

Theoretical and Experimental Investigation of SO₂ Adsorption from Flue Gases in a Fluidized Bed of Copper Oxide

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Abstract

Among the air pollutants, sulfur dioxide has been given special emphasis for posing dangers to the environment. SO₂ emissions in the air have harmful effects on human health and the environment. Respiratory diseases and exacerbation of heart diseases are among dangerous symptoms for human health, especially when high concentrations of SO₂ are emitted. Therefore, in the present study, a wide variety of dry and wet processes were investigated to identify an appropriate process to reduce the amount of sulfur dioxide. Ultimately, the use of a fluidized bed containing metal oxides in a dry process was selected due to the factors such as simplicity of the process, forming a minimum of waste water and gas and ability to reduce pollution levels to acceptable environmental standards. In order to examine the performance of this type of fluidized beds, a laboratory scale set-up was constructed to investigate the effects of various operational parameters including temperature, inlet gas rate and concentration on the amount of sulfur dioxide adsorption by copper oxide.

Key words: Sulfur Dioxide, Fluidized Bed, Copper Oxide, Desulfurization.

Introduction

Desulfurization of raw materials and products is inevitable in oil and gas refineries. SO₂ emissions in the air have harmful effects on human health and the environment. Respiratory diseases and exacerbation of heart diseases are among dangerous outcomes for human health, especially when high concentrations of SO₂ are emitted. In addition, SO₂ causes deposition of fine acid droplets in the environment. This acidic deposition makes the water in rivers and lakes acidic, accelerates degradation of buildings' facade, destroys ancient constructions/monuments and changes the soil chemical composition.

SO₂ pollution appears in the environment most often as "acid rain" or more generally "acidic deposition" with its adverse effects on objects, buildings and ... [1]. The wet type deposition is in the form of rain with acidic pH, acid fog or snow, which flow on the ground and affect a variety of plants and animals. The level and severity of these impacts depend on the amount of rain acidity, soil chemistry and buffering capacity of soil and type of fish, trees and living organisms, whose life is dependent on water. The dry type of acid deposition (dry deposition)

is related to acidic gases and particles suspended in air, which are gradually deposited on the ground. Over 50% of these acidic particles suspending in the air are deposited on the ground and are moved on buildings, cars, homes and trees by wind. These dry sediments are washed out of the trees by the rain and hail and therefore increase the water rain acidity, worsening their effects on the environment. Figure 1 is a schematic diagram of cycling of acid gases, their emissions into air and their return to the soil and Figure 2 shows a schematic picture of production and precipitation mechanism of acid rain. Various experiments and studies conducted by scientists reveal that SO₂ and NO_x are the main causes of acid rain. Reaction of these gases with water, oxygen and other chemicals in the air generates various acidic compounds whose production rates increase by sunlight radiations. The final products of this reaction are mainly sulfuric acid and nitric acid [2].

In order to remove sulfur from flue gases (Flue Gas Desulfurization, FGD), different technologies are accessible, practical application of some of which dating back to several past decades.

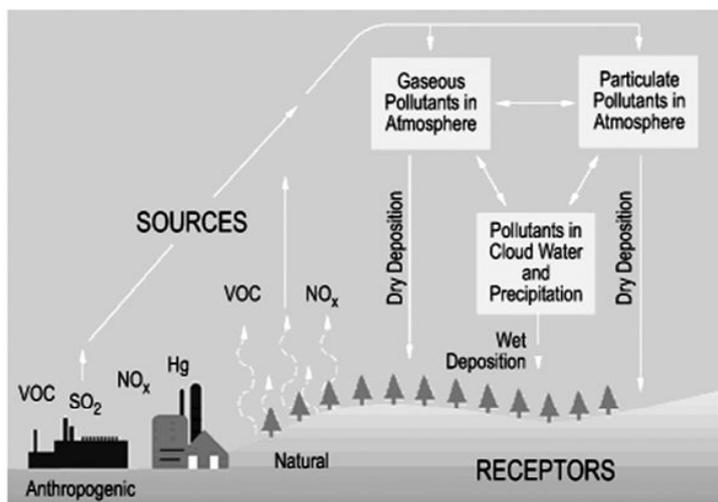


Figure 1. A schematic diagram of acid gases cycling [3]

