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Kinetic studies and reactor modeling of single step H_2S removal using chelated iron solution

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ABSTRACT

Airlift reactor concept was used for hydrogen sulfide removal from acid gases using chelated iron solution. Rate equations for absorption and regeneration reactions were determined and finally, an 'Autosweet' program was developed for design and simulation of the reactor. Variations of the concentration profiles of the reactants and products with time, the required time to achieve steady state conditions, concentration profiles of two phases at steady state and volume of the reactor in absorption and regeneration sections can be calculated based on implemented model in this study. Comparison of theoretical and experimental results shows a good agreement and justifies the model. Based on the model as a second stage of project, a 1 m^3 prototype reactor was designed and constructed at NIOC Research Institute of Petroleum Industry.

Keywords: Kinetics; Modeling; Airlift; Chelated iron; Hydrogen sulfide

1. Introduction

Liquid phase oxidation process using iron chelate catalytic solution (LOCAT) has been employed for treatment of acid gas streams. However, the process was identified economical for up to 850–1050 kg/h of sulfur production, although much larger systems have been installed [1]. Advantages of these systems include the ability to treat both aerobic and non-aerobic gas streams, high H_2S removal efficiencies, great flexibility; essentially 100% turndown on H_2S concentration in feedstock, and quality and the production of innocuous products and byproducts.

The two most common processing schemes encountered in these systems are named "Conventional" and "Autocirculation". The first one is employed for processing gas streams, which are either combustible or cannot be contaminated with air. Here, absorption and regeneration reactions occur in separate vessels. The second one is used for processing acid gas streams (CO_2 and H_2S) or noncombustible streams in which both absorption and regeneration reactions are carried out in a single vessel according to the following equations, respectively:

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

$$H_2O + 2Fe^{2+} + \tfrac{1}{2}O_2 \rightarrow 2Fe^{3+} + 2OH^- \quad (2)$$

The overall reaction is the reaction given in Eq. (3):

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

The autocircualtion scheme of the reactor is illustrated in Fig. 1. The reactor consists of three main zones: riser, downcomer and gas–liquid separator. In riser both absorption and regeneration reactions take place. In the initial section of the riser, in which the reaction of Eq. (1) occurs, acid gas is sparged and absorbed into a catalytic solution. Then, the solution flows in regeneration section in which air is sparged where the reaction of Eq. (2) occurs. The solution circulates due to density difference created between riser and downcomer zones. As seen in Fig. 1, the two spargers for acid gas and air are placed in an appropriate flexible distance to each other. The regener-

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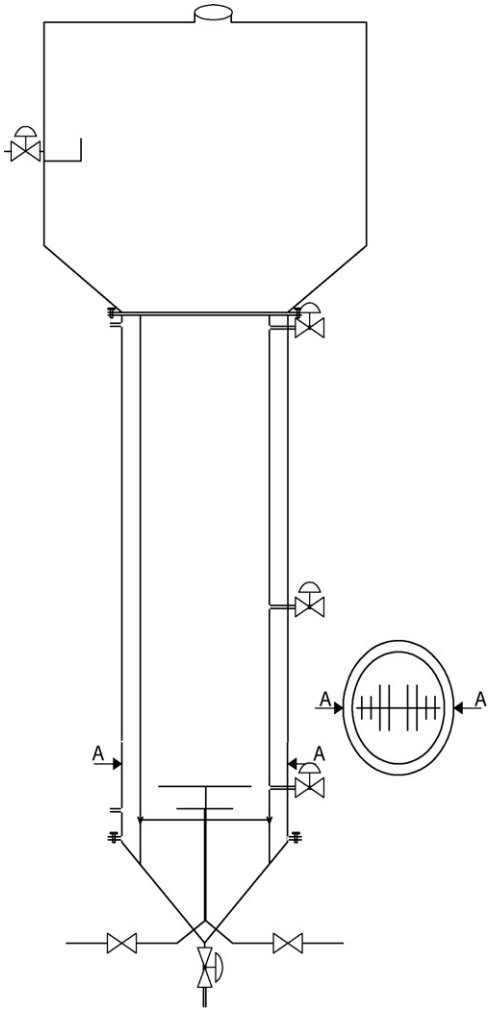

Fig. 1 – Autocirculation scheme of the reactor.

ated catalytic solution re-enters to the riser absorption zone due to the presence of the natural circulation.

