

Flue Gas Desulphurization with Ammine Compound Approach: Introducing a New Iranian Selective Method for Eliminating SO₂

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ABSTRACT

Removing SO₂ from flue gas produced by chemical and petrochemical plants has always been a great concern in diverse countries and many studies due to its obvious harmful and perilous influence on health and environment. Flue gas desulphurization (FGD) is the widest applied technology for reducing SO₂ emissions in the industry. Consisting of many methods, wet flue gas desulphurization (WFGD) is the most widespread one. This study is going to introduce a novel ways of SO₂ elimination from flue gas which is investigated as a selective absorption with high performance in the research center of Abadan Institute of Technology. This experiment done to isolate this dangerous gas and send it out through the stack of cat-cracker unit, whose composition has more than 2000ppm SO₂.

INTRODUCTION

Flue gases from combustion processes normally contain less than 0.5 vol % sulfur dioxide. The relationship between the sulfur content of the fuel and the sulfur dioxide content of the resulting flue gas is shown in Table 1. This table gives the sulfur dioxide content of combustion gases from several typical fuels. On the other hand, stack gas from smelters handling sulfur ores can have very high sulfur dioxide concentrations. Therefore, the economics of recovering sulfur values from such gases can be much more favorable. Of course, the problems of discharging such gases without sulfur dioxide removal are also much more acute.

Most combustion gases contain a small, but significant amount of sulfur trioxide (or sulfuric acid as reaction with water) as well as sulfur dioxide. This component is of considerable importance because of its highly corrosive nature, its effect on the chemistry of many sulfur dioxide recovery processes, and its suspected critical role in air pollution problems. The amount of sulfur trioxide emitted to the atmosphere is a function of combustion air fuel ratio, fuel composition, combustion temperature,

time at combustion temperature, the presence or absence of a catalyst, electrostatic precipitator conditioning with ammonia, and the type of flue gas desulfurization system. The equilibrium concentrations of the principal sulfur species in the combustion gas from a typical fuel oil at several air fuel ratios have been calculated. The results show that in excess air mixtures at equilibrium, SO₂ is the most stable compound above 1000 K, SO₃ is the predominant sulfur compound between 900 and 600°K; while, on further cooling, H₂SO₄ gains dominance over SO₃ [1].

FLUE GAS DESULFURIZATION PROCESS

Emission of flue gas in air was considered as a high importance issue in the world until 1900s [3]. But In the past 20 years, Flue Gas Desulfurization (FGD) technology has made considerable progress in terms of efficiency and reliability since then lots of work has been done to specify the effect of these pollutant on human. To reduce these effects on environment and human governmental legislations were enacted [4,14,15]. One of the main pollutants emitted to the environment contribute in phenomena known as acid rain, is SO₂. SO₂ reacts with water present in rain, to form sulphuric acid (H₂SO₄). Eventually, this 'acid rain' returns to the earth and can cause corrosion structures, soil damages, and lakes resulting in damaged ecosystems. Even short term exposure to SO₂ can contribute to respiratory problems in most individuals, especially those with prior respiratory illnesses, such as asthma [8, 11].

So many technologies were designed to remove SO₂ from flue gas in chemical and petrochemical industry. Among them, wet flue gas desulfurization (WFGD) is the main technology have earned widespread use due to high SO₂ removal efficiency, reliability and low utility consumption [9,13]. These technologies represent a varying degree of commercial readiness. Some

can claim tens of thousands of hours of operational experience, while others

- Types, quantities, qualities, and availabilities of sorbents, water, steam, and power

Table 1 Federal New Source Performance Standards [1].

