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Sulphur recovery process from acid tail gas and environmental implications

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ABSTRACT

Removal of sour gases from acid gas during processing of natural gas is one of the necessary steps towards harnessing fuel efficiency. Our studies on selection of suitable sulfur recovery process from acid gas revealed that liquid phase oxidation process is best suited for safe disposal of acid gas. The liquid redox processes such as LOCAT process (Hydrogen sulphide being absorbed in chelated iron solution) and SulFerox process (converting H₂S in sour gas to elemental sulfur through reaction with ferric ion) were observed highly efficient. Iron chelate based liquid phase oxidation process has been observed most suitable for treating the acid gas generated at Oil and Natural Gas Commission (ONGC) Plant. Both LOCAT and SulFerox processes are, hence, recommended to ONGC in the turnkey package for potential decision support in favour of designing ONGC plant.

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1. Introduction

Increasingly stringent environmental emission standards have raised certain pertinent issues with regard to off-shore gas containing SO₂ (Joseph, 1988; Nagl, 1997) since elemental sulfur has traditionally been a problem in aqueous system due to its extremely insoluble in water, and thus nucleates rapidly forming small particles (Clute,

1982). Among the options available for the ultimate disposal of off-gas containing SO₂, the production of elemental sulphur is highly attractive (Kowszun, 1979). Acid gas treating has traditionally required an amine plant to remove hydrogen sulphide and a Claus unit to convert the concentrated hydrogen sulphide stream to sulfur (Seeger et al., 2011). The SulFerox process on the other hand, is an alternative to these steps, by removing hydrogen sulphide directly from gas streams and converting it to elemental sulphur (Villa and Ramshaw, 1991).

Over the years, acid gas popularly known as sour gas predominantly containing CO₂ and H₂S gas released from the Oil and Natural Gas Commission (ONGC) plant becomes increasingly sour, and it has increased the H₂S gas concentration from 700-800 ppm in 1998-99 to 1200 ppm, and maximum of 1950 ppm occasionally is recorded. This is a potential source for future H₂S hazard, a long term solution for the disposal of such acid gas is, therefore, required. Accordingly, a study for selecting a suitable process to remove the H₂S from acid gases generated in gas sweetening unit (GSU) was undertaken.

2. Process principles

Oil and Natural Gas Commission's western Onshore Process Complex located at Institute of Oil and Gas Production Technology, about 200 km from the Mumbai offshore in India was selected as the location of the study. Oil and gas processing here involved the following steps such as: i. unstabilized crude gets stabilized in Crude Stabilization Units (CSU), ii. gas is compressed in CSU off-gas compressors, iii. slug catchers receive gas along with dropout condensate, iv. condensate Fractionation Unit (CFU) is used to process condensate separated from slug catchers, v. lighter Hydrocarbon and acid gas stripped in stripper column and sent to Gas Sweetening Unit (GSU), and vi. plant delivers the products like stabilized crude, lean gas, LPG, NGL and C₂-C₃ to various end users. Oil and gas from off-shore are received at ONGC plant through separate trunk lines from off shore facilities. Gas separated from slug catcher contains gases like H₂S and CO₂, which are harmful and highly corrosive for operation in down-stream units. These sour gases are removed in sulfinol-D based gas sweetening plant. The sweetened gas is sent for further processing in down-stream units and acid gases released during the regeneration from the regenerator are disposed in the atmosphere with a help on an elevated through a 50 meter high vent stack for smooth dispersion of gases adhering environmental norms.

Gas along with the dropout condensate is received in slug catcher units. Condensate separated from the slug catchers is processed in condensate fractionation unit (CFU) along with the second and third stage condensate generated in CSU off-gas compressor plant. In CFU, the lighter hydrocarbon and acid gases are stripped in stripper column and sent to GSU. The bottom liquid from stripper column is further fractionated in LPG column to produce LPG and Naphtha.

