliant on three main factors: solubility of the unwanted components in the solvent, flow rate and steam requirements. The flow rate is how quickly the solvent is pushed through the apparatus. Solvents with low absorption or that quickly decrease absorbing ability with absorption require a fast flow rate. The faster the flow rate, more solvent and more frequent regeneration are required, greatly increasing cost. Thus maintaining a slow rate of flow is important to cost, but stronger absorption requires more intense steps to regenerate the solvent. The stripping gas used to regenerate the solvent often is steam, too high a flow rate will increase the steam required, but so will too strong an interaction between the acid gas and solvent. A schematic of an amine based, chemical solvent, gas treatment plant is shown in figure 4.[58] A series of field test at the Fajr-e-Jam gas refinery in Iran showed MDEA and aMDEA to have more desirable steam consumption and flow rates with good CO_2 adsorption, whilst DEA gave better H_2S removal.[47] Often a mixture of amines is used to tailor the sweetening fluid to the composition of the gas field whilst giving the best steam consumption and flow rate possible. Occasionally other basic components are added, such as water soluble sodium silicate known as water glass[49] or a buffer,[48,57] to help maintain a certain pH to optimize efficiency.

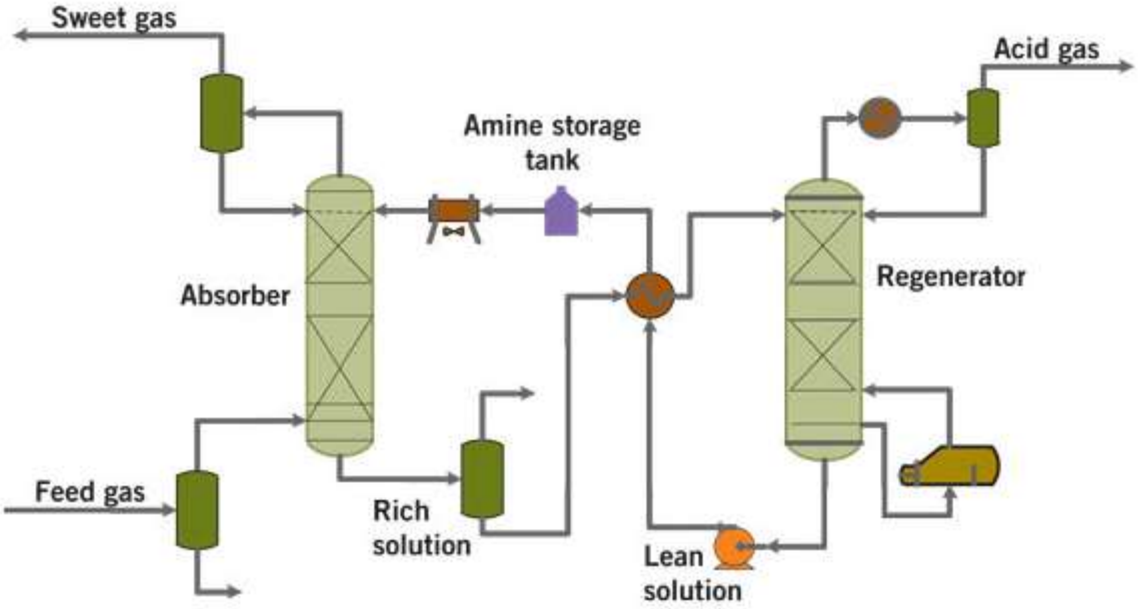


Figure 4. – Schematic of a gas treatment plant which uses amines as chemical solvents for acid gas removal (reproduced with permission from ref. 58).

Strong bases, often NaOH have also been used, and classified, as chemical solvents. Though the lack of reversibility may mean that ‘scavengers’, may be a better label for them (see section 3.7). Similarly to amines, NaOH reacts by a simple acid base mechanism with the acidic components.[59] H_2S reacts with two equivalents of NaOH to form Na_2S and water. Unlike amines, the kinetics of the reaction of NaOH with H_2S and with CO_2 are very similar, leading to the conclusions that CO_2 only reacts in the form of carbonic acid upon dissolution instead of forming carbamates. As NaOH is in aqueous solution the probability of CO_2 dissolution is quite high.

3.3 Membranes

Membranes are used to separate gases by allowing the undesirable products, CO_2 and H_2S, through to a waste steam, whilst leaving the desired natural gas. There are two main characteristics that dictate permeability, and thus selectivity, of a membrane: diffusion and sorption. The rate at which a molecule can diffuse through a membrane decreases with molecular size. So in general terms, smaller molecules find it easier to pass through membranes than large molecules. In glassy polymers diffusion is the main factor dictating separation. Sorption increases with condensability of the gas. This often can relate to the molecular diameter of the molecule, as larger molecules tend to condense more readily, but also more polar components are more condensable than non-polar components. Sorption is the dominant factor of permeability in rubbery polymers. Either glassy or rubbery polymers can be used in separation of acid gases from natural gas as both CO_2 and H_2S have smaller diameters and are more condensable than methane.[60] The kinetic diameters, critical volumes and boiling points are shown in table 1 to illustrate the difference in size and condensability of CO_2, H_2S and methane.

Gas	Kinetic diameter / Å	Critical volume / $cm^3 mol^{-1}$	Boiling point / °C
Carbon dioxide	3.3	91.9	-78.5
Hydrogen sulfide	3.6	87.7	-60.0
Methane	3.8	98.6	-161.5

Table 1. - Kinetic diameter, critical volume and boiling point for CO_2, H_2S and methane.[61]