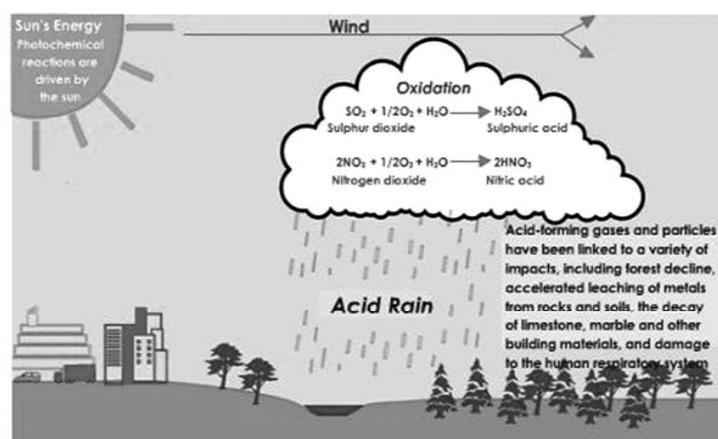


Figure 2. A schematic picture of the production and precipitation mechanism of acid rain [4]

Some of these technologies have been recently used by business units. FGD technologies can generally be divided into two categories:

1- Systems in which the sorbent circulates only once through the system and will not be used again after SO_2 adsorption. These systems are known as once through systems in which there is a permanent link between SO_2 and the resultant material or by-product is considered waste material.

2- Systems in which the sorbent is retrievable and can be used again. These systems are called regenerable systems. In these systems, SO_2 is separated from the sorbent in the retrieval phase and can be used for other purposes such as production of sulfuric acid, elemental sulfur or liquid SO_2 . The regenerated sorbent is returned to the system for reabsorbing SO_2 from flue gas.

Both of the above-mentioned systems can be divided into “wet” and “dry” systems. In wet processes, the produced waste material or by-product is wet and the purified outlet gas is also saturated with humidity. On the other hand, in dry processes, the produced waste material or by-product is a dry material and the outlet gas is free from humidity [5].

Among the above methods, SFGD (Shell Flue Gas Desulfurization) is highly efficient for the following reasons and so this method was selected for further study.

- 1– High efficiency of sulfur dioxide removal.
- 2– No energy waste due to proximity of adsorption and regeneration temperatures.
- 3- Simultaneous removal of SO_2 and NO_x
- 4- Lack of unwanted products/materials
- 5– Capability of treatment of high amounts of outlet gas with good performance and acceptable cost.

Description of the selected process

SFGD is a dry regenerable method in which a fluidized bed of copper oxide is used. It consists of two fluidized bed reactors of copper oxide for sulfur dioxide in which the flue gas coming out of a sulfur production unit is burned up in order to oxidize all the containing sulfur and change it into SO_2 . The outlet gas then enters the fluidized bed reactor to perform SO_2 adsorption process. The first reactor operates at a temperature of about $700 - 800^\circ\text{F}$ and is capable of converting 95% of sulfur dioxide [6]. In the regenerating unit, sulfur dioxide is removed from sorbent solid at the adsorption process temperature (about $750-850^\circ\text{F}$) using a regenerating gas such as hydrogen, methane, or carbon monoxide. Sulfur dioxide produced by regeneration bed can be sent to the first stage of sulfur production unit to be used again for sulfur production. A schematic diagram of the process is shown in Figure 3.