Source Category	Affected Facilities	Maximum Emissions
Fossil-Fueled Steam Generators	Coal- Boilers and Oil-Fired	Solid Fuel: 1.2 lb SO ₂ /106 Btu* Liquid Fuel: 0.8 g SO ₂ /10 ⁶ Btu
Sulfuric Acid plants	Process Equipment	2 kg SO ₂ /metric ton (mton) (4 lb SO ₂ /ton H ₂ SO ₄) and 0.075 kg acid mist/mton H ₂ SO ₄ (0.15 lb acid mist/ton H ₂ SO ₄)
Petroleum Refiners	Refinery Process Equipment including waste-heat boilers and fuel gas combustors	Fuel gas max H ₂ S: 230 mg/dry std m ³ (0.10 g/dry std ft ³)
Primary Copper Smelters	Roaster, Smelting Furnace Copper Converter	0.065% SO ₂ by VOL
Primary Zinc Smelters	Roaster, Sintering Machine	0.065% SO ₂ by VOL
Primary Lead Smelters	Sintering Machine, Dross Reverberam Furnace, Electric Smelting Furnace, and Converter	0.065% SO ₂ by VOL
Petroleum-Refinery Sulfur Recovery Plants	Claus Plant oxidation or reduction with incineration reduction without incineration	0.025% SO ₂ by vol dry at 0% excess air 0.030% by vol reduced sulfur compounds dry at 0% excess air and 0.0010% by vol H ₂ S dry at 0% excess air vol H ₂ S dry at 0% excess

have only recently been demonstrated at commercial plants [2]. Environmental regulations are the driving force behind the need for and selection of flue gas desulfurization (FGD) systems and dictate many design criteria. For example, they limit the amounts of the pollutants which can be discharged to the atmosphere and to any waterway. They also place limits on the concentration of toxic metals and other chemicals in landfilled byproduct, which can significantly affect the FGD process selection [1].

Factors considered in the selection of industrial sulfur dioxide removal systems vary with the type of system, but some important parameters are:

- Gas flow rate (size)
- Inlet and outlet
- Sulfur dioxide concentrations
- Installed cost

- types, quantities, characteristics, and disposal options for solid and liquid byproducts/wastes
- gas side pressure drop
- operating and maintenance labor
- space and sparing requirements
- ease and time of installation
- new versus retrofit
- materials of construction
-

The SO₂ gas produced by many renewable processes can be converted in an auxiliary plant into any of several byproducts, including liquid SO₂, H₂SO₄, and elemental sulfur. The marketability of these products depends on local demand and economic factors.

Amine so₂ absorption processes attracted attentions because of being regenerable and so₂

gathering possibility [12]. SO₂ recovered by this method can be used in refinery sulfuric acid units as a raw material, a reactant in chemical reactions, a refrigerant or a reagent and/or solvent in laboratory tests.

Various processes have been proposed for removing sulfur dioxide from gas streams; however, few of them have attained commercial status. Only the limestone/lime wet FGD systems, predominantly with spray, tray, or packed tower absorbers; and the lime spray dryer systems are widely accepted today. Users have opted for low cost, proven systems that operate with high availability [10]. Selective SO₂ Regenerative process with a cheap initial cost for solvent with no need to separate absorbed SO₂ byproducts lower charge and high absorption rate, increase the performance more than that of lime/limestone, citrate, double alkali or other processes. Amine absorbent used here covers all the characteristics mentioned which specify it from other solvents. To organize many FGD processes that have been developed a new classification is shown in figure 1. We divided FGD processes to recoverable and non-recoverable commonly used by many; however, in a new categorization processes are presented by details.

