Tail gas treatment of sour-SEWGS CO_2 product

H.A.J. van Dijk

Juni 2012
ECN-E--12-025

Acknowledgement

This literature review has been performed as part of the EDGaR *Effect of impurities in $C0_2$ on the CCTS chain optimisation* project (proj.nr. 5.0889).

Abstract

This literature review covers the technologies suitable for the CO_2-H_2S separation within the context of CO_2 purification of a pre-combustion captured stream intended for storage or reuse.

The technologies considered cover existing industrially applied processes, emerging processes as well as processes in development. Several technologies capable of achieving the desired CO_2-H_2S separation were identified. Among them are liquid scrubbing processes Thiopaq and CrystaSulf producing elemental sulphur, selective oxidation to elemental sulphur such as MODOP or based on novel catalysts and sorbent-based (reactive) separations using low-, medium- or high-temperature (reactive) sorbents.

Contents

Summary

Within the EDGaR CO_2 purity project, a literature research was conducted on technologies suitable for CO_2-H_2S separation. The CO_2 results from pre-combustion capture and is intended for geological storage or reuse. The separation involves the removal of typically 1% H_2S from a concentrated CO_2 stream, preferably to <10 ppm.

Industrial processes as well as emerging technologies and research topics were reviewed. Industrial processes cover scrubbing technologies based on chemical, physical and hybrid solvents as well as Claus and related downstream processes. Emerging technologies are related to high-temperature sorbent based systems, liquid scrubbing technologies combining unconventional solvents with elemental sulphur formation, and alternative catalysts for the selective oxidation of H_2S to elemental sulphur. Research topics with potential but at an early stage of development include thermal and electrochemical H_2S decomposition.

For our application, the scrubbing technologies prove unsuitable due to their low H_2S selectivity. Considering Claus tail-gas-treatment technologies, only the MODOP selective oxidation process is promising, together with novel liquid scrubbing applications Thiopaq and CrystaSulf. Nevertheless, promising novel catalysts for the selective oxidation have recently been researched. Considering sorbents, several promising routes can be identified, being i) low temperature PSA with novel sorbents aiming at circumventing the generally observed low H_2S selectivity over CO_2 for conventional sorbents, ii) medium temperature hydrotalcite-based sorbents being developed at ECN, showing promising H_2S sorption characteristics under specific conditions, and iii) high temperature reactive sorbents capable of removing H_2S while resulting in SO_2 upon oxidative regeneration.

1 Introduction

Within the sour-SEWGS scheme, all inorganic sulphur is bound to end up in the CO_2 product stream. This is schematically represented in **Figure 1**. Besides H_2S, this product stream will also contain a certain amount of syngas. The typical characteristics of the CO_2-rich product stream are represented in **Table 1**.

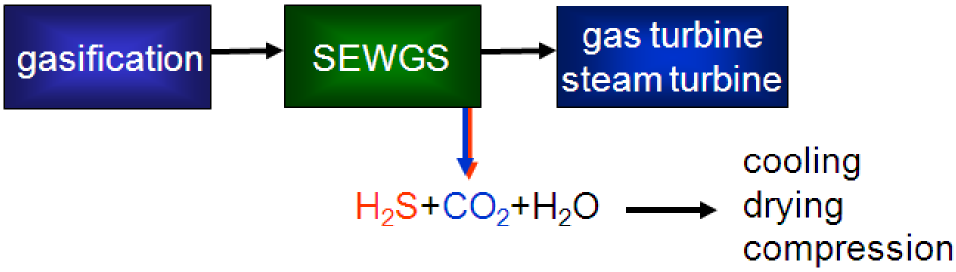

Figure 1: Schematic representation of the fate of H_2S within the sour-SEWGS technology

	Sour-SEWGS feed		Sour-SEWGS product		CO_2 product	
CO	*6*	*%*	*<5*	*%*	*?[a]*	
CO_2	*24*	*%*	*35*	*%*	*>95*	*%*
H_2	*35*	*%*	*<5*	*%*	*?[a]*	
H_2O	*34*	*%*	*60*	*%*	*<100*	*ppm*
H_2S	*2000*	*ppm*	*2500*	*ppm*	*?*	
T	*400*	*°C*	*400*	*°C*	*Ambient*	
P	*25*	*bar*	*1*	*bar*	*110*	*bar*

a this number cannot be specified in detail at this moment. However, it is believed that total volatile composition must be <5%

Table 1: Comparing SEWGS feed and CO_2 product compositions

Prior to transport of the CO_2 product, the captured CO_2 stream generally needs conditioning, consisting minimally of drying and compression. The gas conditioning system has to deal with 3 types of components: water, volatile and condensable components [1].

Volatile components comprise a.o. N_2, Ar, O_2, H_2, CO, NO and CH_4. The content of these components in the CO_2 product can be decreased by flashing or distillation. When applying flashing, a CO_2 recovery of >90% and a CO_2 purity of 95% is readily achieved. Using distillation, however, the CO_2 purity can be boosted to >99%. Moreover, if the content of inerts is small, the volatiles-rich off-gas can be recycled back to the CO_2 capture unit. This assures no loss in CO_2 capture ratio and the reuse of fuel components such as H_2, CO and CH_4. Since with the SEWGS technology the N_2 basically ends up in the H_2, no build-up of N_2 is risked when applying full off-gas recycle. Aspelund and Jordal [1] mention that the capture technology and the volatile recovery within the gas conditioning section should be optimized simultaneaously. In other words, striving for maximal CO_2 purity within the SEWGS system might not be required when considering the entire chain.

Condensable components, having a boiling point in the same range as CO_2, typically are propane, ethane, H_2S, NO_2 and SO_2. Accordingly, these components cannot easily be removed by flashing or distillation and will end up in the CO_2 product unless additional cleaning is applied. Recently, Air Products [2] and the Vattenfall group [3] reported on SO_2 and/or NO_x removal within the CO_2 compression unit. Both components are oxidized in a wet environment towards their acid form (H_2SO_4, HNO_3) with >90% conversion when sufficient residence time is allowed. This technology is reported to be promising to reach high CO_2 purities while the requirements for $DeSO_x$ and $DeNO_x$ units upstream the CO_2 conditioning unit can be relieved. For H_2S, no specific clean-up technologies are mentioned.

The present literature overview presents the technology options for the sour-SEWGS downstream CO_2-H_2S separation. Such a clean-up technology could be applied anywhere within the chain of Sour-SEWGS off-gas to CO_2 product ready for pipeline injection. Typical conditions for the sour-SEWGS CO_2-rich product and the CO_2 ready for pipeline injection are summarized in **Table 1**.

One preliminary question would be: is there a desired S-containing product to be recovered from the H_2S-CO_2 separation unit? Basically, 3 bulk-materials can be produces, being i) elemental sulphur, ii) sulphuric acid and iii) gypsum ($CaSO_4.2H_2O$). All three products are bulk materials and therefore have relatively low commercial value.

Around 75 Mt of elemental sulphur are globally produced on an annual basis, primarily as an involuntary by-product from oil and gas processing [4]. Over 70% of sulphur is used in the production of sulphuric acid for phosphate fertilisers, in addition to a variety of industrial uses, including metal leaching. Sulphur is important to a wide range of industries. Both supply and demand for sulphur correlate strongly with global development. On the demand side, the need for new infrastructure and food for a growing population directly impacts the industry, as sulphur is required in order to produce certain fertilisers for crops, as well as base materials used in construction. On the supply side, additional sulphur production capacity enters the market when new oil and gas processing capacity comes on stream. Since late 2008, pricing had been volatile in the global sulphur market. That volatility is expected to continue for the next few years as a result of tight supply-demand market conditions.

Globally, over 200 Mt of sulphuric acid are consumed on an annual basis [5]. Most sulphuric acid is produced on purpose through sulphur burning for captive use by users including the phosphate fertilizer and base metal sectors. The product is also required in a wide variety of speciality and industrial products such as pulp, paper and batteries. In addition to the burning of sulphur, sulphuric acid is produced as involuntary by-product through the smelting of base metals including copper, nickel and zinc. Smelters are prevalent in Europe, South Korea and Japan. Very similarly to elemental sulphur, demand for sulphuric acid correlates strongly with global development. The need for new infrastructure and food for a growing population directly impacts the industry, as sulphuric acid is required in order to produce certain fertilizers for crops, as well as base metals used in construction. Sulphuric acid is an important raw material for a wide variety of sectors and the outlook is for stable supply and demand conditions.

Global consumption of gypsum was 216 Mt in 2008 [6]. Demand for gypsum is closely linked to general economic activity due to its use in construction in plasterboard, plasters and cement. Overall, world consumption of gypsum dropped 4% between 2006 and 2008, a total reduction of 8Mt, as a result of the global financial crisis and associated recession. Plasterboard and cement production are expected to take at least 2-3 years to regain the 2006 peak levels, but full economic recovery will see growth rates of between 4 and 7%py for cement and plasterboard respectively. Global consumption of gypsum could reach over 300Mt by 2015. Although natural gypsum still dominates the market, use of synthetic gypsum has grown rapidly during the past decade in particular. Three factors are responsible for this major shift in the market; stricter environmental regulations at coal-fired stations resulting in increased output of FGD gypsum, the high cost of environmental measures and resistance to accumulation of waste motivating power companies to sell usable waste products, and the low cost of FGD gypsum compared to natural gypsum. In the future, increased use of FGD and other suitable waste gypsum materials is assured for manufacture of plasterboard, plaster, cement and other materials.

2

Acid gas removal technology

2.1 COS, CS_2 and SO_2 conversion

For tail-gas treatment in a Claus plant, the conversion of COS and CS_2 to H_2S is an important step to increase the total sulphur recovery to 99.9+% levels. Basically 2 processes can be applied: hydrolysis and hydrogenation.

COS hydrolysis is slightly exothermic equimolar reaction:

$$COS\ +\ H_2O \rightarrow CO_2 + H_2S \qquad \Delta H_r =\ -31\ kJ/mol \tag{1}$$

COS hydrolysis is complete at typically 175-275°C and proceeds on activated alumina, titania and zirconia catalysts [7,8]. The main reason for catalyst deactivation is sulphate formation, for which alumina appears to be most sensitive. The hydrolysis of CS_2 is more difficult than that of COS, requiring higher operating temperatures of >300°C. An example of a COS hydrolysis catalyst, Porocel has activated alumina-based catalyst (Hydrocel 640), promoting the COS hydrolysis reaction without promoting reaction of H_2S and CO to form COS and H_2.

The hydrogenation is performed on a CoMo/Al_2O_3 catalyst within the SCOT process, operating at typically 300°C. The COS and CS_2 are mainly hydrolized to H_2S, while elemental sulphur and SO_2 are converted via hydrogenation. In industrial operation of such a hydrogenation reactor in a SCOT unit, a stoichiometric excess of H_2 leads to <10 ppm SO_2, 1 ppm CS_2 and <10 ppm COS [8].