Gas separated from slug catcher contains gases like H₂S and CO₂ which are harmful and highly corrosive for operation in down-stream units. These sour gases from slug catchers is routed to gas sweetening unit (GSU) for removal of H₂S and CO₂. There are two trains (train 12 and 13) of GSU and third one is under construction with each train processing around 5.75 MMSCMD of gas during normal operation. The sour gas first enters into inlet knockout drums (KODs) to knock out any liquid from the gas. Gas from inlet KODs is sent to the absorber column where acid gas like H₂S and CO₂ are removed by counter-current contact with lean amine solution. ONGC plant operated two identical Gas sweetening units (GSU-12 and GSU-13), which were designed based on the Sulfinol-D process. The GSU trains remove acid gases from associated and other gases from offshore & satellite fields. Crude Stabilization Unit (CSU) off-gas and Condensate Fractioning Unit (CFU) off-gas. GSU-12 and GSU-13 are identical, and were designed to treat 5.75 MMSCM/D, each of feed gas containing 4.0% (mol) CO₂ and 450 ppm (mol) of H₂S. The GSU designs are based on a sulfinol-D solvent.

There are various solvents used along with Sulfinol-D. They are expressed as weight percent of pure amine in the aqueous solution. Monoethanolamine (MEA) containing about 20% for removing H₂S and CO₂, and about 32% for removing only CO₂. Diethanolamine (DEA) contains about 20 to 25% for removing H₂S and CO₂. Aqueous solutions of MEA (solutions of MEA in water) are used as a gas steam scrubbing liquid in amine treaters. For example, aqueous MEA is used to remove carbon dioxide (CO₂) from fuel gas. DEA is used as a surfactant and a corrosion inhibitor. It is used to remove hydrogen sulphide and carbon dioxide from natural gas. In oil refineries, a DEA in water solution is commonly used to remove hydrogen sulphide from various process gases. It has an advantage over a similar amine ethanolamine in that a higher concentration may be used for the same corrosion potential. This allows refiners to scrub hydrogen sulphide at a lower circulating amine rate with less overall energy usage. Methyl diethanolamine (MDEA) is a clear, colourless pale yellow liquid with an ammonia odour. MDEA is a

tertiary amine and is widely used as a sweetening agent in chemical, oil refinery, syngas production and natural gas. It has ability to preferentially remove H₂S (and slip CO₂) from sour gas streams.

Gases containing H₂S or both H₂S and CO₂ are commonly referred to as sour gases. The process includes an absorber unit and a regenerator unit as well as accessory equipment called hydrosulphurization. This H₂S-rich stripped gas stream is then usually routed into a Claus process to convert it into elemental sulphur.

2.1. Absorber

In the absorber, the downflowing amine solution absorbs H₂S and CO₂ from the upflowing sour gas to produce a sweetened gas stream (i.e. an H₂S-free gas) as a product and an amine solution rich in the absorbed acid gases. The stripped overhead gas from the regenerator is concentrated H₂S and CO₂. In oil refineries, that stripped gas is mostly H₂S, much of which often comes from a sulphur-removing process.

2.2. Available processes

The acid gas removal can be accomplished by following commercially available processes viz., Claus-Scot, liquid redox (LOCAT and SulFerox) and disposable solids and liquids (Sulfa-Treat, Sulfa-Scrub, etc.). Claus process is best known and most widely used sulphur production process in industry. It is most applicable for production of sulphur from acid gas stream containing from about 20-100% H₂S. This process involves vapour phase oxidation from H₂S with air. Advantages of Claus process are : proven technology, produce bright sulphur, designed to convert COS and destroy ammonia and has relatively low operating cost due to net steam production. However, the disadvantages of the process could be enumerated as it requires acid gas feed stream relatively rich in H₂S (>20%) and maximum sulphur recovery is about 97-98%. Therefore, this process requires a subsequent tail gas clean up unit like Scot.

SCOT process (Shell Claus Off-gas Treating) was developed by Shell, and introduced in the early seventies as a attractive process for improving the efficiency of Sulphur Recovery Unit (SRU), Since the first unit was started-up in 1973 more than 120 units have been built with a wide range of capacities. SRU plant is normally located in Petroleum Refineries in combination with hydrogen sulphide removal plant in a Hydro-sulphurization (HDS). The HDS process is one of the most important key technologies for refining low grade fuels and preventing air pollution from internal combustion engines and burning facilities.

