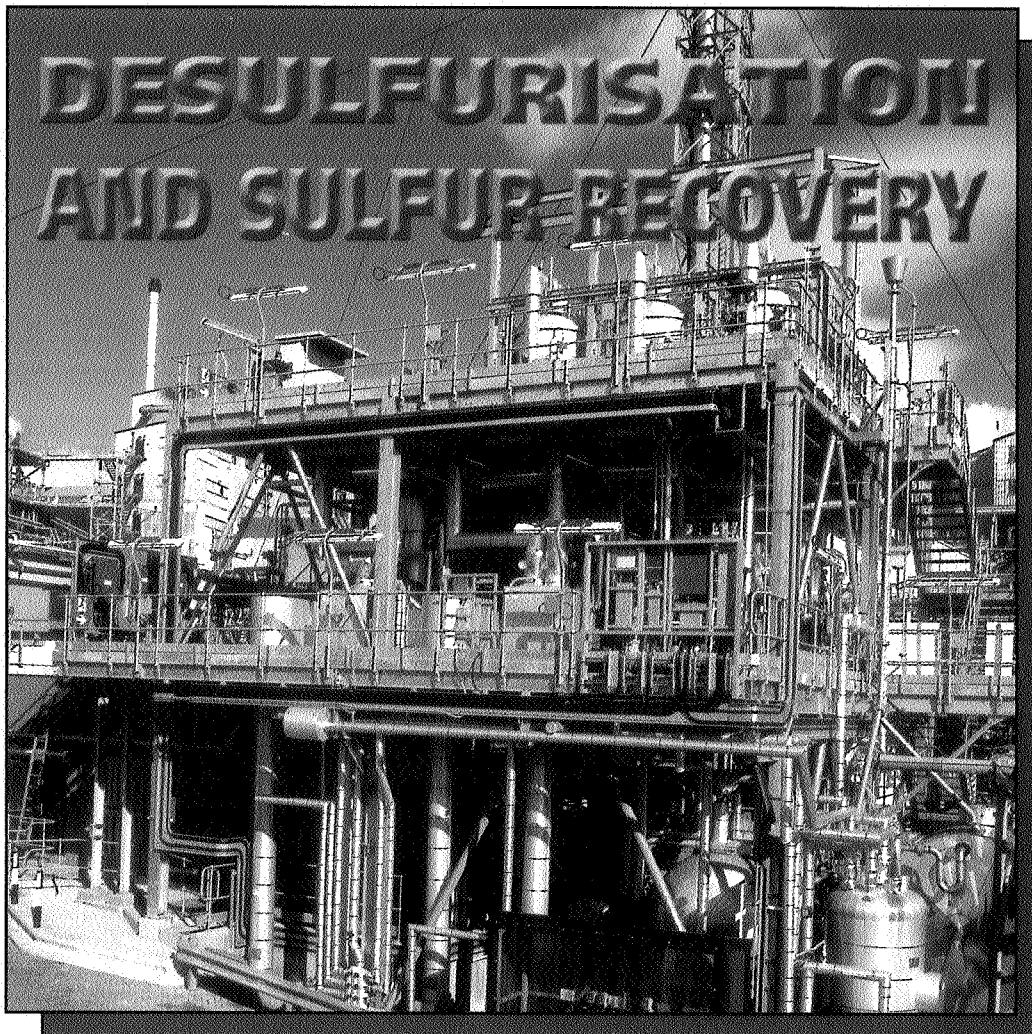


HYDROCARBON ENGINEERING



In this two part article Peter Hughes, Adrian Finn and Lee Scott, Costain Oil, Gas & Process Ltd, UK, present an overview of available sulfur recovery technology and highlight some of the associated technical issues

All hydrocarbons of natural origin, including natural gas, crude oil and coal, may contain sulfur compounds. These compounds range from the simplest form, namely hydrogen sulfide found in natural gas, through simple mercaptans (R-S-H compounds), to very complex molecules.

The combustion products from hydrocarbon fuels form carbonic acid with moisture, but if the fuel contains sulfur compounds, stronger acids are formed. These have an adverse effect on the environment and a high corrosion potential. Therefore there is an incentive to reduce the sulfur content of the fuel, and so decrease the acidic nature of the exhaust gas. Sulfur treating is also necessary if the hydrocarbon is to be fed to high value catalyst based processes.

The environmental effects of burning hydrocarbon fuels have led most world governments to impose stringent specifications on the sulfur content of hydrocarbon fuels.

This article presents some of the experience of Costain Oil, Gas & Process Ltd in selection and design of sulfur treating technology. Due to increasing demands on sulfur treating processes, new technology is continuously being developed and consequently, not all technologies, or technology suppliers may be mentioned.

Selection criteria

The main criteria for selecting sulfur treatment processes are quite simple. Firstly, consider the nature and composition of the sulfur species. This includes consideration of whether the fluid being treated is liquid or gas, and whether the sulfur species appear as hydrogen sulfide, simple mercaptans or other carbon based species, such as carbonyl sulfide or carbon disulfide. Another major consideration is the degree of sulfur removal required, whether the removal efficiency is specified or a target sulfur content is required. The scale of the process should be considered, such that the amount of sulfur processed is known. Finally, environmental regulations for disposal of sulfur compounds and byproducts must be fully considered.