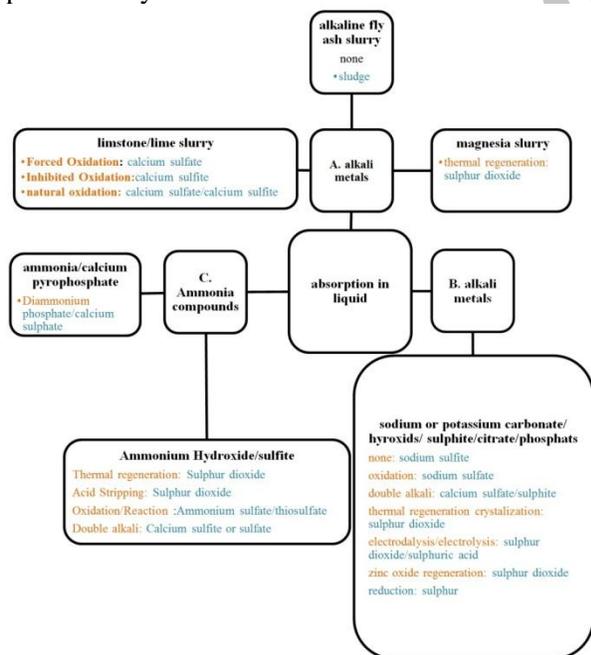


Figure 1 desulfurization categorization

A large number of gas-liquid and gas-solid sulfur dioxide treatment processes have been developed, such as limestone, or lime-based scrubbing, magnesium hydroxide, sodium hydroxide and sodium citrate buffer solution or different solvents for absorption.

Regenerative processes are interesting because they increase the efficiency of raw materials. Thus, some organic solvents are also used as sorbents. The interaction between gas and liquid is related to the absorption efficiency and the ability to recover sulfur dioxide. N,N-dimethylaniline is an aromatic amine used in some applications as sorbent for sulfur dioxide removal because of its affinity.

in this case this interaction between SO₂ and solvent should not strong or weak. This cause an easy absorption and desorption of SO₂. However, the use of scrubbers and other systems in which direct contact between sulfur dioxide and N,N-dimethylaniline occurs leads to several environmental drawbacks. Solvent evaporation and drops dragging take place in the gas stream, leading to solvent losses and its release to the environment [5]. Bassu and Dutta(1987) studied the absorption equilibria and kinetics with regard to the effects of gas concentration, temperature and other variables. They concluded that it is an instantaneous pseudo- first-order reversible reaction when the concentration of N,N-dimethylaniline is high [6].

P Luis et al. (2008) employed N,N-dimethylaniline which is an aromatic amine solvent used in some industrial applications for its sulfur dioxide affinity, leading to a regenerative process. This interaction is neither too strong nor too weak, thus absorption and desorption can occur allowing a regenerative process [5]. As a result, sulfur dioxide can be recovered and converted into a product of high purity by further concentration steps. They showed that about 40%-50% SO₂ absorbed can be recovered.

PROCESS DESCRIPTION

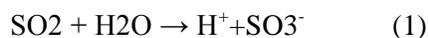
The process is a relatively new FGD process that produces SO₂. It utilizes a proprietary. Thermally regenerable ionic amine-based solution, the discovered absorber, which is non-volatile, stable oxidatively and thermally, and designed to meet applicable health and safety standards. A pilot

plant at Research Center of Petroleum University of Technology has been prepared [7].

The process consists of a gas cooling and pre-scrubbing section, a sulfur dioxide scrubbing section, and a regeneration and solvent purification section. The flue gas cooling and pre-scrubbing equipment, usually are downstream of the particulate removal equipment. Reduces the flue gas temperature, removes most of the strong acids and particulate matter, and saturates the gas with water. The SO₂ is then absorbed from the gas in a countercurrent multistage scrubber. The scrubber utilizes air atomizing nozzles to take advantage of the absorbent's high reactivity and SO₂ capacity to achieve up to approximately 100% SO₂ removal. The absorber has interstage solvent collectors and a mist eliminator downstream of the absorption section. The regenerator, which packed, is equipped with a steam heated reboiler to regenerate the amine and a vacuum pump to ensure that regeneration occurs at low enough temperatures to suppress the disproportionation of regenerable SO₂ into non-regenerable SO₃. The SO₂ from the regenerator is then dried and may be further processed into sulfuric acid or sulfur.

The processes compared were the co-current wet limestone, jet bubbler, countercurrent wet limestone, dry lime, and Wellman-Lord processes. The study showed that the economics for this process can be very favorable when compared with limestone processes in high sulfur applications [7].

