HYDROGEN SULFIDE REMOVAL FROM BIOGAS BY ISET PROCESS

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Abstract:

Hydrogen sulfide is a highly toxic and corrosive gas which is one of the larger pollutants of the atmosphere. The burning of the gas releases sulfur dioxide which is also a corrosive and toxic gas. Cleaning of this gas is necessary not only for pollution abatement but also for effective use of the gas mixtures like natural gas, biogas etc for end use application like power generation in IC engines where the presence of hydrogen sulfide at higher concentration corrodes the internal parts of the engines in a very short operational duration of run. This paper addresses the removal of hydrogen sulfide from biogas generated by ETP's and STP's by a patented ISET process which is a modified liquid redox process developed at CGPL, IISc, Bangalore and which has been tested on commercial scale quite extensively and which has installed power generation capacity of 4.8 MWe.

The hydrogen sulfide concentration is brought down from the designed level (volume percentage of biogas) to less than 50 ppm and the hydrogen sulfide is oxidized to elemental sulfur that is precipitated and is filtered. The process consists of two stage countercurrent scrubbing of hydrogen sulfide from biogas using a chelated polyvalent metal ion which undergoes reduction, followed by removal of precipitated sulfur in the filtration unit and the oxidation of the reduced metal ion using oxygen in the air, for recycling.

As a case study, one of the installation at USWL, which has recorded around 20,000 hours after its installation is considered. The system has scrubbed around 3.6 million m^3 of biogas and generated 5.1 million units of electrical energy during the period. At an average concentration of around 4.5 % hydrogen sulfide in the raw gas, the amount of H_2S removed is 0.16 million m^3 and 200 tons of sulfur precipitated. Use of the scrubber has helped in improving the overall efficiency of conversion to electricity and reduced the emissions. The operating cost works out to be 2.5 US cents per kWh.

1. Introduction:

Industrialization and urbanization of the society in the present world has increased the levels of pollution in all the three sectors, land, air and water due to the wastes generated. Proper treatment and disposal of the same in order to prevent the damage to the natural resources and the environment is being recognized and pursued at various degrees of seriousness around the world. Different methods are in vogue depending on the type of waste, biodegradable or non-biodegradable. One of the most common and effective ways of treating the biodegradable matter is anaerobic digestion and is infact, part of most of the distillery effluent treatment plants and sewage treatment plants. Biogas, the product of anaerobic digestion is a mixture of Methane, Carbon dioxide and Hydrogen sulfide. The composition of biogas is mainly Methane, CH_4, (55-65 %), Carbon dioxide, CO_2, (30 - 40 %) and hydrogen sulfide, H_2S, (0 - 6 %) depending on the type of waste and the temperature of the digester used. The calorific value of biogas is around 24 – 28 MJ/ m^3 (depending on the CH_4 content in the gas) and is a potential and efficient fuel source for power generation using IC engines, if the hydrogen sulfide is removed from it.

1.1 Need for Hydrogen Sulphide Removal:

Hydrogen sulphide is a highly toxic and corrosive gas and is a major pollutant in fossil fuel based industries, sulphur based chemical Industries and biogas based units Sweetening of biogas is essential because of its toxicity which affects the environment and the highly corrosive nature which corrodes the metallic parts like boiler tubes, engines coming in contact with it in few hundred hours of operation. The toxicity of H_2S is more than hydrogen cyanide (1).

IC engine application requires H_2S concentration to be less than 1000 ppm, limit which is dependent on individual engine manufacturer, but lower the level better is for the life of the engine.

2. Processes for removal of Hydrogen sulfide:

Different processes like absorption and desorption by amine followed by Claus process for sulfur recovery, Liquid red-ox process, absorption by caustic solution and the subsequent biological regeneration of the same are being used for scrubbing hydrogen sulfide from the gas stream. Amongst the various methods for removal of hydrogen sulfide, modified versions of Claus process and Liquid red-ox process are the most common and widely used.

Claus process which is a vapor phase oxidation process in multiple stages scrubs hydrogen sulfide at higher concentrations (more than 15% v/v) and converts to sulfur, has an efficiency of around 97 % for a three stage process (1). The Liquid red-ox process can treat gas economically and efficiently, with fluctuating gas flow and with low to medium level (0.5 % – 10 %) but fluctuating hydrogen sulfide concentrations.

3. ISET Process:

ISET process developed by CGPL, IISc, Bangalore, is a modified liquid red-ox process using chelated polyvalent metal ion with a stabilizing agent. The process utilizes the oxidation reduction potential of chelated iron in aqueous medium, for scrubbing hydrogen sulfide from the biogas.

