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## THE INFLUENCE OF TEMPERATURE ON SO<sub>2</sub> RETENTION FROM RESIDUAL GASES BY ABSORPTION INTO DILUTE BASIC SOLUTIONS

Annette Madelene Dancila, Cristina Modrojan, Cristian Onose, Oanamari Orbulet, Cristina Orbeci

Politehnica University of Bucharest, Faculty of Applied Chemistry and Material Science, 1-7 Gheorghe Polizu, Bucharest, [dancila.madelene@yahoo.com](mailto:dancila.madelene@yahoo.com), Romania

### Abstract

The work is part of current concerns regarding the reduction of SO<sub>2</sub> emissions in the atmosphere. The study aimed the SO<sub>2</sub> retaining by absorption in dilute NaOH solutions at different temperatures in the range of 20-60°C.

The analysed parameters were: the pressure variation of SO<sub>2</sub> in the gaseous phase depending on the SO<sub>2</sub> volume injected, the degree of loading of the solution, the pressure variation according to the degree of loading, the amount of SO<sub>2</sub> absorbed depending on the volume of SO<sub>2</sub> injected and the absorption efficiency of the solution depending on the volume of SO<sub>2</sub> injected.

**Keywords:** *absorption, diluted solutions of NaOH, SO<sub>2</sub>*

### Introduction

In latest years, particular attention has been paid to the removal of SO<sub>2</sub> from various industrial sources (Zhu et al 2005, Gómez et al 2007, Jannelli & Minutillo 2007).

Numerous industrial gases have a high content of sulphur, as for example, the gas from coke ovens and thermal power plants, especially those that use fuels with high sulphur content. Certain plants, such as chemical plants producing sulphuric acid, emit gases containing sulphur dioxide, which is considered one of the most dangerous air pollutants. Recourse to the use of natural fuels with low sulphur is limited to availability and high price. There have been developed technologies for flue gas desulfurization system for fuels with high sulphur content (Yan et al 2014). Current studies emphasize the high cost of these operations; besides this, it was not proved on a satisfying manner the possibility of sulphur extension in a desired proportion by the methods of hydrodesulphurisation of coal, oil or residual oil with a high content of residual sulphur (Dupart et al 1993, Spörl et al 2013, Cheng et al 2017, Ladwig & Blythe 2017).

Other methods of solving the pollution problem with sulfur oxides refers to their removal from the exhaust gases and establishing the concentrations limits for harmful gases which may be disposed of into the atmosphere (Kilicarslana & Qatu 2017, Wei et al 2011).

Normally the concentration of sulfur dioxide emission gas from existing sulphuric acid plants is 2,000-3,000 ppm and sometimes reach up to 5,000 ppm. The value of 2,000 ppm is equivalent to the cca. 12.5 kg to 1 tone of H<sub>2</sub>SO<sub>4</sub> produced, and the maximum limit is 2.7 kg/t of H<sub>2</sub>SO<sub>4</sub> produced.

Emissions of sulphur dioxide have decreased by 66% between 1990 and 2005. In 2005, the most significant source of SO<sub>2</sub> emissions was the energy industries sector

(41%), followed by emissions occurring from industrial processes (35%) and industrial energy use (13%) ([www.eea.europa.eu](http://www.eea.europa.eu)).

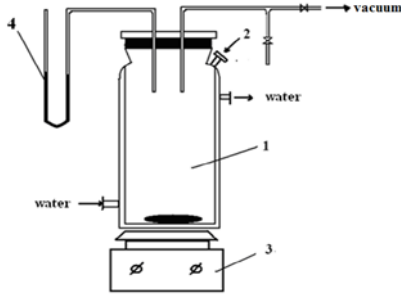
According to the European Directive, CAFE 2008/50/EC, the emission limit values for SO<sub>2</sub> in the atmosphere are comprised between 20 µg/m<sup>3</sup> air per year, 125 µg/m<sup>3</sup> air/24 hours and 350 µg/m<sup>3</sup> air/1 hour. ([www.europarl.europa.eu](http://www.europarl.europa.eu)). Absorption of SO<sub>2</sub> is performed in order to obtain a gas sulphate of high concentration (SO<sub>2</sub>) to enrich the poor gas, which cannot be used directly to obtain sulfuric acid and purification of flue gases with a low content of SO<sub>2</sub>. As an absorbent are used: water, solutions of inorganic and organic compounds or their solutions.