Industrially cellulose acetate membranes are often used. Being relatively cheap and environmentally friendly they make a good choice for industrial application. The selectivity for CO_2 and H_2S over methane is adequate,[62] though modifications, such as the use of cellulose esters,[63] can improve the selectivity. More than one membrane separation step is used to reduce the loss in methane, as selectivity is not so good that methane loss after one membrane can be ignored. The method of using two cellulose acetate membranes has been proven effective at producing sales specification natural gas at a well in East Texas, less than 4 ppm of H_2S.[64] A majority of membranes show a decrease in permeability with pressure, cellulose acetate on the other hand, actually shows an increase.[65] Cellulose acetate swells with the addition of CO_2, with a higher pressure of CO_2 forcing more of the gas into the polymer. The swollen polymer is significantly more permeable that before swelling and this has a negative effect upon methane losses during production. The major downfall associated with cellulose acetate, is that the structure of the membrane is destroyed by liquid water. As almost all natural gas is wet, if not saturated, either a dehydration step is required or careful avoidance of water's dew conditions, which vary with gas composition and amount of water.[66] To circumvent this water sensitivity a range of other polymer membranes including polyamides such as nylon,[67] polyamide-polyether block copolymers,[60,68] polysulfides on polyfluoroethylene[69] and siloxane and alkoxysilyl oligomers[70] have been created. Though none have received the widespread use that cellulose acetate has, usually because of cost, either of the membrane, or of changing already established equipment. Different membranes have different selectivities, for example polyamide-polysulfide block copolymers have a very good selectivity for H_2S, so are used in two membrane systems often along with a cellulose acetate for CO_2 removal.[71,72] This approach has the added advantage that as well as H_2S, the polyamide-polysulfide block copolymer also removes water, greatly increasing the lifespan and efficiency of the cellulose acetate membrane.

Liquid membranes work on the principle that commonly used chemical solvents, such MEA, DEA etc., can separate acid gases from methane. Instead of designing apparatus to handle the liquid, the solvents are immobilized in a membrane. Any of the previously mentioned polymers are potential candidates for the support in a liquid membrane.[73] The nature of the support varies with a majority being micro or meso-porous solids with the solvent filling the pores.[74] Though swelling a polymer with a solvent is known,[73] as in the use of hollow fibres.[75] Though this method is much slower than using the free solvent, it combines the effect of the membrane and the solvent, giving a potentially cleaner final product.

3.4 Clathrate Hydrates

As discussed in section 2.2, clathrate hydrate formation is a big concern in sour gas streams. With the presence of H_2S promoting their formation and resulting in H_2S rich clathrates.[76] Though it is not believed that clathrate formation as a method of sweetening is in use, there is patent literature suggesting that it is possible to use hydrate formation as a method to remove H_2S. The patent states that this is done under thermodynamic conditions, allowing the H_2S clathrate to predominantly form.[77] Once the clathrates have formed they are then heated up carefully, allowing the less stable methane clathrates to dissociate first, resulting in a fuller recovery of the desired natural gas. The H_2S clathrates are then either melted to give a sour gas stream, or disposed of in their solid state, for example by reinjection (see section 3.6).

Reaching thermodynamic equilibrium can be costly in time and requires large apparatus that is not viable in the limited space on offshore platforms. An alternative is to form methane clathrates. A methanol/water mixture is often used to form these kinetically controlled materials. Methanol is a thermodynamic hydrate inhibitor, usually used to help prevent the formation of clathrate hydrates. In this application it aids kinetic formation of the methane clathrate over the thermodynamic formation of the H_2S clathrate as well as increase the solubility of methane in the aqueous medium.[78] Water-only systems have also been developed to address the environmental and cost concerns associated with methanol.[79] Formation of methane clathrates leaves an acid gas rich stream. After multiple methane removals the acid gas stream is sent to waste. The clathrates are then melted to retrieve the desired natural gas. To achieve a sufficiently pure gas and high yield, both the removed stream and gas from the dissociated clathrates must be run through the system multiple times.

In reality both cases mentioned would result in mixed hydrates being formed making removal of a specific component difficult, so it is very unlikely that clathrates would ever find commercial use as a sweetening method. The number of repetitions it would take to converge on a level of purity that would meet sales specification would more than outweigh in time and cost any perceived benefit from using water as cheap and green alternative.

3.5 Distillation

Distillation is also used for removing acid gases from mixed gas streams. A majority of distillations for sour gas sweetening are cryogenic fractionation, requiring the raw natural gas to be cooled to a liquid then heated to distil off the desired gases. Carbon dioxide is renowned for subliming at a range of temperatures and pressure often encountered in distillation apparatus, this has led to two different types apparatus being developed. The first of which sees the sublimation of CO_2 to be a problem that should be avoided leading to the first commercial cryogenic distillation, the Ryan-Holmes process, being developed.[80,81] To prevent solid CO_2 formation solids-preventing agents are used. Solids-preventing agents are often hydrocarbons that are heavier than the natural gas, with a preference for butane. CO_2, and also H_2S, are more soluble in butane than methane, it also successfully decreases the freezing point of CO_2.[81] In gas reservoirs naturally containing heavier hydrocarbons, the heavier hydrocarbons can be used from the produced waste stream, saving the cost of purchasing extra additives.

ExxonMobil submitted a trademark for Controlled Freeze Zone (CFZ), and successfully implemented this technology at Clear Lake gas plant in Texas in 1986, shown in Figure 5.[82] Instead of taking steps to prevent CO_2 freezing, CFZ relies on CO_2 freezing as a method of separating it from the natural gas. Solid CO_2 falls onto a melt tray then this tray is warmed under pressure to allow the CO_2 to melt and the liquid CO_2 is poured out of the column.[82–85] Whilst this forgoes the need for additives, the equipment used is large and bulky so is problematic for offshore applications, though it has been successfully implemented at inland facilities such as the Shute Creek gas treating facility in Wyoming.[82] There is also more to be desired in the energy cost of the operation as the high pressures, 34 bar, and low temperatures, around -60 °C, that are required are expensive to maintain, leading to a hybrid systems that use CFZ in succession with the more traditional non-subliming methods.[80]

Figure 5. CFZ pilot facility in Clear Lake (reproduced with permission from ref. 71).

An alternative method of distillation is vortex distillation. One of the leading implementations of this technology is the Twister Supersonic Separator.[86–88] Twister was first implemented in Petronas/Sarawak Shell Berhad B11 offshore facility in East Malaysia in 2004 after a series of full scale tests in the Netherlands, Nigeria and Norway.[86,87] The B11 offshore facility has been running continuously and successful since its start up, sweetening the sour gas and thus preventing corrosion. Twister operates by causing a drop in temperature by converting pressure into kinetic energy, similar to the way in which a turbo-expander converts pressure into shaft power.[86] After the initial inlet a Laval nozzle is used to expand the gas to supersonic velocity, resulting in a mist of droplets of condensed gases, all components of the sour gas are condensed, the desired natural gas as well as CO_2 and H_2S. The vortex creates a centrifuge that forces the droplets up to the edge of the column. The liquids are separated off by the cyclonic separator and the stripped gas exits the far end. The removed liquid is degased to remove any dissolved methane, which is then added to the sweetened gas. A schematic of the Twister® tube is shown in Figure 6.