2.2 H_2S removal via solvents

Acid gas removal can be done via wet scrubbing. There are 3 types of solvents, namely chemical, physical and hybrid solvents [8,9]. Chemical solvents involve amines that chemically react with acid gasses such as H_2S and CO_2. As a result, the solvent loading is relatively independent of the adsorption pressure, making them the preferred solvents at low (partial) pressures. Accordingly, deep H_2S removal is possible at low feed pressure. Physical solvents involve methanol (Rectisol) or glycols (Selexol). The physical dissolution of the acid gasses obeys Henry's law, making them more efficient at higher system pressures. Hybrid solvents (e.g. Sulfinol) try to combine the best of both the chemical as the physical solvents.

In general, most systems applied today are used for treatment of syngas, refinery gasses, or natural gas. Several hundreds of MDEA plants exist, 55 Selexol plants have been installed, over 200 Sulfinol units have been licensed, and more than 100 Rectisol units exist. Most of the applications deal with H_2S removal, although applications for combined CO_2 and H_2S removal are also exploited. Depending on the application and feed composition, a H_2S rich gas suitable for standard Claus processing can be produced. For deep H_2S removal, COS hydrolysis is often required since for all solvent processes the COS solubility is much less than that for H_2S. For chemical production, where the catalyst processes are sulphur sensitive, Rectisol is mostly used since it capable of achieving <0.1 ppm H_2S.

For all solvent processes, the feed can be dehydrated to some extend because of the relatively low temperature of operation. This is especially the case for physical solvents.

2.2.1 Chemical solvents

Going from mono to secondary to tertiary amines the corrosiveness of the aqueous solvent decreases, the reactivity with COS decreases, and the H_2S/CO_2 selectivity increases. The H_2S adsorption rate is instantaneous, while the CO_2 adsorption rate is much slower. Accordingly, amine scrubbers systems are relatively compact and can be relatively easily operated for selective H_2S removal, which is especially true when using MDEA because of it has the slowest CO_2 reaction rate (1000 times slower than MEA). The regeneration of the sorbent for CO_2+H_2S is done via evaporation of the solvent using steam as heating medium. In general, the steam consumption for amine systems is much larger than for physical solvents, although the electricity use is less. Since amine are diluted in water, high steam consumption results during regeneration. In case the H_2S content must be increased for downstream Claus, flashing of the solvent for CO_2 removal before stripping might be employed.

In general, amine systems produce a Claus stream leaner in H_2S than for physical solvents. For feeds with high CO_2/H_2S ratios, such as IGCC syngas (excluding raw syngas form Shell gasification), amine systems are normally not capable of producing suitable Claus feeds and an acid gas enrichment unit (AGE) is required. For natural gas, the H_2S

content can be much higher and amine systems directly produce a suited Claus feed. Often, treated syngas still contains in the order of 100 ppm H_2S, while 10-20% of the CO_2 is also removed from the IGCC syngas. Additives may be applied to improve the H_2S/CO_2 selectivity. Such a modified MDEA with feed of 12% CO_2, 5500-7800 ppm H_2S is reported to desulphurise to <4 ppm H_2S with 30% CO_2 removal. The calculated Claus feed composition would then be 13-18% H_2S in CO_2.

Although besides the objective of this literature study, amine systems may also be designed for high CO_2 and H_2S removal efficiencies. The CO_2 removal must then be boosted by means of additives. At high P_{CO2} amine solvents act as pseudo physical, and flashing can be applied to already remove large part of CO_2 prior to steam stripping.

An interesting amine system for our application of removing H_2S from CO_2 is the Flexsorb SE process. It uses hindered amine rather than MDEA and is intended as tail-gas treatment system in a Claus plant for H_2S removal with minimization of CO_2 content of the H_2S rich recycle to the Claus plant. Other applications involve Acid Gas Enrichment systems (increasing H_2S content of CO_2-H_2S streams from other solvent systems) and NG treatment. Compared to MDEA, the recirculation rate is lower, leading to a lower utility consumption for solvent regeneration. A Flexsorb brochure from ExxonMobil mentions it requires little more than half of the energy compared to an MDEA system [10]. The H_2S levels in the treated gas can be as low as 10 ppm (Flexsorb SE Plus). For the application in an Acid Gas Enrichment unit, the enrichment performance is represented in **Figure 2**. It can be seen that even with this highly selective H_2S solvent, the H_2S content in our application is too low to directly go to Claus feeds. Moreover, the CO_2 loss via co-capture is significant.

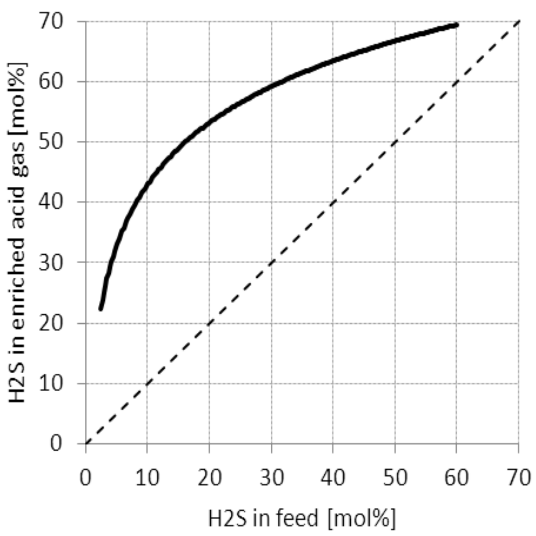

Figure 2: H_2S enrichment of a AGE unit using Flexsorb SE Plus [11]

The most widely applied amine-based Claus tail-gas unit is the SCOT (Shell Claus Off-gas Treatment) process. It is basically a MDEA scrubber applying low adsorber contact times to minimize CO_2 co-adsorption (kinetic separation). For a Claus off-gas, about 10-40% of the CO_2 form the feed is co-adsorbed and H_2S levels of the treated gas can be as low as 10-400 ppm.

2.2.2 Physical solvents

The most common physical solvent systems are Rectisol, using methanol, and Selexol, which is glycol-based. Commercially, there a several other systems (e.g. Purisol, Fluor Solvent polypropylene carbonate) and even more solvents have been and are being studied [8,9].

The regeneration of physical solvents for CO_2 is by means of pressure release. Normally this is done in stages, already producing CO_2 streams at pressure. For bulk CO_2 removal, depressurization is normally sufficient. If deep CO_2 removal is required, stripping with air or N_2 can be applied. Regeneration for H_2S is done by means of stripping with inert gas or steam. If deep H_2S removal at appreciable inlet concentrations is desired, solvent thermal regeneration might be applied. Steam stripping or thermal regeneration are also preferred if downstream processes require high H_2S contents. In general, the hydrocarbon dissolution in physical solvent systems is much larger than for chemical solvent systems. In physical solvents the C_3^+ fraction is almost completely dissolved, while CH_4 can be dissolved as much as 10% of the feed content. They are released from the solvent together with the CO_2 upon pressure release. This is not the case for aromatics, which tends to accumulate in the solvent. Since IGCC syngas hardly contains hydrocarbons, this does not pose a problem. This is of course quite different for NG applications. COS, CS_2 and mercaptans are also quite soluble and thus removed. In a 2-stage process, a first adsorption-regeneration section removes H_2S (steam stripping for H_2S regeneration) and a second adsorption-regeneration section removes CO_2, see **Figure 3**.

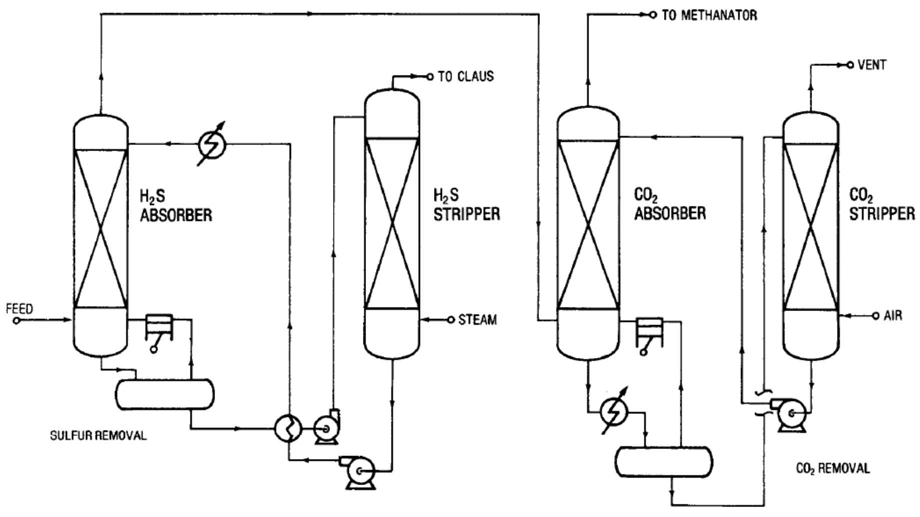

Figure 3: Schematic layout of a Selexol unit for separated H_2S and CO_2 removal [8]

Rectisol always requires refrigeration of the solvent, but is capable of achieving very low H_2S slips of <0.1 ppm. It can also cope with COS. Therefore, it is the preferred system in case the cleaned syngas is intended for chemicals production (e.g. methanol, Fischer-Tropsch). Drawbacks are that the process scheme of a Rectisol plant is relatively complex and refrigeration costs can be high.

In case a Selexol unit is intended for selective H_2S removal, no refrigeration is required. The unit then consists of an adsorber, a flash and a steam heated regenerator. The flash product (CO_2 rich) is then compressed and sent back to the adsorber feed. If both CO_2 and H_2S removal is required, refrigeration is normally applied. A Selexol unit is capable of achieving H_2S removal to typically 10-20 ppm in an IGCC.

Concluding:

- For IGCC syngas, if bulk H_2S removal is required without CO_2 removal for relatively low pressure feeds (<30 bar), MDEA is considered a low cost option. Deep H_2S removal will invoke CO_2 coadsorption.
- At higher pressures, Selexol becomes increasingly attractive.
- For removal of both CO_2 and H_2S, Selexol is more favourable than amine systems.
- Rectisol is considered as most expensive and only suitable when deep H_2S removal is required.

2.2.3 Hybrid solvents

In hybrid or mixed solvents, an amine is mixed with the physical solvent in order to combine the large capacity of physical solvent with the amine's ability for deep acid gas removal in a single step [9]. The most known mixed solvent is the Sulfinol process. The sulphur compounds in the product gas can be reduced to low ppm levels. This process has been developed specifically for treating large quantities of gas, such as natural gas, which are available at elevated pressures. The solvent is composed of Sulfolane, DIPA or MDEA and water. The acid gas loading of the Sulfinol solvent is higher and the energy required for its regeneration is lower than those of purely chemical solvents. A Sulfinol-M process is used for selective absorption of H_2S, COS and mercaptans, while co-absorbing part of the CO_2. Chiyoda Corporation, an authorized licensor for the Sulfinol process has designed Sulfinol-X that can remove acid gas and organic sulfurs in a single absorption column, thereby eliminating the need for organic sulfur removal at a later stage.