The process of SO<sub>2</sub> retention in various liquid fumes is mostly a physical absorption process, accompanied by a chemical reaction, so it is a process of chemisorption. The most widely used methods are: chemisorption-based processes on metallic oxides (MgO, CuO, MnO<sub>2</sub> and especially CaO) (Przepiórski et al 2012, Gaudin et al 2016, Osaka et al 2015, Czyzewski et al 2013); absorbents in suspensions-based processes (e.g. LIME process that uses a suspension consisting of CaO or process water and LIMESTONE, a suspension of CaCO<sub>3</sub> and process water or LIME-LIMESTONE a suspension of CaCO<sub>3</sub>·CaO, and water) (Srivastava 2000, Kohl & Riesenfeld 1985, Dagaonkar et al 2001a, 2001b) sodium citrate (Bekassy-Molnar et al 2005). Other methods used so far are absorbents in ammoniacal solution, process solutions, Wellman-Lord (which uses NaOH as absorbent and Na<sub>2</sub>CO<sub>3</sub>); a disadvantage of this procedure is that in time we obtain Na<sub>2</sub>SO<sub>4</sub> that is inactive against SO<sub>2</sub>. A modified version of this procedure (the ionic process Stone Webster) partially removes these disadvantages by introducing a secondary processing of the solution of Na<sub>2</sub>SO<sub>4</sub> through electrolysis, when recovering NaOH and get H<sub>2</sub>SO<sub>4</sub> (Irabein et al 1992, Wang et al 2011).

### **Materials and Methods**

The study aimed to determine the quantity of SO<sub>2</sub> absorbed depending on the volume of SO<sub>2</sub> and apprehension SO<sub>2</sub> injected into the NaOH solutions of different concentrations, temperatures and degrees of loading. Solutions of NaOH concentrations used in this study were 2, 5 and 10 %, and temperatures of 20, 40 and 60 °C. The plant used to perform the study is shown in Figure 1 and consists of a 1-thermostat absorption vessel in which it was introduced a volume of NaOH solution of different concentrations, 2-airtight device for injecting volumes of SO<sub>2</sub> to the upper side, 3-magnetic stirrer and 4-differential manometer with mercury.

The thermostat vessel is mounted on a magnetic stirrer and has an airtight device for injecting volumes of SO<sub>2</sub> to the upper side. The pressure difference is read on differential manometer with mercury.

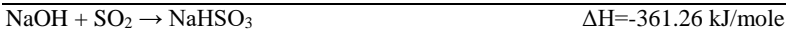


**Figure 1.** Work installation (1-thermostat absorption vessel; 2-airtight device for injecting volumes of SO<sub>2</sub>; 3-magnetic stirrer; 4-differential manometer). Reaction mechanism of absorption of SO<sub>2</sub> in NaOH solutions.

*Version A*



*Version B*



*Version C*



In order to determine which mechanism is more useful for SO<sub>2</sub> retention by absorption, the study tracked several parameters: pressure variation according to the volume of SO<sub>2</sub> injected, the loading degree of the solution, pressure variation according to the loading degree, the amount of SO<sub>2</sub> absorbed depending on the volume of SO<sub>2</sub> injected and the absorption efficiency depending on the volume of SO<sub>2</sub> injected.

