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Removal of Hydrogen Sulfide from Gaseous Streams by a Chemical Method using Ferric Sulfate Solution

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Abstract: Hydrogen sulfide is a toxic and odorous compound present in biogas produced by the anaerobic digestion of biosolids and other organic materials. Reactive absorption of hydrogen sulfide into aqueous ferric sulfate solution is a direct process for H_2S removal and Sulfur recovery. Apart from sulfur, only H_2O is generated in the process and consequently, no waste treatment facilities are required. A distinct advantage of the process is that the reaction of H_2S with is so rapid and complete that there remains no danger of discharging toxic waste gas. Effective operation parameters on this process considered. Results show that high temperature and low pressure are suitable for absorption reaction. Variation of hydrogen sulfide concentration and Fe^{3+} concentration with time in absorption reaction shown that the reaction of ferric sulfate and hydrogen sulfide is first order with respect to the both reactant. At low concentration of $Fe_2(SO_4)$, the absorption rate of H_2S increase with increasing the $Fe_2(SO_4)_3$ concentration. At higher concentration, a decrease in the absorption rate was found. At higher concentration of $Fe_2(SO_4)_3$, the ionic strength and viscosity of solution increase remarkably resulting in a decrease of solubility, diffusivity and hence absorption rate.

Key words: Absorption · Ferric sulfate · Hydrogen sulfide · H_2S removal

INTRODUCTION

Hydrogen sulfide (H_2S) is being produced by many industrial activities such as petroleum refining, natural gas and petrochemical plants, viscose rayon manufacturing craft, pulp manufacturing, food processing, aerobic and anaerobic wastewater treatments and many other industries [1]. The presence of H_2S in gaseous streams proscribes the direct use of these gases because of its toxic properties, the formation of SO_2 upon combustion and the problems it usually gives in downstream processing [2]. Upon inhalation, H_2S reacts with enzymes in the blood stream and inhibits cellular respiration resulting in pulmonary paralysis, sudden collapse and death. Continuous exposure to low (15-50 ppm) concentrations will generally cause irritation to mucous membranes and may also cause headaches, dizziness and nausea. Higher concentrations (200-300 ppm) may result in respiratory arrest leading to coma and unconsciousness [3-6]. This means that it is often necessary to remove H_2S from gas stream prior to use.

Nowadays, researchers and scientists have been focused on developing effective, stable and practicable methods for H_2S removal from gaseous streams. Various solid materials have been developed to capture H_2S from a number of industrial gas effluent streams [7-13]. Several commercial techniques are available for the removal of H_2S, including aqueous NaCl [14], iron-based sorbents [15, 16], activated carbon [17], Fe_2O_3, metal oxides [18, 19] and removal of H_2S using aqueous red mud [20] which is a caustic waste product of alumina industry [21]. Most of the process use gas-liquid contactors in which the H_2S is absorbed into a complexing reagent to give either another dissolved sulfide containing component and problems are the degradation of the solvent [22]. Iron (Fe) is an excellent oxidizing agent to convert H_2S to elemental sulfur (S). During the1960s, intensive researches commenced in England focused on increasing the solubility of elemental Fe^{3+} in aqueous solutions and they realized that Iron is an excellent oxidizing agent to convert H_2S to elemental sulfur (S) [23]. However, there is always research for the development of effective and low-cost method.

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MATERIALS AND METHODS

In this research, the reactive absorption of H_2S into aqueous ferric sulfate ($Fe_2(SO_4)_3$) solution has been studied and design calculations for equipment have been done. An aqueous $Fe_2(SO_4)_3$ solution used an absorbent in this process. H_2S absorbed and oxidized to elemental sulfur and at the same time, Fe^{3+} is reduced to Fe^{2+} according to Eq. 1.

$$H_2S + 2Fe^{3+} \rightarrow S^0 + 2Fe^{2+} + 2H^+ \tag{1}$$

Elemental sulfur is removed from the solution by separator and the reactant Fe^{3+} is regenerated from Fe^{2+} by oxidation in reactor to the following reaction (Eq. 2):

$$Fe^{2+} + H^+ \, 0.25O_2 \rightarrow 2Fe^{3+} + 0.5H_2O \tag{2}$$

Depending on the gas flow rate and the efficiency required several types of absorbers are suitable, such as jet scrubbers, bubble-cap towers or packed towers. The sulfur separator can include filter press, settler and sulfur melters, depending on quality of elemental sulfur required. Apart from sulfur, only H_2O is generated in the process. Thus, this process does not need waste treatment facilities [22].

A distinct advantage of this process is that the reaction of H_2S with $Fe_2(SO_4)_3$, is so rapid and complete that there remains no danger of discharging toxic waste gas. The process is schematically depicted in Fig. 1.

