Biological process for H_2S removal: acidophilic or alkalophilic?

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ABSTRACT. Two prosperous biotechnological processes have been developed for H_2S removal from gaseous streams. These processes can be categorized into acidophilic and alkalophilic processes based on operating condition applied. Both processes are based on the combined action of a chemical absorption step and a biological step for regeneration of the absorbent solution used. Elemental sulfur is the end product. In this paper the feasibility and engineering aspects of theses two processes are discussed and a comparison between both processes is presented.

1 INTRODUCTION

H_2S containing gasses are generated during anaerobic treatment of wastewater containing partially oxidized sulfur components or in petrochemical and natural gas refineries. The adequate removal of H_2S from biogas, natural or industrial gases is an important process because of its toxicity, corrosive properties and bad odor (Weber and Hartmans, 1996). Application of H_2S containing biogas and natural gas for energy generation is furthermore associated with the emission the sulfur moiety as SO_2, an important inducer of acid rain.

Many commercial chemical processes are available for the removal of H_2S from gaseous streams. Most of the processes use gas-liquid contactors in which H_2S is absorbed into a complexing reagent to give either another dissolved sulfide containing component (e.g. alkanol-amine or hydroxide based processes) or elemental sulfur as a precipitate(Wubs and Beenackers, 1993). However, they have high capital costs, demand large energy inputs and result in the generation of secondary hazardous wastes (Pandey and Malhotra, 1999).

Recently, two combined chemical-biological processes have been developed for H_2S removal from gaseous streams, which are based on elemental sulfur production and regeneration of the absorbent solution used. Both processes consist of two stages: in the first stage H_2S is absorbed and in the second stage the absorbent solution is biologically regenerated utilizing chemoautotrophic bacteria (Asai *et al*., 1989; Buisman, 1993; Buisman *et al*., 1990; Buisman *et al*., 1991b; Ebrahimi *et al*., 2003; Pagella *et al*., 1996;

Satoh *et al*., 1988; Sorkin, 1994; Sublette and Sylvester, 1987). These processes can be categorized based on the pH they are operated: an acidophilic and an alkalophilic process. In the acidophilic process an acidic ferric iron solution is used for H_2S absorption and acidophilic ferrous iron oxidizing bacteria are used for regeneration step. In the alkaline process, an alkaline solution is used for H_2S absorption and alkalophilic sulfide oxidizing bacteria are used in the regeneration step. In this contribution, the feasibility and engineering aspect of both the acidophilic and alkalophilic processes will be discussed and a comparison between both processes for H_2S removal in further details will be presented.

2 ACIDOPHILIC PROCESS

In the acidophilic process, H_2S is absorbed from the gas phase into a ferric iron solution and chemically oxidized to elemental sulfur in a scrubber. Ferric iron is reduced to ferrous iron. Elemental sulfur is removed from the solution by a separator and the ferric iron solution is regenerated by biological oxidation in an aerated bioreactor using acidophilic bacteria (Acidithiobacillus or Leptospirillum ferrooxidans) (Figure 1). To avoid ferric iron precipitation the acidophilic process is conducted at low pH values (~2). The major reactions in this process are:

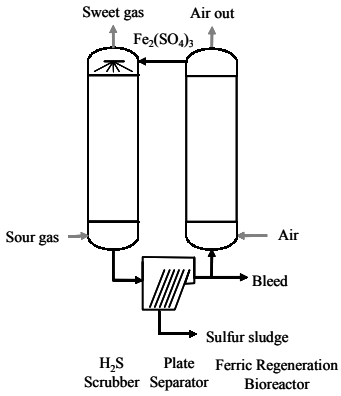

Fig. 1. Schematic representation of the acidophilic process for H_2S removal

H_2S absorption

$$H_2S+2Fe^{3+} \rightarrow S^0+2Fe^{2+}+2H^+ \quad (1)$$

Ferric regeneration

$$2H^++2Fe^{2+}+1/2O2 \rightarrow 2Fe^{3+}+H_2O \quad (2)$$

The overall reaction

$$H_2S+1/2O_2 \rightarrow S^0+H_2O \quad (3)$$

3 ALKALOPHILIC PROCESS

In the alkalophilic process, H_2S is absorbed into an alkaline solution in a scrubber and the solution is fed to an aerobic bioreactor where sulfide is biologically oxidized to elemental sulfur using alkalophilic Thiobacillus bacteria. Elemental sulfur is removed from the solution by a separator, and the regenerated carbonate solution is recirculated to the scrubber (Buisman, 1993). A schematic representation of the process is depicted in Figure 2. The alkalophilic process is conducted at high pH (8-10) to enhance H_2S absorption in the scrubber. The reactions in this case are as follows:

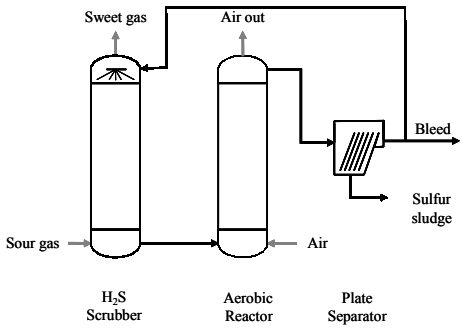

Fig 2. Schematic representation of the alkalophilic process for H_2S removal

H_2S absorption

$$H_2S+OH^- \rightarrow HS^-+H_2O \quad (4)$$

Biological sulfur formation

$$HS^-+1/2O_2 \rightarrow S^0+OH^- \quad (5)$$

The overall reaction

$$H_2S+1/2O_2 \rightarrow S^0+H_2O \quad (6)$$

4 COMPARISON BETWEEN TWO PROCESSES

4.1 H_2S absorber

For the acidophilic process the kinetics of the reactive absorption of H_2S by aqueous $Fe_2(SO_4)_3$ solution has been studied and found to be first order with respect to both H_2S and total Fe^{3+}concentration (Ebrahimi *et al*., 2003). This implies that the absorption rate of H_2S linearly increases with total $Fe_2(SO_4)_3$ concentration with a maximum at about 0.5 mol Fe^{3+}/l. However the studies of the biological regeneration stage indicated that maximum iron concentration applied in the integrated process is limited by biological regeneration stage to about 0.2M (Ebrahimi *et al*., 2005). The pH in the range of 0.6-1.8 doesn't have significant impact on biological iron oxidation process however a higher pH will enhance the chemical absorption of H_2S in the scrubber. But higher pH will lead to precipitation of the iron complexes and unwanted growth of A. ferrooxidans. Therefore, for the combined process an iron concentration of about 0.15-0.2M and a pH of 1.3-1.5 are considered optimal for the inflow of the biological stage. The biological reaction results in an increase of 0.3-0.4 units in the pH of the system therefore for H_2S absorption process pH at the liquid unlet will be in a range of 1.6-1.9.

The H_2S absorption into ferric iron solution is accompanied by a chemical reaction which is so slow that the reaction occurring in the thin boundary layer can be ignored and assumed that the entire reaction takes place in the bulk of the liquid phase. Based on experimental result obtained (Ebrahimi *et al*., 2003), the assumption of negligible reaction in the film is justified in practical conditions, because amount transported through the film (~kl.A.$C_{H2S,i}$) is much bigger than the amount of H_2S converted in the film by chemical reaction (A*δ*kr*$C_{H2S,i}$<< kl.A.$C_{H2S,i}$). Or making use of relation δ=D/kl, if: δkr/kl<<1 or Dkr/kr<<1 this generally written as: $\sqrt{Dkr/k_l^2} = Ha < 1$ this dimensionless group is called Hatta number, Ha. (note: by considering the maximum ferric iron solution of about 0.2M in the integrated acidophilic process, kr=k1,1. C_B will be about 26 1/s, by considering a common value kl value for the packed or spray column it can be shown that Ha number is much lower than 1.)

