INVESTIGATION OF PARAMETERS AFFECTING A SELECTIVE FLUE GAS DESULFURIZATION WITH AN AMINE BASE ABSORBENT

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ABSTRACT: *A novel selective absorption of SO_2 from a produced stream containing SO_2, CO_2, N_2 and steam mixture with amine solution was investigated using an absorption/stripping columns in laboratory scale. SO_2 concentration, stripper temperature, gas to liquid ratio and solvent pH were considered as working parameters to investigate their effect on SO_2 removal efficiency from the flue gas. According to the experiments, sulfur dioxide which was in the range of 4000 ppm to 8000 ppm in gas mixture was reduced to less than 200 ppm and 1000 ppm respectively.Furthermore the selectivity of the absorption is tested by performing an8 days test which showed the selectivity of more than 99.8 %. Observation showed the effectiveness of parameters ranked to the least as pH, stripper temperature, inlet SO_2 concentration and gas to the liquid ratio.*

Keywords SO_2 absorption, regeneration, amine solution,parameters

INTRODUCTION

As sulphur dioxide is a major atmospheric pollutant generating acid deposits, its abatement in flue gases is of important industrial concern[1,2].Fossil fuels,combustion in power plants, boilers, incinerators, roasting of sulphide ore in metallurgy and sulphuric acid industry are the major sources of sulphur oxide. Although SO_2 is a dangerous gas to humanhealth, it's destructive to environment. Large part of sulphur oxides is also added in air due to volcanic eruption. These amount of SO_2 in atmosphere leads to air pollution and acid rain [3,4]. Due to presence of moisture in atmospheric air these oxides react with moisture and forms sulphurous acid. The oxides react in the atmosphere forming sulphuric acid, which leads to acid rain. Because of the lowering of the permissible emission limits, there has been a rising interest in new treatment processes for absorbing gaseous SO_2, using various reactants[5]. Many processes have been developed, so far. Among them limestone, calcium hydroxide and magnesium hydroxide slurries, sodium hydroxide solutions, and some organic solvents are used as absorbent in those processes[6,7,8].The most well-known flue gas desulfurization processes are mainly based on scrubbing with limestone slurries of the flue gas. These are known as non-regenerative processes [9,10]. Typically, the by-product is either discarded in a landfill or converted into gypsum for use in wallboard and cement manufacturing. Disposal in a landfill requires a large initial capital investment as well as significant resources to maintain the landfill throughout the life of the plant[11].

There are also regenerative SO_2 removal processes like Wellmann-Lord and the citrate processes [9,12] In these processes, SO_2 is absorbed by aqueous solution, then recovered from the SO_2 rich solution either as SO_2 by steam stripping or as elemental sulphur by reacting to H_2S[12,13,14].

The recovery and recycling of sulphur are being aided by the commercial introduction of generable selective SO_2 scrubbing from gas streams. This new process can reduce emissions to air while providing a new tool to solve the recycling puzzle[15].

The selectivity of this process with high performance separate this process from others, which can have lots of usage in industries. In this process Sulphur, in the form of sulphur dioxide (SO_2) is recovered, which can be used in bleaching as a feed chemical, hydrosulphite manufacture, pH adjustment and residual peroxide destruction.

1. Absorption mechanism

In water solution, SO_2dissolve reversiblyin a hydration and ionization equilibrium reaction. In the first reaction SO_2 molecules are covered with water molecules. Then the result reacts with water to form sulphurous acid according to reaction (2). Then sulphurous acid appears to contribute in an equilibrium to release proton as indicated in reaction (3).

$$SO_{2\,(g)} \leftrightarrow SO_{2\,(aq)} \quad (1)$$

$$SO_{2\,(aq)} + H_2O_{\,(L)} \leftrightarrow H_2SO_{3(L)} \quad (2)$$

$$H_2SO_{3\,(L)} \leftrightarrow HSO_3^- + H^+ \leftrightarrow SO_2 + 2H^+ \quad (3)$$

