



# Reduction and regeneration of SO<sub>x</sub> from flue gases

<sup>1</sup>Swarnabh Mandal and <sup>2</sup>BSVSR Krishna

Department of Chemical Engineering, Manipal Institute of Technology, Manipal University, Karnataka, India  
Email: <sup>2</sup>Krishna.bandaru@manipal.edu

**Abstract** - Sulphur Dioxide (SO<sub>2</sub>) is one of the main pollutants which will come from refineries, flue gases, power generation units and industrial boilers. Among the various approaches for SO<sub>2</sub> removal from flue gases, regenerative processes are better and employing aqueous solutions of organic and inorganic buffering agents are being used. Experiments have been conducted to find the better suitable amine solutions to facilitate the maximum SO<sub>2</sub> absorption from flue gases and the same will be regenerated for separating SO<sub>2</sub> gas stream to increase the efficiency of the sulfuric acid plants. Experiments also conducted to check the possible solvent degradation.

**Keywords:** Sulphur Dioxide, Amine solution, Absorption, regeneration.

## I. INTRODUCTION

Sulfur dioxide (SO<sub>2</sub>), one of the main pollutants from industrial off gases and causes damage to the man's Eco system. This SO<sub>2</sub> can result in various respiratory and cardiovascular diseases for the humans or animal, moreover the sulfur dioxide along with NO<sub>x</sub> was the precursors for acid rain which may cause heavy damage to the flora [1]. The awareness of these problems led many scientists and Industrials for controlling these SO<sub>2</sub> and NO<sub>x</sub> release to the atmosphere at source. Same time government has made stringent measures for release of these gases into atmosphere. Mostly these gases can be recovered at source itself.

Sulfur dioxide emission in India was controlled mainly via scrubbing by the use of caustic systems but the major drawback was the un-recyclability of the caustics. This resulted in large scale treatment or disposal of the caustics. In the last few years, many regenerative processes with comparatively lower costs have been developed, including the use of various aqueous solutions of organic and inorganic buffering agents and being used for various types of flue gas applications i.e. Refinery Claus sulfur recovery unit tail gas treatment, power plant flue gas, sulfuric acid plant feed gas treatment, tail gas treatment etc.

Many methods have been developed in recent times for stripping of sulfur dioxide from the flue gas.

- Wellman-Lord Process [1,2, 3]: This process requires concentrated sodium sulfite solution for stripping of sulfur dioxide from the influent gases. Captured sulfur dioxide in the solution by the process of

absorption is released or desulfurised by thermal treatment in an evaporator.

- Belco's Labsorb Process [4]: The phosphate solution is the solvent used for absorption of the sulfur dioxide and thermally treated for regeneration of the solution.

- Cansolv Process[5] : It utilizes the amine solution for absorption of sulfur dioxide, and later thermal regeneration is done.

\*Major disadvantage in the later process is that the amines are highly toxic.

Sulfur dioxide is acidic in nature and has a pKa value of 1.81 at 25 °C, the pKa value of -2 to 12 in water is considered as a weak acid, therefore, weak bases may be used for its absorption. However strong bases like caustic soda, alkyl amines etc are more effective in sulfur dioxide absorption but associated problems with these processes is thermal regeneration is difficult. An option for this case is weak bases. The weak bases around 5-7 pKa is preferred for the absorption, because a weak base have the tendency to decrease the basicity while heating and hence resulting in the regeneration of the absorbed SO<sub>2</sub> gas. This process can be verified via the Wellman-Lord and Belco's process where the sodium sulfite and phosphate pH solution used respectively have a pKa value of around 7. But the main drawbacks of these solvents are unstable and have a decrease in the basicity upon increase in temperature, which leads to cost ineffectiveness. On the contrary the amines used in the Cansolv process have a pKa value of around 5.7 at 25 °C and can be recycled even though it has lower basicity than the former solvents. Additionally, it can be used in the regeneration of the sweet gases as well i.e. H<sub>2</sub>S and CO<sub>2</sub> in the regeneration chamber. Hence, amines are the preferred solvents to be used in SO<sub>2</sub> regeneration process. Present work is focused on scrutinizing the solvents which will give better absorption and more recovery of SO<sub>2</sub> in regeneration step.