Hydrocarbon streams are normally contaminated with sulfur compounds of similar volatility to the hydrocarbon components and the following provides a summary of common sulfur contaminated streams, to indicate the range of likely treatments.²

- Natural gas. Raw natural gas can contain significant quantities of hydrogen sulfide and some light mercaptans. Sulfur compounds must normally be removed to achieve national pipeline transportation standards so as to avoid corrosion and minimise odour and toxic effects. Sulfur compounds also need to be removed to minimise sulfur oxides in flue gases from combustion processes.
- Sour gases. Refinery or petrochemical processes liberate light hydrocarbon gases that contain sulfur species. These must be treated before the gas is used as fuel within the refinery or elsewhere. Hydrogen sulfide is normally the major sulfur species, though other sulfur compounds can also be present depending on the upstream process.
- Acid gases. These are normally streams that contain a high concentration of hydrogen sulfide and are usually treated to remove elemental sulfur to high efficiency.
- Liquefied petroleum gas (LPG). Untreated LPG can contain significant quantities of mercaptans and some hydrogen sulfide, carbonyl sulfide and carbon disulfide. The method of treating depends on what is required of the products. It may be that the butane/butylene fraction will not require treatment, but

the propane/propylene will. Thus, rather than treating the combined stream, it is first fractionated and then the relevant stream is treated for removal of sulfur compounds.

- Motor spirits. Untreated hydrocarbon spirits can contain a range of sulfur compounds and must be treated, either to make them acceptable for motor spirit blending or conditioned for further processing. Consequently, the most common process routes are either hydrotreating to reduce the sulfur compounds to hydrogen sulfide, or else the mercaptans are oxidised into disulfide compounds (R₁-S-S-R₂). The latter process does not remove the sulfur, but modifies it into a more acceptable species.
- Heavier hydrocarbons. As the size of the hydrocarbon molecule increases, so does the stability of the sulfur compounds. Consequently, more aggressive treatments are required, normally of the hydrotreating type. Treating requirements are similar to motor spirits, mainly to achieve fuel specifications, but in some cases there is a need for further processing.
- Sour water. In some hydrocarbon processes, either physical or chemical, water is in contact with a hydrogen sulfide contaminated stream. The hydrogen sulfide preferentially dissolves in the water to produce sour water, which must be treated before reuse or release as effluent.
- Tail gas. Sulfur removal processes are not 100% efficient and for high sulfur throughput processes, the residual sulfur content of a treated gas could mean significant quantities of sulfur are released into the atmosphere. This residual gas, known as 'tail gas', is usually the effluent of a Claus sulfur recovery plant and generally contains inert gases with traces of hydrogen sulfide and sulfur dioxide. These may require further treating before being released to the atmosphere with other flue gases.

Figure 1. Selection based on gas flow.

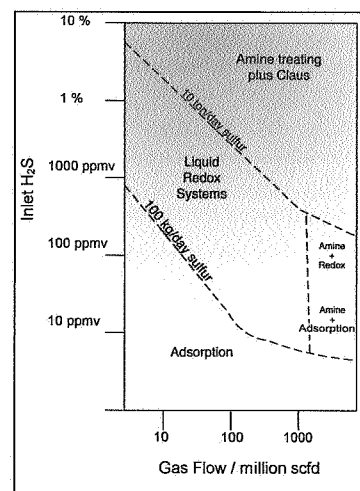
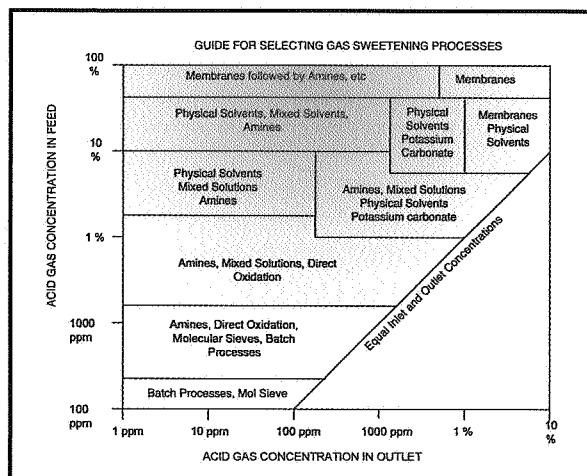


Figure 2. Selection based on product concentration.



Generic process types

There are basically three main types of sulfur treatment process:

- Polishing for removal of comparatively small amounts of sulfur.
- Reduction - oxidation (redox) processes for intermediate amounts of sulfur.
- High capacity processes.

Two nomographs are presented in Figures 1 and 2 to provide some guidance.

Polishing processes

These processes typically remove small amounts of sulfur compounds from relatively clean streams. They can be relatively expensive to run due to consumption of process chemicals but this is offset by their comparatively low capital cost.

There are two main types of processes – those that use physical adsorption onto a solid bed and those that undergo a chemical reaction to form modified products.

Typical examples of the former include activated alumina, molecular sieve and activated carbon.²

Chemical reaction processes employ various chemicals such as zinc oxide or caustic to react with the sulfur compounds. Examples include Chemsweet (Natco), Merox (UOP), Slurrissweet (Gas Sweetening Association), Sofnilime RG (Modular Products), Sulfa-Check (Exxon), Sulfascrub (Quaker), SulfaTreat (Sulfa Treat Co) and Puraspec (Synetix).³

A disadvantage of some polishing processes is that the product can be contaminated. For example, liquid systems will potentially rehydrate a dry gas; metal oxide based fixed beds react with hydrogen sulfide to produce water and some fixed bed processes require the gas to be hydrated for optimum service. These processes should be installed upstream of any dehydration facility, providing their use is justified.⁵

Selection between the various fixed bed technologies should account for: the capital and operating costs of the process; removal efficiency; unwanted products; spent material disposal and handling issues. Other issues may prevail, such as maintaining a gas in a dry condition or operating temperature.