Adding the amine, to the water leads to an increasein quantity of SO_2 dissolved. According to equation (4), the amine drives the above equilibria to the right by reacting with the hydrogen ions. The overall reaction, indicates that by increasing concentration of SO_2 in the feed gas, the equilibrium moves to the right, i.e. the quantity of SO_2 dissolved in the rich solvent increases. Therefore, the scrubbing of more concentrated gas streams requires a less than the proportional increase in solvent circulation rate.

$$R_1R_2R_3N + H^+ \qquad R_1R_2R_3NH^+ \quad (4)$$

2. MATERIAL AND METHODS

A pilot plant designed and set up for the acid gas removal from flue gas, prepared to remove SO_2 from the simulated gas (figure 1). It is specially designed for the experiments and using an amine absorber with an innovative formulation. The pilot consists of absorption and stripper tower, with a diameter of 15cm and a height of 150cm, and the experiments were done using the gas to liquid ratio ranging from 375 (V/V) to 500(V/V).

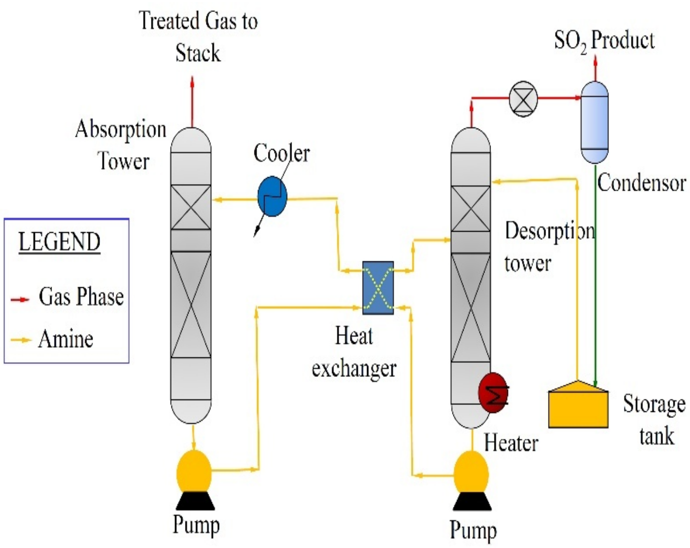

Figure 1. The pilot plant designed for absorption and regeneration of SO_2.

In order to prepare the solvent solution, two kilograms of the prepared amino compound absorber were added to 40 litters of water. So the concentration of 43 grams per litter is prepared, in this case the volumetric percent of 6.6 is reached with a pH of 11.

According to previous studies, the pH should be in a range of 5-6 for the best SO_2 absorption [16,17]. Therefore Sulphuric acid was chosenand added to the solvent to reduce pH and help SO_2 absorption due to its features. Thus, 2.5 litters of sulphuric acid, with a concentration of 99 percent were added to the solvent solution to reach the desired pH. The pH of the overall solution then reached 6.01.

Two elements each with the power of 2000 Watts are used in the stripper column that heatsupthe absorber solution to approximately 120 °C. Each element is connected to temperature controllers to be set as desired. Heating up to 120 °C will cause the pressure to increase up to 0.8-0.9 (bar). At the top of this tower, a thermocouple is placed to measure the temperature and set the top temperature and pressure at a desired point.

Solvent flow rate varies from 100 to 400 millilitres per minute at the entrance of absorber column. After solvent entrance, it is sent to desorption column via a 750 (w) pump. Then the absorber flow is preheated in a shell and tube heat exchanger illustrated in figure 1, prior to entering the desorption tower.

Feed gas is produced by using three gas cylinders, N_2, CO_2 and SO_2 and a boiler to produce steam. The CO_2 and N_2 gases were commercial grades with a purity of 99.99%, and the SO_2 gas was used with a high purity of 99.9%. All these components are mixed in a collector designed for this purpose. Figure 1 shows a scheme of the pilot plant employed in the experiments. The employed absorber and regenerator were made of 316 stainless steel with an internal diameter of 15 cm, and a height of 1.5 (m). The absorbent flows through the pipes to the absorber and set by using the rotameter to the desired point. All the experiment conditions are achieved and set by using equipment designed in the pilot. The inlet produced flue gas is analysed by using TESTO 350 containing sensors which can report the concentration of SO_X, CO_2 and NO_X.