Calculation of the load of the solution with SO<sub>2</sub> were made on the basis of formulas:

$$\beta = \frac{\text{moles } \text{SO}_2}{\text{moles } \text{NaOH}} \quad (1)$$

where:

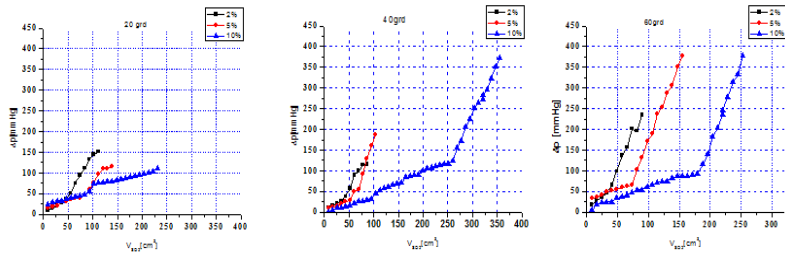
$$\text{moles } \text{SO}_2 = \frac{V_{\text{SO}_2 \text{ corrected}}}{22400} \quad (2)$$

V<sub>SO<sub>2</sub> corrected</sub> = the volume of SO<sub>2</sub> injected, brought under normal circumstances

$$\text{moles } \text{NaOH} = \frac{V_{\text{NaOH}} \cdot \rho_{\text{NaOH}} \cdot C_{\text{NaOH}}}{100} \cdot \frac{1}{M_{\text{NaOH}}} \quad (3)$$

## Results and Discussion

### Pressure variation depending on the volume of SO<sub>2</sub> injection



**Figure 2.** SO<sub>2</sub> absorption in various solutions of NaOH at 20, 40 and 60 °C.

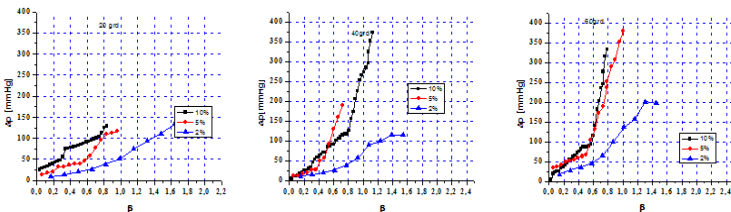
Comparative analysis of curves, coordinate  $\Delta P = f(V_{SO_2})$  where  $\Delta P$  is the partially pressure variation of the SO<sub>2</sub> in the gas phase, lead to the conclusion that as increases SO<sub>2</sub> injected amount, increases the SO<sub>2</sub> pressure in the gaseous phase, which highlights the fact that SO<sub>2</sub> absorption in solutions of NaOH is not total. Increasing the temperature of the NaOH solution favours retaining of a larger SO<sub>2</sub> volume.

NaOH solution 10% concentrated can retain more SO<sub>2</sub>, which is observed by lower SO<sub>2</sub> pressure values in the gaseous phase than at 2% and 5% NaOH solutions.

The low temperature of 20 °C favours the dissolution (physical absorption) of SO<sub>2</sub> in solutions, regardless of the concentrations. At 40 °C temperature, NaOH solutions of 2% and 5% the physical absorption is shorter, SO<sub>2</sub> being retained by chemical absorption, the reaction mechanism to this temperature resulting from version A to obtain NaHSO<sub>3</sub>.

The temperature of 60 °C leads to SO<sub>2</sub> retention in the case of 2% solutions only by chemical reaction, and in the case of 5 and 10% solutions the SO<sub>2</sub> absorption takes place first in the form of physical absorption and then as chemical absorption made after the reaction Version B.

### Pressure variation depending on the degree of loading solutions of NaOH



**Figure 3.** The loading degree of NaOH solutions at 20, 40 and 60 °C temperature.

Figure 3 illustrates the loading degree of NaOH solutions according to temperature. At 20 °C temperature, loading of solutions is low compared to solutions that retain SO<sub>2</sub> at temperatures of 40 or 60 °C. The 2% solution saturates much faster regardless of the temperature of the solutions. Solutions of 5% and 10%, respectively, can retain higher volumes of SO<sub>2</sub>.