Polishing processes may also be tailored to a particular species, such as the Sofnilime process for extracting carbonyl sulfide from liquid propane/propylene streams.

Redox processes

Reduction/oxidation processes extract intermediate amounts of sulfur (up to approximately 20 tpd) to give a low sulfur content product. These processes have the advantage of generally producing elemental sulfur in a direct fashion.⁴

Examples of redox processes are the BG Technology Stretford process, USFilter LO-CAT II and the SulFerox process.³ Most processes are iron based. Iron or iron chelates chemically absorb hydrogen sulfide, which is then oxidised with air to create a liquid phase sulfur product. Sulfur is then recovered by filtration or skimming. The vanadium used in the Stretford process may preclude its use.

Mention should be made of biological technology, such as the Shell-Paques process, which is claimed to be an alternative to redox technology. In this process, the sour gas is passed through a caustic scrubber, where the hydrogen sulfide is extracted as a sulfide and sulfur bacteria convert it to elemental sulfur, ready for further processing. However, experience as yet is limited.

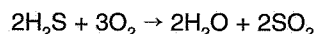
High capacity processes

These processes cater for capacities from approximately 10 tpd of sulfur upwards. They are characterised by an initial extraction process, mainly for removing hydrogen sulfide. The hydrogen sulfide is then released to form a concentrated acid gas stream and can be converted to elemental sulfur in a Claus plant.

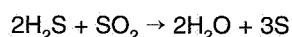
The basic extraction process does not vary much. The process fluid is initially contacted against a solvent, which absorbs the hydrogen sulfide. The hydrogen sulfide is released when the solvent is regenerated in a second column. The main process variant is the type of solvent used; most use amine based solvents that chemically extract the hydrogen sulfide. Simpler processes use commodity amines such as monoethanolamine (MEA) and diethanolamine (DEA), whereas proprietary processes use more complex amines, such as di-isopropanolamine (DIPA) and methyl diethanolamine (MDEA).²

Physical solvents are also used commonly. These rely on the solubility of the hydrogen sulfide in the solvent being higher than the hydrocarbon streams. Regeneration is achieved by reducing the rich solvent pressure, and desorbing the hydrogen sulfide. Commonly used physical solvents include methanol and pyrolidine.

Acid gas removed from the treated stream is normally routed to a Claus unit, where the hydrogen sulfide is converted to elemental sulfur. The Claus process for sulfur production is well established. In this process, hydrogen sulfide is reduced to sulfur by burning in a limited oxygen environment, as illustrated by the following equations:



The sulfur dioxide then oxidises hydrogen sulfide to produce elemental sulfur:



The actual reactions are more complicated than this and other intermediates are formed and lost. However, the outcome is that approximately 94 - 98% of the sulfur is recovered as elemental sulfur and an inert flue gas is produced.

The basic Claus process has been developed and modified due to environmental pressures to improve sulfur recovery efficiencies and increase throughput. This is normally achieved by adding air or pure oxygen at various stages of the process. Examples of this are TPA Claus Plus, Stork SuperClaus, Lurgi OxyClaus, TPA Oxygen Injection, Goar Allison COPE and BOC/Parsons SURE processes.³

Tied to a Claus plant will be a receiver for the liquid sulfur product, where further licensed technology may be required. Some hydrogen sulfide will be entrained in the sulfur, which can desorb on standing. This can lead to noxious atmospheres around the sulfur pit, and degassing equipment may be needed. In its simplest form, this requires removal of gases containing a high concentration of noxious hydrogen sulfide. Proprietary technology is available for improved degassing processes from Shell, TPA and others.

Process descriptions

The following section gives brief descriptions of a number of proven processes. It is not intended to be fully exhaustive but highlights the processes most widely employed by the authors.

Molecular sieve technology

Molecular sieve systems work by passing the process stream through a bed of aluminosilicate zeolites, which by nature of their polarity, 'filter' out the sulfur species. After a certain time, the bed becomes loaded with the sulfur species, and outlet content starts to increase. At this point, the bed will have a reduced treating effect and should be regenerated. The regenerant is passed in the opposite direction through the bed to desorb the sulfur species, until the bed is completely regenerated.³

When the feed composition and conditions are established, product quality and the regenerant agreed, information is normally submitted to a sieve vendor (such as UOP, Grace or Ceca). More than one vendor should be contacted, as some vendors will select a proprietary sieve rather than a commodity product. The vendor provides a bed size and conditions for regeneration. The vendor should also advise on engineering issues such as ceramic support loadings which need to be considered when sizing the vessel.

Choice of regenerant can be complex. Treated product from the exit of the treating bed is often used, but the regenerant may then have to be flared or further treated. If the material being treated has a high value, this will not be acceptable. Alternatives could be to use a lower value process stream from elsewhere in the plant, or an inert stream, such as nitrogen. The latter could also be costly, in which case a recycle system could be specified using a blower.

Molecular sieves have been successfully used for a number of sulfur species, such as hydrogen sulfide and mercaptans. A major incentive for the use of molecular sieves is that other contaminants can be removed, including carbon dioxide and water.

The molecular sieve bed size depends on the time required for adsorption and regeneration, which in turn depends on the regeneration conditions. Most regeneration cycles require elevated temperatures and reduced pressures. The higher the regeneration temperature, the more expensive may be the utility supply but the shorter the regeneration cycle. There are a number of factors to consider in optimising process design.⁷

Puraspec process

The Puraspec process is typical of a number of fixed bed proprietary processes, which are suitable for removal of very small (ppm) levels of sulfur compounds. Puraspec, developed by Syntex, formerly ICI Katalco, is a proprietary blend of copper, zinc and aluminium oxides on a binder. Costain has provided several Puraspec systems for treating natural gas from the North Sea and for propane treating.