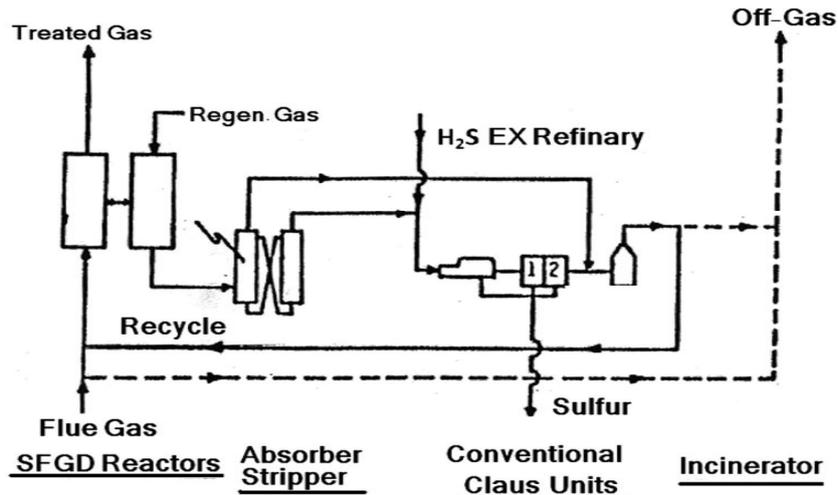
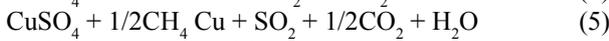
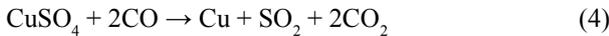
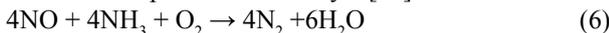


Figure 3. A schematic diagram of SFGD Process



If hydrogen is used for copper sulfate regeneration, as shown in Equation (3), copper is regenerated and SO₂ is released at 200 °C. If methane is used as the regenerative gas, the regeneration rate is slower than when hydrogen is used as regenerative gas. Of the three introduced regenerative gases, methane has the lowest reaction rate. If enough time is allowed to the system, it will be possible to reduce sulfur concentration in the solid adsorbent by 1 wt % using methane as the regenerating gas. It is also possible to use solid adsorbents in multiple regeneration and adsorption cycles [10]. In addition, copper oxide and copper sulfate act as catalysts in selective removal of nitrogen oxides in fluidized beds. To do so, ammonia is injected into the gas stream containing contaminants before entering the fluidized bed to react with nitrogen oxides in the presence of catalyst [11].



An initial economic estimate indicates that process economy is a function of the amount of consumed solid adsorbent. Therefore, it is possible to reduce the process

cost to a minimum by using a suitable solid adsorbent.

Experimentation

In order to study the process practically, a pilot scale set-up, whose processing flow and general diagrams are shown in Figures 4 and 5, respectively, was constructed. As it can be observed in these figures, the SO₂ polluted air enters into the reactor unit with a known concentration. When the polluted air passes through the bed, SO₂ reacts with copper oxide. SO₂ concentration in the inlet and outlet air is measured by a standard volumetric method [12]. The unit consists of the following parts:

1- Air compressor: The required air is provided by a 12 m³/hr compressor. A regulator valve is used to regulate the inlet air.

2- Ejector: Since the produced SO₂ pressure is lower than the air pressure, an ejector is used to inject SO₂ into the air stream.

3- SO₂ production system: In this system, a saturated solution of sodium sulfite reacts with hydrochloric acid to produce SO₂, as shown by the following reaction:

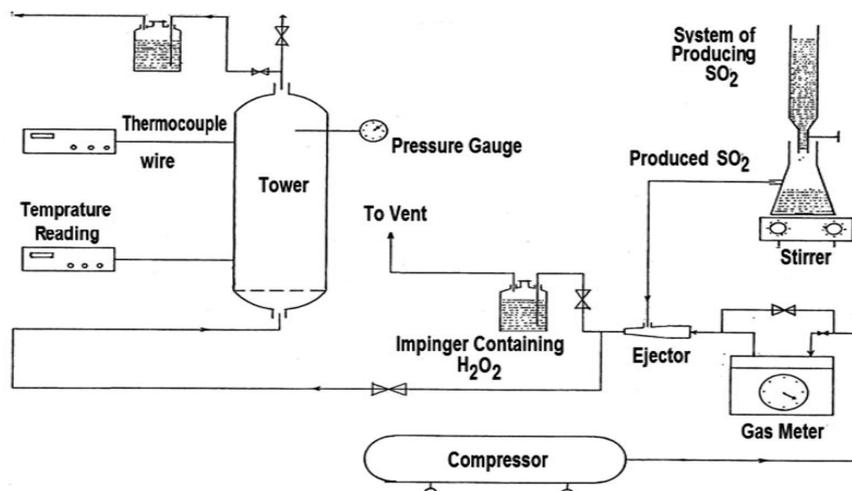
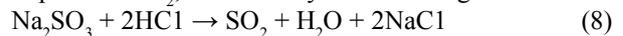