3

Claus process

3.1 General description

The Claus process is the most important industrial process for sulphur recovery [8,12]. In short, a H_2S-rich process gas is converted into elemental sulphur with up to 99.5% sulphur recovery. The recovered sulphur is generally of high quality, but due to excess availability hardly has any economic value.

In the original process, the Claus reaction was a catalytic single step selective oxidation (also referred to as direct oxidation):

$$H_2S + {}^{1}\!/_{2}\, O_2 \rightarrow {}^{1}\!/_{n}\, S_n + H_2O \tag{2}$$

Because the heat of reaction was dissipated by radiation alone, sulphur yields of 80–90% were possible only if the H_2S space velocity was low. Processing capacity was not significantly increased by installing cooling coils within the catalyst bed, nor by recycling cooled waste gas through the reactor.

In 1930's IG Farben industry in Germany introduced a revolutionary development which gave improved efficiency at much higher space velocities and also allowed waste heat to be recovered as steam. This consisted of separately stoichiometric burning one-third of the H_2S to SO_2 in a flame, cooling the hot gases in a waste heat boiler, and introducing them, with the remaining two-thirds of the H_2S, to the catalytic reactor at 200–300°C. Later, this was modified so that the entire H_2S-rich stream enters the burner and only enough air is fed to burn 1/3 of the H_2S. Following the burner, heat is reclaimed and the first sulphur condensation occurs. Then one, two, or three further catalytic stages, in which the gases leaving the sulphur condenser of the previous stage are reheated and passed through another catalytic reactor, followed by another sulphur condenser. This version has become known as the modified Claus process, but is nowadays simply referred to as the Claus process. A total sulphur recovery of 92–94% is typically reached.

The reactions taking place are:

$$H_2S + {}^3\!/_2\, O_2 \rightarrow SO_2 + H_2O \qquad \text{Combustion} \qquad (3)$$

$$2\,H_2S + SO_2 \leftrightarrow {}^3\!/_n\, S_n + 2\,H_2O \qquad \text{Claus equilibrium} \qquad (4)$$

$$H_2S + {}^1\!/_2\, O_2 \rightarrow {}^1\!/_n\, S_n + H_2O \qquad \text{Overall} \qquad (5)$$

Because of the Claus equilibrium reaction, sulphur condensers are required to allow the thermodynamically limited H_2S-SO_2 reaction to proceed. Typically, the chemical reactions involved do not go to completion, rendering the process sensitive to any perturbations. Despite the enormous accumulated experience in design and operation of Claus plants, the process is inherently difficult to maintain at full efficiency.

3.2 H_2S equilibrium chemistry

Elemental sulphur is known to consist of several species, ranging from S_2 to S_8. At low temperature S_8 is abundant, while S_2 prevails at high temperature, as can be seen in the left hand side of **Figure 4**. At low temperature, therefore, the partial pressure of sulphur is lower than at increased temperature.

For a stoichiometric air-H_2S mixture the equilibrium H_2S conversion is given on the right hand side of **Figure 4**. At the lower temperature of this figure (<400°C), the equilibrium between O_2 and H_2S is shown. Due to the splitting of S_8 into molecules with fewer S-atoms, the partial sulphur pressure increases and the equilibrium H_2S conversion drops sharply.

Above 550-600°C, this effect tails of as the predominant elemental sulphur species is S_2. The increase in H_2S conversion at increasing temperature then results from the thermal decomposition equilibrium of H_2S into elemental sulphur. This is the main mechanism by which sulphur is produced in the sulphur furnace. When the hot gas from the burner is cooled, the sulphur conversion at first drops to the minimum represented on graphic, as the dissociated hydrogen and sulphur recombine, and then rises along the left portion of the curve, as the oxidation of hydrogen sulphide progresses. However, as the temperature is lowered, the reaction becomes progressively slower until, below about 350°C, it is too slow to be of practical use. At this temperature, the best theoretical yield (assuming the system has reached equilibrium) is only about 80–85 %. It is not possible to increase burner conversion efficiency by using excess oxygen, because although a great proportion of the H_2S reacts, it forms SO_2 rather than sulphur. Conversion is, however, favoured, if the hydrogen sulphide is highly concentrated, and it is further increased if the nitrogen content of the combustion air is reduced or eliminated altogether. Because of the equilibrium reaction, a high moisture loading in the feed gas has a detrimental effect on conversion efficiency.

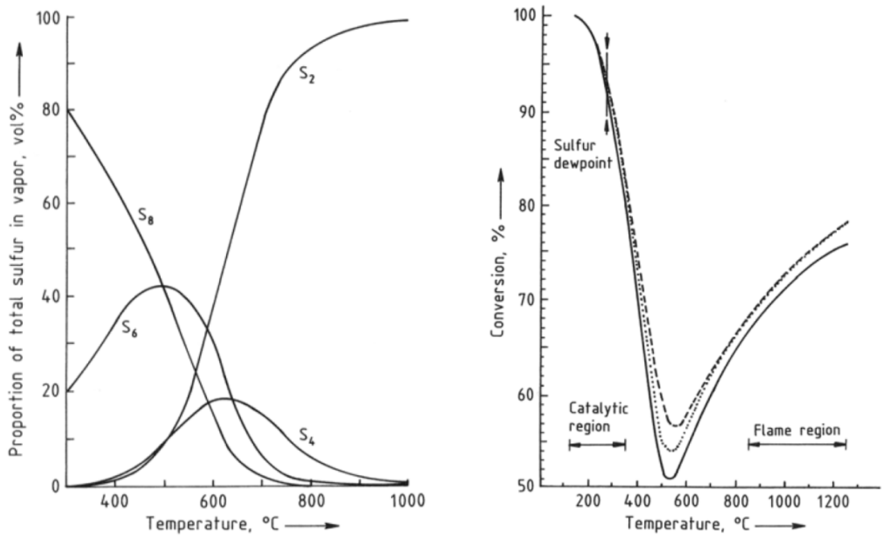

Figure 4: H_2S conversion and sulphur composition according to temperature [12]

The function of the downstream cascade of sulphur condensers and catalytic stages is to increase the sulphur yield along the low temperature side of the right-hand curve of **Figure 4**.

Side reactions [7,8,12] in the burner are the formation of COS, CS_2 and SO_2. These are partially again hydrolysed or hydrogenated to H_2S in the first catalytic Claus reactor, which is normally operated at a slightly higher temperature to do so. The burner also effectively removes components such as NH_3, HCN and hydrocarbons when it is operated at sufficiently high flame temperature and residence time. The destruction of hydrocarbons within the burner prevents deactivation of the downstream Claus catalyst. Removal of NH_3 prevents ammoniasulfite deposition in downstream equipment.

3.3 Claus plant configurations

In **Figure 5** a standard process configuration for a Claus unit is represented. It consists of a burner, followed by a sulphur condenser and a cascade of 3 catalytic stages each followed by a sulphur condenser. This configuration can reach sulphur removal efficiencies of up to 98% when a highly concentrated H_2S feed of >70% is used and drops to 96% at 40% H_2S feeds [8]. For feeds containing 20-40% H_2S, a split flow configuration is often applied to maintain high sulphur recoveries of 94-96%, in which 1/3 of the feed is fed to a burner to produce the SO_2, while the rest of the feed bypasses the furnace. A drawback is that the pollutants in the bypass flow (e.g. hydrocarbons, NH_3) enter the Claus catalysts, potentially causing catalyst hot-spot formation and deactivation. Below about 15% H_2S content in the feed gas other means have to be used to maintain a stable temperature in the furnace, such as feed air preheating or oxygen enrichment. Such a lean H_2S feed gas results in low sulphur recovery efficiencies and high unit costs. Besides, oxygen-blown Claus is regularly also applied to improve the flexibility of the plant with respect to the feed composition. Often, this still covers enriched H_2S feeds of 40-70%. Since O_2-enrichment mainly focusses on stabilization of the flame, the sulphur recovery is hardly increased. For H_2S lean feeds (<15%), therefore, installing an acid gas enrichment unit (amine unit) followed by a standard Claus is often more economical.

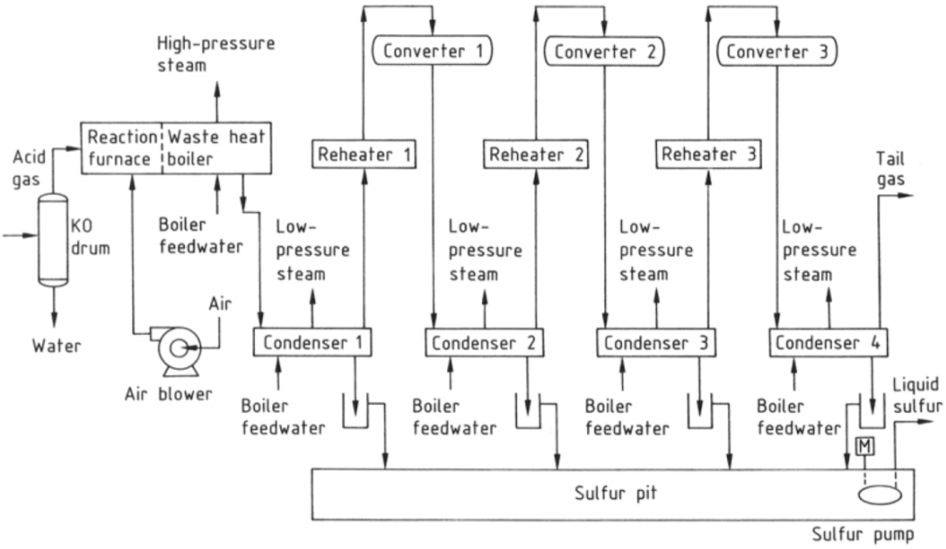

Figure 5: Claus plant schemas Straight-Through Configuration [8]

3.3.1 Adaptations to the Claus process

There is a large range of technologies to improve the overall sulphur recovery from a Claus plant, see **Figure 6**. More than 25 processes are commercially available, based on catalytic conversion or enrichment via solid sorbents or solvents.

One way to boost the sulphur recovery of the Claus process to 99-99.7% is to adapt to the Claus unit itself. In the extended-bed Claus processes, the adaptation is the addition of an extra catalytic stage at the end of the Claus process. This can be gas phase catalytic processes such as the SuperClaus and EuroClaus, or sub-dewpoint processes such as the e.g. the Sulfreen process.