Process Design Calculations: In this work it was assumed that a packed tower used as absorber, continuous filter used as solid-liquid separator to separate sulfur from outlet liquid and a back mixing reactor used as oxidizer to regenerate Fe^{2+} to Fe^{3+}. According to these assumptions and for known gas flow rate (100000 kg/day sour gas, contain ≈ 4% v/v H_2S), design calculations have been done.

Calculations have been done for a packed tower with 2 inches raschig rings as packing and 0.1 molar $Fe_2(SO_4)_3$ concentration. Onda's method used to calculate k_G and k_L, gas and liquid side mass transfer coefficient (Eqs. 3, 4, 5).

$$\frac{aw}{a} = 1 - \exp\left[-1.45\left(\frac{\sigma_C}{\sigma L}\right)^{0.75}\left(\frac{L_w^*}{a.\mu_L}\right)^{0.1}\left(\frac{L_w^* a}{\rho_{L.g}^2}\right)^{-0.05}\left(\frac{L_w^{*2}}{\rho L^{\sigma} L^a}\right)^{0.2}\right] \tag{3}$$

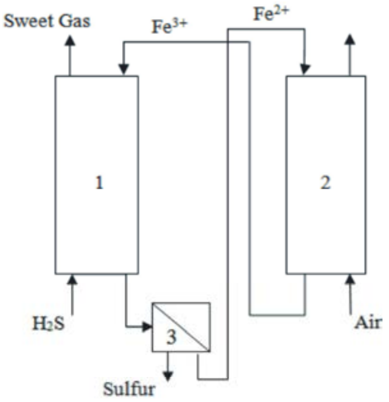

Fig. 1: Process scheme of process for H_2S removal, 1- Absorber, 2- Oxidizer, 3- Solid-liquid separator

$$k_L\left(\frac{\rho L}{\mu_{L.g}}\right)^{1/3} = 0.0051\left(\frac{L_w^*}{a_w \mu_L}\right)^{2/3}\left(\frac{\mu_L}{\rho_L . D_L}\right)^{-1/2}\left(a.d_p\right)^{0.4} \tag{4}$$

$$\frac{k_G}{a} . \frac{RT}{D_V} = 5.23\left(\frac{V_w^*}{a.\mu_v}\right)^{0.7}\left(\frac{\mu_v}{\rho_v D_v}\right)^{1/3}\left(a.d_p\right)^{-2.0} \tag{5}$$

The height of liquid and gas-film transfer units (H_G, H_L) and overall gas-phase transfer unit [2] are obtained from Eqs. 6 to 8.

$$H_G = \frac{G_m}{k_G . a_w . p} \tag{6}$$

$$H_L = \frac{L_m}{k_L . a_w . C_t} \tag{7}$$

$$H_{OG} = \frac{G_m}{k_G . a . P} \tag{8}$$

And after calculations, tower's height (Z) calculated (Eq. 9).

$$Z = H_{OG} . N_{OG} \tag{9}$$

Subsequently, Diameter and height of absorption tower are 3.6 ft and 12.5 ft and pressure drop is 0.35 inH_2O/ft packing [24-26].

In this process assumed that Oxidizer is a back mixing reactor. According to this assume, calculations have been done for oxidizer. Fe^{3+} is regenerated from Fe^{2+} according to equation 2 and it is relatively slow reaction. The reaction is first order with respect to oxygen and is 0.536 with respect to Fe^{2+}, as follow (Eq. 10):

$$-r_{Fe^2+} = 4.39\times 10^4 \exp\left(\frac{-23.3}{R.T}\right).C_{Fe^{2+}}^{0.536}.C_{O2} \qquad (10)$$

Consequently, Oxidizer's height and diameter are 2.45 ft and 4.9 ft [27-29].

RESULTS AND DISCUSSION

Variations of Reactant Concentration: As other researchers found before[19], this experimental results also showed that the absorption reaction of hydrogen sulfide by $Fe_2(SO_4)_3$ solution appears irreversibly and is first order with regard to both reactants. Variations of concentration profile of the reactants calculated in recent studies. These profiles had shown in Fig. 2 and Fig. 3.

