STUDIES ON ONE STEP REMOVAL OF H₂S AIMS AND DESIGN CRITERIA FOR A PILOT PLANT

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ABSTRACT : *In an attempt ot develop a one step process for the removal of H₂S from sour gas, the engineering considerations were dealt with in two steps. In the first step it was attempted to derive the data required for establishing the design criteria for a pilot plant, by experimenting with a small bench scale.*
In this paper the results of the bench scale studies are summarized.

INTRODUCTION:

Much of the natural gas produced around the world is sour, i.e contain H₂S levels from as low as a few parts per million to as high as 35 volume percent [1]. The presence of H₂S in such streams is accompanied by serious environmental and corrosion problems and its removal is one of the utmost engineering tasks in all petroleum and petrochemical processing plants.

There are many natural gas reserviors in Iran and presently considerable amounts of associated gas are being wastefully burnt due to lack of a simple and readily deployable process for treating small streams of sour gas to either produce fuel grade gas or injection gas.

Besides one of the main problems in current

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petroleum refining plants is the thermal instability of the Claus process in response to feed variations, leading to operation shut downs and consequently large amounts of H_2S are burned in flares.

Although amineClaus process is still being extensively used in gas treatments of high sulfur capacity it is increasingly being replaced by direct conversion method, for low sulfur capacities (up to 15 tons sulfur/day) specifically when environmental considerations restrains the burning of sour gas in the atmosphere.

The aim of the investigation undertaken here was to use a bench scale set up to obtain reliable design criteria and operating parameters for the direct continuous conversion process in a pilot plant.

EXPERIMENTAL :
Process description

Liquid oxidation process functions by absorbing H_2S into a mildly alkaline (pH = 8−8.5)aqueous solution of oxidized chelated iron and converting it immediately and selectively to elemental sulfur. The catalyst used in this process has been produced in the *gas department of the Petroleum Research Institute of National Iranian Oil Company* at Ray [2].

As shown in Fig. 1 the sour gas enters absorption column where it comes in contact with the liquid catalyst and H_2S is converted to elemental sulfur in the form of fine sulfur particles that are subsequently separated by settling and pumped out of the system. The iron solution is regenerated by contact with atmospheric air in the oxidizing vessel.

Review of design criteria

As previously mentioned the following equipments are required for this process:

       A : Gas - Liquid contactors

       B : Oxidation vessel

       C : Sulfur separation equipment

1- Gas - Liquid contactors : Common types of equipment used for this purpose are packed towers, bubble columns and venturi scrubbers.

In the case of packed towers the important design parameters are its diameter and height. The standard method for determining the diameter is based on flooding point [3,4]. Many absorption processes involve some chemical reactions, however despite the complexities involved some satisfactory correlations can be derived. One of the conventional approaches is based on the mean mass transfer coefficient k_{OG} a. This parameter is usually related to liquid and gas flow rates according to following relation or is repesented by curves like in Fig. 2.

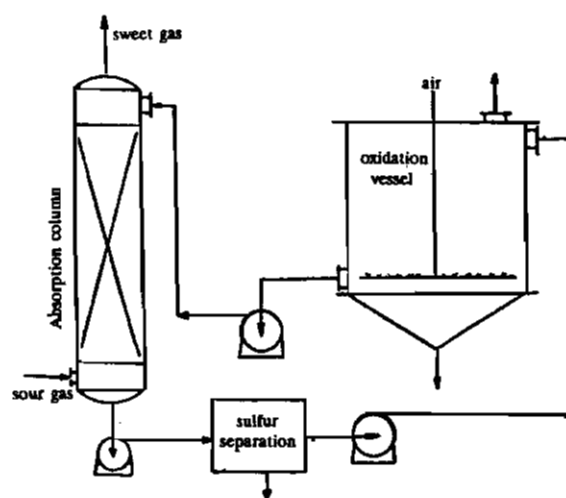$$k_{OG} \cdot a = \alpha \cdot L^\beta \cdot G^\gamma \qquad (1)$$

Fig.1 : Process flow diagram for one step removal

Mean Mass Transfer Coefficients Ceramic ¼"