(Notations: A ,interface area m^2; D, diffusion coefficient, m^2/s ; C_{H_2S} ,concentration of H_2S in the liquid, $kmol/m^3$; k_L, liquid side mass transfer coefficient, m/s; k_r second order reaction rate constant, m^3/kmol.s, d, liquid film thickness, m)

On the other hand, the chemical reaction is fast enough (Vkr<<Akl)which results in the bulk concentration of H_2S very small. Therefore, the H_2S transport process in the acidophilic system is determined by the mass transport through the boundary layer (J=kla.$C_{H2S,I}$). Therefore a gas liquid contactor with a high liquid side mass transfer capacity is preferred for H_2S absorption into ferric iron solution.

The alkalophilic process is conducted at high pH values (8-10). In this condition, H_2S removal rate is very fast due to instantaneous complexation in the liquid phase. Absorption rates therefore are limited by the mass transport rate of the H_2S in the gas

phase, this has been confirmed experimentally(Ebrahimi *et al*., 2003). As a result the H_2S absorber size in alkalophilic process becomes smaller than that of acidophilic process.

4.2 Bioreactor

Regarding the ferric iron regeneration stage, the important sub-process in the integrated in acidophilic process, the kinetics of the biological ferrous iron oxidation of acidophilic bacteria had already been studied in our department (Boon *et al*., 1999a; Boon *et al*., 1999b; van Scherpenzeel *et al*., 1998). The rates for biological ferrous iron oxidation obtained with suspended microorganisms were found to be far too low to favor the biological regeneration concept in the integrated process for H_2S removal. Recently, several studies have focused on the improvement of the volumetric acidophilic ferrous iron oxidation rates. It has been realized that by immobilization of the acidophilic ferrous iron-oxidizing bacteria on a carrier materials in packed, fluidized bed or airlift reactors high volumetric oxidation rates can be achieved (Ebrahimi *et al*., 2005; Grishin and Tuovinen, 1988; Kinnunen and Puhakka, 2004; Mazuelos *et al*., 2001; Mesa and Cantero, 2002). In our previous study, to improve the biological oxidation rate the immobilization of ferrous iron oxidizing bacteria in an airlift reactor was investigated (Ebrahimi *et al*., 2005). In this way, the high oxygen mass transfer capacity in the airlift reactor was combined with the high biofilm surface area and biomass concentration in the reactor. Consequently, a high ferrous iron oxidation capacity at short hydraulic residence times can be achieved by using this concept. The maximum ferrous iron oxidation rate achieved in this study was about 145 $molFe^{2+}/m^3.h$ at hydraulic residence time of 0.25h, which is limited by the gas-liquid oxygen transfer rate. Results demonstrate that the ferric iron precipitates generated in the reactor are highly suitable as a carrier material for the immobilization of ferrous iron oxidizing bacteria due to their high specific surface area, stability and the optimal settling velocity of the biofilm formed. As a conclusion, the airlift reactor with precipitate attached biofilm was found to be a promising concept for high-rate biological ferrous oxidation at pH-values as low as about 1-1.5.

Biological oxidation of sulfide is the most important subprocess in the alkalophilic process. The oxidation of sulfide must be controlled in such a way that mainly sulfur is produced instead of sulfate. The sulfate production rate can suppress by controlling the oxygen concentration. In order to increase the sulfide oxidation rate the oxygen concentration should be high. But applicable oxygen concentration limited by the problem of oxidation of the elemental sulfur produced to sulfate at higher oxygen concentration. The reported sulfide oxidation rates with free cell suspensions are in the order of 0.2 $kgS/m^3.h$ (Buisman *et al*., 1991a). The sulfide oxidation has been improved by immobilized biomass in fixed bed and gas lift bioreactors. The maximum oxidation rate reported is 0.4 $kgS/m^3.h$ (Buisman, 1993).

Based on our experimental results, the iron oxidation capacity in the acidophilic process using a biofilm airlift reactor can be substantially higher than the corresponding oxidation capacities that can be achieved in the alkalophilic process, at least 5 fold. Consequently, the bioreactor in the acidophilic process using biofilm airlift reactor can be significantly smaller than the bioreactor in the alkalophilic process.