The need for developing a modified liquid redox process mainly arose due to lack of a suitable and reliable indigenous technology in the country and the imported liquid redox systems being expensive. The present technology is about a third of the cost of the one of the technologies available outside India (1). The systems based on Claus process are likely to be far more expensive at the flow rates of relevance to applications considered here (600 m^3 per hr at 7.5 % hydrogen sulfide in the gas that corresponds of 1.5 tonnes per day of sulfur)

3.1 Process:

The two stage counter current process consists of Reduction and Oxidation stages.

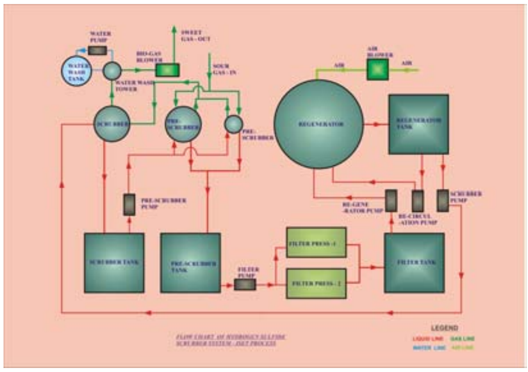

Fig 1. Flow Chart ISET Process

3.1.1Reduction:

The dissolved sulfur ions reduce the Fe^{3+} ion to Fe^{2+} ion in two stages. The sour gas consisting hydrogen sulfide first enters the Pre-scrubber, which is a packed column with larger size packing, from the bottom. The scrubbing liquid is uniformly distributed using liquid header form the top, over the packing. The liquid from the tower having maximum precipitated sulfur is pumped to the filter press for sulfur removal. The counter-current contact of the scrubbing solution with the gas, scrubs most of the hydrogen sulfide from the raw gas and nearly sweet gas enters the second stage scrubbing in the scrubber. Scrubber consists of smaller size packing for larger contact area to remove the hydrogen sulfide to the desired ppm levels and the scrubbing solution is pumped from the regenerator uniformly using a liquid header counter to the gas flow. The clean gas after passing through the mist eliminator of the scrubber is washed with water in the wash tower to remove any small liquid carry over by the gas.

$$H_2S + H_2O \longrightarrow 2H^+ + S^{2-} \quad 1$$
$$2Fe^{3+} + S^{2-} \longrightarrow 2Fe^{2+} + S \quad 2$$

3.1.2 Oxidation:

The liquid containing ferrous ions after the sulfur filtration stage is pumped into a packed column regenerator which provides large contact area. Oxygen in the air from the bottom comes in counter current contact with the reduced scrubbing solution, oxidizes the ferrous ion back to ferric ion and the solution is recycled back to the scrubber.

$$2Fe^{2+} + H_2O + O_2 \longrightarrow 4Fe^{3+} + 2OH^- \quad 3$$

The process uses packed columns for adsorption and regeneration combined with online sulfur removal from the liquid before it enters the regenerator. The usage of packed columns for adsorption and regeneration provides larger surface area for the reaction to occur, reduce the cost of pumping the gas/air compared to other liquid redox processes which employ spargers for gas/air pumping and eliminate the blockages encountered in sparging systems due to the sulfur present in the solution. Online removal of sulfur after the reduction stage in the present process ensures clear liquid going to the regenerator which facilitates better air liquid contact due to the absence of sulfur in the stream and also prevents the blocking of the regenerator column. The system can handle large fluctuations in biogas flow rates meaning a high turndown ratio, which can be as low as 1:5. The power consumption is around 8 – 10 % of the maximum designed power level which is comparable or slightly less with other liquid redox processes (6)

Sulfur produced by the process is very fine in nature due to nucleation of the insoluble sulfur produced in during precipitation (2). The sulfur precipitated has a particle size of between 1 – 8 microns with 90 % of the particles below 5 microns (particle size is measured using Laser diffraction technique) and a purity of more than 98 % is easily achieved by simple washing with water. The sulfur produced by liquid redox process is amorphous in nature and finer particle size compared to the sulfur produced by Claus process. The sulfur produced is being used in agricultural fields as soil amendment for pH adjustment, nutrient and a pesticide (3). The finer particle size, higher the dispersability and presence of small quantities of iron in the sulfur from this process make this sulfur easily absorbed, highly reactive and more suitable for agricultural purpose compared to the sulfur produced by Claus process. This would mean a better economical value for this grade of sulfur which can be readily used without any further processing. Typically the sulfur by this route should fetch about three times the price compared to the sulfur used in sulphuric acid production.