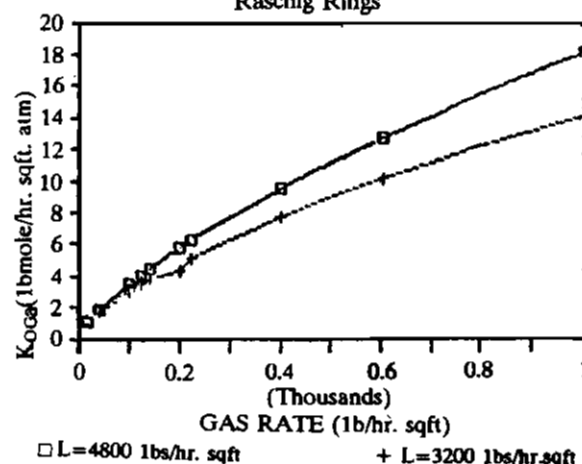□ L=4800 lbs/hr. sqft   + L=3200 lbs/hr.sqft

Fig. 2 : Mean mass transfer coefficient of H_2S in to aqueous solution

The data required for proper estimation of $k_{OG}a$ value may be obtained in a pilot plant by varying the liquid and gas flow rates and measuring H_2S concentrations at the upper and the lower ends of the contactor. Material balance along with Eq.(2) allows the overall mass transfer coefficient to be calculated [4]:

$$k_{OG} \cdot a = \frac{N}{V. \Delta P_{Ln}} \qquad (2)$$

The reaction between Fe^{3+} and H_2S is very fast and therefore assumed to be controlled by mass transfer and the Shulman equation [3] may be safely applied to calculate the mass transfer coefficient.

The ejector venturi scrubber is a device which utilizes the velocity action of a contacting fluid to pump out, scrub, and/or absorb the entrained gas. This action is economical and specially beneficial in handling highly corrosive gases such as H_2S. It eliminates the need for the costly corrosive resistant blower or compressor to pump the gas through the system.

The device is primarily comprises a conventional venturi section and spiral- type nozzle which imparts a combination of axial and tangential velocities to the liquid jet stream. The spiral angle and the size of the orifice are arranged so as to;

1) Impart sufficient tangential velocity to form a spray cone which fills the entire venturi throat area.

2) Break up the motive liquid into proper drop sizes to permit efficient scrubbing or absorption of the entrained gas.

3) Impart a sufficient combination of axial and tangential velocities to obtain the desired pumping characteristics, Fig. 3.

To predict the performance of this device, the number of transfer units were calculated using the following relation [5]:

$$N_{toG.} = Ln \ [y_1(1 - y_2)/y_2(1 - y_1)] \qquad (3)$$

Experimental data used in the primary design of the venturi is shown in Fig. 4.

Experimental data

2- Oxidation vessel (Bubble column): As mentioned earlier, the catalyst solution is regenerated by contact with air in an oxidizer vessel (a bubble column type reactor).

The regeneration step is controlled by the reaction rate hence requiring a specific residence time. In order to determine the residence time the dispersed plug model may be applied [6]. Using the rate Eq. (4)[7] and applying the disperse plug model relations, one can solve the
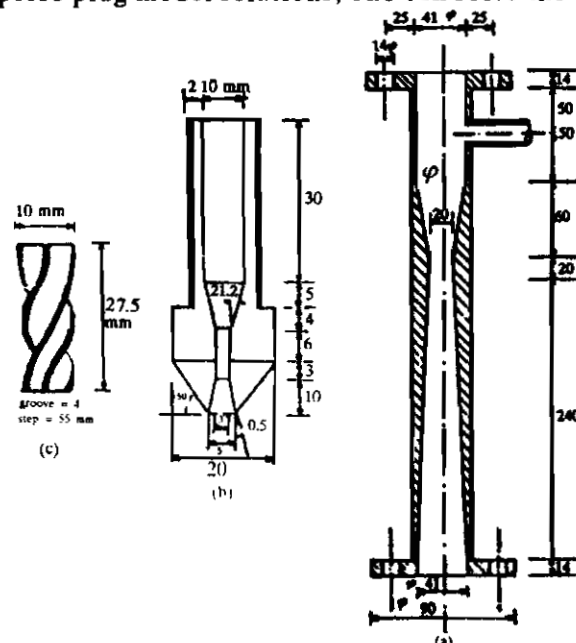