## II. EXPERIMENTAL

I) Materials used: The following gases are procured from the supplier: Nitrogen gas (99.99%), SO<sub>2</sub> gas (99.99%), anhydrous amines (more than 98%), Iodine

solution (N/10),  $\text{H}_2\text{SO}_4$  (97%),  $\text{H}_2\text{O}_2$  solutions (50% v/v), NaOH pellets (97%), HCl (35%) and sodium thiosulfate (N/10). The above pure gases are used to prepare the gas mixtures of required mole/mass percentage mixtures for experimentation.

II) Methods: Batch and a continuous, scale bench scale apparatus had used to estimate the absorption of  $\text{SO}_2$  from three different solvents. Further, the extent of regeneration of the  $\text{SO}_2$  gas was estimated from these solvents with the increase of the temperature.

III) Experimental: Schematic diagram of experimental was shown in Fig.1.

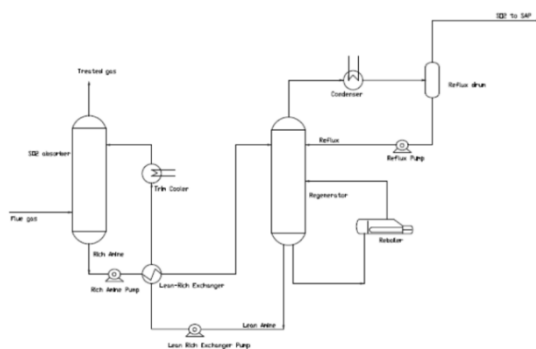


Figure 1: Schematic experimental setup

The Experimental setup consists of following sections i.e.  $\text{SO}_2$  absorber, solvent regenerator, re-boiler, condenser, heat exchangers, pumps and storage tanks. In absorber the flue gas which contains  $\text{SO}_2$  was flows upward while the lean liquid which contains amine with low or negligible  $\text{SO}_2$  counter-currently flows from top to bottom. In absorption  $\text{SO}_2$  was absorbed from flue gas by lean amine solution at low temperature. The lean was sent to the bottom of regeneration tank to raise the temperature such that the  $\text{SO}_2$  was stripped off from amine solution. Pure  $\text{SO}_2$  was raised from through the regeneration column and this gas moves to the reflux drum via condenser and the lean amine stripped of the  $\text{SO}_2$  moves to the trim cooler to reduce the amine temperature to enable it's recycle procedure. Three solvents were selected for this study i.e. Solvent-1, 2 and 3, after an extensive study on  $\text{SO}_2$  absorption capabilities of the amine based solvents.

A batch and a continuous, laboratory scale bench scale unit was used to estimate the  $\text{SO}_2$  absorption in the Solvent1, Solvent-2 and Solvent-3. Similarly the extent of regeneration of the  $\text{SO}_2$  gas was estimated from the above three solvents rich in  $\text{SO}_2$  with the increase of the temperature.

### III. ABSORPTION:

#### Batch process

The absorption under batch process was conducted by passing a customized gas mixture of  $\text{N}_2$  and  $\text{SO}_2$  through the selected amines to analyze the  $\text{SO}_2$  concentration in feed and off gas as well to estimate the amount of  $\text{SO}_2$

absorbed by the amines. Before starting of the experiment the following clean in process have done to ensure the proper function of absorber. Water vapour was sent through gas assembly unit then gas was sparged from the bottom the vessel to enable proficient absorption of gas into the liquid. The temperature was maintained  $40\text{--}42^\circ\text{C}$  in the vessel to enable the best suitable condition for absorption of the gas. Now  $\text{SO}_2$  &  $\text{N}_2$  gas mixture was sent under controlled flow rate. The gas stream was directed through a 3-way valve. A set of two absorber chambers were setup to ensure complete absorption of  $\text{SO}_2$ .  $\text{H}_2\text{SO}_4$  was formed as a result of the  $\text{SO}_2$  gas being absorbed by 3%  $\text{H}_2\text{O}_2$ . The  $\text{H}_2\text{SO}_4$  concentration was estimated with NaOH solution. This titrate value was used to determine the  $\text{SO}_2$  concentration in the gas mixture.  $\text{SO}_2$  on absorption yields  $\text{HSO}_3^-$  and  $\text{S}_2\text{O}_3^{2-}$  ions, which when oxidised forms  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$  ions. The acidified solution of iodine was titrated against the amine solution before and after the absorption of  $\text{SO}_2$  gas to estimate the ionic concentration of  $\text{SO}_x^{-n}$  ions in the amines.