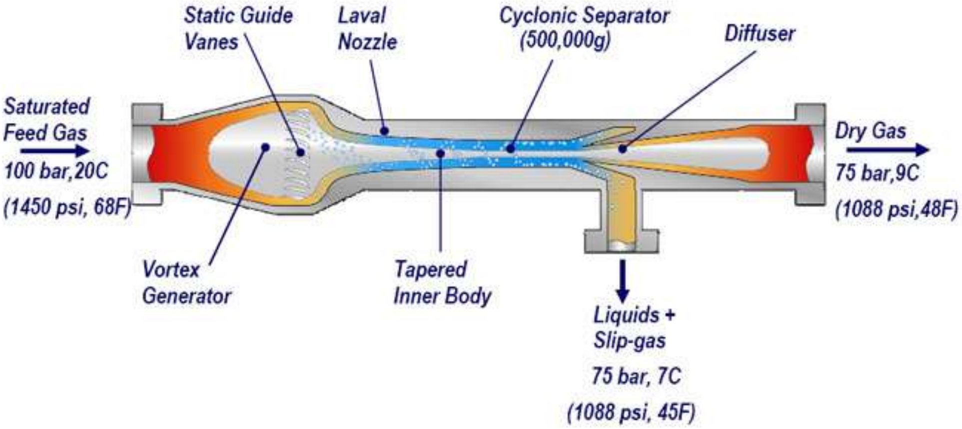


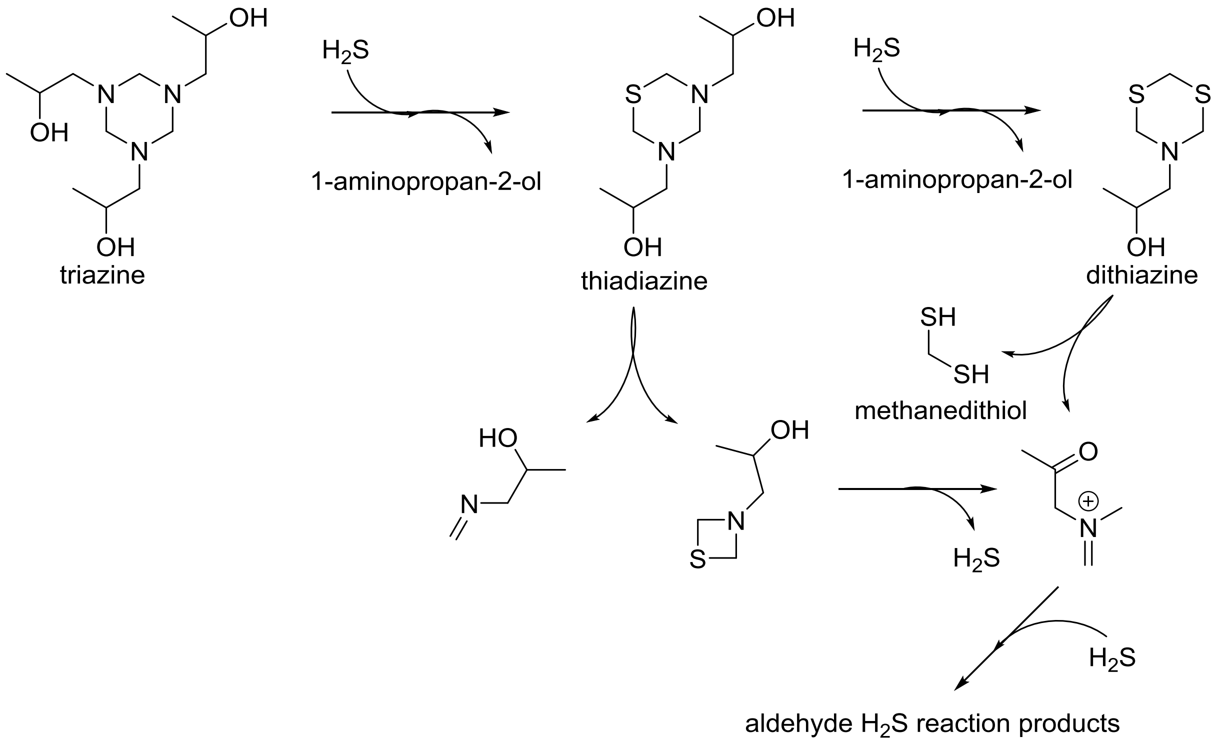
Figure 6 – schematic cross section of the Twister tube.[86]

Ethane forms an azeotrope with CO_2, making their separation difficult. It is supposedly possible to add an azeotrope inhibitor, also called an entrainer, to help prevent this, though as the patent literature on the matter only describes the invention as an inorganic or organic compound that disrupts or inhibits formation of an azeotrope formed by a sour species and a light hydrocarbon, it is unlikely such inhibitors are in use.[89] Though no example of these chemicals is given, the theory behind the inhibitor is to add a compound that is structurally similar to the sour component. The inhibitor then replaces the sour component in the azeotrope, allowing full removal. Even though no specific chemicals were named, the underlying concept is sound as similar technologies have been used for other purposes such as distilling ethanol from water by the addition of benzene.[90]

3.6 Scavengers

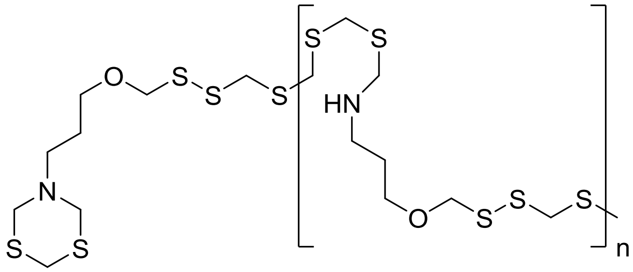
A scavenger is a compound that reacts with acid gases irreversibly. This is a one-use reagent that cannot be regenerated and is suitable in situations where the acid components are in very low quantity, but a very lean final product is desired.