The aqueous amine solvent used in this process is very stable and highly selective for SO₂. In water solution, dissolved SO₂ undergoes reversible hydration and deionization to produce bisulphite and sulphite according to the following equations:



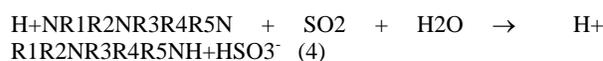
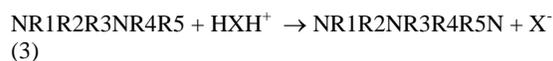
Adding a buffer, such as an amine, to the water increases the quantity of SO₂ dissolved. The buffer drives the above equilibria to the right by reacting with the hydrogen ions to form ammonium salts.



Reaction 2, the overall reaction, indicates that as the concentration of SO₂ in the feed gas increases, the equilibrium moves to the right, i.e. the quantity of SO₂ dissolved in the rich solvent increases. Thus, the scrubbing of more concentrated gas streams requires a less than proportional increase in solvent circulation rate. Since the gas volume, and therefore the gas side equipment, remains constant, a relatively small total cost increase is caused by an increase in feed SO₂ concentration.

Steam stripping of the SO₂ loaded solvent in a counter-current multi-stage column will force the equilibrium of reaction (1) to the left and consequently, reactions (1) - (2) are reversed, regenerating the absorbent.

The process is based on a unique class of amine absorbents that optimally balance the ability to absorb and regenerate sulphur dioxide. One absorbent molecule has two amine functionalities. One of the amine functionalities is strongly basic and non-heat-regenerable. Once it has reacted with SO₂ or a stronger acid, it remains in salt form in the scrubbing process. The resulting mono protonated amine in reaction (3) is the lean amine system that scrubs the SO₂. The second amine functionality is less basic than the first and is referred to as the "sorbing nitrogen"; it operates in the buffering range that gives the optimal balance for absorption and regeneration of SO₂ in reaction (4). This amine functionality is the essence of the CANSOLV® system technology.



Expressed in other terms, the absorbent used in the process is a diamine, one amine function always being in salt form. This prevents volatilization and therefore loss of solvent to the cleaned gas, as well as avoiding contamination of the byproduct SO₂ with the solvent. Through an optimum balance of SO₂ absorption and desorption tendencies, the process is able to achieve high purity in the treated gas while using a minimum of regeneration energy.

Process is very robust and easy to operate. Sulphur dioxide removal to <100 ppmv can easily be obtained in most applications and treated gas

purities of <10 ppm are usually attainable, at a slight increase in capital expense and regeneration steam use. The amine absorbents provide the following significant advantages:

- Selectivity of SO₂ over CO₂
- High thermal and chemical stability, even in the presence of oxygen in the treated gas
- High water solubility, giving a homogeneous liquid absorbent of relatively low toxicity (no mortality at 20.0 g/kg, rats)
- Low foaming tendency (due to lack of conditions responsible for foaming)
- The versatility and regenerability of the process enables its application to scrubbing almost any gas stream containing SO₂

It should be noted that FGD systems are not the only method of controlling flue gas SO₂ emissions. Other potential methods are fuel cleaning, switching, and blending; unit retirement; purchase of SO₂ emission allowances (in the U.S.); and the use of other technologies such as atmospheric fluidized bed combustion, pressurized fluidized bed combustion, gasification with fuel gas clean-up, etc.

EXPERIMENTAL

Selective SO₂ absorption is done to isolate this dangerous gas and send it out through the stack of cat-cracker unit in the research center of Abadan Institute of Technology. The tests were done in an experimental plant in the laboratory of the research center. The plant is specially designed for the experiments and uses an industrial amine absorber with an innovative formulation. In the plant, the absorption tower, with a diameter of 15cm and a height of 150cm was designed and the experiments were done using an absorber solution rate ranging from 50 to 400 ml/min.

While running the plant, the gas flow from three capsules of SO₂, CO₂ and N₂ enter the absorption column. In addition, produced steam from the

boiler enters the tower in order to help improved distribution of the absorber.