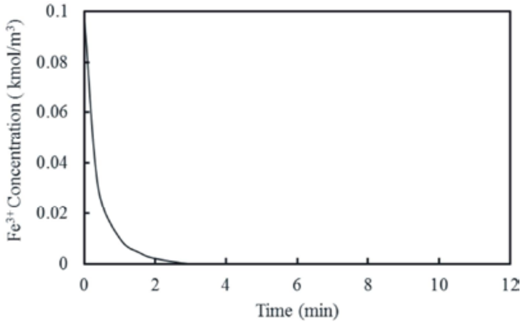

Fig. 2: Fe^{3+} Concentration profile

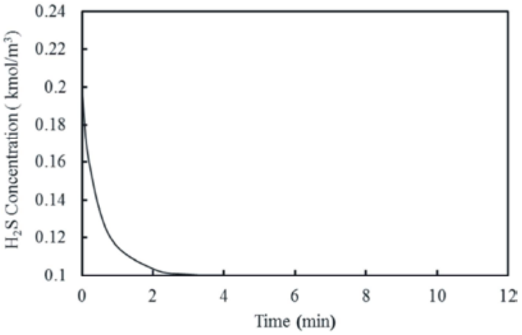

Fig. 3: H_2S Concentration profile

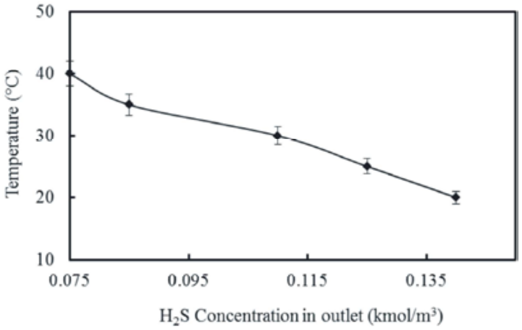

Fig. 4: Influence of temperature on H_2S concentration in outlet

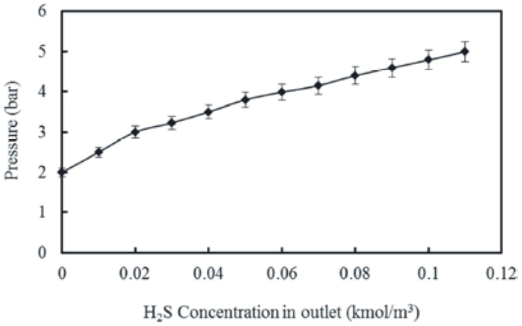

Fig. 5: Influence pressure on H_2S concentration in outlet

Recent studies have resulted at low $Fe_2(SO_4)_3$ concentrations (up to 0.3 M) the absorption rate of H_2S increase with total $Fe_2(SO_4)_3$ concentration. At higher $Fe_2(SO_4)_3$ concentrations a decrease in the absorption rate was found. At higher concentration of $Fe_2(SO_4)_3$ the ionic strength and viscosity of the solution increase remarkably resulting in a decrease of the solubility, diffusivity and liquid side mass transfer coefficient of H_2S and hence absorption rate [22].

Influence of Temperature and Pressure on the Process: It is important to have an exact control on effective parameters in reaction to have high efficiency and low cost and energy consumption. Therefore, some effective parameters in this process are considered. Results shown that high temperature and low pressure is appropriate condition for absorption reaction as shown in Fig. 4 and Fig. 5.

CONCLUSIONS

The preferred treatment method for sulfur containing gas streams depends on the source of the gas. H_2S removal from gas streams using aqueous ferric solution as absorbent has been studied theoretically and calculations for absorber and oxidizer have been done and their dimensions are obtained for a known sour gas flow rate. The absorption reaction is first ordered with respect to both H_2S and ferric iron concentration and influence of temperature and pressure on H_2S absorption show that in high pressure and low temperature the process should have higher efficiency and optimum concentration of $Fe_2(SO_4)_3$ should be used in the process due to increasing the ionic strength and viscosity of the solution at higher concentration of $Fe_2(SO_4)_3$, consequently, resulting in a decrease of the solubility, diffusivity and liquid side mass transfer coefficient of H_2S and hence absorption rate.

NOMENCLATURE

a	Surface area of interface per unit volume of column, m^2/m^3
σ	Surfacetension, J/m^2
μ_L	Viscosity of liquid, Ns/m^2
μ_V	Viscosity of liquid, Ns/m^2
ρ_L	Density of liquid, kg/m^3
ρ_V	Density of gas, kg/m^3
D_L	Liquid phase diffusivity, m^2/s
D_V	Vapour phase diffusivity, m^2/s
k_L	Liquid side mass transfer coefficient, m/s
k_G	Gas side mass transfer coefficient, kmol/m^2 atm s
H_L	Height of transfer unit-liquid film, m
H_G	Height of transfer unit-gas film, m
H_{OG}	Height of transfer unit-overall (gas concentrations), m
K_L	Overall liquid-phase transfer coefficient, m/s
K_G	Overall gas-phase transfer coefficient, s/m
G_m	Molar rate of gas per unit cross-section, kmol/m^2 s
L_m	Molar rate of liquid per unit cross-section, kmol/m^2 s
L_W^*	Liquid flow rate (mass) per unit cross-section, kg/m^2 s
V_W^*	Gas flow rate (mass) per unit cross-section, kg/m^2 s
dp	Packing size, m
C_T	Total molar concentration, kmol/m^3
R	Universal gas constant, J/kmol K
Z	Height of packed column, m
g	Acceleration due to gravity, m/s^2
P	Total pressure, N/m^2
T	Absolute temperature, K

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