Gas from SRU is heated via inline burner and introduced into reactor (R-1). All sulphur compounds in the gas, leaving the SRU excluding H₂S e.g. SO₂, COS, CS₂ elemental sulfur are converted into H₂S by a reducing agent such as hydrogen over a special catalyst at an elevated temperature. Hot H₂S-containing gas leaving the reactor is cooled in two stages; first a waste heat boiler producing low pressure steam, and then a quench column, in which steam present in the gas is condensed and set to a sour water stripper. The cooled gas is subsequently treated in an amine absorber (C-2) and the fat solvent (rich-amine) from C-2 is sent for regeneration, the absorbed gas is stripped out in regenerator (C-2). The regenerated solvent (lean amine) is sent back to C-2. The OVHD gas containing the H₂S is returned to SRU unit and the off gas from Scot containing small amounts of H₂S is routed to an incinerator. As a result, almost all the sulphur compounds introduced into SRU are converted to elemental sulphur by the combined system of SRU and Scot process.

Liquid redox processes employ aqueous-based solutions containing metal ions, usually iron, which are capable of transferring electrons in reduction-oxidation (redox) reactions. Currently, the redox process of choice is the LOCAT process, which is licensed by Gas Technology Products LLC. In this process, a non-toxic, chelated iron catalyst is employed to accelerate the reaction between H₂S and oxygen to form elemental sulphur. As implied by its generic name, liquid redox, all of the reactions in the LOCAT process occur in the liquid phase in spite of the fact that it involves vapour phase reaction. In the process, the sour gas is contacted in an absorber with the aqueous, chelated iron solution where the H₂S is absorbed and ionizes into sulphide and hydrogen ions. This reaction is mass transfer limited. The dissolved sulphide ions then react with chelated, ferric ions to form elemental sulphur. This reaction is very fast and is not equilibrium limited. In addition, since the reactions are occurring at ambient temperatures, the sulphur is formed as a solid. The solution is then contacted with air in an oxidizer where oxygen is absorbed into the solution and the ferrous ions are converted back to the active ferric state.

SulFerox is a redox-based process that converts the hydrogen sulphide in sour gas to elemental sulphur through reaction with aqueous ferric ion. The process forms solid sulphur particles that are easily filtered out. There are three steps in the process : absorption, regeneration and sulphur recovery. During absorption, the sour gas stream comes into contact with a liquid containing soluble iron (III), and hydrogen sulphide is selectively

oxidised to form elemental sulphur. Regeneration involves reoxidation of the iron(II) to maintain a supply of active iron(III). To maximise sulphur recovery, the elemental sulphur formed in the first reaction is concentrated in a surge tank and then filtered out. The filtrate is returned to the process for maximum ferric iron solution recovery. Acid-gas treating has traditionally required an amine plant to remove hydrogen sulphide and a Claus unit to convert the concentrated hydrogen sulphide stream to sulphur. The SulFerox process is an alternative to these steps and consequently offers substantial savings in capital and operating costs by removing hydrogen sulphide directly from gas streams and converting it to elemental sulphur.

3. Experimental results

The successful utilization of H₂S by converting it to sulphur and H₂ attains the triple objective of waste minimization, resource utilization and environmental pollution reduction (Eow, 2002). The selection of suitable sulphur removal process is mainly governed by the total sulphur loading, which in turn depends upon the acid gas flow rate and H₂S concentration. Application range and suitability of various processes commonly followed by the industry provide fair option for the process selection (Fig.1). Various acid gas parameters used in ONGC plant have undergone substantial changes, especially the concentration of SO₂ gas (Table 1). Design base of ONGC plant is further described (Table 2).

Table 1
Changes in acid-gas parameters over time (1998-2013).