4. Experimental Work

Basic studies to understand the reduction of hydrogen sulfide to sulfur, the oxidation of the ferrous ions to ferric ions and chelate degradation studies were carried out to understand and optimize the process parameters. The reduction studies are not discussed here as they have been extensively studied and documented earlier (4, 5).

Experimental studies to study the oxidation reactions were carried out in HDPE column of 200 mm in dia and 2000 mm height including the space above the packing for the liquid header and mist eliminator. Raschig rings were used as packing material and the packing height was 1000 mm. The liquid containing ferrous ions was pumped from the top of the column using a liquid header and the air was drawn from the bottom of the regenerator. Catalyst iron concentrations used for the experimental studies were in the range of 0.19 to 0.21 M.

The experiments were carried out with different liquid and air flow rates. The flow rates were measured using flow meters. The experimental results show that the oxidation rate is similar for the two different air flow rates (higher and lower) suggesting that increase in the air flow rate does not increase the oxidation rate as the reaction is controlled by slower rate of dissolution of oxygen present in the air. The experimental results also show the regeneration rate at the end of each run for particular air and liquid flux is 15 – 20 % of the original ferric ion concentration.

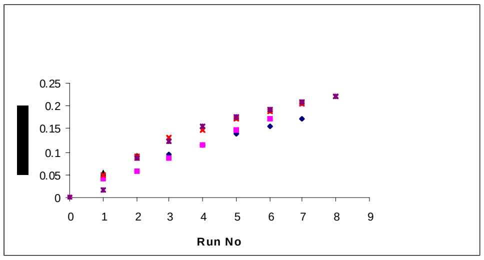

Figure 2: Regeneration results

Chelate degradation occurs during the oxidation stage (7) and is an inherent drawback with any liquid redox systems. Various processes employ stabilizing agents and specific operation conditions to minimize the chelate degradation. Studies were conducted with and without stabilizing agents and it were found that the addition of stabilizing agents in small quantities (0.01 M) helps in improving the chelate stability.

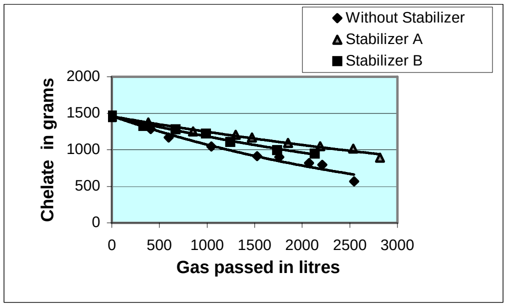

Figure 3: Chelate Degradation

5. Field Installations and Performance of ISET scrubbers

5.1 Field Installations

Table 1

Sl. No	Location	Type of User	Design Capacity	Status
1	UP Jal Nigam, Kanpur, India	STP	900 m^3/hr 3 % H_2S 1.6 MWe	Running for 6 – 8 hrs a day H_2S in Sweet Gas < 10 ppm
2	UP Jal Nigam, Allahabad, India	STP	600 m^3/hr 3 % H_2S 1.1 MWe	Running for 4 - 6 hrs a day H_2S in Sweet Gas < 10 ppm.
3	KCPSIC Ltd, Vuyyuru, Andhra Pradesh, India	ETP	600 m^3/hr 7.5 % H_2S 1.0 MWe	3.0 million kWh generated H_2S in Sweet Gas < 50 ppm
4	USWL, Ugar Khurd, Belgaum, Karnataka India	ETP	600 m^3/hr 7.5 % H_2S 1.0 MWe	7.0million kWh generated H_2S in Sweet Gas < 50 ppm
5	VISHTEC, Melvisharam Ranipet, Tamilnadu, India	Leather fleshings	13.5 m^3/hr 3.0 % H_2S 30 kWe	Running for 6 hrs a day. H_2S in Sweet Gas < 10 ppm

5.2 Performance

ISET scrubbers have been designed and installed for 24 hrs X 7 days. The scrubbed gas is used for power production in IC Engines either in duel fuel mode in diesel/fuel oil engines or in gas engines. As can be observed from the above table the H_2S concentration in the scrubbed gas in all the installations is less than 50 ppm at the maximum.

5.3 Case Study – Ugar Sugar Works Limited.

Effluent from the distillery is treated mainly through anaerobic path to reduce the COD and BOD of the effluent and recover the calorific value of the effluent organics as Biogas. The design capacity of the ISET scrubber installed at USWL is 600 m^3/hr (max) of biogas flow rate and 7.5 % inlet H_2S (max). The achievable power production is around 1 MWe at a CH_4 concentration of around 65 %. The present operating gas flow rate and the inlet H_2S concentration is around 200 m^3/hr and 4 % respectively. The plant is being operated 24 hrs X 7 days X 330 days. The plant has recorded more than 20000 hrs till date and the outlet H_2S concentration has been less than 10 ppm on average. The graph below show a typical loading pattern on one of the days where the average gas flow rate is 75 % of the design capacity.