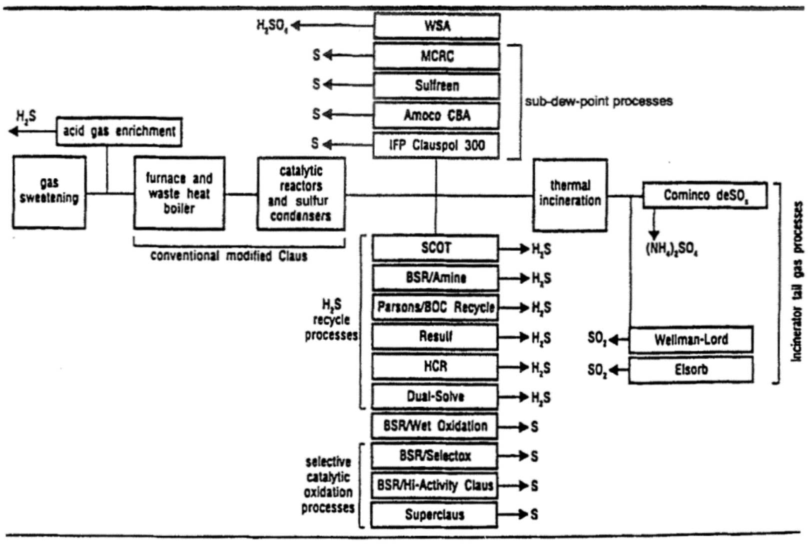

Figure 6: Technology options to improve sulphur recovery from Claus plant [ref in 7]

In the Super-Claus process a direct oxidation catalytic stage is added downstream the last catalytic Claus reactor. The Claus burner is operated with a lower O_2 feed than normal, resulting in a higher H_2S and much lower SO_2 content of the gas leaving the last Claus stage. This allows an efficient direct oxidation of H_2S to elemental sulphur in the direct oxidation catalytic stage, boosting the overall sulphur recovery up to 99% (SuperClaus-99). The catalyst (a.o. FeCr-oxide/Al_2O_3) generally has a H_2S conversion >85% and is insensitive to excess air and steam, and does not promote the (reverse) Claus reaction nor COS and CS_2 formation. In fact, at least a 10-fold of excess O_2 is required for catalyst stability. An even higher recovery of 99.5% (SuperClaus-99.5) is reached when a hydrogenation reactor is installed upstream the direct oxidation reactor in order to optimize the H_2S content. In this case, the Claus burner is operated with the conventional amount of air. In the similar EuroClaus process, the syngas present in the feed is used to reduce the SO_2 not only to H_2S but also to elemental sulphur. Following sulphur condensation, the feed mainly contains H_2S as sulphur species, which is further reduced in a direct oxidation reactor.

The MODOP process is basically another extended-bed Claus process, applying catalytic direct oxidation. First the Claus tail gas is hydrogenated to convert COS, SO_2 and CS_2 into H_2S at about 280°C. The gas is then cooled and water is condensed, since water is a main problem for the direct oxidation reaction and decreases sulphur recovery rate [13]. After the addition of stoichiometric amounts of air the H_2S is converted to sulphur by direct oxidation aver a TiO_2 catalyst at a temperature above 250-280°C. About 90% of H_2S is converted to elemental sulphur, which is recovered as a liquid on cooling the gas in a condenser. If higher recoveries are required, additional oxidation stages may be added. The vent gas leaving the final condenser is incinerated before it is released to the stack.

SulfaTreat DO is a catalytic direct oxidation process developed by TDA Research, capable of dealing with H_2S containing streams ranging from a few ppm to 3%. The O_2 feed is typically stoichiometric. At least 90% H_2S conversion and 99% selectivity is reported. The steam content of the feed does not influence the catalyst operation. The catalyst is a proprietary supported base metal oxide.

In contrast to the above mentioned processes, the addition of a sub-dewpoint catalytic stage can also be applied. Among such processes are Sulfreen (Lurgi and SNEA), CBA (BP Amoco), and MCRC (Delta Hudson). The processes are very similar, with the exception of how the regeneration gas stream is handled. In the sub-dewpoint catalytic reactors, the equilibrium is pushed to the product side while sulphur condenses on the Claus catalyst. At an operating temperature of 125–150°C, the sulphur recovery is increased to 99.5%. Cyclic regeneration with a hot stream is required for recovery and ensures sustainable catalytic activity. A further improvement to 99.5–99.7% recovery is reached when the COS and CS_2 are converted into H_2S prior to the sub-dewpoint reactor (Hydrosulfreen). In another variant, a downstream direct oxidation reactor is installed to further convert the H_2S to elemental sulphur at temperatures comparable to the Sulfreen process (Doxosulfreen). The upstream process is steered such that the H_2S content is higher and SO_2 is lower than normal, resulting in an efficient operation of the direct oxidation stage. Total sulphur recoveries of 99.9 % can be reached.

Another adaptation of the Claus process concerns the burner. In the Selectox process, the Claus burner is replaced by catalytic stage to burn 1/3rd of the H_2S into SO_2, followed by the Claus catalytic stages with intermediate sulphur condensation. The recycle Selectox process is designed to treat lean acid gas streams, typically containing 40 mol% H_2S with an overall sulfur recovery of 94–97%. For the once-through configuration, the incoming H_2S content can be as low as 1-5%. At these low levels, however, the sulphur recovery is also lower at 85-90%.

3.3.2 Claus tail-gas treatment

Besides the adaptation of the Claus process itself, another way of boosting the sulphur recovery of the Claus process is to implement a tail-gas treatment process. These technologies can be subdivided into separation and reaction processes.

A established separation processes is the SCOT process, in which SO_2, COS and CS_2 present in the Claus tail-gas are converted into H_2S via hydrogenation/hydrolysis over a CoMo/Al_2O_3 catalyst. The required syngas is often already present in the Claus tail-gas. The H_2S is then washed by an amine scrubber and send back to the feed of the Claus unit. As **Figure 6** illustrates, more commercial processes are based on H_2S separation and recycle. Alternatively, all sulphur components in the Claus tail-gas are incinerated to SO_2, which is then washed and recycled back to the Claus unit (Clintox process). In the Wellman–Lord process the SO_2 generated by incineration is not send back to the Claus process but further processed to elemental sulphur, sulphuric acid or liquid SO_2 within a separate unit.

Another tail-gas treatment is the Wet Sulphuric Acid process by Haldor Topsøe [14,15], which incinerates the tail-gas and catalytically oxidizes the SO_2 further to SO_3, followed by SO_3 hydration to gaseous sulphuric acid and sulphuric acid condensation. All these processes are highly exothermal and the plant can be operated autothermally and even with export of steam. Feeds containing H_2S levels of 3-5% can be processed, but the feed requires a certain caloric value for the thermal incineration to be effective. If the feed caloric value is too low, support fuel must be added. Additionally, the SO_3 conversion efficiency might drops when the feed H_2S content is too low. For 3% H_2S feeds, conversion efficiencies of 99.5% are reported.

3.4 Liquid processes

In the liquid oxidation process, the H_2S is converted into elemental sulphur via aqueous phase RedOx processes at ambient temperature and atmospheric pressure. It represents an isothermal, low operating cost method for carrying out the direct oxidation of H_2S to elemental sulphur. It is cost-effectively applied for relatively small feed streams. Although high sulphur purities can be obtained, its grade is lower than that resulting from a Claus plant and accordingly has a lower marketing potential.

Two variants are commercially applied, being the LOCAT process [16,17] and the Stretford process [18]. The LOCAT process uses Fe^{2+}/Fe^{3+} RedOx couple to convert Fe^{3+} and dissolved HS^- into elementary sulphur and Fe^{2+}. Alternative processes using the same RedOx couple are the Sulferox and the Sulfint processes [19]. Regeneration of Fe^{2+} is then performed by bubbling air. Sulphur removal efficiencies of >99% are reported at H_2S feed contents of 3%. Thus as Claus tail-gas technology it easily boosts overall sulphur recoveries to the 99.9% level. But extensive SO_2 hydrogenation to H_2S is required to reach that, since only H_2S can be treated. Moreover, SO_2 reacts with the buffer solution, producing salts and calling for continuous reagents addition. In case the feed has a high CO_2 content, carbonates and bicarbonates are formed in the solution, leading to precipitation of salts and a decreased capability of H_2S and O_2 uptake.

The Stretford process is rather similar, but utilizing a different RedOx reagent in the form of vanadium. An alternative process using the same RedOx couple is the Unisulf process [19]. In contrast to the LOCAT process, CO_2 dissolution forms much less of a problem when using vanadium solution. The sulphur removal performances of the Stretford and the LOCAT process are very similar.

In contrast to the O_2–assisted regeneration of the LOCAT and Stretford processes, electrochemical regeneration can also be applied. This is discussed in more detail in section 6.

Another interesting aqueous phase process is based on bacterial conversion of H_2S into sulphur, such as in the Thiopaq process [12,20,21]. The H_2S is first stripped from the feed with an aqueous carbonate solution, taking the H_2S as HS^-. It is reported that SO_2 in the feed is also dissolved [12]. Feed H_2S levels can be from a few 100 ppm up to tens of per cents and H_2S removal down to <25 ppm is reported. This carbonate solution is then fed to a bio-reactor, where under air addition the bacteria convert the sulphide into sulphur. The process is suitable for desulphurization of natural gas, biogas and syngas and can also be operated at increased pressure. The produced sulphur is very suitable to be used as additive in fertilizers because of the hydrophilic character of the sulphur and the presence of traces of the bacteria. Questions remain whether this process would be suitable with very high CO_2 partial pressure and whether it would guarantee a near quantitative CO_2 recovery, since CO_2 does interact strongly with carbonates forming less soluble bicarbonates and affecting significantly pH of aqueous medium.

The CrystaSulf process removes H_2S from sour gas and converts it to elemental sulphur via a non-aqueous liquid-phase modified Claus reaction [22,23]. **Figure 7** gives a flow-diagram of the technology. The H_2S reacts with dissolved SO_2 to produce dissolved elemental sulphur, which has a high solubility in the CrystaSulf solution (in contrast to water-based systems). The solution is then passed through a colder crystallization unit where the sulphur is removed. The solvent must be fed with SO_2 from an external source, which can be an incinerated sidestream of the feed, liquid SO_2 from a tank or part of the produced sulphur can be burned to SO_2. In a NG application, the unit removes H_2S down to 0.1 to 1 ppmv. Feeds with high CO_2 contents can be treated, since carbonates or bicarbonates are not formed in the non-aqueous solvent. No CO_2 is removed from the feed. Since it involves the Claus reaction, high sulphur recoveries require COS and CS_2 present in the feed to be hydrolysed to H_2S. A CrystaSulf demonstration unit removed 2000 ppmv of H_2S from 85% CO_2 at 20 bar feed pressure [23]. Since the solution can be loaded with high SO_2 contents, the desulphurization efficiency is much less sensitive to fluctuations in the H_2S content of the feed.