Figure 4. Process flow diagram of SFGD method



Figure 5. The general picture of the pilot scale unit

4- Sulfur dioxide concentration measurement system:

A sampling pot containing hydrogen peroxide is placed inside the gas inlet and outlet of the tower to collect the sulfur dioxide contained in the air for a given period. When sulfur dioxide is absorbed by hydrogen peroxide, the resultant sulfuric acid is titrated with standard sodium hydroxide to determine the initial sulfur dioxide concentration.

5- Adsorber Tower: The used adsorber tower is a steel cylinder with 6 cm diameter and a height of 50 cm, which consists of a pressure gauge chamber and two openings for inserting the thermometer.

6- Heating system: Three 1000 W electric elements are used in order to generate the required heat for the reaction.

7- Thermometer and temperature controller: The bed temperature is measured in two points by two chromium allumel thermocouples. The system also contains a controller to control the temperature.

Results

The effects of various operating parameters on sulfur dioxide adsorption have been investigated in order to identify the optimal conditions for the process and the following results were obtained from the conducted experiments:

Effect of Adsorbent Types

Hydrogen peroxide test is used to calculate SO_2 con-

centration under different conditions. The obtained results for two different types of adsorbents are presented in Tables 1 and 2.

In these tests, the efficiency of the existing copper oxide adsorbents on alumina base is controlled and the percentages of SO_2 removal are determined. Various regenerating gases such as hydrogen, methane, and carbon monoxide can be used in order to regenerate the produced copper sulfate. Considering the higher rate of reaction between hydrogen and copper sulfate, hydrogen has been used in these tests, as was shown in equations 3 to 6.

Effect of Temperature:

Figure 6 shows the effects of different temperatures on sulfur dioxide adsorption in the bed. As it is evident from the figure, the percentage of SO_2 removal increases with temperature. The reason is that an increase in the temperature leads to the increased rate of reaction between copper oxide and SO_2 existing in the air. Though, as it can be observed, at temperatures above 375°C , SO_2 removal efficiency will fall down with a rise in the temperature due to overcoming subsidiary reactions over the main reaction at temperatures above 375°C . As a result, 375°C is the optimal temperature for this process. In addition, SO_2 removal efficiency reduces with time at a constant temperature, indicating that the catalyst is saturated with time.

Table 1. Results obtained from the reactor with C18 catalyst and a bed length of 30 cm

Bed Temperature ($^\circ\text{C}$)	375	350	400	300	250
Superficial Velocity (cm/sec)	200	195	210	180	180
Inlet SO_2 Concentration (ppm)	2100	2500	2000	2000	2100
Outlet SO_2 Concentration (ppm)	290	550	700	800	1600
Removal Efficiency (%)	86	78	65	60	23.8

Table 2. Results obtained from the reactor with redox catalyst and a bed length of 30 cm

Bed Temperature ($^\circ\text{C}$)	375	350	300	350
Superficial Velocity (cm/sec)	200	200	160	160
Inlet SO_2 Concentration (ppm)	2100	2100	1500	1800
Outlet SO_2 Concentration (ppm)	609	651	570	540
Removal Efficiency (%)	71	69	62	70

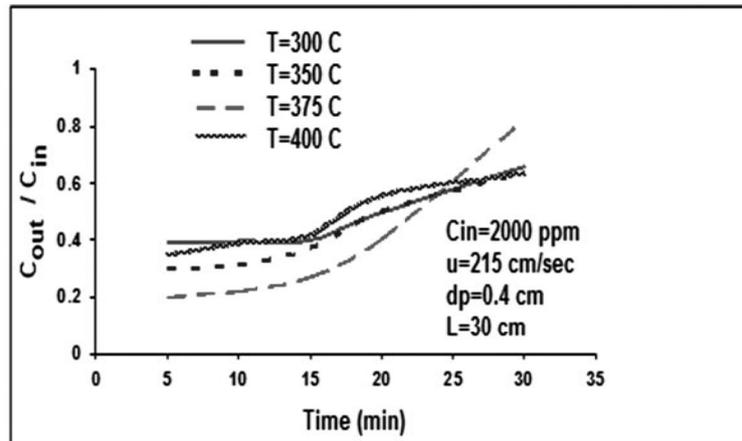


Figure 6. Variation of SO_2 removal efficiency with time at different temperatures