Azines are often used as scavengers, with wide range of triazines having been produced, tested and successfully used to sweeten sour gas. For example, hexahydro-1,3,5-tris(2-hydroxyethyl)-S-triazine proved effective at reducing the level of H_2S in an operating well in West Texas.[91] Another example is 1,3,5-hexahydro-1,3,5-tert-butyltriazine that can be easily synthesized by slowly adding tert-butylamine to formaldehyde.[92] Comparison to other triazines in lab trials showed 1,3,5-hexahydro-1,3,5-tert-butyltriazine to be particularly effective at removing H_2S.[92] In 2009 Kelland[93] stated that one of the most preferred triazines in use was 1,3,5-tri-methoxypropyl-hexahydro-1,3,5-triazine (MOPA hexahydro-triazine). The reaction scheme of a triazine with H_2S is shown in scheme 4.



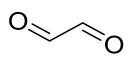
Scheme 4. Proposed reaction scheme of 1,3,5-(2-hydroxypropyl)-hexahydro-s-triazine with H_2S.[94]

The main problem with using triazines as scavengers is fouling, the formation of a solid byproduct that may interfere with later processes or cause blockages. The fouling product from triazine reacting with H_2S is a dithiazine polymer, one example of which is shown in structure (**10**).[95] It has been suggested that the carbon sulfur chains necessary for the polymer to form arise from the formation of methanedithiol that occurs when dithiazines decompose as seen in scheme 4.[95] Removal or replacement one of the hydroxy groups could possibly prevent the formation of methanedithiol, as the third hydroxy group is necessary to form methanedithiol. One issue with removing the tertiary hydroxy group is the decrease in water solubility that may increase the probability of triazine precipitation and in fact worsen the fouling problem.[94]



(10)

Glyoxal (**11**) has been suggested as a scavenger, though many additives have been used to improve the efficiency. Originally glyoxal was used along with other aldehydes to form water soluble products.[96] The problem with this method was that at lower pH, around 5.5, these products are no longer soluble. In acid gas environments lower pHs are expected and the production of solids blocks part of the equipment. A later invention[97] used only glyoxal in a high loading resulting in insoluble products. More additives were required to remove these solids, resulting in a process that is not economically viable. Adding polypropyleneoxide (**12**) has a synergistic effect on the glyoxal, reducing the amount needed and thus the cost and amount of solid formed.[98]



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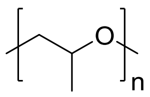


(12)

Zinc compounds are often used in the removal of H_2S.[99] A preferred compound is ZnO, that is cheap, readily available and has minimum associated health risks. A slurry of ZnO particles is made in a solvent, often water, and the sour gas is passed through. H_2S reacts with ZnO to form ZnS, an inert, insoluble solid that is simple to easily and safely dispose of.

To minimize the required amount of scavenger, bactericides can be added to the oil well to minimize the initial amount of H_2S produced.[100] Many oil wells, especially those found in the North Sea, contain sulfate reducing bacteria that produce H_2S and are the reason for many fields becoming sour. In the Skjold reservoir in the Danish North Sea, tetrakishydroxymethylphosphonium sulfate is added to kill sulfate reducing bacteria.[100] It was shown to successfully reduce the amount of H_2S produced in the reservoir by up to 50 % and is not deactivated by H_2S like the traditionally used aldehyde based bactericide. Bactericides only reduce the amount of H_2S, additional scavengers are also required to reach pipeline specifications.

3.7 Oxidation

An effective way of removing H_2S from a gas stream is to convert it into something less harmful and easier to remove. A range of metal complexes can be used to oxidize H_2S into solid elemental sulfur, which can then be simply filtered out of the gas stream. As these additives are often catalytic they do not come under the classification of scavenger. Metals typically used include, iron, cobalt, nickel, and vanadium, though many others are may be potential candidates.[101–103] During the sweetening process H_2S is oxidized to elemental sulfur, and the metal catalyst is reduced. To regenerate the catalyst oxygen, introduced either as pure oxygen, air or oxygen-enriched air, is used to oxidize the metal back to its starting oxidation state. The overall reaction for the oxidation of H_2S is shown in equation 3.

$$H_2S + \tfrac{1}{2}O_2 \longrightarrow S^0 + H_2O \tag{3}$$

Vanadium is applied as a V^{2+} salt in aqueous solution with a boron compound and quinone. The boron compound complexes to the vanadium, preventing the formation of any unwanted side products that would deactivate the catalyst, such as vanadium sulfide or V^{3+}. An added advantage of including a boron compound is it works as a buffer, keeping the pH in a workable range between 8.5 and 9.3.[104] The quinone is added as a catalyst to reoxidize the spent vanadium and is itself regenerated by the addition of oxygen.[104]

A large disadvantage of vanadium is its toxicity. Environmental regulations state that it cannot be released in the environment in concentrations above 25 ppm. Iron is a much more environmentally, and economically, friendly option. Iron is often used as chelate complex, forgoing the need for the addition of a boron compound to prevent unwanted species. The chelating ligand stops the formation of iron hydroxides that would form, then subsequently precipitate out, in neutral to basic conditions. Desire for cost efficiency usually leads to the chelating ligand being a relatively cheap and easily available compound such as ethylenediaminetetraacetic acid (EDTA), though the list of ligands used is quite extensive.[101,103,105] A mixture of ligands is often used. For example, EDTA is an effective ligand at low pH whilst saccharides are effective at high pH. A mixture of the two gives stability across the whole range of pHs that are encountered in natural gas processing.[105] Iron catalysts also require re-oxidizing before reuse. In a similar way to vanadium, either flushing with oxygen, or oxygen enriched gas can be used, as can adding an oxidizing agent such as quinone. The bacterium thiobacillus ferroidans can also be used to regenerate iron catalysts.[106] While this method is not yet in common use, it is a green and innovative and may show potential in the future.

Non-solution based methods of H_2S oxidation have also been used, the most common of which being the iron sponge method. Wood shavings are coated in a layer of iron oxide and packed into a purification column. The acid contaminated gas flows up through the sponge. The H_2S reacts with the iron oxide to form iron sulfide. A source of oxygen is then passed though the sponge, returning the FeS to FeO and giving elemental sulfur. When the sponge becomes saturated with sulfur, it is removed and disposed of. Problems may arise with removal, as often during the sponge's life time it hardens into a solid mass, resisting easy removal. Disposal is also accompanied by strong sulfurous smell, which while not harmful, is rather unpleasant for workers. Addition of secondary amines to the sponge prolongs life, prevents hardening of the material and removes the sulfurous smell. [107] Metal oxides can also be supported upon porous materials such as alumina.[108] Vanadium oxide supported on alumina can effectively remove H_2S from a gas steam. H_2S is absorbed onto the vanadium oxide, during the regeneration step involving heat and flushing with nitrogen, the H_2S is desorbed and 26 % is oxidized to elemental sulfur. As only 26 % is converted to harmless by-products, this is not the most industrially useful method.