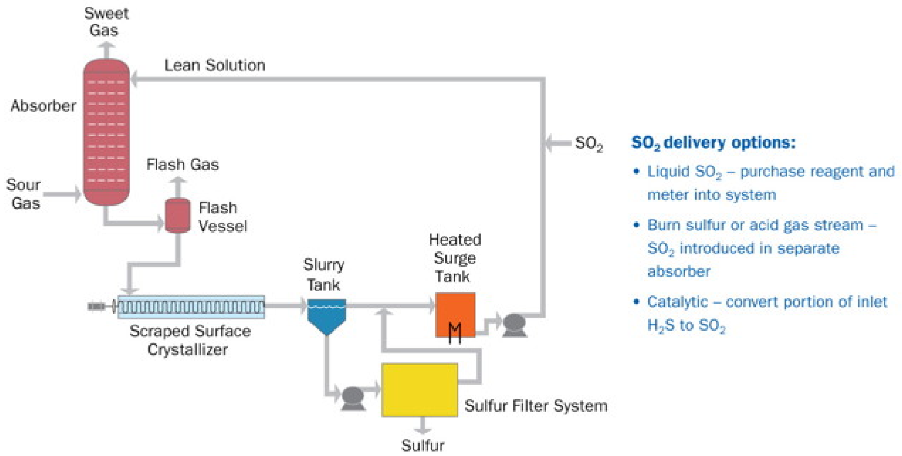

Figure 7: Schematic representation of the CrystaSulf process [23]

3.5 Novel catalytic processes

Although direct oxidation is already applied in commercial extended-bed and Claus tail gas treatment systems, the selectivity and stability of the used catalysts could be improved. The 3 major drawbacks of the commercial processes are [24]: i) relatively low selectivity due to direct oxidation of H_2S into SO_2 or the oxidation of elemental sulphur, ii) the presence of water must often be low since the catalysts can promote the reverse Claus reaction of elemental sulphur to H_2S and SO_2, and iii) the formation of sulphates on the oxidic support in the presence of steam, SO_2 and O_2.

Therefore, catalyst optimization is still being investigated. At the CNRS in Strasbourg, Fe- and Nibased catalysts were developed for the direct selective oxidation of H_2S into elemental sulphur via:

$$H_2S + 0.5\,O_2 \rightarrow {}^{1}/_{n}\ S_n + H_2O \qquad (6)$$

Fe supported on β-SiC proved effective in fully converting H_2S with a >90% selectivity to elemental sulphur at temperatures in the range of 210-250°C [25,26]. The feed contained 1% H_2S, 2.3% O_2, which is 4.6 the stoichiometric amount, and 20% steam. Catalyst stability is reported to be very good, which is in sharp contrast to alumina or titania based catalysts which rapidly loose activity and selectivity in the presence of steam. High H_2S conversions (>97%) together with high selectivities (>95%) are also reported by a different group on Fe-Ce-based catalysts using stoichiometric O_2 amounts at 250°C, but in the absence of steam [27].

Additionally, sub-dewpoint operation on NiS/β-SiC catalysts has shown 100% H_2S conversion at a 100% selectivity, in combination with a high S-loading of the catalyst before regeneration was required [24,28]. The feed contained 2000 ppm H_2S, 3200 ppm O_2 (λ=3.2) and 20% H_2O. A sulphur loading of the catalyst of up to 80 wt% was reported before the catalyst needed to be regenerated. The catalyst was stable during multiple reaction and regeneration cycles. The nature of the SiC support proved essential in this operation. It is reasoned that the β-SiC contains hydrophilic patches of mixed oxidic-carbidic silica, responsible for steam adsorption. The steam adsorbed in these zones act as a conveyer belt to remove sulphur particles resulting from the direct oxidation reaction away from the active centres, thus maintaining catalyst activity at high sulphur loadings of the catalyst.

The above mentioned catalytic systems differ from other metal-oxide based systems mentioned in literature in the sense that they seem to supress the retro-Claus reaction (reverse of reaction 2) and the further oxidation of elemental sulphur into SO_2. Both these reactions lead to a loss of selectivity towards elemental sulphur.

Alternatively, activated carbon as non-metal-oxide catalysts are also researched extensively throughout the years [29]. At sub-dewpoint temperatures, these catalysts have high selectivity. Regeneration of the sulphur from the pores, however, proves difficult and progressive loss of capacity was observed due to pore plugging and loss of surface area [28]. For gas-phase operation at >150°C, these catalysts rapidly loose selectivity and oxidation of the carbon is readily observed at >200°C.

4

Sorbent based desulphurization

4.1 Regenerative processes

Regenerative hot-syngas desulphurization by means of solid sorbents has been a research topic for decades. This technology is meant to improve the IGCC efficiency by performing the syngas cleaning at high temperature. Several good recent review articles thus give a good overview of the characteristics of the different sorbents investigated [30,31]. Furthermore, Kohl and Nielsen give a good overview [9]. The main interest is to maintain a high temperature while treating IGCC (or biomass gasification) syngas. Typically, a lot of research has been performed on these type of sorbents, but no commercial applications have emerged as yet, only some demonstrations [8,9]. In general, the disadvantages are: i) fixed bed systems require high-T and high-P valves and generate changing regeneration gas compositions, ii) fluidized bed systems are prone to particle attrition and are less suitable for high-P operation, iii) the sulphur is released as SO_2, which is more difficult to dispose than H_2S. The production of elemental sulphur requires a reducing agent, and sulphuric acid of pure SO_2 is difficult to market.

In general, the sorption systems under consideration remove H_2S from a feed stream according to the general equation:

$$M_xO_y(s) + H_2S(g) \rightarrow M_xS_y(s) + H_2O(g) \tag{7}$$

Considering thermodynamics, candidate systems can be based on oxides or carbonates of Barium, Calcium, Cobalt, Copper, Iron, Manganese, Molybdenum, Strontium, Tungsten, Vanadium, rare earths and Zinc [31]. Of these, Zinc, Manganese, Copper, Iron, and Calcium are among the most promising and most extensively studied materials. An important factor is the availability and thus price of the sorbent. In general, the adsorption kinetics are 1st order in H_2S concentration. Other properties can be important as well, such as reducibility of the oxide, the capability to form carbides, and the catalytic activity for e.g. the WGS reaction. Generally, the temperature levels considered are between 300°C and 800°C, with the oxidative regeneration generally at higher temperature than the adsorption. Apart from O_2, regeneration using steam or SO_2 can also be considered via:

$$M_xS_y(s) + O_2(g) \rightarrow M_xO_y(s) + SO_2(g) \tag{8}$$
$$M_xS_y(s) + H_2O(g) \rightarrow M_xO_y(s) + H_2S(g) \tag{9}$$
$$M_xS_y(s) + SO_2(g) \rightarrow M_xO_y(s) + S(g) \tag{10}$$
$$M_xS_y(s) + O_2(g) \rightarrow M_xSO_4(s) \tag{11}$$

Although it is normally assumed that the regeneration with steam causes the release of H_2S, it is often observed that it can also lead to the release of SO_2. Regeneration with O_2 is highly exothermal (e.g. Δ_rH=-779 kJ/mol for ZnS), low O_2 contents are usually applied to prevent sorbent overheating and sintering. Besides, high O_2 contents can also cause sulphate formation via reaction (10), which is an important side reaction leading to loss of sorbent capacity since sulfates may not be regenerated under mild conditions. Sulphate formation is enhanced at low temperature and high O_2 and SO_2 concentrations. Moreover, sulphates have larger specific volumes which can lead to physical particle damage. Regeneration with the production of elemental sulphur has been studied for Ce- and Mn-based systems.

Regeneration normally produces 1.5-5% SO_2 in N_2 and which must be further processed [9]. Concentration can be performed by a Wellman-Lord process. Further processing to elemental sulphur can be done by hydrogenation to H_2S and subsequent treated. Alternatively, the RTI direct sulphur recovery process can be used, which uses syngas to convert SO_2 into elemental sulphur via reactions of SO_2 with H_2 and CO. Another option for treating the regeneration off-gas is the application of a Flue Gas Desulphurization (FGD) unit to produce gypsum.

All sorbents mentioned below have been tested at relatively dry conditions and in the absence of other components such as HCl, CO_2 or hydrocarbons. Thermodynamics suggests that steam is generally unfavourable for reaching high desulphurization levels for oxidic materials. But for Zn-based materials, deep desulphurization in the presence of steam is still possible up to 500°C. This is also confirmed by experiments. The Z-Sorb Ni-ZnO material, for example, has been demonstrated up to 15% steam. A clear understanding of other contaminants such as HCl is still lacking. With HCl there is a possibility of metal-chloride formation. In the presence of CO and CO_2, the formation of COS is possible and could reduce the total desulphurization capability of a sorbent. In the presence of unsaturated hydrocarbons, vulcanisation has been observed leading to brownish deposits downstream the adsorber reactor.

4.1.1 Zinc-based sorbents

Desulphurization by ZnO of natural gas at low temperature (370°C) is well established. The material has a high capacity associated with bulk ZnS formation. Unfortunately ZnS has a higher density than ZnO, leading to diffusion problems in deep utilization. At temperatures >600°C, ZnO reduction can lead to evaporation of elemental Zn.

Therefore, developments within hot syngas desulphurization focus on stabilization of Zn. Zinc Ferrite (ZnFe-oxide) has high efficiency (ppm level H_2S) and capacity (20 wt%) at 500°C. At much higher temperature, disintegration into the oxide components occurs. The addition of Ti partially counteracts the separation. Complete regeneration is achieved at elevated temperatures (750°C) with 2%O_2 in N_2. For this TSA operation, the development focusses on a dual fluidized bed configuration. In coal gas, FeC formation resulting in soot formation can be an issue in this type of sorbent. The other class of materials is Zinc Titanate (ZnTi-oxide). The addition of Ti is the most effective method to stabilize ZnO from reduction and vaporization, thereby increasing the temperature window of H_2S adsorption. Efficient H_2S removal from simulated coal gas with up to 50% steam has been observed below 500°C. Additions of various elements has been performed to increase sulphidation rates and to limit capacity loss upon regeneration (e.g. due to sintering at increased regeneration temperature).

An interesting demonstrations for syngas desulphurization is the RTI developed dual bed transport reactor using a proprietary ZnO-containing material [9,33]. It removes 8000 ppm H_2S from a gasifier syngas to <20 ppm and is regenerated with O_2, releasing the sulphur as SO_2. This concept has been demonstrated for 3000 hours. The resulting SO_2 stream is either send to a sulphuric acid reactor or to their in-house developed Direct Sulphur Recovery Process (DSRP), where part of the syngas is used to react SO_2 to elemental sulphur, having COS and H_2S as by-products. The Nickel-ZnO material used in the Z-Sorb process, which is a reactive desulphurization process for desulphurization of gasoline [9,33], was also successfully tested for the desulphurization of IGCC syngas.