Effect of Inlet Gas Velocity

As it is clear from Figure 7, an increase in inlet gas velocity results in a decrease in SO_2 removal efficiency. The reason is the decrease of the gas residence time in the reactor and as a result, the reaction rate between copper oxide and SO_2 in the air will decrease with increasing the gas velocity.

Effect of SO_2 Concentration on the Inlet Gas

As shown in Figure 8, an increase in SO_2 concentration in the inlet gas results in a decrease in SO_2 removal efficiency or an increase in outlet SO_2 concentration. However, the decrease in removal efficiency is negligible such that increasing inlet concentration by eight times will result in only eight percent decrease in removal efficiency.

Since the reaction rate between copper oxide and SO_2 is a function of the amount of reacting solid copper, the copper quantity in the solids has been investigated in addition to the above operating parameters. To do so, two types of catalysts (C18 and Redox) containing different amounts of copper were tested.

Effect of Copper Quantity in the Solid Catalyst

As previously mentioned, the reaction rate constant is

a function of k_{so} , which itself varies with variations in the copper quantity. The results of various experiments have revealed that when copper quantity is higher, the percentage of sulfur dioxide removal is higher as well (See Figure 9). Of course, it should be noted that a very high percentage of copper oxide based on the alumina base opening may increase fracture and corrosion rate of copper oxide particles, which is considered as an adverse effect. Therefore, the amount of copper oxide equal to 9 to 15% is experientially determined as appropriate [13].

Effect of Adsorbing Capacity of Adsorbent at Different Adsorption and Regeneration Cycles

In order to control re-adsorbing capacity of adsorbent after multiple adsorption and regeneration cycles, the adsorbent solid bed was tested for adsorption and regeneration several times. The results of the experiments, shown in Figure 10, indicate that significant changes were observed in the first few cycles, i.e. all the produced sulfate in the adsorbent is not regenerated in the first few cycles and after multiple adsorption and regeneration cycles, adsorbing capacity of adsorbent remains stable.

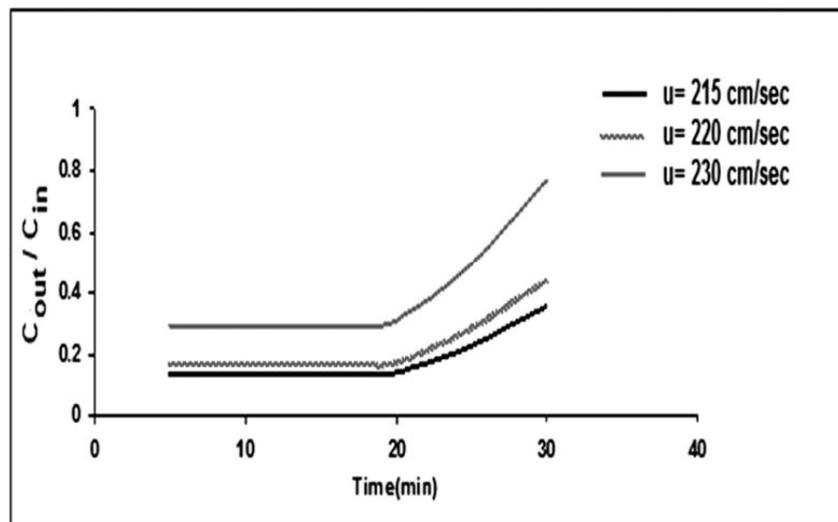


Figure 7. Variation of SO_2 removal efficiency with time at different inlet gas velocity

