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# Selective absorption of $H_2S$ with High $CO_2$ concentration in mixture in a rotating packed bed

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## ABSTRACT

There is an increasing interest in the selective removal of hydrogen sulphide ($H_2S$) from gas streams with a high concentration of carbon dioxide ($CO_2$). In this study, a rotating packed bed (RPB) with short gas-liquid residence time and high mass-transfer efficiency is used for the selective absorption of $H_2S$ from gas mixtures with a high $CO_2$ concentration with dinuclear cobalt-phthalocyanine sulfonate (PDS) as the catalyst. The effects of rotation speed, gas-liquid volume ratio, temperature, $Na_2CO_3$ and PDS concentrations on the desulfurization efficiency and selectivity were investigated. The experimental results show that the removal rates of $H_2S$ and $CO_2$ are 99.13% and < 1%, respectively, at a rotation speed of 1000 r/min, a liquid-gas ratio of 8.5 $L/m^3$, a temperature of 32 ± 2°C, a PDS concentration of 1.5 ppm, and a $Na_2CO_3$ concentration of 10 g/L. The high gravity technology has the advantages of high desulfurization selectivity and efficiency, and low liquid-gas ratio and $Na_2CO_3$ consumption.

## 1. Introduction

Hydrogen sulphide ($H_2S$) is a toxic gas widely present in industrial gases, such as tail gas from ammonia synthesis, natural gas, coke oven gas, and refinery gas [1]. There is an increasing interest in the selective removal of $H_2S$ from gas streams with a high ratio of carbon dioxide ($CO_2$) to $H_2S$. However, a considerable quantity of $CO_2$ can also be removed in the conventional desulfurization process by the wet oxidation method because both $H_2S$ and $CO_2$ are acidic and similar in many physical and chemicals aspects, which can increase the circulation volume of the absorption liquid and aggravate the energy load of the solution regeneration system [2–4]. Therefore, there is a need to selectively absorb $H_2S$ in the presence of $CO_2$, which will greatly improve the process efficiency and bring significant social and economic benefits.

The methods of selective removal of $H_2S$ vary depending on the composition and pressure of the raw gas. Wet oxidation, which has high desulfurization efficiency and low operation cost, can directly convert $H_2S$ to elemental sulfur and thus contribute significantly to pollution control and resource reclamation [5,6]. The basic principles of wet oxidation method for $H_2S$ removal is based on absorption of $H_2S$ by the alkali solution (carbonate solution or ammonia water) and under the action of desulfurizing catalyst the hydrosulfide formed thereby via the oxidation-regeneration reaction is transformed into elementary sulfur, which can be recovered [7,8]. Therefore, the key of this method is the performance of the catalyst.

At present, ADA (anthraquinone disulfonate method) and MSQ (hydroquinone, salicylic acid and manganese sulfate compound catalyst) methods had been widely used in industrial gas desulfurization process, but they have different levels of poor activity, low sulfur capacity and high cost. PDS catalyst is a hot spot in the research of wet desulfurization technology due to its high activity, high selectivity, high life span and high sulfur capacity [9–11]. The commercial PDS consisting of dinuclear cobalt-PDS (see Fig. 1) is effective in removing $H_2S$ and preventing sulfur deposition and blockage of packing and pipeline, making it an attractive catalyst for the desulfurization of synthesis gas, coke oven gas, fuel gas, biogas, etc. [9]. However, the method used in the traditional absorption tower can hardly achieve high selective desulfurization when there is a high $CO_2/H_2S$ ratio in raw gas.

A selective absorption process for the removal of $H_2S$ requires high mass transfer and short residence time to avoid unwanted time dependent reactions, which can be readily achieved by using a rotating packed bed (RPB) [11]. As a process intensification method, high gravity technology has been applied to absorption [12–15], distillation [16–18], preparation of materials [19,20] and chemical reactions [21]. The reaction of $H_2S$ with $Na_2CO_3$ is essentially instantaneous, whereas that of $CO_2$ with $Na_2CO_3$ is relatively slow. Thus, it is highly possible to selectively absorb $H_2S$ in the presence of bulk $CO_2$ using a RPB which

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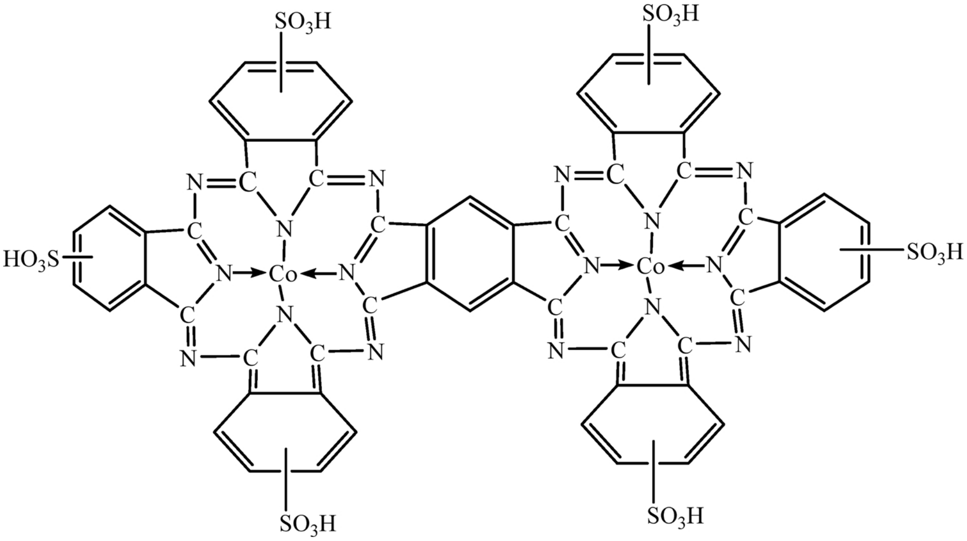