#### Continuous process

The customized gas mixture and the flow are similar to that of the batch setup experiment performed already. The column was packed with glass beads (small tubes of  $4\text{mm} \times 4\text{mm}$ ). Gas flow rate was maintained  $42.75$  lph. The liquid flow rate was maintained at  $2.5$  lph from bottom, while the gas was sent to the column through the bottom of absorber counter-currently. The liquid level was controlled in the column via a control valve by maintaining a minute pressure inside and the temperature was controlled by thermostated water supply through the outer jacket of the column. pH was measured at the bottom of the column and carried till pH was stable. The sample was collected from the bottom of the column with the titrations being carried out for  $\text{SO}_2$  rich solvents at regular time intervals.

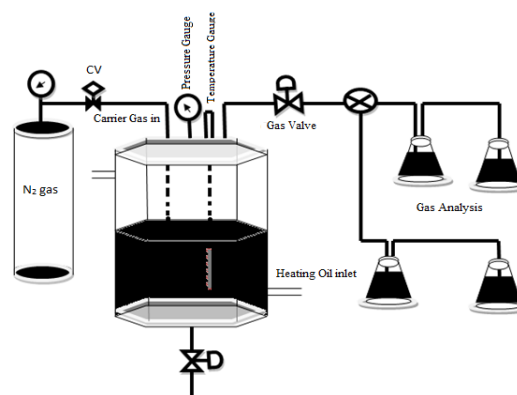


Figure 2.  $\text{SO}_2$  regeneration setup

#### $\text{SO}_2$ Regeneration

A regeneration vessel was shown in Fig. 2, fitted with pressure gauge and thermometer. The rich amine was heated by oil and nitrogen gas was used as carrier to strip the  $\text{SO}_2$  by exploiting the desorption phenomenon and is sent to the analyzer section through a gas outlet.

In the analyzer section the SO<sub>2</sub> gas was absorbed in hydrogen peroxide solution and titrated with respect to time for the analysis of the SO<sub>2</sub> at regular time intervals.

#### IV. RESULTS AND DISCUSSION

##### 1. Solvent Screening

SO<sub>2</sub> absorption was carried out using ten different amine solutions with known quantity of pure SO<sub>2</sub> gas. The absorption quantity was measured with respect to time taken for absorption in each of the solvents. The absorption was conducted at 45-50<sup>0</sup>C, followed by heating the rich SO<sub>2</sub>amine to facilitate desorption; the amines were heated to 90-100 <sup>0</sup>C for regeneration of SO<sub>2</sub>.The SO<sub>2</sub>concentration was measured by the iodometric titration, while the SO<sub>2</sub> regeneration after heating was determined by titrating it in hydrogen peroxide against NaOH.

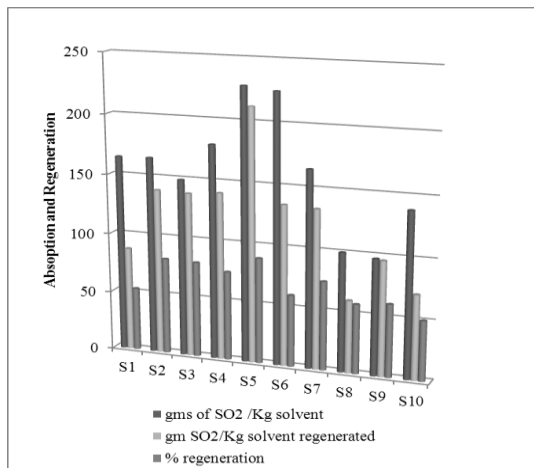


Fig 3. Variation of SO<sub>2</sub> absorption and desorption for 10 solvents.

Figure 3 show the data of absorption and regeneration for ten solvents for fixed quantity of SO<sub>2</sub> and fixed final time. Though Solvent 5 has shown high absorption and desorption due to the cost of solvent and handling problems solvent 1, 2, 3 have chosen due to less time for absorption and desorption while other solvents have taken moderate time for absorption and desorption of SO<sub>2</sub>. To reduce overall time and expenditure present Author’s chosen these three solvents for further experimentation [6].