CrystaSulf is a non-aqueous oxidative method for removing H_2S, that results in dissolved sulfur avoiding the problem of clogging.[109,110] CrystaSulf uses a hydrocarbon based solvent loaded with SO_2. The H_2S reacts with the SO_2 to produce elemental sulfur that remains in solution. The rich solvent is taken to a cooling stage. The dissolved sulfur crystallizes out of solution and the solvent can then be reused. SO_2 in small scale facilities is added as a liquid drip into the solvent.

In much larger facilities some of the produced elemental sulfur is burned to produce SO_2 gas that is bubbled through the solvent to give a loaded solvent. In 2004 CrystaSulf was successfully implemented at the Emden site in Germany, replacing the old molecular sieve towers previously used and successfully meeting the newly enforced 3.3 ppm sulfur limit.[110,111]

All oxidation methods only remove H_2S, as other acidic compounds, such as CO_2, are already fully oxidized. In some situations retention of the CO_2 is desirable. For the majority of cases in which it is not, these methods must be employed with another to remove all acidic components.

3.8 Disposal of waste gas

After the acid gases have been removed, they have to be disposed of. There is not much of a market for H_2S and CO_2 requires further scrubbing to remove residual H_2S before it can be used. There are a number of methods in use of dealing with waste gases.

One method, that is becoming more commonly used, is re-injection.[112,113] The acid gases are injected back into the well they were brought up from. This is a continuous process, whilst the next gas extracted from the well will be more sour, there is less of a drop in pressure, allowing a more through extraction. After a majority of desired gas has been removed, the well is sealed off again. If the waste components ever become needed or profitable, the well can be reopened and the acid gases extracted. One disadvantage is the high pressure that is required to re-inject the gas, requiring compression pumps. These pumps can achieve gas pressures of up to 1000 bar, though operating pressures as low as 150 bar can be used.[114] Clathrates can be added in their solid form, not requiring pressurization, similarly the liquid acid gases from CFZ can be added without further processing.[82] The gas reinjection well at the Shute Creek facility in Wyoming is shown in Figure 7.

Figure 7. Acid gas injection well at Shute Creek, Wyoming (reproduced with permission from ref. 71).

Space can be very limited at the well site, especially offshore. Whilst making desirable products from the waste gas is a very common solution, there is often not space to build a plant to do this. This leads to a need to safely transport the acid gases. Again, H_2S clathrates can lend themselves to this application. They are stable, even above the usual melting point for water, allowing for relatively easy and safe transport. Another method is transportation in a solvent. Acid rich physical solvents can be transported, though diffusion is hard to control so may pose a significant health risk. Chemical solvents on the other hand, require heating to release the acid gases and so at low to ambient temperatures they are perfectly stable. The fact that the acid gases have been neutralized also allows for transportation through pipelines without fear of corrosion.[52]

Hydrogen sulfide is not a particularly commonly used chemical. A number of processes exist to convert it into more profitable materials. Oxidation of H_2S to sulfur is discussed in section 3.8, as it is a commonly used method of removing H_2S from a natural gas stream. This is becoming less popular as the demand for sulfur is currently quite low. The elemental sulfur is usually just disposed of as a solid. A more useful process is converting the H_2S to sulfuric acid. For small quantities of H_2S, the acid gas is incinerated, though it is not desirable to release large quantities of the SO_2 produced to the atmosphere.[50,115]

It is also worth noting that many sweetening methods result in large quantities of sour water, which in turn need sweetening. Methods are often analogous to the sour gas sweetening methods such as use of scavengers,[116] oxidizing H_2S to less harmful substances,[117,118] or finding applications where the sour components do not require removal[119] to name but a few. Detailed discussion of sour water processing is beyond the scope of this review, though Knudsen *et al.* give a brief introduction to several methods in their paper for the seventh SPE international conference.[120]

4 Corrosion and hydrate inhibition

Some sites find space, or small enough technologies, to remove the acid gas components at the offshore rig, for example the Petronas/SSB B11 platform off the shore of Malaysia removes acid components using vortex distillation before transport to an onshore processing plant.[87] Though the limited amount of space at many well sites, can often lead to a desire to transport the sour gas in its raw state and perform all necessary acid gas removal in larger plants onshore. So instead of removing the acid gas components, it becomes prudent to prevent their undesirable effects, namely formation of clathrate hydrates and pipe corrosion.

4.1 Corrosion inhibition

One method of preventing corrosion is to make the pipeline out of a resistant material. For example, the oxide layer on aluminum prevents it from oxidative forms of corrosion as the exposed parts of the metal are already oxidized. The problem is aluminum is far too expensive to build pipelines from and may not have all the required physical properties. When designing an alloy the cost of the components, the effects they have on the materials physical properties and the corrosion resistance must all be taken into consideration.

Like many large scale metal applications, the principal metal has traditionally been iron. As elemental iron is brittle and general does not exhibit many workable properties, it is often mixed with carbon and other additives to form steel. Carbon is added to aid strength and processability, and then smaller amounts of more expensive metals are added to give resistance to corrosion. Chromium is added to help increase corrosion resistance and molybdenum is added, occasionally with tungsten, to give pitting resistance.[121] All three of these metals are expensive when compared to iron, so are used in as small an amount as possible to still give adequate resistance.

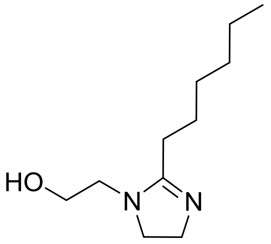
Too much molybdenum and tungsten decrease the workability of the alloy, but tungsten also increases the resistance to sulfide stress cracking and contributes to the strength of the alloy.