The Puraspec process maximises adsorbent activity and this is reflected in a smaller bed size than many other proprietary fixed bed processes.

The normal process arrangement is to provide two vessels, which are operated in series, in a 'lead-guard' fashion. Thus, when the outlet content of the lead bed starts to rise, process gas is routed through the guard bed. At a predetermined point, the guard bed is brought into lead duty, and the first bed is depressured, purged, reloaded and put back in service as guard bed. In this way, the use of adsorbent is maximised. However, it may be preferable to provide a single large bed and bypass, for infrequent bed changeout. This gives a lower capital cost.

The bed is sized to give acceptable time between reload operations. The frequency is typically between one and three years and should be optimised on a case by case basis.

To polish natural gas to sales quality, 100% removal is

not required, and consequently a controlled bypass is used to minimise bed use. This allows either a smaller bed to be specified or a longer life between change-outs.

A benefit of the Puraspec process is that it operates on dry gas. However, the removal of hydrogen sulfide releases water, which may be an issue in terms of product specification.

Regenerative caustic processes

Regenerative caustic processes are used for a wide range of sulfur treating duties and especially for refinery applications. The most familiar is the UOP Merox process but similar processes are offered by IFP and Merichem to nullify the odours of mercaptans by oxidation, or in certain circumstances, to completely remove them. Each licensor uses a proprietary catalyst.

Process configurations vary depending on the material being treated and the amount of effluent allowed. The original and simplest process mixes a gasoline stream with caustic and a cobalt based liquid catalyst. Mercaptans are oxidised (by hydrogen removal) to disulfides, but remain preferentially dissolved in the hydrocarbon. The caustic and catalyst is decanted and recycled, and the hydrocarbon stream is finally polished to remove liquid in a sand filter.⁵

As the caustic gradually becomes spent, some is slip-streamed for disposal. This stream is normally further treated before reaching the main plant effluent, as it can be alkaline and rich in phenolic compounds. To minimise production of this effluent, a minimum alkali process was developed, in which instead of circulating the catalyst, a modified catalyst is absorbed onto a fixed bed, and the hydrocarbon passes across the bed with air and a more dilute caustic stream. A continuous stream of spent caustic is produced, which again must be treated before final disposal. The gaseous product is normally incinerated.

For lighter hydrocarbon streams, such as LPG, NGL or light naphthas, the mercaptans can be extracted as disulfides due to their preferential solubility in caustic solution.

Due to the alkalinity of these processes, the hydrocarbon stream is normally firstly amine treated to remove hydrogen sulfide and carbon dioxide before caustic treatment. The hydrocarbon is pre-washed in weak caustic, to neutralise residues of the acidic species and is then mixed with strong caustic and the catalyst. The resulting mercaptides are then extracted into the caustic stream and the hydrocarbon is sand filtered to remove traces of caustic. The contaminated caustic is heated with air and a disulfide oil is produced. The caustic and catalyst are re-used until spent, the disulfide oil is blended off and the gaseous effluent is incinerated.

Simplified wash processes have been used for natural gas processing based on caustic washing. These are effective, but suffer from high chemical consumption costs as the caustic removes all acidic components, not just the unwanted contaminants.

In the second part of this article, further processes will be presented and their appropriateness for certain applications commented upon. These will include some more redox type processes and bulk sulfur removal technology.

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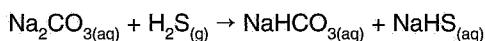
In this second part of the article, further appropriate sulfur recovery technology is discussed.

Stretford process

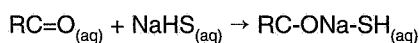
The Stretford process was developed by British Gas (now part of the BG Group) from the earlier Manchester process. It is a typical liquid redox process for removal of low concentrations of hydrogen sulfide from natural gas or other hydrocarbon gases. This type of process can be appropriate when moderate amounts of sulfur are to be recovered, typically hundreds of kilograms a day.

Some variants of the Stretford process use vanadium salts. These salts can be toxic and environmentally sensitive. For this reason, the Stretford process may prove to be unacceptable in many parts of the world.

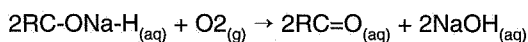
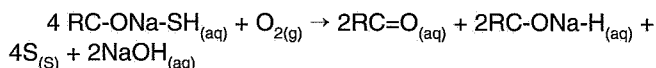
The reaction is water based, so the first part of the process is absorption of hydrogen sulfide from the gas stream, by extraction with a sodium carbonate solution in a spray tower. This absorber is prone to plugging and an open design of splash plate is necessary:



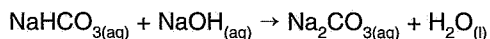
After absorption, the process chemistry becomes quite complex, and reaction kinetics have an effect. The rate determining step, where sodium bisulfide is reacted with anthraquinone disulfonic acid takes approximately 45 mins, therefore a holding volume is built into the bottom of the absorber tower and the liquor is pressured into a separate heated reaction vessel. Residual absorbed gas may need to be vented from this vessel:



The liquor then passes into an oxidiser vessel, where air is bubbled through it to initiate the next steps in the reaction. Careful design of the air distributor is necessary to ensure adequate mixing. The anthraquinone complex is first oxidised to produce elemental sulfur as a precipitate, then further oxidised to regenerate the anthraquinone disulfonic acid:



Finally, the sodium carbonate is regenerated by neutralisation with the stronger sodium hydroxide base:



Sulfur is recovered by froth floatation from the top of the oxidiser vessel into a sulfur slurry vessel. Sulfur precipitate is recovered by pumping with a progressing helical cavity screw pump to a centrifuge, the decanted liquor is then returned to the process and the sulfur further processed as necessary.