Fig. 3 : a - Main body of venturi jet scrubber used in the pilot plant.

b - Spray nozzle

c - Helical core of spray nozzle

Effect of Flow Ratio (L/G) on Number of Transfer Units (N_{toG})
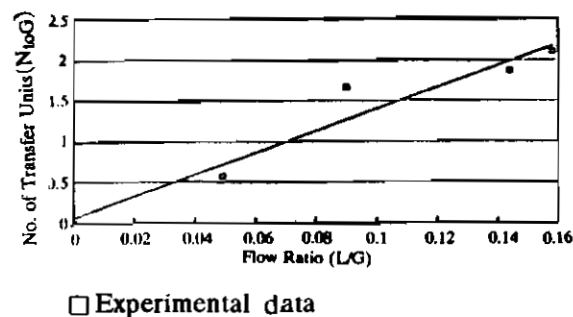

□ Experimental data

Fig. 4 : Experiment data for venturi scrubber

differential equation, and obtain concentration profile and the reactor volume using a computer program [8].

$$-r_A = 1.09 \times 10^4 \exp(-23.3/RT). \, C_{Fe^{2+}}^{0.536} . \, C_{O_2} \tag{4}$$

Since the regenerating solution is essentially saturated with oxygen the reaction is assumed to be a function of the iron concentration only.

The vessel volume may be calculated based on either of the following approaches:

1- Ideal mixed flow pattern (not considered here).
2- Dispersion model and considering the following differential equation:

$$\frac{d^2c_A}{dz^2} - \frac{u_L}{D_E} \cdot \frac{dc_A}{dz} - \frac{k_r C_A^n}{D_E} = 0 \tag{5}$$

In the case of first order reactions, the solutions of Eq. (5) are presented in Fig. 5 [9]. In which P represents the following relation:

$$P = \frac{D_E}{3600 u_L z_F} \tag{6}$$

Then the ratio of liquid height (z_P) to plug flow

liquid height is calculated.

For plug flow reactors the solving of Eq. (5)yields :

$$x_A = 1 - \frac{c_A}{c_{Ao}} = 1 - \exp\left(\frac{-k_r z_{f,plug}}{3600 u_L}\right) \tag{7}$$

Fig. 5 also represents graphical solutions for the dispersed plug model involving a first order reaction in a closed vessel [6,9].

Similar graphical representations have been produced for second order reactions. To estimate reaction performance for orders different from one and two, one may extrapolate or interpolate the curves.

The numerical solutions of Eq.(5) for n= 0.536 and different dispersion coefficients are presented in Fig. 6. It is thus seemed that there are no sensible differences between two approaches.

To check the mass transfer coefficient for oxygen in the vessel, the following relation may be applied [3].

$$sh_L = 2 + 0.0187(Sc)_L^{0.546} \times (Re)_G^{0.779} \times$$
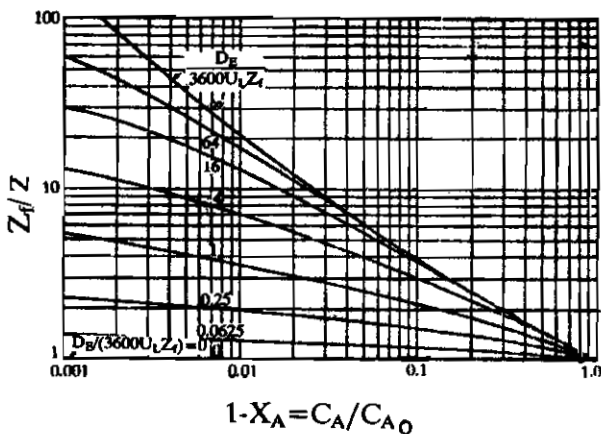
$$\left(\frac{d_p g^{1/3}}{D_L^{2/3}}\right)^{0.116} \tag{8}$$

$$1\text{-}X_A = C_A/C_{A_O}$$

Fig. 5 : Comparison of real and plug flow reactors for the first order reaction

A ⟶ Products [9]