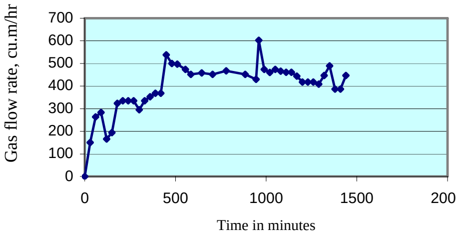

Fig 4. Typical plant loading of Hydrogen sulphide scrubbing system

The monthly average of gas scrubbed and power generated around 90,000 m3 and 140,000 kWh respectively as shown in Fig. 5. One m3 of gas used for power generation yields roughly 1.5 kWh of power on an average. This is mainly a function of the methane content of the gas.

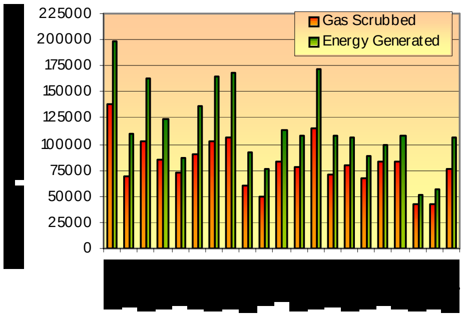

Fig 5. Monthly Gas Scrubbed and Energy Generated

Though the scrubbers have been in operation continuously through out the year, the amount of gas scrubbed and power generated is only around 30 % of the designed capacity on an average because of either the limitation in gas production at the source and due to lack of evacuating power produced using the scrubbed gas.

The present total operating cost is about Rs. 1.70 (US Cents – 4.0) per unit of power produced. This is mainly due to the fact that the power produced is only around 25 % of the designed Plant Load factor and this will come down to around Rs. 1.15 per unit of power produced (US Cents 2.5 – 3.0) at a PLF of around 85 %. Presently net revenue generated while operating at 30 % PLF is around Rs. 200,000 (USD 4500) per month, the same would go up to Rs. 2,000,000 (USD 45,000) per month which is a ten fold increase over the present revenue earned as can be seen from Figure 6. The net energy revenue considered is after deducting the inhouse energy consumption and also all the operating expenses. This would mean that at a PLF of 85 % and for the investment of Rs. 18,000,000 (USD 335,000 - inclusive of Building, Scrubber and Gas engines) incurred by the client, the pay back period would be around 1 year considering interest rate 12 % and linear depreciation for 10 years. This improvement in the revenue generated at low and high PLF is basically because of decrease in manpower cost/unit of energy generated and inhouse power consumption per unit of power generated that decreases as the PLF increases.

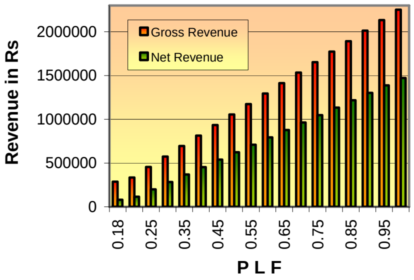

Figure 6: Revenue Earned as a function of Plant Load Factor (PLF)

Table 2: Techno-economics for Biogas power plant with ISET process for Hydrogen sulfide scrubbing (H_2S concentration – 3.0 %

No	**Description**	**Cost in Million Rs**		
		0.5 MW	**1.0 MW**	**2.0 MW**
1	Gas Engine directly coupled with alternator	8.0	15.0	28.0
2	***ISET*** H_2S scrubber	6.0	10.0	18.0
3	Building and Infrastructure	2.0	3.5	5.0
4	Capital Investment (1+2+3)	16.0	28.5	51.0
5	Energy generated for 7000 hrs running time per year (million units)	3.5	7.0	14.0
6	In-house energy consumption for 7000 hrs	0.3	0.6	1.2
7	Revenue earned/ annum by power generation at energy cost of Rs 4.0/kWh	14.0	28.0	56.0
8	Scrubber operating cost	3.0	5.5	10.5
9	Engine operating cost	1.0	2.0	3.5
10	Revenue generated by sulfur sale (Rs0.06/kWh)	0.21	0.42	0.84
11	Interest payment @ rate of 12.0 %	1.8	3.3	5.9
12	Linear Depreciation for 10 years	1.35	2.5	4.4
13	Revenue earned/annum per including running cost, loan repayment and depreciation	7.05	15.1	32.5
14	Pay Back period in years	2.3	1.9	1.6

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