3. RESULTS AND DISCUSSIONS

As SO_2 is an acidic gas, the increase of efficiency by increasing pH of absorption solution is expected to be favourable to absorption[18]. Aqueous amine compound has base properties so its pH affects the absorption process significantly. Figure 2 indicates the absorption variation with pH at a certain operational condition. Conditions chosen here due to better efficiency were desorption temperature of 120 ºC, G/L ratio of 375 and SO_2 concentration of 6200 ppm.

By changing the proportion between the amount of sulphuric acid and amine, the pH value of the absorption solvent is adjusted. The desulfurization efficiency increases asymptotically with the increase in pH. It is observed that the SO_2 concentration has strongly changed in the outlet of absorption tower. In the other word the absorption efficiency highly depends on pH variation. As it is shown in Figure 2 by increasing absorbent pH, absorption efficiencysharply increased due to the increase in SO_2 absorption affinity. The highly tendency of solvent to absorbed can beinterpret along of proton reduction and needs of more SO_2 to be absorbed. However in low PH value a decrease in the number of active groups for absorption are seen, while a pH value that is too high leads to an increase of volatile loss, so a suitable PH value must be found.

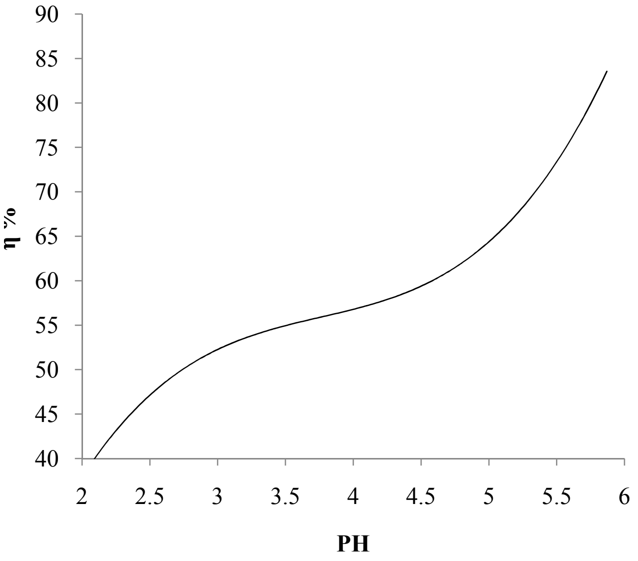

Figure 2. Effect of PH on desulfurization in the average SO_2 concentration of 6100 ppm, at 120 °C and G/L ratio of 375.

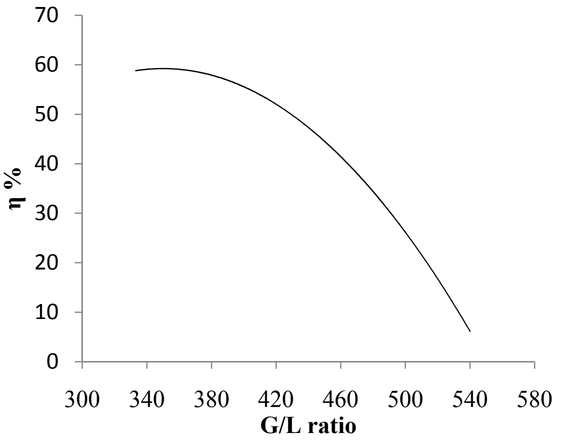

Figure 3. Absorption variation vs. Variation of G/L in SO_2 concentration of 6100 ppm, at 110 °C and PH of 4.

Figure. 3, represents the absorption variation with gas to liquid ratio. Absorption behaviour shows the increase of gas to liquid ratio, cause a sharply decrease in efficiency. At constant liquid flow rate, a decrease in the gas film thickness occurs by increasing the inlet gas flow rate, and gas-liquid mass transfer area and coefficient increase a little, which is favourable to absorb but on the other hand, an increase in the inlet gas rate decreases the gas-liquid contact time, which reduce the absorption efficiency and effects dominantly on efficiency decrease.