4.3 Feasibility and technological advantages

The first commercial application of the acidophilic process was built in 1984, at Kosaka works of Barium Chemicals, Ltd., in Japan (Satoh *et al*., 1988). In this process H_2S from a sour gas with a flow rate of 200 Nm^3/h containing 70% H_2S is removed to a

level of less than 1 0 ppm (99.99% removal efficiency). This process produces 5ton/day sulfur and sells it as raw material for sulfuric acid production. And some successful pilot plant study have been reported for H_2S removal from Amine gas and Clause gas containing H_2S of 0.4-1.9% and 85-93% respectively (Satoh *et al*., 1988). It is estimated that the total cost of this process to be about one-third that of the conventional caustic soda absorption process (Imaizumi, 1986). Evidently, using outcome of the recent improvement on the acidophilic ferrous iron-oxidizing rate can further boost the economical efficiency of this process.

Full-scale alkalophilic processes for biogas treatment were installed worldwide during the last 5 years. Beside biogas, high-pressure natural gas can be treated in a similar way. A long duration test in a large pilot-plant for treatment of high pressure natural gas has demonstrated very smooth operation of the process, after a successful pilot study, a full scale high pressure unit was started in Canada in 2001(Groenestijn and Kraakman, 2005). H_2S in the sweet gas is guaranteed to be below 4 ppmv, while the total design amount of sulfur to be removed per day is approximately 1 ton. It is claimed that this process is competitive compared to the other chemical processes, mostly in the range 0.1-15 ton S/day (Janssen *et al*., 2000). Compared to conventional caustic soda scrubbing processes, this process leads to a reduction of soda consumption by over 95%. Only limited use of casuistic soda is therefore required, which means the operating costs are very low, amounting \$60-\$100/tonne S^0 compared to that of the conventional caustic process, \$1250 /tonne S^0 (Buisman *et al*., 2002).

In comparison to the physical-chemical processes, major advantages of using biological processes for H_2S removal include: high cost effectiveness, very high removal efficiency, safe process operating at ambient temperature and atmospheric or flexible pressure, closed system with regeneration of absorbent solution and finally, production of elemental sulfur as a valuable end product.

Compared to the alkalophilic process, the main advantages of the acidophilic process described here is the closed system without any byproduct (stoichiometric formation of S_0 from H_2S), whereas in alkalophilic process 3-10% of the sulfide is oxidized to sulfate (Buisman, 1993). In order to avoid accumulation of sulfate, a continuous bleed stream from the bioreactor is required. Make up water is needed to prevent acidification of the medium in the reactor, sulfate produced need to be neutralized for example with sodium hydroxide and sodium bicarbonate. Furthermore, treatment of the bleed stream is required. To avoid the complete production of any bleed, an option is to continuously recycle a part of the bioreactor content over a sulfate-reducing stage where sulfate is converted to hydrogen sulfide.

$$SO_4^{2-} + 4H_2 \rightarrow HS^- + OH^- + 3H_2O \qquad (7)$$

The formed sulfide can subsequently be recycled to the sulfur producing bioreactor. But applying this option will lead to increase of the investment and operating cost of the alkalophilic process.

The alkalophilic process produces hydrophilic sulfur that does not stick or have plugging tendencies. As the Thiobacillus microorganisms excrete the sulfur particles they coat the sulfur with a protein coating. This coating changes the characteristics of the sulfur and imparts hydrophilic tendencies. This ensures that no plugging or fouling occurs in either of the bio-reactor, absorber vessel or the transfer piping. However, there is no report about possible problem concerning hydrophilic sulfur produced during acidophilic process.

5 CONCLUSIONS

The both acidophilic and alkalophilic biological processes for H_2S removal with subsequent production of elemental sulfur has been proven both on pilot and industrial scale and are mature technologies. Both processes are an efficient and robust alternatives for chemical processes used for H_2S removal from the gas streams such as refinery or industrial sour gas, natural gas and biogas. A major feature of these process is their highly energy saving nature combined with a closed liquid loop.

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