An advantage of this process is that there is little or no loss of reagent, so operating costs are low. Some effluent will be produced, due to the chemical formation of water, and occasional addition of sodium bicarbonate and anthraquinone disulfonic acid will be required. The quality of the sulfur produced is very high, being chemically precipitated and uncontaminated.

SulFerox process

The SulFerox process was originally developed by Shell and Dow for removal of moderate amounts of sulfur from contaminated gases but is now offered by USFilter. It is a redox

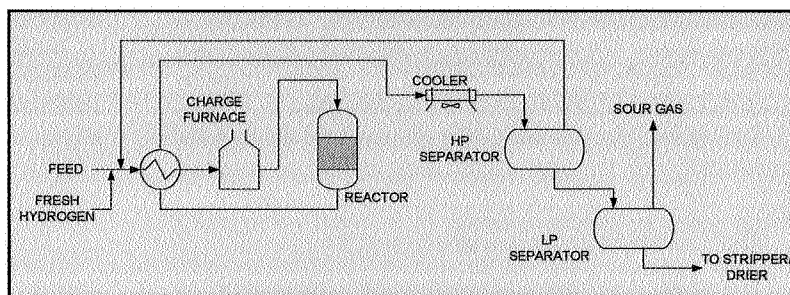


Figure 1. Typical hydrotreating process.

process capable of extracting hundreds of kilograms of sulfur per day directly from hydrogen sulfide, in a comparatively low operating cost process. The process features a high degree of sulfur removal, and so a plant bypass can be used to blend a sales gas product.

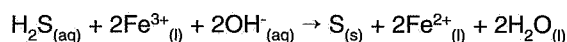
The species used for extracting the sulfur is a proprietary iron salt, known as a chelate, in which the iron ions are stabilised with organic complexes known as ligands. The salt was developed so that a high concentration can be used to reduce circulation flowrate. The reaction is fast and proceeds to completion, and consequently the reaction vessel hold-up time is minimal. This has the benefit that any hydrogen sulfide in the reaction liquor is converted to sulfur.

The process operates at ambient temperatures and is flexible to flowrate and feed concentration. It therefore lends itself to adaption to duties such as tail gas treating.

The sulfur product is not of the highest quality, as firstly it is delivered as a wet cake. Despite washing, the sulfur is contaminated with trace amounts of chelate salt and possibly residual sand entrained from the sour feed gas. The latter may be embedded in the sulfur particles as precipitation nuclei.

The sour feed gas may require pretreatment to remove residual heavy hydrocarbons or liquids, which are foam precursors. Following pretreatment, the gas is passed upflow concurrently with some reaction liquor. A mist flow regime is required, which passes over a proprietary packed column into a separator vessel. The tower is packed with static mixers, which ensure thorough gas/liquid mixing. All parts in contact with SulFerox liquor must be electro-polished 304 stainless steel, due to the corrosivity of the solution (slightly alkaline).

Hydrogen sulfide reacts almost instantaneously with the alkaline iron chelate solution and is oxidised directly to sulfur. The iron is reduced from the trivalent to the divalent species:



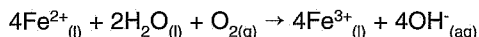
Any iron species contaminating the feed, such as oxide rust, sulfide scale or similar compounds are detrimental to reactivity and must be minimised.

The sulfur containing mist passes into a separator vessel, fitted with a demister pad, where the liquor collects in the conical bottom. Supernatant liquor from the side of the vessel is fed directly back into the contactor column, to minimise the size of sulfur recovery equipment. A slightly thicker slurry is withdrawn from the conical bottom and is passed for regeneration and sulfur recovery. The gas passes through the demister pad and into a knockout vessel for further liquid recovery. This vessel is also fitted with a demister pad. The sweetened gas is passed on for further processing or sales. Any liquid collected is returned to the contactor vessel with the supernatant liquor from the separator.

Sulfur slurry from the bottom of the separator is let down into the first of two flash vessels, to desorb residual gases. The first vessel operates at a pressure suitable for producing

fuel gas, and the second produces low pressure gas that is normally flared. An inline heater is provided between the two flash vessels, to warm the liquid to ambient temperatures and enhance desorption of residual gases.

The liquor then passes into an oxidiser vessel for regeneration of the iron compound, using compressed air:



The liquor is not oxidised to complete regeneration, to avoid excess oxygen being dissolved in the liquor fed to the contactor. This would lead to a risk of combustion of the process or flash gases.

Supernatant liquor is pumped back to the contactor to continue the process. However, it is returned with some caustic soda, to regulate the alkalinity, and a sulfur conditioning chemical to regulate the size of the sulfur particles.

The thickened slurry from the regenerator is then pumped with a helical cavity pump to a rotary vacuum filter. The vacuum is raised by a liquid ring pump, and the recovered filtrate is passed back to the regenerator vessel. It is possible to wash the sulfur cake formed on the cloth, which also provides more liquor for recycling. A sulfur cake is then available for sale or disposal.

Solvent systems

Solvent systems are normally used when the hydrogen sulfide concentration in the sour gas or LPG is moderately high. Although predominantly used for hydrogen sulfide removal, solvents can be tailored to other sulfur species and for carbon dioxide removal.