	1998-99	2012-13
Average pressure (Kg/cm ² a) outlet of GSU	1.2	1.4
Average temperature (OC)	40-42	42-45
Present acid gas flow rate (NM ³ /Hr/Unit)	~6000	~5000
Molecular weight		43.45
Composition (mole %)		
C1	1.50	1.63
C2	0.58	0.51
C3	0.60	0.64
iC4	0.06	0.08
nC4	0.11	0.13
iC5	0.02	0.01
nC5	0.00	0.00
C6+	0.22	0.00
CO ₂	95.80	96.60
N ₂	0.30	0.39
H ₂ S concentration (ppm)	770	1950

The existing tail-gas clean-up technologies can be classified into two groups.: those that attain 99% overall sulfur recovery efficiency, and those that achieve 99.9% efficiency, including the sulphur recovered in Claus units (Eow, 2002). Claus process is most applicable for production of sulphur from acid gas stream containing from about 20-100% H₂S. This process involves vapour phase oxidation of H₂S with air. In addition, process is well proven technology to produce bright sulphur, designed to convert COS and destroy ammonia and HCN and requires relatively low operating cost due to net stream production. However, this process has certain distinct disadvantages viz., process requires acid gas feed stream relatively rich in H₂S (>20%) and maximum sulphur recovery is about 97-98%. Therefore, it requires a subsequent tail gas clean up unit like Scot process. Scot process possess: i. high reliability and stability in operation, ii. sulfur recovery efficiency exceeding 99.9%, and iii. flexible design alternatives, applying various reducing gases, using different solvents and so on. The only disadvantage is that it requires regular clean up which is expensive.

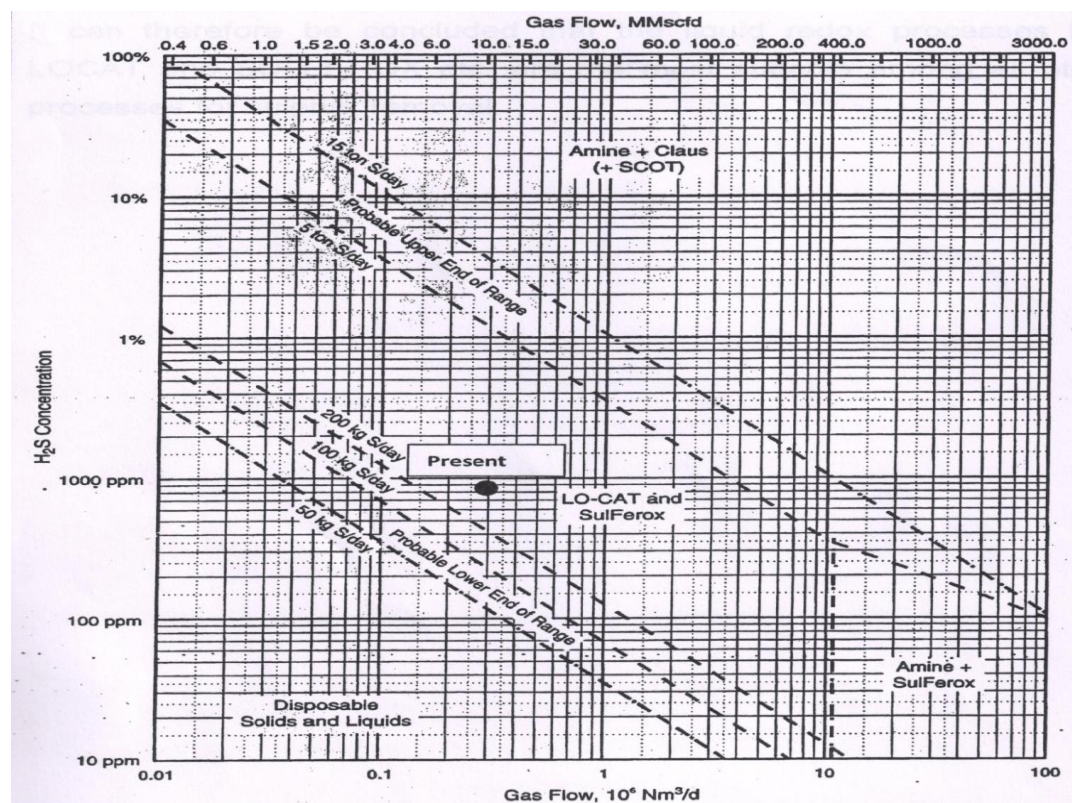


Fig. 1. Application range and suitability of various sulfur recovery processes.