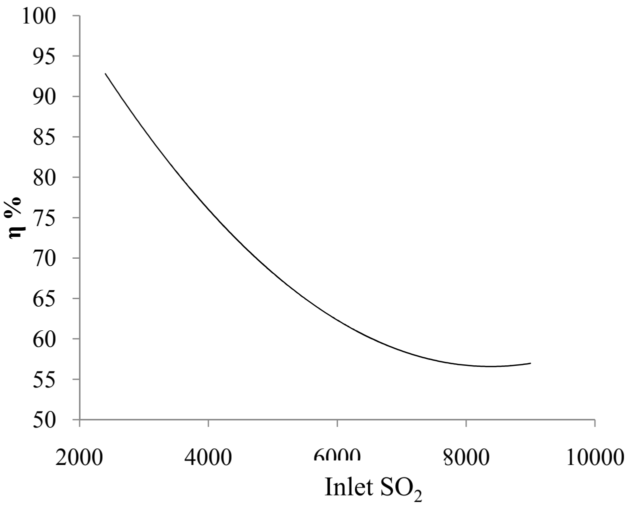

Figure 4. Absorption variation vs. Variation of SO_2 concentration, at 110 °C, G/L of 375 and PH of 4.

The effect of SO_2 concentration on absorption is also investigated. From figure 4 it can be concluded that the efficiency of absorption into amine solution decrease with an increasing in SO_2 concentration of the inlet gas. By increasing the SO_2 concentration the capability of solvent to absorb SO_2 decrease and this is due to absorbent saturation at higher concentration[19] To justify the effect of solvent on absorption the SO_2 inlet concentration was increased from 2400 ppm to 9000 ppm. The concentration of SO_2 in the outlet of absorption tower showed that the SO_2 absorption efficiency decreased from 94 % to 55%. When the SO_2 concentration exceeds 7000 ppm, the buffer capacity declines and influence hardly on SO_2 removal efficiency.This shows that SO_2 concentration is one of the most important parameters affecting on desulfurization while a small change in SO_2 concentration in produced flue gas would result in a high change inabsorption efficiency[20].

Figure 5 indicates that at 110 °C, the best absorptionefficiency is reached.Absorption variation with desorption temperature shows that by increasing temprature from 100 to 110 an increasing in effiency is observed which is due to approximately complete bounds recovery between SO_2 and solvent molecules. By more increasing temperature a decrease in efficiency is observed. Experiment shows that by increasing temperature to 120 °C absorption highly decrease from 79% to 63%. While the temperature increased to 120 °C, the pressure increase from 0.3 bar to about 0.85 bar and does not permit the absorbent to desorb the dissolved SO_2.

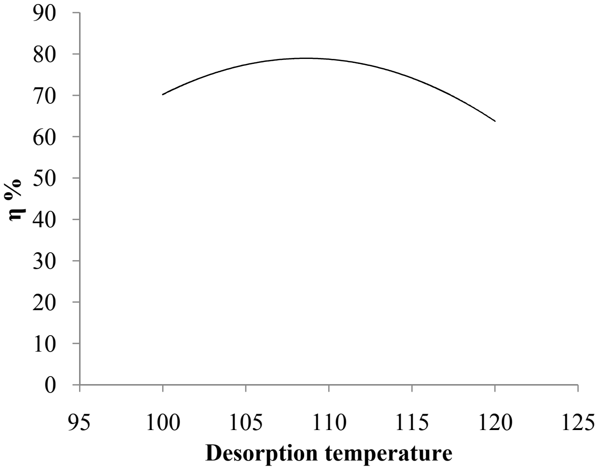

Figure 5. Absorption variation vs. temperature Variation in SO_2 concentration of 6100 ppm, at 110 °C and PH of 4.

4. Analysis of the Safety and Economy

In the explained process a novel solvent with a little toxicity, inexpensive (about 2 $ per kg), high selectivity and absorption efficiency is emplayed. The process is preformed at atmospheric pressure and a temperature of lower than 110 ºC which reduce the dangerous condition due to low pressure and temperature. In addition, the pH range of using absorbent is near 6 and obtained by addition of sulphuric acid to decreases the volatility of amine and increase pH. Therefore, the damage of the absorbent on air can be nearly ignored due to approximately neutral pH an less evaporation. Furthermore, corrosion of equipment at this acidic pH should be considered[20].