**Fig. 1.** Molecular structure of dinuclear cobalt-phthalocyanine sulfonate (PDS).

has short residence time and high mass transfer efficiency. There are some reports concerning the $H_2S$ removal in aqueous solutions in an RPB. Qi et al [7] adopted the PDS method for experimental study on removal of hydrogen sulfide from chemical sour gas (at a maximum throughput of $10000m^3/h$) in the RPB, the work has achieved a desulfurization rate exceeding 98%, which has verified the viability of the high gravity technology of wet oxidation process for removing $H_2S$ from sour gas. Qian et al [1] investigated experimentally and theoretically selective absorption of $H_2S$ from a gas mixture with $CO_2$ into N-methyldiethanolamine (MDEA) with laboratory scale in an RPB with laboratory- sized equipment. The experimental results showed that a high $H_2S$ removal efficiency of around 99.76% as well as the $CO_2$ removal efficiency is merely around 9.50%, which indicates high gravity technology has high selectivity. Two years later, an industrial test for methyldiethanolamine (MDEA) selective removal of $H_2S$ in an RPB is proposed. The results showed that $CO_2$ coabsorption rate for the RPB process is about 4.5% and for the packed tower process is about 77.1%, which indicates the residence time of the amine liquid in the packing of an RPB is too short to sufficiently absorb $CO_2$, but the amine liquid in the packed bed has adequate time to absorb more $CO_2$ [22]. Guo et al [23] optimize the length of packing of a RPB used for pilot-scale $H_2S$ removal, the optimized RPB removes 99.8% of $H_2S$ (15 vol% to 0.03 vol %) from the system.

The purpose of this study is to investigate selective absorption of $H_2S$ in the aqueous $NaCO_3$ solution with PDS as the catalyst in a RPB. The effects of liquid-gas volume ratio, rotation speed, temperature, initial PDS and $Na_2CO_3$ concentration on the $H_2S$ removal efficiency and pressure drop are studied. The results can provide some insights into the applicability of an RPB to selective desulfurization.

## 2. Reactions of $H_2S$ and $CO_2$ in aqueous $NaCO_3$ solution

When $H_2S$ and $CO_2$ are absorbed into an aqueous solution of $NaCO_3$, several reactions occur in the solution, which are as follows:

$$CO_2 + H_2\ O \rightarrow H_2CO_3 \tag{1}$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \tag{2}$$

$$HCO_3^- + H^+ + Na_2CO_3 \rightarrow 2NaHCO_3 \tag{3}$$

$$H_2S(g) \rightarrow H_2S(l) \tag{4}$$

$$H_2S(l) \rightarrow H^+ + HS^- \tag{5}$$

$$H^+ + HS^- + NaCO_3 \rightarrow NaHS + NaHCO_3 \tag{6}$$

$$NaHS + NaHCO_3 \xrightarrow{PDS} Na_2S + CO_2 + H_2O \tag{7}$$

$CO_2$ reacts with $H_2O$ to form $H_2CO_3$ before reacting with the $Na_2CO_3$ solution, because reaction (3) is a slow reaction, which is the control step for the adsorption of $CO_2$ in the $NaCO_3$ solution [24,25]. Therefore, the reaction process is very slow. But at the same time $NaCO_3$ solution absorbs $H_2S$ into the liquid phase, which can be dissociated into $HS^-$ and $H^+$ at once (reaction (5)). $H^+$ can react rapidly with the $NaCO_3$ solution (reacrion (6)), so the absorption rate of $H_2S$ in $NaCO_3$ solution is very fast, and the absorption resistance is controlled by gas film resistance [26,27].

The presence of $O_2$ in the gas leads to sulfur suspension by reactions (8) and (9), which accounts for the blockage of packing and pipeline in industrial applications.

$$NaHS + O_2 \xrightarrow{PDS} NaOH + S\downarrow \tag{8}$$

$$Na_2S_x + {}^{1}\!/_{2}O_2 + H_2O \xrightarrow{PDS} 2NaOH + S_x\downarrow \tag{9}$$

The dissolved oxygen can be easily adsorbed on the PDS surface. In the reproductive processes, $HS^-$ is oxidized quickly by reactive oxygen to generate elemental sulfur.

In summary, the $H_2S$-$NaCO_3$ reaction is a faster reaction, $H_2S$ enters liquid phase through gas-liquid interface and reacts with $NaCO_3$ solution to achieve chemical equilibrium instantly. The absorption rate of $H_2S$ is mainly limited by the mass transfer rate. However, the $CO_2$-$NaCO_3$ reaction is relatively slow, $CO_2$ first enters water through a gas-liquid interface and then hydrolyzes to $H^+$ and $HCO_3^-$.So reducing gas liquid contact time can reduce the $CO_2$ absorbed by $NaCO_3$ solution, thus improve the desulfurization selectivity. Meanwhile, The reason for the selectivity of $H_2S$ absorption for an RPB being higher than that for a packed tower is that the residence time of the amine liquid in the packing of an RPB falls short of 1 s, while it stays about 40 s in the packing of a packed tower [22]. The residence time of the sodium carbonate solution in the packing of an RPB is too short to sufficiently absorb $CO_2$, but the sodium carbonate solution in the packed bed has adequate time to absorb more $CO_2$. Therefore, it is possible to effectively absorb $H_2S$ and reduce $CO_2$ absorption of by reducing the gas-liquid contact time.