Effect of Dispersion Coefficient on BCR Conversion Profile

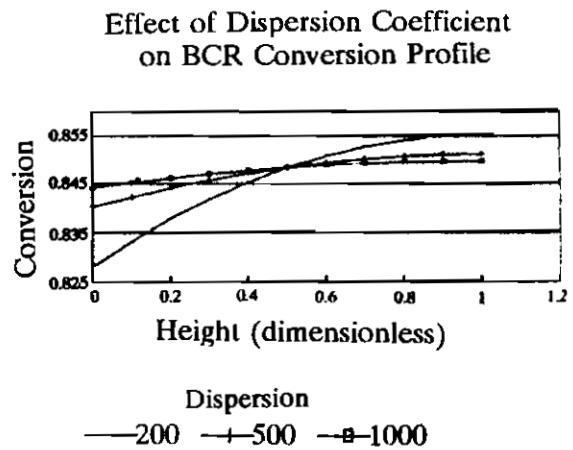Height (dimensionless)

Dispersion

—200 —+—500 —ɐ—1000

Fig. 6: Numerical solution of Eq. (5) for various dispersion coefficient [8]
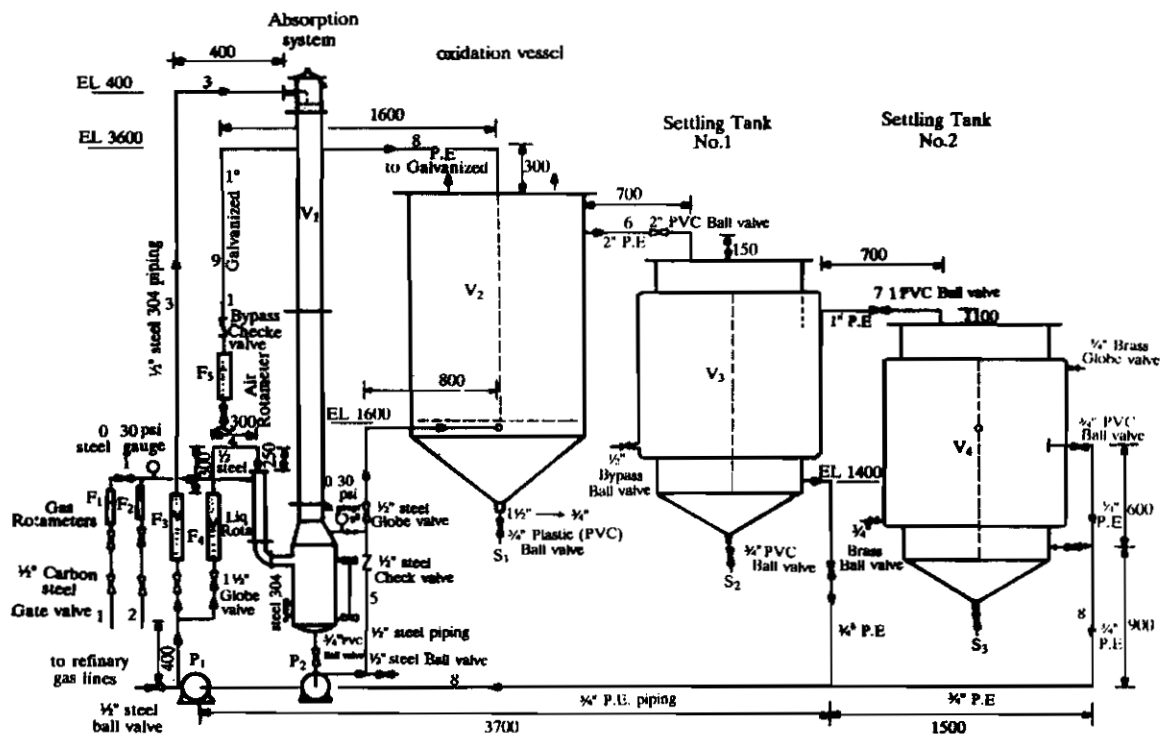
Fig. 7: Pilot plant flow diagram and layout

3- Sulfur seperation equipment: The circulating catalyst solution which contains elemental sulfur in a slurry form, flows from the absorber back to the oxidizer. The larger solid particles of sulfur (0.02 - 0.2 mm) settle out and are removed from the process by a clarifier. The colloidal sulfur (less than 10 μm) are not required to be removed completely [10,11].

