REMOVAL OF SULFUR DIOXIDE FROM SULFURIC ACID PLANT EMISSIONS

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ABSTRACT

A bench scale system was built to study the absorption of sulfur dioxide by sodium hydroxide. The system included means for the generation of sulfur dioxide, incorporation of it in a stream of air to simulate polluted air at various concentrations and absorption packed beds. The absorption was carried out using a counter-current stream of NaOH solution of various concentrations. The method of Box-Wilson experimental design was employed for the determination of the optimum conditions which give the highest absorption efficiency. At high concentration of SO_2 in air, high absorption efficiency was attained for a constant NaOH concentration. The best absorbent was found to be 0.33 g mol.L^{-1}.

INTRODUCTION

The removal of sulfur dioxide from gas stream by adsorption on activated solids was investigated using several adsorbing solids, such as zeolite[1], silica gel[2], carbon[3] and ion exchange resin[4]. Only the carbon adsorption processes found practical commercial significance but have some difficulties such as the instability of carbon in the presence of the gas oxygen, the cost of recirculating the very high amounts of carbon required as well as the cost of the heat and the reducing agent[4].

The recovery may be performed by catalytic oxidation of SO_2 into SO_3 with the flue gas excess oxygen in the presence of vanadium pentoxide catalyst. The resulting SO_3 combines with water vapor in the flue gas to form sulfuric acid which is condensed by cooling and separated from the gas stream[5].

Sulfur dioxide may be absorbed from the gas stream in a spray or packed bed tower in counter current flow streams. The absorbent can be water, ammonia solution, lime slurry, limestone slurry, sodium hydroxide solution.

Thau[6] describes the improvement of water scrubbing process for the adsorption of SO_2 from coal burning. For high SO_2 levels, 45-58 tons of water were required for each ton of coal burned due to the limited amount of SO_2 adsorption to the saturation point and low absorption rate[2]. Also, Lehl[7] reported pollution problems of large quantity of acidic waste water withdrawn.

In the absorption with ammonia[8], two separate scrubbers built one have the other were used and ammoniacal solution added from the top of the column. The process requires careful control of pH levels to be installed in both scrubbing units to prevent heavy fogging conditions. The produced ammonium sulfate represented both economic and pollution problems to get rid of, even into fertilizer industry, because it was the least acceptable and low grade fertilizer[3]. In addition, the cost of ammonia used in scrubbing is high in comparison with other materials[2,3]. The disadvantage of the process were confirmed by Sander et al of Lurgi GmbH[9].

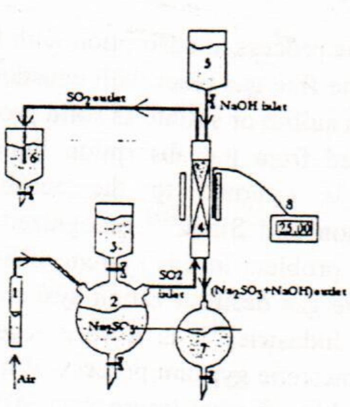
In the process of adsorption with lime, SO_2 and O_2 in the flue gas react with caustic lime to form calcium sulfite or sulfate as solid products that are separated from the absorption liquor. The clear liquid is returned to the scrubbing unit[10]. Johanston and Singh[11] recognized scaling as a serious problem in this system of SO_2 scrubbing. The flue gas desulfurization system of Kawasaki Heavy Industries[12] is a very recent simplified lime/limestone gypsum process. While the system was highly efficient (more than 90% absorption) and reliable, it is large in size and the equipment cost is slightly high[12].

EXPERIMENTAL WORK

Absorption System

Air was introduced into the absorber at a constant flow rate throughout the work (2 m^3h^{-1}). Sodium hydroxide solution of the desired concentration with a constant flow rate of 12.50 Lh^{-1} (3.125 L during the run time of 15 min) was allowed to flow counter-current to the air flow in the packed bed.

A glass column (0.1 m diameter and 0.5 m height) was packed with rashing rings. Sulfur dioxide was synthesized and introduced to the air stream in accordance with a recent procedure[13] by dropping sulfuric acid of the desired concentration onto a liter of aqueous sodium sulfite (0.28 Molar) contained in a 10-L three-neck glass flask. The air flowing through this container will carry SO_2 gas to the button of the packed absorber bed to be absorbed chemically by sodium hydroxide of the desired concentration flowing downward from 5-L glass vessel. The outlet liquid stream was collected from the bottom in a 20-L glass container (product vessel). The outlet gas stream (from the top of the packed bed) was introduced into iodine solution of known concentration to absorb any residual SO_2. In order to determine the amount of SO_2 absorbed in each experiment, another set of experiments was performed under the same conditions and excluding the absorbent, where SO_2 is directly absorbed by the iodine lime solution. The overall system including the SO_2 generation and absorption column is schematically shown in Fig. (1).



1- Rotameter.
2- SO2 generation flask.
3- H2SO4 container
4- Packed bed.
5-NaOH vessel.
6- Iodine solution vessel.
7- Product vessel.
8- Digital thermometer.

Fig. (1) Absorption system overall schematic diagram

Chemicals

Sodium sulfite was of industrial grade with 86.0% anhydrous Na_2SO_3 content. Sodium hydroxide was an analytical grade reagent supplied from BDH, England. Sulfuric acid (98%) was a product of Al-Furat State Co. for Chemical Industries. Other relevant chemicals and reagents were of analytical grade to be used for analysis and standardization.