4.1.2 Copper-based sorbents

Copper-based sorbents are very promising for their thermodynamic deep H_2S removal capability. Prime requirement is that the copper-oxide is not reduced, since its sulphidation activity is an order of magnitude lower than that of Cu_2O and CuO. The addition of Cr proves effective in this respect. The formed Copper Chromite ($CuCr_2O_4$) has the lowest reducibility reported in literature. H_2S levels <5 ppm prior to breakthrough were found at 650-850°C operating conditions. Similar performance is reported for Copper loaded on an Alumina-Manganese oxide. High temperature oxidative regeneration is generally required to suppress stable sulphate formation on Copper containing materials.

4.1.3 Manganese-based sorbents

Manganese oxide of higher oxidation states are likely to be reduced in hot syngas desulphurization to MnO in the 400-1000°C window. Although the thermodynamics of MnO sulphidation are not as favourable as for Zinc or Copper oxide, it is not further reduced to metallic Manganese. The disadvantage is that it has to be applied at high temperatures, both for the H_2S uptake as for the regeneration. Moreover, these high temperatures (900°C) are required to suppress sulphate formation during oxidative regeneration. Regeneration using steam at 600°C proves to be an alternative to O_2-assisted regeneration.

4.1.4 Iron-based sorbents

Due to the low costs of Iron containing materials, these have been studied intensively. The potential of Iron-oxide is somewhat limited due to the excessive reduction and FeC formation at increased temperature. Due to thermodynamics, the H_2S slip during adsorption is higher than for Zn or Cu materials and levels of 50-200 ppm are reported. During regeneration, the formation of elemental sulphur can occur due to the Claus reaction between SO_2 and H_2S or FeS. Iron is a well-known catalyst for this reaction.

4.1.5 Rare Earths-based sorbents

Rare Earth sorbents are promising in the sense that they form stable oxides in reducing environments at increased temperature that have a favourable sulfidation equilibrium. Moreover, these materials have the potential to directly produce elemental sulphur in the regeneration. The addition of Zirconia is also mentioned to increase the reducibility of Cerium-oxide and to supress Ceria sintering. The presence of CO_2 in the feed, however, caused a serious decrease in sulphur capacity.

4.1.6 Sn-based sorbents

Haldor Topsøe developed a SnO-based sorbent that adsorbs H_2S in a 350-500°C range. In contrast to the above sorbents, the Sn-based sorbent can be regenerated with steam to produce H_2S. It is argued that a regeneration giving an enriched H_2S stream that can be sent to a Claus unit is preferred over sorbent processes giving diluted SO_2 streams, for which basically FGD is the main option for treatment. Within the Haldor Topsøe process, the feed must contain significant amounts of steam to prevent SnO reduction. Moreover, the regeneration also requires significant amounts of superheated steam. This process was demonstrated at pilot scale, but due to the high steam consumption was not developed further.

4.2 Low temperature sorbents

Molecular sieve are very effective in low temperature regenerative adsorption of polarisable compounds such as H_2O, CO_2, H_2S, SO_2, NH_3, COS and mercaptans. In principle, H_2S is adsorbed slightly stronger than CO_2, leaving room for deep H_2S removal [9]. Such a process is used for NG treatment when only the H_2S has to be removed. For instance Air Products patent AU200920280 discloses a novel sour PSA system in which removal of H_2S is carried out with low elemental S deposition on the sorbent that can adsorbed CO_2 and does not lose more than 2% capacity H_2S loading. Their claimed sorbent is a cross linked resin supported on SiO_2 - TiO_2 having no ionic groups or H_2S reactive functional groups. Typical feed gas that may be used contain at least 2000 ppmv H_2S, at least 50vol% H_2, and at least 80% CO_2+H_2. The process, however, also co-captures CO_2 contained in the feed and high selectivities over CO_2 are not likely to be achieved. Ma et al. [34] describes a sorbent where an amine is linked to MCM-41 on which the adsorption of CO_2 and H_2S were identified to be temperature dependant. Low temperatures (22°C) induced preferential H_2S adsorption, while high temperature (75°C) favoured CO_2 adsorption. By means of tuning the adsorption temperature, they describe a dual column system where the first column preferentially removes CO_2, while the second column removes H_2S. Unfortunately, the ultimate H_2S removal efficiency was not reported. Note that a high H_2S capacity was only achieved when CO_2 was firstly removed from the feed. Sorbent regeneration is performed via TSA to 110°C.

New developments in separation with PSA system are ongoing with impregnated activated carbons or system where solid particles are “coated” with a liquid layer that selectively takes up the H_2S, leading to a better uptake by the solid [35]. Envisioned applications are the removal of H_2S from NG and biogas in emerging economies.

4.3 Semi-regenerative sorbent based processes

For the removal of trace amounts of sulphur, non-regenerative sorbent processes can be considered. Commercially, all major catalyst companies have ZnO-based sorbents available for H_2S removal. The addition of Cu also allows COS removal and the incorporation of active metals such as Ni allows for organic sulphur removal, mainly targeting mercaptans. Some CuZn-oxide sorbents are also reported to be regenerative by mild oxidation. Another type of cheap scavenging sorbent is Iron-oxide.

SüdChemie ActiSorb-S series are CuOZnO-based materials for deep H_2S removal, ZnO-based for bulk H_2S removal and Ni-based for organic-S removal. They also have a reactive adsorption desulphurization material based on CuO-MoO_3 on ZnO for hydrodesulphurization of organic-sulphur from natural gas.

Haldor Topsøe also offers CuO-based (ST-series) and ZnO-based sorbents (HTZ-series) for deep and bulk H_2S removal, respectively.

BASF Selexsorb SG series is tailored for the removal of various sulphur species. It is an alumina based material with a RedOx promotor (Ag) intended for low temperature capture of inorganic S and mercaptanes, sulphides, disulfides and thiophenes. Regeneration is performed at increased temperature in an O_2 containing stream. Applications include Natural Gas treating and CO_2 stream purification.

Johnson Matthey has a series of sorbents for CO_2 stream purification from H_2S, COS, CS_2 called Puraspec-2000 series. One variant can also deal with trace amounts of organic-S. Their Katalco-32 series (former ICI products) covers ZnO materials for bulk H_2S removal.

The Katalco-2084 is their ultra-purification catalytically active sulphur sorbent for desulphurization of hydrocarbon feeds, typically to protect reformer catalysts.

Axens has a ZnO-based non-regenerative H_2S removal adsorbent for syngas purification, called AxTrap 401. In their AxSorb series, they have regenerative promoted aluminas for the removal of H_2S, COS and CS_2.

Merichem commercializes a non-regenerative H_2S capturing technology based on Iron-oxide as sorbent, called Sulphur-Rite. It typically consists of a plural bed configuration with material unloading facilities once the sorbent is saturated. It is only economical for small scale installations. In principle, this is a semi-batch process, since exposure of spent Fe-based sorbent leads to the formation of elemental sulphur and Fe-oxide, which can again react with H_2S. After several cycles, the material loses its H_2S adsorption capacity due to sulphur build-up. H_2S adsorption performance improves when the material is kept moist. A similar commercial technology is the SulphaTreat process developed by TDA Research.

Another class of solid sorbent scavengers are alkaline sorbents, basically consisting of NaOH as active component. This is transformed to Na_2S. However, such a sorbent will also interact with CO_2 to form carbonates.

Besides these solid sorbent processes, similar chemical systems also exist as aqueous liquid phase processes. These include Fe-based and Zn-based slurries. Advantages are the ease of reagent replacement and partial regeneration by air injection in a separate vessel (in case of Fe-based slurry). For zinc-based systems zinc-acetate is used. By controlling the pH, CO_2 adsorption can be minimized. The zinc-acetate, however, is a relatively expensive reagent, making the process uneconomical for large volumes.

In the SulfaCheck process, a solution of $NaNO_2$ is used to adsorb H_2S and convert it into elemental sulphur. The produces NaOH will react with CO_2 and the reaction with H_2S gives NH_3 and some NO_x.

Other reacting solvents that are reported include the reaction of H_2S with formaldehyde and with a polyamide. Both result in complete H_2S removal. Caustic can also be used, with the production of NaSH as waste product. The latter has the advantage of using a bulk chemical rather than the specialty chemicals of the first two processes.

5

CO_2 gas conditioning

As mentioned in the introduction, the captured CO_2 stream generally needs conditioning prior to transport of the CO_2 product. The gas conditioning system has to deal with 3 types of components: water, volatile and condensable components [1]. H_2S is typically a condensable product, ending up in the CO_2 upon compression. Recently, Air Products [36] developed a low-temperature sour-PSA system, separating CO_2-H_2S from H_2 similar as with our sour-SEWGS. Their solution to deal with the H_2S is to combust it with O_2 in a specially designed low-BTU burner and perform the SO_2 removal within the CO_2 compression unit. The SO_2 is removed as H_2SO_4, which formation is catalyzed by the presence of a small quantity of NO_x. The NO_x would result the combustion in O_2. For the acid formation during the wet compression, an O_2 surplus is required for the oxidation reactions. This wet reactive compression unit is similar to that applied within the oxy-coal scheme of the Schwarze Pumpe pilot plant, as described in the introduction.

6

Thermal and electrochemical H_2S decomposition

The decomposition of H_2S result in H_2 and elemental sulphur, both of which have an economic value. In contrast, the Claus process converts the valuable H_2 into water to produce elemental sulphur. The caloric value of H_2 is reduced to low grade heat (300-350°C).

The thermal H_2S decomposition, however, is a strongly thermodynamic limited reaction and requires high temperatures to get some conversion. The H_2S conversion at <550°C is less than 1% and approached 20% at 1000°C [37]. The reaction is catalysed by several types of transition metal oxides and sulphides, with MoS as of the most active sulfided catalyst and Vanadium- and Iron-oxide as most active oxidic catalysts [38]. To prevent intensive gas heating and cooling, plasma reactors are also considered. Unfortunately, the plasma energy consumption for the different types of plasma reactors is still too high (ranging from 10,000 to 350 kJ/mol H_2) for an economical H_2 production [39]. More promising, although still in explorative stage, are H_2-membrane assisted H_2S decomposition reactors. Because of the high temperature needed, either metallic membranes (Niobium [40]) or ceramic membranes (Zr-Si on alumina tube [38]) are used in combination with a decomposition catalyst mentioned above. Experimentally, 2-fold increases in conversion compared to equilibrium have been demonstrated [41].