The sour fluid is passed through a column counter-current with the solvent and the hydrogen sulfide is absorbed chemically, physically or by a combination of these two means.⁴

As previously noted, solvents are grouped into chemical and physical absorption methods. Chemical solvents are normally amine based, and may be commodity or proprietary chemicals, whereas physical solvents are normal commodity chemicals. Both can achieve low acid gas levels in the treated gas, but chemical treating generally reaches lower levels.

Of the chemical solvents, the primary amines such as MEA are the most reactive, and extract not only hydrogen sulfide, but also carbon dioxide. This reactivity means that sales specifications can be easily achieved but the solvent is just as easily contaminated and degraded by absorbing carbonyl sulfide and carbon disulfide, which makes regeneration difficult. MEA is highly corrosive compared to secondary and tertiary amines and is not used much today. DEA is less reactive and is usually preferred when either carbon disulfide or carbonyl sulfide is present. DEA also has little selectivity between hydrogen sulfide and carbon dioxide. This is not usually a problem in refinery applications, where carbon dioxide content is low, but the high reactivity means contaminants can build up in the recirculating solvent, requiring disposal of a slip-stream or ion-exchange based cleanup.

Tertiary and sterically hindered secondary amines are even less reactive, reducing corrosion risks, but are reactive enough to absorb carbon dioxide. Typical of these amine types are tri-ethanolamine (TEA) and methyl-diethanolamine (MDEA). Di-isopropanolamine (DIPA) should be considered

if extraction of carbonyl sulfide is a priority.⁵

MDEA based solvents are very popular due to their low corrosivity and can provide selectivity to extract hydrogen sulfide and less reactive species. MDEA is the basis of many processes, such as those from BASF, UOP (Amine Guard FS), Dow Gas Spec and Shell ADIP.³ The low corrosivity means higher strength amine can be used, typically 40 - 55%, as compared to DEA, which is usually 20 - 35%. This has many benefits in terms of smaller plant size and lower capital costs, as well as lower operating costs.

Physical solvents are not often selected, other than for very high acid gas content feeds, due to their higher operating cost and lower hydrogen sulfide removal efficiency. However, the less extreme conditions for regeneration do give improved corrosion resistance. UOP/Union Carbide has had some success with SELEXOL,³ especially with high carbon dioxide content streams and where removal of heavier hydrocarbon from the feed gas is beneficial. Others include the Lurgi Purisol process (N-methyl 2 pyrrolidone), Linde's Rectisol (methanol solvent, mostly for cryogenic applications) and BASF's Sepsolv, the TPA DGA based process and the IFP methanol based IFPEXOL process.^{3,5}

Mixed systems of chemical and physical solvents are offered by Lurgi (Amisol), Exxon (Flexorb), UOP (Hi-Pure) and Shell (Sulfinol)³ and may be appropriate in certain circumstances.

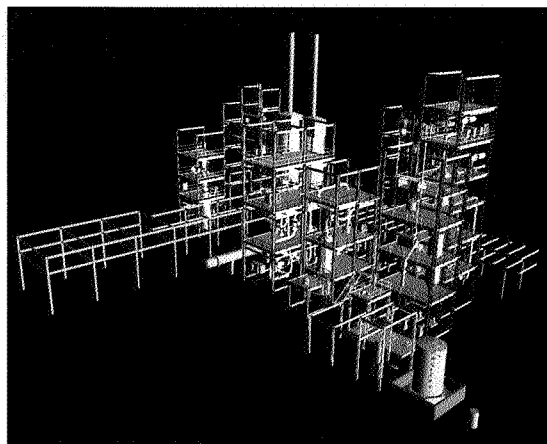
In the typical chemical process, lean amine passes down the absorption column and is contacted with upflowing sour fluid. The amine extracts the acid species, and a rich amine solution collects at the bottom. The rich amine solution must then be regenerated. Where carbon dioxide is present in only minor quantities, the regenerator produces a high concentration hydrogen sulfide acid gas (more than 90% hydrogen sulfide). Physical solvents absorb hydrogen sulfide also yielding a rich solvent, which is regenerated by reducing the operating pressure.

The hydrogen sulfide then desorbs out, but usually the solvent must also be steam stripped to fully regenerate. Flash vessels are also used in some chemical systems to remove gas from the solvent prior to regeneration.

Corrosion potential must be considered when selecting the solvent as the high temperatures found in the regenerator can cause high corrosion rates. This can be countered by stress relieving and proprietary corrosion inhibitors. Poor corrosion control not only leads to rapid amine degradation, but the formation of corrosion products known as heat stable salts. If not removed, these can lead to further amine degradation and corrosion. The usual removal method is to filter a 10% slip stream of lean amine, although the more amine that is filtered, the longer the amine life. Filtration capacity down to 5 microns should also be considered.

Carbon filters are also included on the slipstream, again for amine clean up. Solvent additives may be required if heat stable salts present problems.

Any sour gas feed to an amine system must be scrubbed to remove traces of liquid hydrocarbon, as these cause foaming. Foams can be eliminated by the use of anti-foam chemicals, but these are expensive and are normally rendered unnecessary by good design. Anti-foam chemicals can also cause as many problems as they solve.



Model arrangement for SulFerox plant.