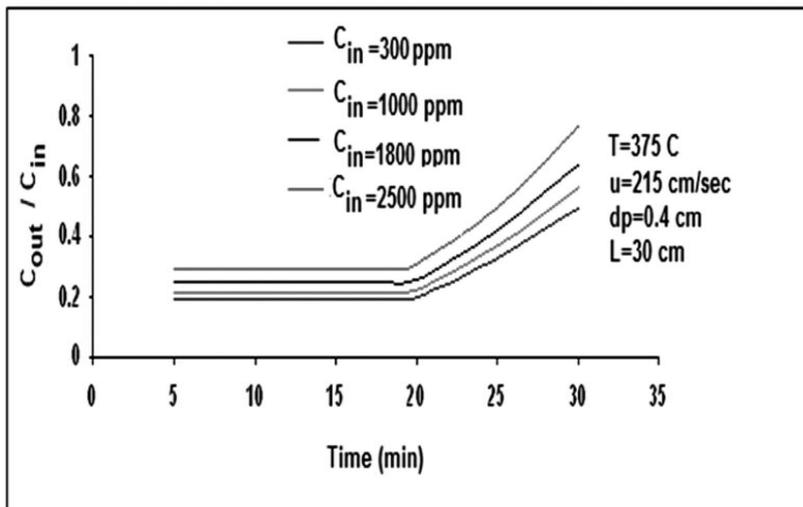


Figure 8. Variation of SO₂ removal efficiency with time at different inlet SO₂ concentration

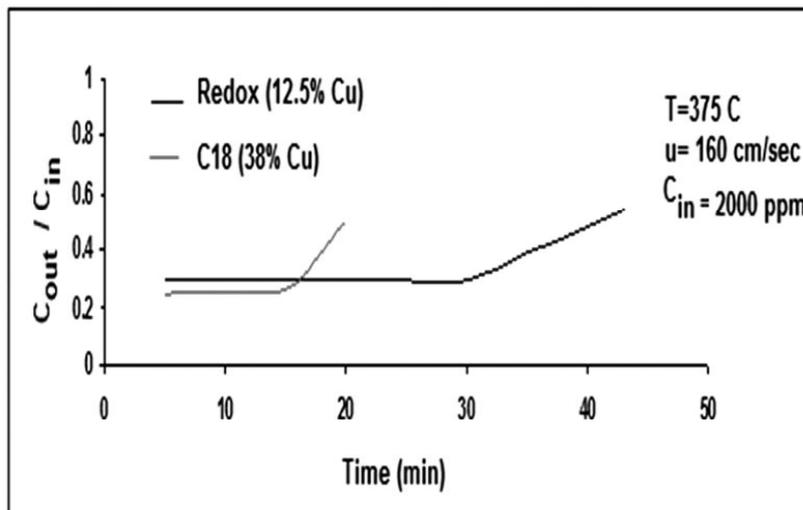


Figure 9. Variation of SO₂ removal efficiency with time for different catalysts

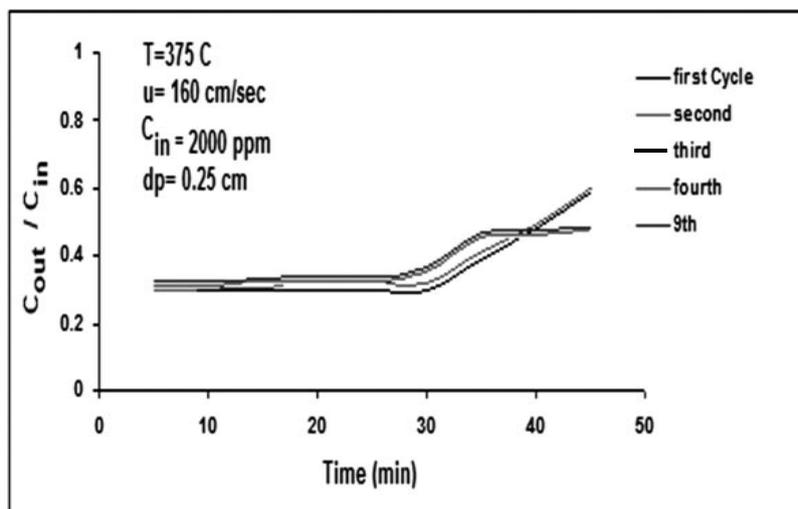


Figure 10. Variation of SO₂ removal efficiency with time for different cycles

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