5. Selectivity investigation.

To produce a real flue gas with the desired composition, a mixture of diesel and mercaptan is burned in a furnace to produce flue gas with SO_2 concentration of 2400 ppm.The increase in CO_2 concentration is due to the decrease in air oxygen by burning diesel in indoor air. The selectivity of absorption to SO_2 is presented in figure 6 and figure 7 respectively. Figure 6 shows the concentration variation ofCO_2in the inlet and outlet of absorption column. As it can be seen, the difference between the outlet and inlet is about 0.04 % which shows the selectivity of about 99.8% for SO_2. Figure 7indicates the comparision of SO_2 concentration variation in the outlet and inlet of absorption tower. the SO_2 concentration in the outlet of the desorption tower is approximately constant on the average of 270 ppm, which shows the performance of about 90%.Table 1 presents the operating conditionFor this observation. In this table any parameter that may affect the absorption and regeneration are presented. It can be noted from this table that the performance for the absorbent with the concentration of 0.05% (V/V) is good enough to introduce the absorbentas a selective high efficient desulfurization process.

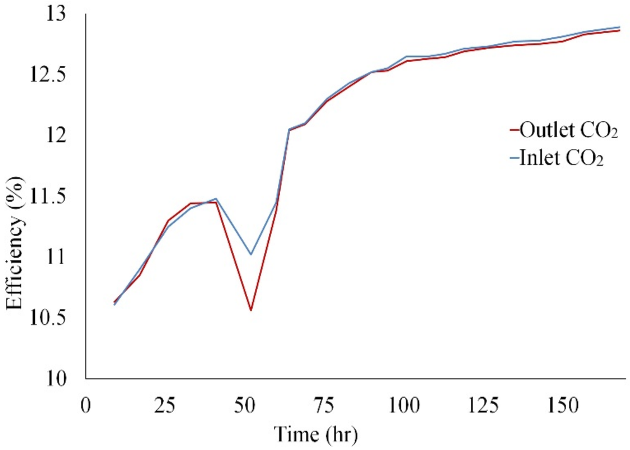

Figure 6.CO_2 variation in the five hour plot of the flue gas desulfurization

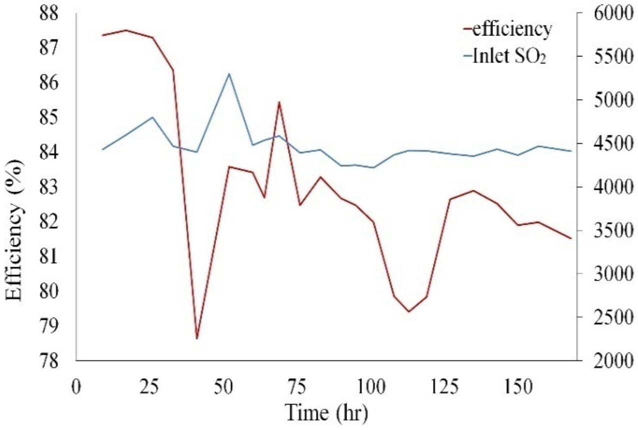

Figure7. SO_2 variation in the Five hour plot of the flue gas desulfurization

Table1. Arbitrary operating conditions for 8 days hour testing**.**

Inlet SO2	Absorption tower T (° C)	Absorption tower P (kpa)	Desorption Top T	Desorption Tower top P (bar)	Desorption Tower bottom P (bar)	Solvent concentration (gr/lit)
2430	61	8	108	0.8	0.85	0.05
2600	60	8	105	0.75	0.8	0.05
2800	61	8	104	0.75	0.8	0.05
2470	59	8	107	0.8	0.85	0.05
2400	62	8	110	0.8	0.85	0.05
3300	57	8	110	0.8	0.85	0.05
2480	58	8	116	0.85	0.9	0.05
2536	55	8	110	0.8	0.85	0.05
2587	57	8	106	0.75	0.8	0.05
2394	59	8	110	0.8	0.85	0.05
2426	61	8	109	0.8	0.85	0.05
2242	60	8	107	0.8	0.85	0.05
2250	59	8	105	0.75	0.8	0.05
2220	52	8	110	0.8	0.85	0.05

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