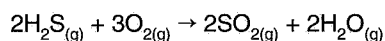
In recent years, improved understanding of the corrosion mechanisms inherent in acid gas treating has led to improved design and operation. Properly designed and well operated units should not incur problems with foaming, amine losses, heat stable salts or corrosion due to improved attention to upstream treatment, flash vessel design, good filtration, water washing, metallurgy selection, post weld heat treatment and stress relieving.⁵

As noted earlier, solvent systems can be used to treat both sour gases and light hydrocarbon liquids. However, solvent treatment of liquids can lead to high hydrocarbon losses, and so is only a preferred solution in certain circumstances.⁶

Simple Claus process

The Claus process is perhaps the classic process for sulfur recovery, and is probably the most common. It was originally developed at the end of the nineteenth century for partial combustion of acid gases containing 20 - 100% hydrogen sulfide, to form sulfur. Most Claus plants can achieve conversions of approximately 95%, but higher efficiencies can be achieved. The basic Claus process, as installed, has many variations, so a generic process will be described.¹

The first stage, after initial scrubbing, is the partial combustion of approximately one third of the hydrogen sulfide to sulfur dioxide:



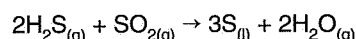
The design of combustion equipment for the Claus reaction is comparatively specialised, as it is categorised as a 'reaction' burner. If burner conditions are not correct, sulfur will be produced on the burner nozzle itself, leading to plugging. Incorrect combustion conditions at startup, when burning fuel gas can lead to carbon deposits on the burner.

The acid gas feed must be scrubbed of any hydrocarbon liquid, as this will be partially burned in the furnace to carbon, which turns the sulfur product an unacceptable black colour.

As the partial combustion process causes other reactions to occur, some sulfur is produced. Since this is an exothermic reaction, heat is released and this is recovered in a waste heat boiler. The flue gases are cooled, allowing the sulfur to be condensed, and a liquid forms. This must be drained from the waste heat boiler before the gas is reheated for feeding to the first reactor. The reheating is carried out in one of a number of ways. It could be by further partial combustion of hydrogen sulfide in an inline burner, or else in a heat exchanger. The former has lower operating costs, but the latter, typically using steam, allows better control of the temperature of the gas fed to the reactor.

The reactor is filled with a bauxite based catalyst. The performance of these catalysts is constantly being improved. The decision as to how to reheat is influenced by catalyst selection. If a very high level of sulfur recovery is required, an advanced grade of catalyst is needed, which in turn requires a stable reactor feed temperature. This is difficult to support with inline burners. This is exacerbated if the operator requires high turn down, and a steam reheater is normally specified for a high conversion process. If tail gas treating is installed, a lower sulfur recovery can be tolerated and, consequently, a lower operating cost process could be specified, which includes inline burners. Reactor instabilities may lead to catalyst deactivation by sulfur filling the catalyst pores, but it is possible to regenerate by burning off the sulfur. However, the reactor beds may then require frequent replacement.

An endothermic reaction occurs in the reactor bed, which encourages the formation of sulfur:



The gases are passed back through the waste heat boiler,

which allows more sulfur to condense. The process continues through cycles of reheat, catalysis and condensation to achieve a conversion target. A two step process is usual but up to four steps is conventional to achieve high recovery. Modern Claus processes usually feature two cycles followed by a tail gas recovery process.

At the end of the Claus process, a final knockout pot is provided for recovery of residual droplets of sulfur, which would foul cool equipment downstream.

A major factor in the operability of a Claus process is the stability of the process, which is influenced by the amount of air injected. Too little or too much air leads to reduced conversion, so the air injection rate is normally controlled by the ratio of hydrogen sulfide to sulfur dioxide in the exhaust gas. This is known as the tail gas ratio, and should be analysed continually. The better the analyser, the better the control of air injection and the better the conversion control. A ratio of 2:1 is the normal target.

Process design is influenced by the need to handle liquid sulfur at a tightly controlled temperature. Jacketed pipework is normal to ensure that the sulfur is maintained at approximately 140 °C as otherwise the viscosity of the liquid increases unacceptably. Pipework should be designed for free draining into a pipe, but dip-legs need to be incorporated to avoid blowing exhaust gases through the sulfur drains. These dip-legs can be proprietary designs, due to the need to check flows. All pipework should be in small flanged sections to allow disassembly for clearing, and any right angled bends should be provided with rodding eyes. It is a fact that wherever there is a low flow point, sulfur will collect, solidify and require clearing. A typical example of this is flame detectors, which should be constantly purged with nitrogen or air and also fitted with rodding eyes to clear sulfur plugs.

A liquid sulfur storage vessel is usually provided. Typically this is an underground vessel fitted with steam coils to maintain the product in the liquid form.

Sulfur degassing may be needed as residual hydrogen sulfide dissolves in the sulfur. This will desorb in the storage vessel, creating a hydrogen sulfide atmosphere above the sulfur. This causes problems when handling the sulfur but systems can be provided to degas the liquid. The simplest process involves educting the vapour space into an incinerator or flare.

Enhanced Claus processes

Most licensors offer enhancements to the basic Claus process. Some are aimed at new plants, some at existing plant revamps. The latter are very common, due to increased demands on existing facilities for increased sulfur recovery. Most of these processes involve injection of gaseous oxygen, either in the feed to increase plant throughput or downstream to increase sulfur conversion. A thorough review of the existing equipment is necessary to determine whether the higher temperatures produced by the revamp are acceptable. More advanced catalysts are also usually needed.

Enhanced Claus processes have also been developed for the recovery of sulfur from leaner acid gases. These direct oxidation processes are not generally competitive with redox processes, as the acid gas dilutant is usually carbon dioxide rather than flammable hydrocarbons. However, a redox process could be used on a lean acid gas stream.