##### 2 SO<sub>2</sub> absorption in presence of CO<sub>2</sub>

Mostly the effluent consists of NO<sub>x</sub> and CO<sub>2</sub> from the Sulphuric plants. Experiments conducted to check the effect of CO<sub>2</sub> present in effluent while absorption taking place. A mixture of CO<sub>2</sub> and SO<sub>2</sub> was used to check the effect of absorption in these amine solutions. The absorbed SO<sub>2</sub> was analyzed similarly through iodometric titrations [7]. Figure 4 shows absorption of SO<sub>2</sub> with time and presence and absence of CO<sub>2</sub> as independent parameter. It was observed that the rate of absorption was more in absence of CO<sub>2</sub> for solvents I and II, while it was notable that, Solvent-III showed no effect of CO<sub>2</sub> presence.

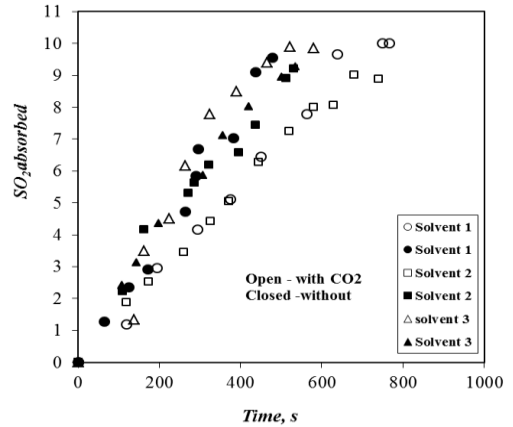


Fig 4 Variation of SO<sub>2</sub> absorption in presence of CO<sub>2</sub>

##### 3. Solvent degradation

Solvent degradation was identified using the following procedure: The chosen sets of solvents were subjected to high temperatures of around 85 -95 <sup>0</sup>C and at 6atm followed by pH titration. These results were plotted in Figure 5 as variation of pH with volume of HCl. One can observe from the figure that treated and untreated amines solvent have performed same manner. The net intake was same. This shows that, life span of solvent for absorption and desorption was more.

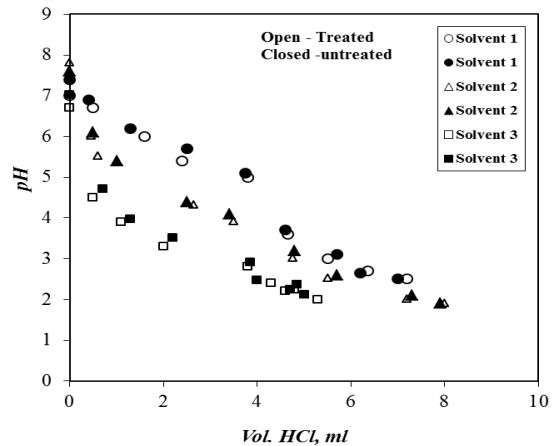


Fig5. Study on degradation of solvents for treated and untreated solvents.

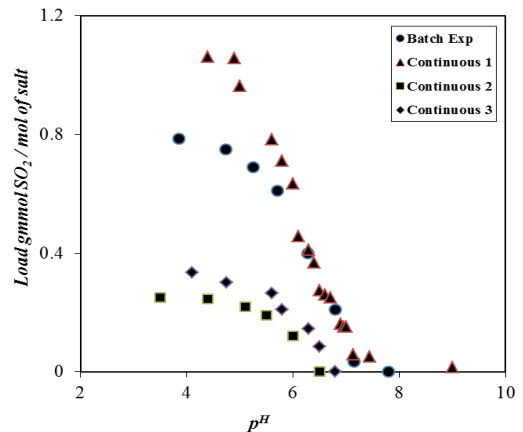


Fig 6. Rate of SO<sub>2</sub> absorption through Continuous and Batch Runs

#### 4 Rate of SO<sub>2</sub> absorption

Solvent 2 was selected as a specimen solvent to conduct continuous experiments and compare the same with batch experimental data. The three continuous experiments were done at different p<sup>H</sup>s, so as to understand the maximum loading rate [9, 10]. It was found, the loading was high to quite an extent on the continuous run-I at 8.7-8.9 p<sup>H</sup>, which reduced in the second run with 7.1-7.25 p<sup>H</sup> value and so on the loading reduced even more at a slight lesser 6.5-6.6 p<sup>H</sup> on Continuous run-III. A batch run was also conducted on Sol-II at 8.5 p<sup>H</sup>, as expected it was observed that the SO<sub>2</sub> loading in the amine sol-II was more in the Batch run than in the Continuous run-I. The same was represented graphically in figure 6. The temperature was maintained 27<sup>o</sup>C during the experiment.