The tests were done in 100, 200, 300, 400 ml/min levels. Examining the optimum point of absorption, the desorption temperature and pH were taken as variables; the first of which was analyzed in five levels of 105, 110, 115, 120, and 127°C, and the latter was observed in levels of 3, 4, and 6. Analysis of the output gas from the stack of cat-cracker unit after passing through the designed plant illustrates that the gas contains %65 Nitrogen, %19 water steam, and %12 Carbon dioxide. The concentration of the consumed absorber was 0.78 gr/lit; noting its low concentration in proportion to the input SO₂ of the absorption tower, the efficiency is to the nearest 100 percent that is quite unique and desirable and more than what is expected from the cat-cracker unit. Consequently, the amount of SO₂ inlet to the absorption column was tested in three levels of 4800, 6800, and 8800 ppm. The results of the experiment demonstrate that the absorber -even with a low concentration- has strong absorption ability so that it can reduce the amount of 8800 ppm of SO₂ feed to 10 ppm in the outlet.

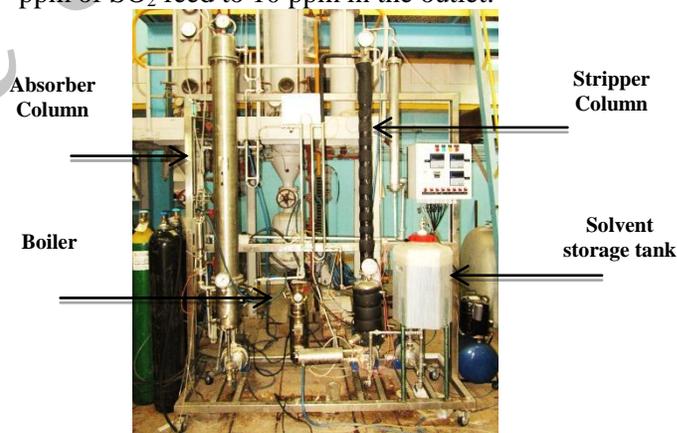


Figure 2 desulfurization plant which is designed at research center of Petroleum University of Technology

The data were then optimized using “Taguchi” statistical method. It was concluded that the absorber has the ability of full (%100) absorption in a condition with a pH of 4, absorption temperature of 120° C, absorber flow rate of 400 ml/min, and SO₂ concentration of 6800 in the inlet. Analysis of the output gas flow demonstrates an average absorption of %99.95 for the absorber solution with a concentration of 0.78

gr/lit. The history of the process shows that it is the first time that selective SO₂ absorption is done

3	2	1	test #
4	4	4	PH
6600	6500	6300	SO ₂
400	400	400	solvent flowrate
120	120	120	desorbition bottom T
9	9	9	gas flowrate lit/min)
62	63	63	Absorption tower T (° C)
0.03	0.03	0.03	Absorption tower P (bar)
114	112	113	desorbition Top T
1	1	1	Desorption Tower top P (bar)
1.1	1.1	1.1	Desorption Tower bottom P (bar)
0.78	0.78	0.78	solvent concentration (gr/lit)
6.1	5.8	5	% CO ₂ inlet
10.9	10.7	12.1	% O ₂ inlet
6.1	5.8	5	%CO ₂ outlet
10.9	10.7	12.1	%O ₂ outlet
1	1	0	SO ₂ outlet (ppm)
≈20	≈20	≈20	%H ₂ O inlet

Figure 3 Gained Values by experiments in 3 test.
Quantity of SO₂ at the outlet is shown

in pilot scale in Iran with such a unique efficiency. Formerly, the license of this process belonged to the Canadian 'Cansolve' Company that had reached the same efficiency for absorption. Hence, the industrial execution of this process in the country may create lots of new challenges.