Although iron-based, liquid redox processes have gained acceptance as evidenced by over 150 units being licenced worldwide, there are still areas in the process, which need to be improved upon. Operating costs for aqueous iron-based redox systems are composed of replacing chemicals which are either oxidised in the unit or which are physically lost from the unit. Sulfur produced from liquid redox system has the same chemical assay as Claus sulfur, and it does have several commercial uses in its unmelted form. On the other hand, LOCAT and SulFerox Process, a liquid redox processes employ aqueous-based solutions containing metal ion, usually iron which are capable of transferring electrons in reduction-oxidation (redox) reactions (Table 3). In this process, a non-toxic, chelated iron catalyst is employed to accelerate the reaction between H₂S and oxygen to form elemental sulphur. The conventional mode of operation for a Claus unit is to convert one third of the H₂S to SO₂, which then reacts with remaining H₂S to form elemental sulfur. This is accomplished by carefully controlling the quantity of oxygen entering the system. Due to equilibrium limitations, some of the SO₂ leaves the system with the tail gas. If the unit is operated in a manner such that there is insufficient oxygen to complete the reaction giving SO₂, then there will be insufficient SO₂ produced to complete the reaction yielding sulfur and then H₂S removal efficiency will be reduced. However, the amount of unreacted SO₂ in the tail gas will also decrease.

Table 2

Design base of the ONGC plant.

Parameter	Value
Acid gas flow rate (MMSCMD)	0.24
Pressure (Kg/cm ²)	1.4
Temperature(OC)	50
Inlet H ₂ S content (ppm)	2000
Outlet H ₂ S (ppm)	4

Disposable solids and liquids like Sulfa-Treat, Sulfa-Scrub, etc. are used for removal of small amount of H₂S; say sulphur less than 50-200 Kg/d. Disposal cost can often exceed the first cost of scavenger chemical sulphur

recovery with these processes is usually uneconomic. It can, therefore, be concluded that the liquid redox processes like LOCAT and SulFerox etc. are the most suitable among all other processes for sulphur removal (Table 3).

Table 3

Features of different sulfur recovery processes tested in ONGC plant.

Parameter	Present case	Claus-Scot	LOCAT/SulFerox	Disposable
Flow rate (MMSCMD)	0.24	All range	< 10	< 7
H ₂ S (%)	0.2	> 20	All range	< 1
Sulphur load (Kg/d)	680	> 15000	200-1500	< 100

Claus units can easily achieve hydrogen sulphide removal efficiencies exceeding 99.9% by employing a liquid redox system such as LOCAT as a tail gas treating unit. The combination of Claus and liquid redox has a significantly lower capital cost than conventional amine-based tail gas units which offsets its higher operating costs. In addition, the liquid redox unit will significantly reduce the inherent sensitivity of the Claus unit to changes in feed gas composition and flow rate (Kowszun, 1979; Clute, 1982; Dalrymple et al., 1989).

Liquid phase oxidation systems have undergone considerable evolution during 20th century, and this will continue into the 21st century. Foreseeable developments for the near future will be smaller equipment sizes and lower operating costs which will be achieved by the development of better oxygen mass transfer devices reducing the amount of air required and the size of oxidizers made by the addition of free radical scavengers into the system.

4. Conclusion

The conclusions drawn from the studies conducted comprised of :

Maximum sulfur recovery of 97-98% was obtained with Claus process. Therefore, this process requires a subsequent tail gas clean up unit like Scot process.

SulFerox proved to be flexible system (with regard to changes in gas volume and H₂S content) with comparatively lower operating cost (suitable at both low and high pressure) and non-toxic elemental sulfur product.

Use of chelated iron enables desired acceleration in reaction between H₂S and O₂ to form elemental sulfur.

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