#### 5 SO<sub>2</sub> regeneration

The SO<sub>2</sub> loading in Sol-II was done at a pH 8.5 for the SO<sub>2</sub> regeneration experiment; here the temperature was maintained at around 130 <sup>o</sup>C with a pressure between 1-2 atm. Figure 7 shows the rate of loading and the rate of regeneration with respect to time. The regeneration experiment was carried out till the rate of regeneration was reduced substantially [8,9,10].

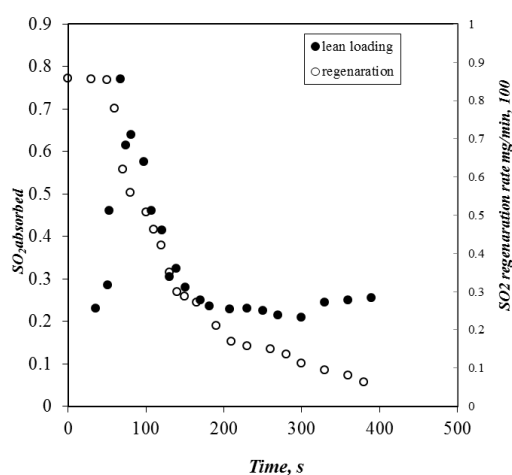


Fig7. Loading and Regeneration in Sol-II

#### V. CONCLUSIONS

The following conclusions can draw from the above study. A set of ten amine solvents were chosen and screening was done based on their rate of absorption and desorption of SO<sub>2</sub> gas. Three solvents namely solvent 1, 2, 3 were shown better performance than other solvents. It was observed that the rate of absorption was more in absence of CO<sub>2</sub> for solvents I and II, while it was notable that, Solvent-III showed no effect of CO<sub>2</sub>



presence. Continuous experiments along with batch experiments also conducted to verify the experimental set up can used for continuous mode or not.

#### ACKNOWLEDGEMENT

The Authors would like acknowledge Mr. D.K Sarkar (DGM), Mr. Kaushik Ghosh Mazumder (Deputy Manager) and Mr. Karthik B (Senior Engineer) from R&D Department of Engineers India Limited for providing the kind help valuable support, laboratory facility.

#### REFERENCE

- [1] Neumann, U., "The Wellman-Lord Process", in "Sulfur Dioxide and Nitrogen Oxides in Industrial Waste Gases: Emission, Legislation and Abatement", D. Van Velzen, Kluwer academic publishers, 1991.
- [2] Berichte V.D.I., "Emissionsminderung bei Feuerungsanlagen SO<sub>2</sub>-NOX-Staub", VDI-Verlag GmbH, Düsseldorf, 1983.
- [3] Weiss, L. H., Evaluating sulfur-producing FGD processes, Chem Systems Inc., N.Y., 1976, 125-133
- [4] Jensen F. A., Erga, P.E., "The Elsoorb Process: New Re-generable Process for SO<sub>2</sub> recovery", ICHIME Symposium Series No. 131, pg-197.
- [5] Stevens D. K. and Tonjes M. R., 54<sup>th</sup> Annual Laurance Reid Gas Conditioning Conference February 23, 2004.
- [6] Atanasova D. D, Velkova E. R, Ljutzkanov, L., Kolev, N., Kolev, D., Journal of Chemical Technology & Metallurgy, 48, 5, 2013 p 457-464.
- [7] Kamps, A.P., Xia J., and Maurer G., "Solubility of CO<sub>2</sub> in (H<sub>2</sub>O+Piperazine) and in (H<sub>2</sub>O+MDEA+Piperazine)", AIChE Journal, Vol. 48(10), 2003, pg-2662.
- [8] Hakka, L., "SO<sub>2</sub> recirculation as an economic alternative to double absorption", Sulphur 2000 Conference, San Francisco, California, USA, October 2000.
- [9] Zahiril M.R., Mehrara. H, Rouzbehani. B, "Investigation of parameters affecting a selective flue gas desulfurization with an amine base absorbent", Sci.Int.(Lahore), 25(2), 225-228, 2013.
- [10] Mehrara, H, Shishesaz M.R., Rouzbehani, B. "A Novel Selective Flue Gas SO<sub>2</sub> Removal with an Amine Absorbent", Int. J Sci. Emerging Tech Vol-6 No 1, July 2013.