The electrochemical conversion of H_2S into either elemental sulphur (proton conducting membrane) or SO_2 w/wo elemental sulphur (oxygen conducting membrane) has been studied for several years to some extent. Compared to H_2, H_2S is much more challenging due to its corrosive character and the formation of stable sulphides and sulphates. The high temperature application of H_2S as a fuel has been reported to have great potential [42], but is not as mature as conventional SOFC technology. Obviously, alternatives to Ni-based anodes are being investigated, such as Pt-based. The formation of too stable PtS causes degradation of the performance. The formation of stable non-conductive sulphates within the electrolyte can also occur. Stable SOFC electrolyte materials based on doped Ceria, however, have been reported [43].

The reverse electrochemical conversion, i.e. electrolysis, has also been considered for H_2S decomposition into elemental sulphur and H_2 [44]. Several aqueous RedOx systems have been proposed, such as iodide-based, Iron-Chloride ($FeCl_3/FeCl_2$), Iron complexes (Iron Chelate, in analogy to the LOCAT process) and Vanadium-Oxide (VO_2^+/VO^{2+} in analogy to the Stretford process). The H_2S is adsorbed into the aqueous solution and oxidized to elemental sulphur. After sulphur separation, the solution is regenerated via electrolysis producing H_2 and the oxidized complex. The electrolysis can be done directly (electrodes in the solution), or indirectly via an electrochemical membrane. In the LOCAT and Stretford processes, the oxidative regeneration of the RedOx couple is done by reaction with O_2, while in electrolysis mode water splitting at the anode occurs, producing protons that recombine at the cathode to H_2. Similar to the LOCAT and Stretford process, CO_2 in the feed can be problematic in forming stable carbonates in the solution. Moreover, the resulting sulphur can be of poor quality and difficult to recover and purify.

7

Discussion

The goal of this literature overview is to identify technology leads that could be used for an efficient CO_2-H_2S separation of the sour-SEWGS CO_2–rich product gas. The conditions of the sour-SEWGS CO_2 product, together with the characteristics of the CO_2 stream ready for transport is repeated in **Table 2**. As follows from this table, the range of conditions where an efficient CO_2-H_2S separation could be applied is rather broad. Roughly it goes from hot, wet low-pressure sour-SEWGS product to cold, dry, high-pressure CO_2 product.

	Sour-SEWGS feed		Sour-SEWGS product		CO_2 product	
CO	*6*	*%*	*<5*	*%*	*?*[a]	
CO_2	*24*	*%*	*35*	*%*	*>95*	*%*
H_2	*35*	*%*	*<5*	*%*	*?*[a]	
H_2O	*34*	*%*	*60*	*%*	*<100*	*ppm*
H_2S	*2000*	*ppm*	*2500*	*ppm*	*?*	
T	*400*	*°C*	*400*	*°C*	*Ambient*	
P	*25*	*bar*	*1*	*bar*	*110*	*bar*

a this number cannot be specified in detail at this moment. However, it is believed that total volatile composition must be <5%

Table 2: Comparing SEWGS feed and CO_2 product compositions

Firstly, wet absorption systems were reviewed, both amine systems as physical or mixed solvents. In general it can be concluded that all of them can be configured to selectively remove H_2S from a sour stream. Note that the sour-SEWGS product has a very high CO_2/H_2S ratio. Amine systems, however, will result in a considerable CO_2 co-adsorption and are likely to produce a H_2S-enriched stream not suitable for Claus, requiring additional acid gas enrichment or an adapted Claus operation. Nevertheless, CO_2 sent to the Claus unit cannot be captured, thereby reducing the CO_2 capture ratio. Illustrative, **Figure 8** represents calculations on the CO_2 loss from our sour-SEWGS product as a function of the H_2S content of the enriched acid gas. It illustrates that CO_2 loss can be considerable. Acid gas enrichment systems, which are intended to increase the H_2S content of an acid stream, cannot enrich our sour-SEWGS product to Claus feed standards (meaning from 7500 ppm H_2S to 40%). The required enrichment is too severe. Moreover, amine systems for this feed probably results in a H_2S slip of typically 100 ppm. In contrast, physical or mixed solvents will display lower CO_2 co-adsorption, producing a Claus feed richer in H_2S and thereby limiting the loss of CO_2 capture ratio. Selexol and Rectisol normally desulphurize down to 10-20 ppm H_2S. Rectisol can go lower, but at considerable cost increase. In conclusion, it can be stated that chemical solvents are not suitable and that physical or mixed solvent systems could be designed for such high enrichments but are rather expensive solutions with a potential high rate of CO_2 co-capture.

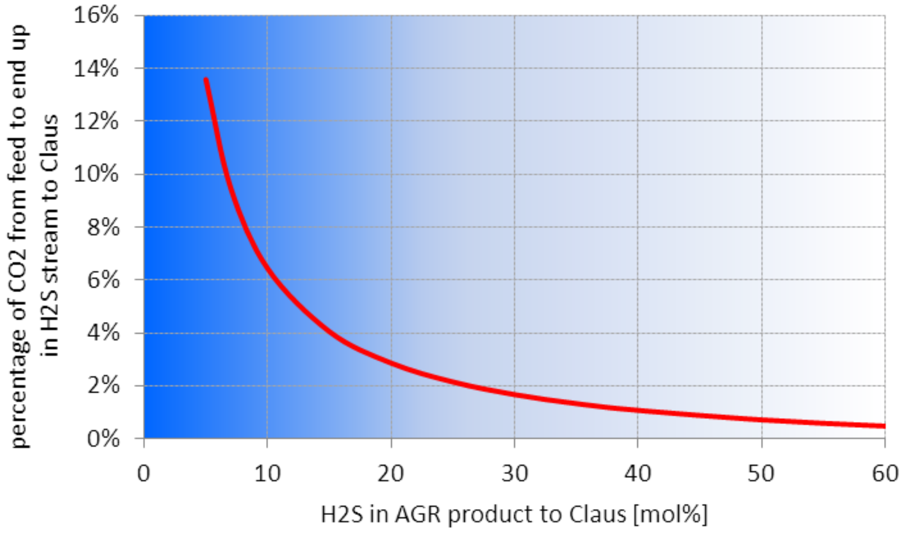

Figure 8: Relation between percentage of CO_2 that is lost via the H_2S stream going to Claus as a function of the H_2S content of that stream

Although the Claus process in itself cannot be applied for our problem, some Claus adaptations and tail-gas-treatment technologies are promising. The direct oxidation step in the SuperClaus and EuroClaus processes is capable of H_2S conversions to elemental sulphur of typically >85% with considerable selectivities. The catalysts used, however, require a 10 fold surplus of O_2 to remain stable. Applying such a catalytic stage to our case would lead to a CO_2 stream still containing considerable amounts of H_2S and SO_2. The H_2S and SO_2 contents of the CO_2 product are plotted in **Figure 9** as a function of the H_2S conversion at various values for the selectivity to elemental sulphur. It can be seen that very high conversion together with very high selectivities are required for deep sulphur removal from the CO_2 stream. Moreover, the required surplus of O_2 leads to an O_2 content of the CO_2 stream in the order of 5%.

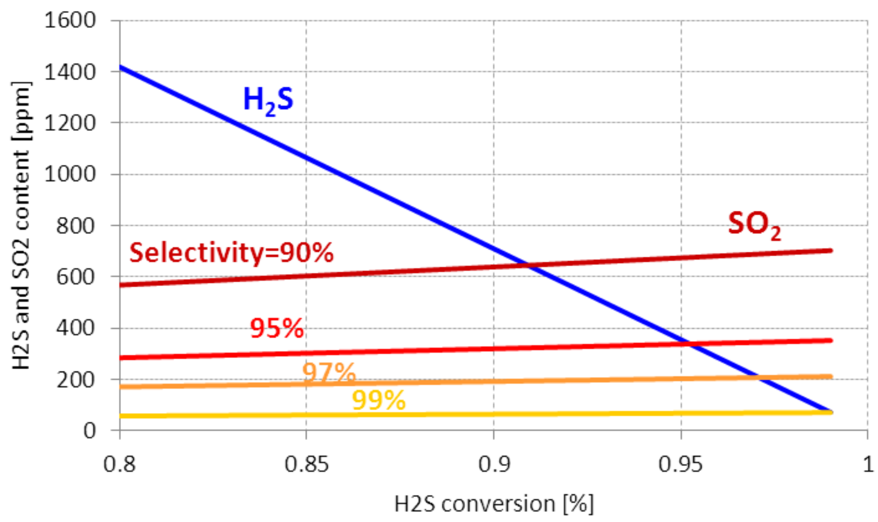

Figure 9: H_2S and SO_2 contents of the CO_2 product for a selective oxidation treatment as a function of the H_2S conversion and sulphur selectivity (feed=7100 ppm H_2S in CO_2)

The direct oxidation catalyst of the MODOP process operates with stoichiometric O_2 contents, but does not tolerate steam in the feed. It thus eliminates the addition of significant amounts of O_2 to the CO_2, but necessitates pre and post drying. Drying prior to the direct oxidation stage is required because of catalyst stability and selectivity, while drying downstream the direct oxidation step is because of the 7000 ppm H_2O produced by the oxidation and the requirement of a CO_2 product without free water.

The SulfaTreat DO is a catalytic direct oxidation process combining a stoichiometric O_2 feed with a tolerance for steam. A H_2S conversion of >90% and selectivity of >99% are reported, resulting in our case in <700 ppm H_2S and <70 ppm SO_2. Novel catalysts based on Fe/SiC or Fe-Ce-oxide are reported to have high conversions, but relatively low selectivities (<97%).

In contrast to these gas-phase catalytic processes, sub-dewpoint direct oxidation reactors combine high conversion with high selectivities. A novel NiS/SiC catalyst is reported to have “near 100%” conversion and “near 100%” selectivity at a 3-fold O_2 surplus and requires steam in the feed for good operation. These processes are interesting for our application.

Other Claus tail-gas-treatment systems such as SCOT, Wellman or WSA are not considered suitable. Scott basically is an amine scrubber. For WSA our feed has a too low caloric value. Moreover, the process is intended for venting the treated gas stream, which does not stroke with our intention of CO_2 capture. First of all, the burner should be operated with O_2 instead of air and the surplus of O_2 should be minimized. It is not likely that this process can be adapted to treat our feed.

Considering liquid oxidation processes, the LOCAT and Stretford processes are not very suitable because of the surplus of air required to regenerate the liquid. In current configurations, at least part of this air will end up in the CO_2. Moreover, the high CO_2 feed content poses dissolution problems for the LOCAT process.