High nickel alloys give much better corrosion resistance in highly corrosive environments. The nickel percentage is often between 35 and 55 %.[121–125] In these alloys the iron is the balance metal used to fill up the remaining percentage after the desire ratio of components has been added, so the nickel based alloys cannot necessarily be classed as steel. Similar to steels, chromium and molybdenum are added to give corrosion resistance. Another common additive is aluminum. Whilst it is always the case that aluminum must be present, its effects and dosing vary with different alloys. Some patents have claimed that aluminum decreases the alloy strength[123] whilst others say it increases it.[122,125] It can generally be agreed that too high loading results in a decrease in workability. Titanium is added to increase strength and works synergistically with aluminum to maximize the lattice mismatch between the phases in the alloy that results in an increase in strength. Copper can be added to increase corrosion resistance in non-oxidative environments and works synergistically with Mo.[122,125] Niobium is added to increase strength and help prevent the formation of molybdenum and chromium carbides that are detrimental to the mechanical properties.[125]

Whilst resistant alloys help improve the life time of pipelines, addition of a chemical corrosion inhibitor can improve it even further. Information on the exact nature of many chemical corrosion inhibitors is closely guarded intellectual property making an in depth scientific review difficult

Corrosion is often thought of as an electrochemical process, with both cathodic and anodic corrosion present in most systems. There are two ways of preventing corrosion: blocking active sites on the metal, or adjusting the potential of the surface to promote the formation of a protective scale.[35] In general, the second option is rarely used and often scale inhibitors are even added. Whilst a scale can be protective, it is hard to maintain a complete and even layer with breakdown of the scale leading to the accelerated corrosion of mesa pitting.

A majority of the organic inhibitors used are nitrogen containing compounds, such as long-chain amines, amides, hydroxyalkyl imidazolines[126] **(13)** and salts of these species. Occasionally similarly structured polymers are used, such as N-substituted polyamines **(14)**.[127] A small contribution of their effect is raising the pH of the system and neutralizing the acid gases,[128] though often their main method of action is forming a protective film on the metal surface. Inhibitors that form protective films are referred to as barrier inhibitors. Traditionally, the inhibitor is a filming amine with minimum interaction with the metal surface. More recently vapor corrosion inhibitors (VpCIs) have become more prominent, as they interact with the surface of the metal and allow for self-healing by maintaining a steady partial pressure of inhibitor.[129,130] This prevents pitting that occurs when a small section of protective layer breaks down by adsorbing more VpCI. Being vaporized before addition to the pipeline, minimizes the time is takes for adsorption to occur. VpCIs are also compatible with a range of drag reducers, which keep the pipeline flowing quickly, minimizing the time in which corrosion can occur.[35,129]



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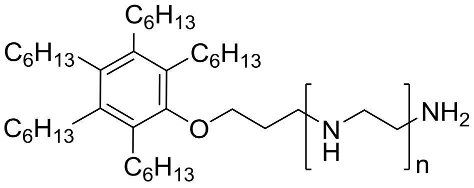

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Many barrier inhibitors are surfactant-like compounds, with polar head groups and long aliphatic tails. The polar head groups adsorb onto the metal whilst the tails stay in the transported material. This forms an effective coating that helps prevent corrosion of the covered metal. The film is commonly believed to work by changing the wettability of the surface. Adsorption of the surfactant results in a much more hydrophobic surface, helping repel water in the pipeline and without water present neither H_2S nor CO_2 are corrosive. The inhibitor can also desorb and encapsulate the water, working as an emulsifier to keep the water in the transported medium instead of seeking out the more polar metal surfaces.[131] This type of inhibitor requires constant addition to replenish the layer. If part of the layer starts to break down, it can lead to localized corrosion such as pitting.

Similar to barrier inhibitors, pipelines can be coated with a resistant material. Occasionally this is a more resistant metal such as zinc or cadmium but more often an epoxy or polymer layer. A range of materials exist for different applications, especially at the wellhead and other above ground equipment exposed to sour gas, but most coatings are not used for the pipelines themselves, as any breaks in the layer would require line downtime and high cost to replace.

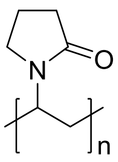
Inorganic inhibitors are relatively rare. Metals used include: vanadium, antimony, tin and bismuth.[132] As well as often being more expensive than their organic counterparts, they are all toxic metals and potentially environmentally damaging. This is problematic for workers and disastrous in the tragic event of a leak. Metal salts are electrochemical inhibitors, oxidizing damaged areas of the pipe and replenishing it.[133,134] The exact salt does not appear to matter as long as the oxidation state is correct. For example, as long as vanadium is in its plus 4 or 5 oxidation state, it is possible to use its oxides, halide, cyanates and sulfates to name but a few.[134] The selection of salt type does greatly change the inhibitors solubility and cost, so these factors must be taken into consideration. Many metal salts are added with alkanolamines to improve the corrosion resistance and dispersion.

The final corrosion inhibition technique is cathodic protection.[35] The aim of cathodic protection is to minimize the potential difference in the system that allows the corrosion to proceed. One method is a sacrificial anode. This involves adding an anode that is more reactive than the pipe. As reacting with the anode is more favorable, the anode corrodes whilst the pipe remains whole. The other method is impressed current cathodic protection. In this case the anode is essentially inert, for example a platinum electrode, and the potential difference is impressed by a power supply. To save on costs, it has been proven possible to power the electrode by solar energy, giving adequate protection from corrosion.[135] Cathodic protection is usually used in conjunction with a coating, helping prolong the coating's life and the coating further protects the surface of the pipe.

4.2 Hydrate Inhibition

In all pipelines, formation of clathrate hydrates is a significant concern and in sour systems they are even more likely to form. In mild climates working with sweet gas reserves, adding a hydrate inhibitor might not be necessary. Any small build up can be cleared by frequent pigging, that would also remove and sand or other any other contaminant that may have built up in the line.[136,137] Pigging involves pushing a usually metal, polymer or gel device, called a pig, down the pipeline either to clean, coat or detect defects in the pipeline. In colder environments and especially in sour gas fields, the pigging frequency required would no longer be cost effective and hydrate plugs can form fast enough to make pigging impossible.