Determination of Absorption Efficiency

The absorption efficiency (E%) is defined as the weight percentage of absorbed sulfur dioxide to that originally fed to the absorption column. The following sequence is used:

a. A fixed volume of 20 ml sample of iodine solution (used to absorb residual SO_2 in the leaving gas stream) is titrated with standard sodium thiosulfate solution (1.0 N), in the presence of starch as indicator. The equivalent volume of sodium thiosulfate solution (V_t) is recorded, and normality of iodine solution (NI) is:

$N_I = (V_t \times 1.0)/20$

b. The weight of iodine equivalent to the residual SO_2 in iodine (w_t) is: $w_t = w_{Io} - (N_I \times 253.8 \times V_t)/100$ where V_t is the volume of iodine solution equivalent to the residual SO_2 concentration and w_o is the initial weight of iodine in the solution.

c. The weight of the residual SO_2 (w_R is calculated according to the stiochiometry $w_R = (w_I \times 64.06)/253.8$ where 64.06 and 253.8 are the mol. wt. of SO_2 and I_2.

d. The weight of SO_2 fed to the absorber: Steps (a) to (c) were used again to estimate the weight of SO_2 fed to the system (w_s), but a V_t of sample of iodine solution taken from the identical experiment without absorbent existence. Thus,

$$E\% = [(w_s - w_R) \times 100)/w_s$$

RESULTS AND DISCUSSION

The effects of the inlet SO_2 level and absorbent (NaOH) concentration on the absorption efficiency of each run, calculated by the titration method are presented in Table (1). Graphical representation of absorption efficiency values versus SO_2 levels and absorbent concentrations are shown in Fig. (2 and 3) respectively.

Effect of Sulfur Dioxide Concentration

Fig. (2) shows that at high levels of SO_2 in air higher absorption efficiency was attained at constant NaOH concentration. This can be attributed to the greater driving force for removal and consequently higher absorption efficiencies are more easily attained, because the rate of absorption increases proportionally with the driving force, as explained by Charles et al[14].

Table (1) The absorption efficiency and residual SO_2 for several SO_2 and NaOH concentrations

Run No.	SO_2 inlet level, ppm	NaOH conc., molL^{-1}	Residual SO_2 conc., ppm	Absorption efficiency, %
1	8	0.10	0.752	90.60
2	20	0.10	1.400	93.00
3	32	0.10	2.11	93.40
4	8	0.17	0.60	92.50
5	20	0.17	1.15	94.25
6	32	0.17	1.69	94.70
7	8	0.25	0.5	93.75
8	20	0.25	0.94	95.30
9	32	0.25	1.41	95.60
10	8	0.33	0.44	94.50
11	20	0.33	0.78	96.10
12	32	0.33	1.12	96.51
13	8	0.40	0.43	94.60
14	20	0.40	0.76	96.20
15	32	0.40	1.08	96.61

Effect of Sodium Hydroxide Concentration

The effect of NaOH concentration on absorption efficiency is shown in Fig. (3). It is clear that as NaOH concentration increases, the efficiency increases regularly, but the rate of increase descends as the concentration reaches 0.33 mol L^{-1}. This is due to the reduction in the removal driving force between phases. Thus, operating the absorber with NaOH of concentration greater than 0.33 mol.L^{-1} would improve the efficiency only slightly. Such a concentration level compromises both cost and efficiency. Similar effect was noticed by Cornell and Dahlstrom[15].

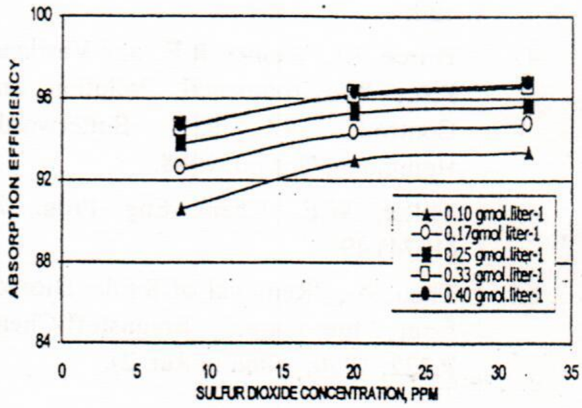


Fig. (2) The effect of SO_2 concentration on absorption efficiency at different NaOH concentrations

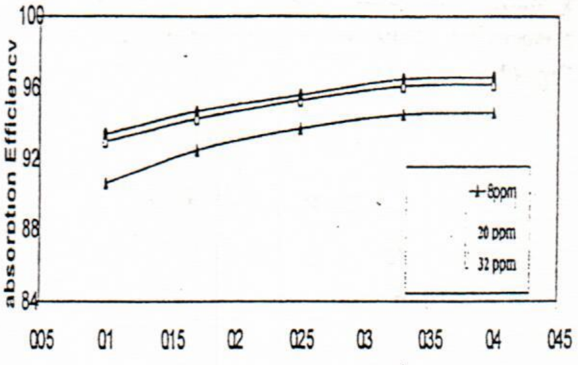


Fig. (3) The effect of NaOH concentration on absorption efficiency at different SO_2 concentrations

CONCLUSIONS

1. High levels of SO_2 in air higher absorption efficiency was attained at constant NaOH concentration.
2. The optimum concentration of NaOH which gives maximum absorption efficiency is 0.33 $mol.L^{-1}$.

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