In contrast, the liquid phase Thiopaq and CrystaSulf processes appear promising. In the Thiopaq process, an aqueous carbonate is used to remove H_2S to <25ppm. The bio-based regeneration produces a sulphur with good biological characteristics, potentially increasing its market value. In the CrystaSulf process, a non-aqueous solution strips the H_2S down to 0.1 to 1 ppm and produces elemental sulphur in the liquid phase by reaction with dissolved SO_2. A zero CO_2 uptake of the solution is reported. Both processes can be operated at increased pressure. While the Thiopaq process will probably lead to a water saturated CO_2 product, this is not the case for the CrystaSulf process.

Considering high temperature regenerative sorbents, Zn- and Cu-based systems seem most promising because of their relatively low operating temperature, especially for the regeneration. Other oxidic materials such as Mn-, Fe-, or Ce-based sorbents generally require high temperature (>600°C) oxidative regeneration. Besides, Fe- and Ce-based materials may promote the Claus equilibrium reaction, producing elemental sulphur upon regeneration. With Zn- and Cu-materials, deep regenerative desulphurization has been reported. The main challenge is to maintain sorbent capacity by preventing i) sorbent reduction (metallic Zn is volatile, metallic Cu has low reactivity to H_2S), ii) material sintering during the exothermal regeneration the and iii) formation of stable sulphates. To this extend, ZnFe and ZnTi are mentioned as candidates, as well as supported Ni-ZnO-based materials. Promising results are reported for the Z-Sorb and the RTI processes.

Another interesting regenerative sorbent is the Selexsorb-SG from BASF, which is based on Ag-oxide/Ag-sulfide looping via TSA.

A major disadvantage of these regenerative sorbents is that they produce a diluted SO_2 stream, which is not trivial to be used for sulphuric acid production. Flue gas desulphurization might be applied.

Commercially, ZnO, CuO and Fe-oxide based sorbents are offered by almost all catalyst manufacturers. They are generally intended for one-through use for deep desulphurization with high loading capacity.

The progress on thermal and electrochemical H_2S decomposition is considered to be too poor to be considered as suitable technologies.

8

References

1 Aspelund, A., Jordal, K., *Gas conditioning-The interface between CO_2 capture and transport*. International Journal of Greenhouse Gas Control **2007**, 1 (3), 343-354

2 Torrente-Murciano, L., White, V., Chadwick, D., *Removal of SO_x and NO_x from oxyfuel-derived CO_2*, 1st Oxyfuel Combustion Conference, **2009**

3 Yan, J., Anheden, M., Faber, R., Starfelt, F., Preusche, R., Ecke, H., Padban, N., Kosel, D., Jentsch, N., Lindgren, G., *Flue Gas Cleaning for CO_2 Capture from Coal-fired Oxyfuel Combustion Power Generation*, Energy Procedia **2011**, 4, 900–907

4 http://www.icis.com/fertilizers/sulphur/

5 http://www.icis.com/fertilizers/sulphuric-acid/

6 http://www.icis.com/fertilizers/sulphate-of-potash/

7 Pieplu, A., Saur, O., Lavalley, J.C., *Claus catalysis and H_2S selective oxidation*, Catal. Rev. Sci. Eng. **1998**, 40(4), 409-450

8 Nick Korens, Dale R. Simbeck, Donald J. Wilhelm, *Process screening analysis of alternative gas treating and sulphur removal for gasification*, SFA Pacific, Inc. Mountain View, California **2002**

9 A.L. Kohl, R.B. Nielsen, *Gas purification*, Gulf Publishing companu, Houston, Texas, 5th edition **1997**

10 *FLEXSORB® SE/SE PLUS, Solvents for Selective H_2S Removal*, Sellsheet, ExxonMobile Research and Engineering, **2007**

11 D. Perry, L. Parks, R. Fedich, *FLEXSORB® SE A Proven Reliable Acid Gas Enrichment Solvent*, Presentation at GPA’s 89th Annual Convention, Austin, Texas, March 21, **2010**

12 Wolfgang Nehb, Karel Vydra, *Sulphur*, Ullmann's Encyclopedia of Industrial Chemistry , **2006** Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

13 S.W. Shun et al., *Selective oxidation of H_2S to elemental sulphur over TiO_2/SiO_2 catalysts*, Applied Catalysis B, **1998**, 16(3), 235-243

14 ROSENBERG, H., *Topsoe wet gas sulphuric acid (WSA) technology—an attractive alternative for reduction of sulphur emissions from furnaces and converters*. International Platinum Conference ‘Platinum Surges Ahead’, The Southern African Institute of Mining and Metallurgy, 2006 (http://www.saimm.co.za/Conferences/Pt2006/191-198_Rosenberg.pdf)

15 Uhelná, WSA case story, 2008, *WSA for cleaning of acid gas from gasifier* , http://www.topsoe.com/business_areas/gasification_based/Processes/WSA/~/media/PDF%20files/WSA/Topsoe_wsa_clean_acid_gas_gasifier.ashx

16 LO-CAT http://www.merichem.com/resources/technical_papers/optimization.php

17 G.J. Nagl, *Liquid redox enhances Claus process*, Sulfur, **2001** (274), 1-6

18 Stretford process http://www.technicalmetals.com/sulphur.htm

19 A. de Angelis, *Natural gas removal of H_2S and mercaptans*, Appl.CatalB, **2012** (113-114), 37-42

20 http://www.paques.nl/pageid=67/THIOPAQ®.html

21 E. van den Brink, *Efficiënte biologische ontzwaveling van gassen*, Biochem, **2008** (04/08), 12-15, juli 2008

22 Dennis Dalrymple, *CrystaSulf revisited*, SULPHUR 2007 (308 Jan Feb)

23 David M Seeger, Bryan J Petrinec, Jenny M Dávila, *Liquid-phase Claus process medium-scale hydrogen sulphide removal technology*, Hydrocarbon World, **2011**, 6(1), 46-49

24 Nicolas Keller, Ricardo Vieira, Jean-Mario Nhut, Cuong Pham-Huu and Marc J. Ledoux, *New Catalysts Based on Silicon Carbide Support for Improvements in the Sulfur Recovery. Silicon Carbide as Support for the Selective H_2S Oxidation*, J. Braz. Chem. Soc. **2005**, 16 (2), 202-209

25 Nicolas Keller, Cuong Pham-Huu, Marc J.Ledoux, *Continuous process for selective oxidation of H_2S over SiC-supported iron catalysts into elemental sulphur above its dewpoint,* Appl. Catal. **2001**, 217, 205-217

26 Patrick Nguyen, Jean-Mario Nhut, Charlotte Pham, Marc J. Ledoux, Cuong Pham-Huu *Fe_2O_3/β-SiC: A new high efficient catalyst for the selective oxidation of H_2S into elemental sulphur*, Catal. Today, **2009**, 141, 397-402

27 Koyuncu, D.D.E., Yasyerli, S., *Selectivity and stability enhancement of Iron Oxide by Ceria incorporation for selective oxidation of H_2S to sulfur*, Ind. Eng. Chem. Res. **2009**, 48 (11), 5223-5229

28 Nicolas Keller, Cuong Pham-Huu, Claude Estournes, Marc J.Ledoux, *Low temperature use of Si-C based catalyst for selective H_2S oxidation. Role of Si-C surface heterogeneity and nature of the active phase*, Appl. Catal. **2002**, 234, 191-205

29 Shinkarev, V.V., Glushenkov, A.M., Kuvshinov, D.G., Kuvshinov, G.G., *New effective catalysts based on mesoporous nanofibrous carbon for selective oxidation of hydrogen sulfide*, Appl. Catal. B, **2009** (85), 180-191

30 X. Meng, W. de Jong, R. Pal, A.H.M. Verkooijen, *In bed and sownstream hot gas desulphurization during solid fuel gasification: A review*, Fuel Processing Technology, **2010** (91), 964-981

31 S. Cheah, D.L. Carpenter, K.A. Magrini-Bair, *Review of Mid- to High-Temperature Sulfur Sorbents for Desulfurization of Biomass- and Coal-derived Syngas*, Energy Fuels, **2009**, 23 (11), 5291–5307

32 I.V. Babich, J.A. Moulijn, *Science and technology of novel processes for deep desulfurization of oil refinery streams: a review*, Fuel 82, **2003**, 607–631

33 C. Song, *an overview of new approaches to deep desulphurization for ultra-clean gasoline, diesel and jet fuel*, Catalysis Today, **2003** (86), 211-263

34 Ma, X., Wang, X., Song, c., *Molecular basket sorbents for separation of CO2 and H2S from various gas streams*, J. Am. Chem. Soc., **2009**, 131, 5777-5783

35 L. Zhou, M. Yu, L. Zhong, Y. Zhou, Feasibility study on pressure swing sorption for removing H_2S from natural gas

36 J. Hufton, T. Golden, R. Quinn, J. Kloosterman, A. Wright, C. Schaffer, R. Hendershot, V. White, K. Fogash, *Advanced Hydrogen and CO_2 Capture Technology for Sour Syngas*, Energy Procedia **2011** (4), 1082–1089

37 Kaloidas, V.E., Papayannakos, N.G., *Hydrogen production from the decomposition of hydrogen sulphide equilibrium studies on the system $H_2S/H_2/S_i$ in the gas phase*, Int. J. Hydrogen Energy, **1987**, 12(6), 403-409

38 Reshetenko, T.V., Khairulin, S.R., Ismagilov, Z.R., Kuznetsov, V.V., *Study of the reaction of high temperature H2S decomposition on metal oxides*, Int. J. Hydrogen Energy, **2002**, 27, 378-394

39 John et al., *Energy efficiency of hydrogen sulfide decomposition in a pulsed corona discharge reactor*, Chem. Eng Sci, **2009**, 64, 4826-4834

40 Chan, et al., *Modeling and simulation of non-isothermal catalytic packed bed membrane reactor for H_2S decomposition*, Catal. Today, **2000**, 63, 379-385

41 Chan, P.Y.P, *Design and verification of catalytic membrane reactor for H_2 recovery from H_2S*, Thesis, **2007**, University of New South Wales, Sydney, Australia

42 M. Liu, P. He, J.L. Luo, A.R. Sanger, K.T. Chuang, *Performance of a solid oxide fuel cell utilizing hydrogen sulphide as fuel*, Journal of Power Sources, **2001**, 94, 20-25

43 J. Winnick, *A hydrogen sulfide solid oxide fuel cell*, project E-19-X46, Georgia Tech sponsored research, Annual Report to the National Science Foundation on Grant No . CTS-9321968, **1994**

44 Huang, H., Yu, Y., Chung, K.H., *Recovery of H_2 and Sulfur by indirect electrolysis of H_2S*, Energy Fuels, **2009**, 23 (9), 4420–4425

ECN

Westerduinweg 3
1755 LE Petten
The Netherlands

P.O. Box 1
1755 LG Petten
The Netherlands

Tel + 31 88 515 49 49
info@ ecn.nl
www.ecn.nl