In comparison with the conventional scheme, the unique feature of the autocirculation reactor is that no pumps are required to circulate solution between absorber and oxidizer. Therefore, these are generally less expensive units with few operational problems related to sulfur plugging than usually reported for the other scheme. However, due to presence of oxygen and sulfide ions, these units may produce more byproducts.

Hydrodynamic parameters of this scheme such as gas holdup, liquid velocity, pressure distribution and bubble diameter were determined in another work [2]. The main objective of this paper is to determine reaction kinetic parameters for both absorption and regeneration reactions and then presenting a model to simulate the reactor behavior using airlift reactor concept which is commonly used for fermentation or bio-reactions.

In fact, a little information concerning kinetic data has been revealed in the literature. The absorption reaction between H_2S and catalytic solution is fast and as soon as H_2S reaches to interface plane, the absorption reaction takes place between two phases [3]. The method of how to measure the kinetics parameters and how to imply an appropriate model interpreting the experimental data is very important for determination of rate constant and the other required parameters. In addition the literature shows a great controversy regarding kinetics parameters. The investigations commonly confirm that the regeneration reaction can be considered first order with respect to the oxygen concentration [4–6], but there are different information can be found regarding the order of reaction with respect to the chelated iron II concentration. For example, Sada et al. reported this order equal to 0.536 [4], however, the other investigators reported it to be mostly equal one and two [5]. Reviewing some papers shows that the order varies between one and two when pH and concentration of chelated iron solution change.

Here, an experimental investigation is performed to determine rate equations for RIPI20,[1] iron chelate catalytic solution (i.e. Fe–EDTA complex), and a model is developed to predict variations of the concentration of the reactants and products with time. The "Autosweet" program is also developed to estimate the time needed to steady state conditions, concentration profile of two phases at steady state and volume of the reactor needed to take place the absorption and regeneration reactions within the safe zone operation and for a given condition. Experimental data obtained from a bench scale reactor are in a good agreement with simulated reactor using the program.

2. Experimental

2.1. Experimental setup

Kinetic experiments were carried out in a glass reactor illustrated in Fig. 2. The reactor has 10 cm diameter and 20 cm height in which gas and liquid can be contacted. Both phases are well mixed via two impellers located at two positions in the bulk of gas and liquid on the agitator shaft. The agitator speed in all experiments is constant and equal to 300 rpm. Six baffles, 1 cm in width, are placed symmetrically to avoid the formation of vortex inside the reactor and make agitation to take place completely.

Variations of iron concentration and dissolved oxygen in liquid phase are measured and saved using an oxidation–reduction probe (ORP) and a DO electrode. Depending on the purpose of experiment the electrodes are connected to a PentiumII personal computer for data acquisition. Containers, V_2, V_3 and V_4, are dry nitrogen, hydrogen sulfide and air cylinders, respectively. A vacuum pump is used for evacuation of the reactor and charging the catalytic solution from container V_6. Off gases from the reactor can be gathered in vessel V_5.

2.2. Absorption reaction kinetics

The reaction mechanism is as follows:

$$H_2S_{(g)} + H_2O_{(L)} \rightarrow H_2S_{(aq)} + H_2O_{(L)} \quad (4)$$

$$H_2S_{(aq)} \rightarrow H^+ + HS^- \quad (5)$$

$$HS^- + 2Fe^{3+} \rightarrow S^0 + 2Fe^{2+} + H^+ \quad (6)$$

Eqs. (4) and (5) represent the absorption of H_2S into the aqueous chelated iron solution and its subsequent ionization, while Eq. (6) represents the oxidation of the sulfide ions to elemental sulfur and the accompanying reduction of the ferric iron to the ferrous state. The overall absorption reaction fol-

[1] RIPI20 is formulated by RIPI.