Thermodynamic inhibitors, like methanol, are commonly used to prevent pipe blockages by clathrate hydrates. The requirement for very high loading, between 20 and 50 %,[138] makes them a very costly method of inhibition, though less costly than cleaning up after and repairing a ruptured pipe. A desire for a less high loading, and thus, less expensive, inhibitors started research into low dosage hydrate inhibitors (LDHIs). Water soluble synthetic polymers were tested as a method of inhibiting hydrate formation, as many such polymers were already in use for other applications so readily and cheaply available for testing. It was found by Colorado School of Mines that polyvinylpyrrolidone (PVP) **(15)**, a polymer already used for a wide range of applications from blood plasma expanders[139] to hair curling,[140] showed potential as a hydrate inhibitor.[138] Though PVP is not as effective as anti-freeze proteins at hydrate inhibition,[141] it is effective enough to prevent blockages during the timeframe and conditions required and the relative cost of production makes it much more desirable in an industrial setting. The low toxicity of PVP is an added bonus, as this would minimize the environmental impact of a pipe rupture, if one should occur. Replacement of methanol with PVP has been successfully implemented at many sites, including a Texaco site in southwest Wyoming for example.[142] These inhibitors are referred to as kinetic hydrate inhibitors (KHIs) as they do not make it thermodynamically unfavorable to form clathrates, just delay their formation until it is no longer a concern.



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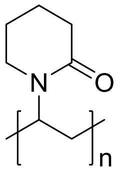

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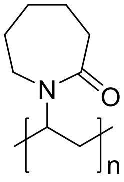
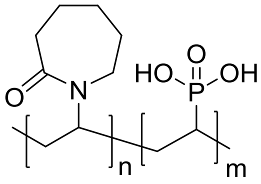


(17)

To further improve the efficiency of the inhibitor other similar compounds were tested. Polyvinylcaprolactam (PVCap) **(17)** shows a greater ability than PVP to inhibit hydrate formation, though the reason for this is not fully understood.[143] A range[144] of copolymers have also proven effective, an example of which being a vinylcaprolactam (VCap)/vinylpyrollidone (VP)/dimethylaminoethyl methacrylate terpolmer.[138] Copolymers show greater hydrate inhibition than PVP alone, whilst bringing down the costs of using solely the more expensive PVCap. Addition of a third type of monomer can impart other desirable properties, such as increasing the cloud point, corrosion resistance or helping improve compatibility with existing pipeline corrosion inhibitors. A VCap/phosphoric acid copolymer **(18)** is an example of adjusting the properties of PVCap by copolymerisations.[145] The phosphoric acid groups make the polymer an effective corrosion inhibitor and anti-agglomerant as well as a KHI, forgoing the need of multiple additives to control the corrosion and hydrate formation that occur in sour pipelines.

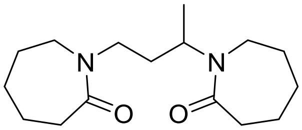


(18)

With PVP and PVCap being effective hydrate inhibitors, it would be expected that the 6-membered lactam analogue, polyvinylpipiridone (PVPip), also referred to as polyvinylvalerolactam **(16)**, would be so as well. Chua *et al.*[143] tested the hydrate inhibiting ability of PVPip compared to PVP and PVCap. They did find PVPip to be an effective inhibitor, better in fact than PVP. Though still less effective than PVCap. PVPip is not as effective as the current inhibitors, and the monomer is not commercially available, raising the cost. Though there are no examples of PVPip based polymers being used in an operating system, they have been patented for use as hydrate inhibitors,[146,147] so may come into use if economic considerations allow.

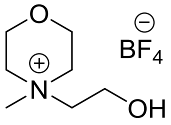
Inspiration for designing LDHIs can also be taken from nature, as a number of biological systems have developed natural antifreezes.[141,148] Cold water fish, such as winter flounder, live in polar regions, yet their blood does not freeze in the sub-zero temperatures they encounter. Antifreeze proteins, high in hydrophilic amino acids, prevent ice from forming in the blood.[148] Synthesis of these proteins has been successful and their ability of hydrate inhibition is as good as expected.[138] Unfortunately, it is not an economically viable option, with protein synthesis being costly and time consuming.

To further the understanding of the mechanisms in systems using polymers, it is often advantageous to use model compounds. Polymers are large and have a range of chain lengths making them difficult to study by common techniques such as NMR. Suitable models can be as small as a monomer up to moderate sized oligomers, with the longer chain lengths being more true to polymer, but harder to analyze. Davenport *et al.*[149] synthesized a vinylcaprolactam dimer **(19)**, which infrared spectroscopic analysis shows to interact with water in a very similar fashion to the polymer, making it a suitable model for the inhibitor. Simulating polymers can also be very computationally expensive so similar model compounds are used in simulations. Kuznetsova *et al.*[150] used up to a PVP octamer in their simulations with methane and water. Oligomers around this length have also been shown to be more effective as inhibitors than the larger polymers,[151] making an octamer a good model to choose when wishing to observe how hydrate inhibition occurs. They established that PVP does not interact with the surface of a forming hydrate, but may create a barrier between the aqueous and hydrocarbon phase. The barrier slows down diffusion of the natural gas into the water, slowing the onset of clathrate formation. Contrastingly, a small angle neutron study of PVP in water by Hutter *et al.*[152] concluded that PVP does adsorb onto the surface of the forming ice. Anderson *et al.*[153] proposed a two-step mechanism based on molecular dynamics simulations. The first step is that KHIs disrupt the local organization of the water molecules making nucleation much more difficult. The second step occurs after nucleation, the KHI adsorbs onto the hydrate blocking further growth. A number of different KHIs were modelled and they hypothesized that the more effective inhibitors would bind more strongly to the forming hydrate with the simulations agreeing. Molecular dynamic simulations by Moon *et al.*[154] however, do not come to the same conclusion. In their simulation the KHI, PVP in this case, does not bind to the forming hydrate. They state that the PVP resides in an environment independent of the hydrate and remains typically two solvation shells away from the hydrate. Instead it is concluded that PVP forms halos of ordered water around the lactam functionalities, which whilst being more ordered than bulk water, actually disrupt the ordering required for nucleation. These contrasting conclusions suggest that more research into the mechanism of hydrate inhibition is needed before the mode of action can be fully understood.



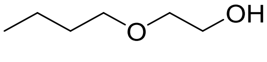
(19)

As all commercial KHIs are water soluble polymers, Kim[155] looked into non-polymeric alternatives. A range of ionic liquids were created with the criteria of being hydrophilic so they will be in the same phase as the water and possessing a hydroxyl or other oxygen based group to allow strong hydrogen bonding interactions with the water. In tests timing the onset of hydrate formation it was found that all the ionic liquids examined were effective. Hydroxyethylmethylmorpholinium boron tetrafluoride [HEMM][BF_4] **(20)** was particularly effective, offsetting clathrate formation for 107.5 min compared to the same loading of PVCap that offset formation for 43 min. By measuring the dissociation of clathrate hydrates formed in the presence of these ionic liquid it was shown that they also behave as thermodynamic inhibitors as well as KHIs, this has not been observed before in any other systems. Though promising, ionic liquids as KHIs have yet to be implemented due to their very high costs.