Sour water stripping

A number of hydrocarbon processes liberate free water that is contaminated with hydrogen sulfide. This gives the water a strong smell and so it is usually known as 'sour water'. This corrosive water cannot usually be used anywhere else on a plant and must be treated. Plant effluents also cannot

be allowed to contain significant concentrations of hydrogen sulfide and the water must be stripped. Hydrogen sulfide stripping is normally carried out in a column, with direct steam injection. The stripped vapours are either incinerated to convert the hydrogen sulfide to sulfur dioxide, or treated to completely remove the sulfur and then released into the atmosphere.

Ammonia is also often present in sour water. Under normal circumstances this must be stripped out, but the stripping duty is higher than for hydrogen sulfide. Consequently, stripping steam ratios can typically be over double those for hydrogen sulfide alone.

One factor to consider with the design of sour water stripping units is the capacity of the feed drums, as sour water production rates can be highly variable. Not only must there be sufficient capacity to 'shave out' peaks but there should be sufficient residence time for hydrocarbon liquids to be skimmed off.

The process scheme typically includes a column, normally packed, for ease of internals replacement. This is a highly aggressive duty for packings, so either regular replacement is necessary or exotic metallurgy is required.

A feed/bottoms exchanger provides most of the heat input, with the rest being provided by direct steam input. The stripped water normally requires cooling prior to disposal or reuse.

Tail gas treating

Tail gas treating has become an issue in sulfur processing in recent years. Prior to this, the residual gases from a Claus plant with 94 - 96% sulfur recovery would be incinerated, together with sour water stripper offgases. However, recent environmental constraints have meant releases of sulfur in whatever form must be limited. Consequently, processes have been developed for the treatment of these tail gases.

Incineration has traditionally been the main method of hydrogen sulfide removal: burning it at high temperature for a short residence time, to form sulfur dioxide. This may still be acceptable in some areas but not in Europe and North America. Residence times of approximately 0.5 s and temperatures in excess of 700 °C are normally required. Catalytic incineration is another process route to ensure complete combustion.

Many processes have been developed for tail gas treatment and it has been noted that the SulFerox or other redox processes may be considered. MDEA based extraction processes are also becoming popular, such as the TPA Result process. Here, the residual hydrogen sulfide is absorbed in a circulating amine solution, and the liberated acid gas reprocessed in the Claus unit.

Consideration should be given to the sulfur component composition of the tail gas. Claus units are normally controlled to give a 2:1 ratio of hydrogen sulfide to sulfur dioxide. This indicates that under normal conditions, sulfur dioxide will also be present in the tail gas. This is not absorbed in any amine system, so either the Claus conditions must be changed to reduce the sulfur dioxide content (and so the Claus conversion) or the sulfur dioxide must be hydrogenated. Hydrogenation is favoured to minimise tail gas treater capacity. The tail gas is reacted with hydrogen over a catalyst, with the latter being produced by air limited combustion of fuel gas. The TPA Result and Shell SCOT technologies are typical of these processes.³

A major consideration in process selection is the routing after treatment. Most treated tail gases are passed to flue

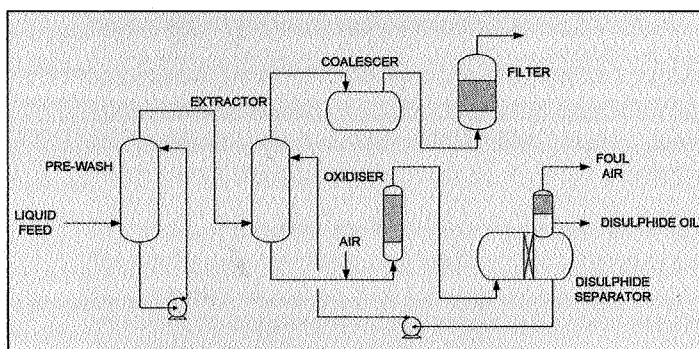


Figure 2. Typical regenerative caustic process.

stacks, so the tail gas must remain at a high temperature. This precludes water based processes. The alternative is to have a separate vent for the tail gas.

Hydrotreating

As noted, all natural hydrocarbon streams can include sulfur species in a stable form. When using hydrocarbons as a fuel, the sulfur must be eliminated without losing the valuable hydrocarbon. The normal way to do this is to hydrotreat using hydrogen at high temperatures (approx 350 °C) and elevated pressures (30 - 50 barg) over a cobalt-molybdenum based catalyst. This process, also known as hydrodesulfurisation, liberates hydrogen sulfide.

The process normally features a two stage separation system after post reaction cooling. The first liberates sour hydrogen for recycling; the second, lower pressure separator desorbs a sour fuel gas that is normally processed in an amine unit for hydrogen sulfide extraction. A number of licensors offer such technology.

The hydrotreating process can be made more severe where hydrogen is used to crack long chain hydrocarbons into smaller, higher value molecules. This is also known as hydrocracking. Hydrotreating is a very complex subject and it is not considered appropriate to fully describe the design issues in this article.

Fuel oil treatment

The vapour space above fuel oils can contain noxious amounts of hydrogen sulfide from delayed desorption of the gas following refinery processing. Chemical treatment of the fuel oil is available to reduce the concentrations of the hydrogen sulfide, but a vapour purge system may be preferred.

Conclusion

Sulfur removal technology must be properly selected to achieve the purpose for which it was designed. Existing technology, which has been proven by experience, is being constantly improved to give better performance and reliability. New technologies are also being developed for new plant and retrofits to limit the environmental effect of sulfur processing. As environmental limits become more stringent, it will be increasingly important to review process selection and design issues.

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