Vessel dimensions in pilot and lab. scale

In order to better estimate of vessels in pilot scale and to discover the operating problems involved, a glass continuous lab scale system, consisting of the following components was designed: a 7 cm I.D./30 cm. height absorption column containing ¼ inch ceramic Raschig rings; a 25 liter oxidizer vessel through which air is introduced via an inlet distributor located at its bottom.

The Liquid was circulated throught the system at a rate of 1-2.5 L per minute (LPM)and the sulfur was removed by hydrocarbon floatation. Based on experiences obtained from

the above mentioned system, a 10 kg sulfur /day pilot plant was designed fabricated and transported to Tehran refinery.

The pilot consists of following components: a 12.5 cm. I.D./240 cm height absorber, a 900 liter oxidizer vessel (I.D. = 90 cm), two 700 liter settling tanks (Fig. 7).

The catalysist solution was circulated through the system at a rate of 30 LPM by two $\frac{1}{3}$ hp pumps and sulfur particles were removed from the bottom of settlers by a 0.5 m^2 simple filters.

RESULTS AND DISCUSSION :
Pilot aims and schedule

One of the most important purposes of the pilot is to investigate the operating problems and to check the design procedure. Also reliable nomographs and correlations are obtained which may be used in optimizing the design of the large scale plants.

The other objective is to find the best method for removing sulfur particles, i.e. To decide between the hydrocylone and continuous

centrifugation.

An improved design for treating sour gases not containing flamable components named Autocirculation system is also scheduled in pilot plant operations [12].

In this system as the acid gas, bubbles up through the solution, H_2S is absorbed and forms elemental sulfur. The ferric iron in the solution is reduced to ferrous ion which is automatically recirculated back into the oxidizer section of the vessel. It is thus obvious that the previous system may be replaced by just one step.

The Autocirculation system needs no circulating pumps, temperature controls, or any complicated machinary of any sort. A small 70 literAutocirculation system has been designed and is to be tested in pilot plant operations [13].

CONCLUSIONS :

A process for one step removal of hydrogen sulfide and its direct conversion to elemental sulfur comprising of three separate steps was developed and successfully tested. In this process hydrogen sulfide is first absorbed by iron solution and oxidized to sulfur. This reaction appears to be fast and requiring a short residence time gas contactors. The second step is the regeneration of the spent iron solution by bubbling of air in a bubble column with enough residence time. In the third step sulfur particles are settled out in an appropriate vessel designed based on settling velocity of the particles.

The data were used to size a pilot scale system for producing maximum 10 kgs/day sulfur by reducing 99.99 percent of H_2S content of the gas.

Notations :

a = Interfacial area per unit of packing volume
sq.ft./cu.ft

c_A = Concentration of component A
lb mole/cu.ft

c_{Fe}^{2+} = Concentration of Fe(II)
lb mole/cu.ft

c_{O2} = Dissolved oxygen concentration
lb mole/cu.ft

D_E = Axial dispersion coefficient
sq.ft/hr

D_L = Diffusivity coefficient in liquid phase
sq.ft/hr

d_b = Bubble diameter
ft

g_c = Gravity acceleration
ft/sq.sec

G = Superfacial gas velocity
lb mole/hr. ft^2

k , k_r = Reaction rate constants

K_{OG} . a = Mean mass transfer coefficient
lb mole/ft^3.atm

L = superfacial liquid velocity
lb mole/hr. ft^2

n = Reaction order
—

N = moles of H_2S obsorbed
lb mole/hr. sq. ft

N_{TOG} = Number of transfer units in gas phase
—

P = Peclet number
—

R = Universal gas constant
kJ/k mole. °R

r_A = Reaction rate
lb mole/cu. ft. hr

Re = Reynolds number
—

Sc = Schmidts number
—

sh_L = Sherwood number in liquid phase
—

T = Temperature
°R

u_L = Liquid average velocity
ft./sec

V = Packing volume
cu. ft

V_s = Slip velocity
ft./sec

x_A = Conversion of a component A
—

y_1 , y_2 = Mole fraction in gas phase
—

z_f/z = Reactor height

$z_{t,plug}$ = Reactor height in plug flow region   ft

α, β, γ = Constant coefficients   ft

ΔP_{Ln} = Log mean pressure diffrence   —

μ_L = Liquid viscosity   atm

ρ_L = Liquid density   1b./ft. sec

        1b./cu. ft

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