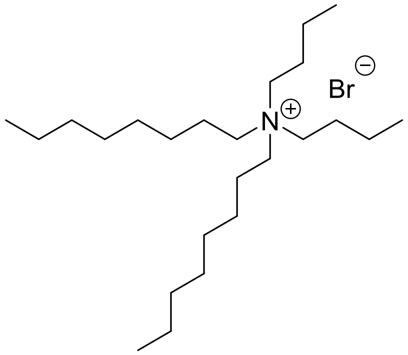
(20)

Most polymeric KHIs are not sold as pure polymer. The polymer powder is messy to handle and does not easily disperse in the pipeline, so is often sold in a solution. The solvent chosen can have a big effect on the efficiency of the inhibitor. Whilst some solvents may retard the inhibitor, others actually improve it. One such solvent is butoxyethanol **(21)** that can act as a synergist.[147]

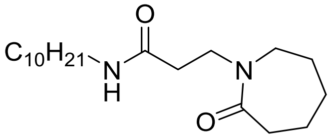


(21)

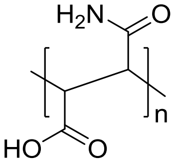
Butoxyethanol is also a weak hydrate inhibitor of a different class called anti-agglomerants (AA). AAs are surfactant like compounds that surround forming clathrates prevent them agglomerating. This allows the clathrates to be transported as a slurry, avoiding plugging.[156] Many AAs are long chain quaternary amines[157] **(22)**, occasionally with multiple aliphatic chains to help induce curvature and help with surrounding clathrate particles. AAs work at lower subcooling than KHIs, so can be used in cold conditions, though a disadvantage is that quaternary ammonium salts are often toxic.[158] There is research into creating biologically compatible and still cost effective alternatives, mostly focusing on neutral and zwitterionic compounds.[147] Kelland *et al.*[159] synthesized a range of alkylamides loosely based on the structures of known KHIs, for example caprolactam with a long alkyl chain **(23)**. Some of these, like the caprolactam derivative, are still toxic. But some, like those containing an acryloylpyrroldine head group **(24)**, give good inhibition and acceptable biocompatibility.



(22)

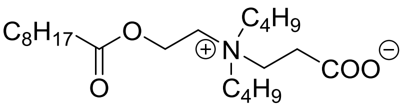


(23)

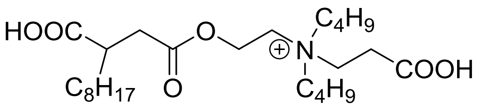


(24)

It was found that zwitterions **(25)** are much more biologically compatible than the corresponding quaternary ammonium salt with free ions.[147] Unfortunately, their ability as an AA was significantly hampered by attaching the anion. Addition of a second carboxyl group **(26)** placed further away from the head group increases the inhibition ability. It is suggested that the charge can be localized on the second carboxylic acid group, much further away from the cationic head group. This is closer to the traditional quaternary ammonium salts in which the anion is free to move away from the head group.



(25)



(26)

It has been suggested that the presence of acid gases can decrease the efficiency of some hydrate inhibitors.[28] However, there are no published studies showing whether this problem arises because the sour components prevent the KHI functioning properly, or that more inhibitor is required in a sour system because of the increased likelihood of clathrate formation in the presence of good guest species such as H_2S (see section 2.2). In contrast, the efficiency of AAs is the same irrespective of gas composition. This is possibly because they do not stop hydrates forming, so the promotion of hydrate formation does not affect the AAs operation. This makes AAs often a more desirable choice in sour systems. Though there are examples of sour systems where KHIs have been successfully implemented.[28] Blends of MeOH and 5-10 % KHI were used successfully in three different gas fields, reducing the required methanol injection by around 65 %, showing KHIs to still be an effective method of hydrate inhibition in sour systems.

The interactions between hydrate inhibitor and corrosion inhibitor can greatly hamper the efficiency of one, or both, of the additives. Which inhibitors are compatible is well studied, with each company establishing a combination of additives that work without any disruption to either's capability. Unfortunately, none of the published literature names what any of the additives are for reasons of intellectual property, making a scientific analysis of why some combinations are disruptive impossible.[136,160,161] Though hydrate and corrosion inhibiting polymers, such as the PVCap/phosphonic acid copolymer (**18**), could be an effective solution to this difficulty.[145]

5 Conclusion

As sweet gas fields are becoming few and far between, it is becoming essential that the sour fields are used, even with the potential dangers and difficulties they raise. The toxicity of H_2S can be avoided by careful site practice and the other hazards, such as clathrate hydrate formation and pipeline corrosion, can be prevented by removal of the acid gases or inhibiting their effects.

An extensive range of methods and ideas to remove or inhibit acid gases have been explored over the years, with chemical and physical solvent based approaches being among the most common. Some of the most effective methods involve a combination of multiple approaches and there remains considerable scope for improved processes, scavengers, membranes and inhibitors. With the increased need for using sour gas fields, surely more innovative combinations and new ideas will surface in the future, however the unreactive nature of CO_2 and the high toxicity of H_2S coupled with the relative large amounts of each gas that must be removed and disposed of makes the area an ongoing challenge.

6 Acknowledgements

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7 Abbreviations

AA, anti-agglomerant; aMDEA, activated alkanolamines; CFZ, Controlled Freeze Zone; DEA, diethanolamine; DEPG, dimethyl ether of polyethylene glycol; EDTA, ethylenediaminetetraacetic acid; H, hexagonal structure; HEMM, Hydroxyethylmethylmorpholinium; Ih, ice phase; KHI, kinetic hydrate inhibitor; LDHI, low dosage hydrate inhibitor; MDEA, methyldiethanolamine; MEA, monoethanolamine; NMP, N-methyl pyrrolidone; NMR, nuclear magnetic resonance spectroscopy; PC, propylene carbonate; PVCap, poly(N-vinylcaprolactam); PVP, poly(N-vinylpyrrolidone); PVPip, poly(N-vinylpiperidone); T, trigonal structure; VCap, N-vinylcaprolactam; VP, N-vinylpyrrolidone; VpCI, vapor corrosion inhibitor.

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