CONCLUSION

Al in al, in order to highly pure selectivity in this FGD method which some important parameters are bolded in it like: comfortably and completely regeneration of solvent, low initial cost of the process makes it so hi-tech and reliable. High performance and low initial cost for running this technology into an industrial unit and moreover long period of absorber responsibility could make this process to be strong component for the Cansolve license. Due to necessities of the elimination of SO₂ emission from industrial plants and also highly range of releasing caused

by these pollutant units and also its irrecoverable consequences, importance of this kind of studies in a large scale and in an industrial aspect leads our oil and gas technologies to a better quality basis.

- 1- Kohl and Richard Nielsen. (1997). gas purification. 5th edition, Gulf Publishing Company Book Division P.O. BOX2.
- 2- Xiaoxun Ma, Takao Kaneko, Tsutomu Tashimo, Tadashi Yoshida, Kunio Kato. (2000). Use of limestone for SO₂ removal from flue gas in the semidry FGD process with a powder-particle spouted bed, Journal of chemical Engineering Science 55, 4643- 4652.
- 3- J.C. Mycock, J.D. McKenna, L. Theodore. (1995). the air pollution problem, Handbook of Air Pollution Control Engineering and Technology, CRC Press, Inc, USA, pp. 1-4.
- 4- Environmental impacts of coal power: air pollution. http://www.ucsusa.org/clean_energy/coalvswind/c02c.html (accessed June 22, 2009).
- 5- P Luis, A Garea and A. Irabien. (2008). Sulfur dioxide non-dispersive absorption in N,N-dimethylaniline using a ceramic membrane contacto. Journal of Chemical Technology & Biotechnology 83, 1570-1577
- 6- Basu RK and Dutta BK. (1987). Kinetics of absorption of sulfur-dioxide in dimethylaniline solution. Can Journal of Chemical Engineering 65,27 - 35.
- 7- Hakka, L. E., Birnbaum, R. W., and Singleton, M., (1991). "Pilot Testing of the CANSOLV System FGD Process," paper presented at the EPRYEP/DOE 1991 SO₂ Control Symposium, Washington, D.C Dec. 3-6
- 8- Yan Liu, Teresa M. Bisson, Hongqun Yang, Zhenghe Xu. (2010). Review Recent developments in novel sorbents for flue gas clean up, Journal of Fuel Processing Technology 91,1175-1197
- 9- Xiang Gao, Honglei Ding a, Zhen Dua, Zuliang Wub, Mengxiang Fanga, Zhongyang Luo, Kefa Cen. (2010) . Gas-liquid absorption reaction between (NH₄)₂SO₃ solution and SO₂ for ammonia-based wet flue gas desulfurization, J Applied Energy 87, 2647-2651
- 10- Schwieger, R., and Haynes, A. (1985). Reliability Concerns, Regulations Lead to Virtual Standardization of Air-Pollution-Control Systems.journal of Power, pp. 8 1-93.
- 11- H. Chu, T.W. Chien, S.Y. Li, Simultaneous absorption of SO₂ and NO from flue gas with KMnO₄/NaOH solutions, J The Science of the Total Environment 275 (2001) 127-135

12- L. Marocco, F. Inzoli. (2009). Multiphase Euler-Lagrange CFD simulation applied to wet flue gas desulphurization technology, *Int. J. Multiphase Flow* 35, 185–194.

13- Hongliang Gao, Caiting Li, Guangming Zeng, Wei Zhang, Lin Shi, Shanhong Li, Yanan Zeng, Xiaopeng Fan, Qingbo Wen, Xin Shu. (2011). Flue gas desulphurization based on limestone-gypsum with a novel wet-type PCF device, *Journal of Separation and Purification Technology* 76 ,253–260

14- Gutierrez Ortiz FJ, Vidal F, Ollero P, Salvador L, Cortes V, Gimenez , (2006), A. Pilot-plant technical assessment of wet flue gas desulfurization using limestone. *Publication of Industrial and Engineering Chemistry Research*, 45:1466–77.

15- Zhang J, Wang Y, Wu D. (2003). Effect investigation of ZnO additive on Mn–Fe/c-Al₂O₃ sorbents for hot gas desulfurization. *Energy Convers Manage*, 44:357–67.

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