Initially, SO<sub>2</sub> retention occurs by physically absorption at temperature of 40 °C up to a β = 0.3 load. For the solution at 60 °C temperature the physical absorption of SO<sub>2</sub> takes place up to a load of β = 0.5, then the retention is done by chemical reaction with obtaining of sodium sulphite acid. The fact that all graphs have ascending curves leads to the conclusion that the process is not complete, the solutions are not saturated.

In case of retention at 40 and 60 degrees, the absorption process is a two-stage process: first, a slow increase in pressure, which can be interpreted by a physical SO<sub>2</sub> absorption process in the solution and the second stage, evidenced by accentuated pressure increase caused by beginning chemical absorption characterized by a lower speed than dissolution rate.

*The variance quantity of SO<sub>2</sub> absorbed depending on the volume of SO<sub>2</sub> injection*

The amount of SO<sub>2</sub> absorbed was calculated according to the relations:

$$m_{SO_2} = \frac{V_{SO_2 \text{ absorbed}}}{22400} \cdot 64 \quad (4)$$

Where:

$V_{SO_2 \text{ absorbed}}$  = the volume of SO<sub>2</sub> absorbed into solution of NaOH

$$V_{SO_2 \text{ absorbed}} = V_{gas} - V_{precinct} \quad (5)$$

$V_{gas}$  = the volume of the mixture of air and SO<sub>2</sub> which lies above the liquid phase

$V_{precinct}$  = the volume of the vessel after the injection of SO<sub>2</sub> and absorption in solution

$$V_{gas} = (273 + t) \cdot \frac{(V_{precinct} + V_{SO_2 \text{ corrected}}) \cdot 756}{293 \cdot (756 + \Delta P)} \quad (6)$$

$$V_{precinct} = V_{vessel} + \frac{0.1256 \cdot \Delta P}{V_{SO_2 \text{ inj}}} - V_{NaOH} \quad (7)$$

where:

$V_{SO_2 \text{ inj}}$  = the constant volume of SO<sub>2</sub> injection

$V_{NaOH}$  = the volume of NaOH solution introduced in the absorption vessel

$V_{vessel}$  = the volume absorption vessel was determined experimentally and it is 147.35 cm<sup>3</sup>

The graphs are in the form  $m_{SO_2 \text{ absorbit}} = f(V_{SO_2 \text{ corrected}})$

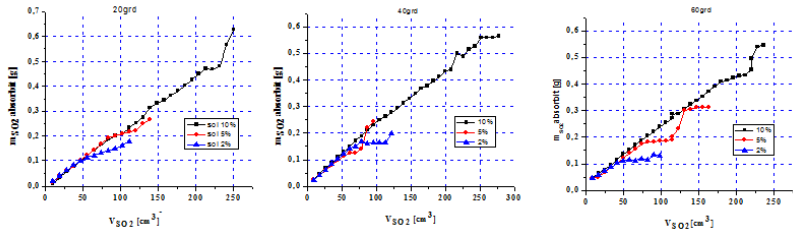


Figure 4. The variance of SO<sub>2</sub> quantity absorbed at 20, 40 and 60 °C.

At constant temperature solutions with a higher NaOH concentration retain a higher quantity of SO<sub>2</sub> as shown in Figure 4.

Thus, in the case of 10% NaOH solution at 40 °C temperature, the amount of SO<sub>2</sub> absorbed increases up to a volume of about 250 cm<sup>3</sup> of SO<sub>2</sub> injected, instead at 60 °C temperature, the amount of SO<sub>2</sub> absorbed is slightly lower for the same volume of SO<sub>2</sub> injected, then it reaches a level characteristic to the saturated solution.

In case of reaction at 40 °C temperature the process is a two stages process, both through dissolution and chemical reaction; while at 60 °C temperature the process flows only through chemical reaction, the amount of SO<sub>2</sub> physically restrained being much smaller due to the decrease of SO<sub>2</sub> solubility into solution.

In the case of NaOH 5 % solution the rise of temperature leads to an increase of the SO<sub>2</sub> amount absorbed into solution. The explanation of what we have observed is that gas is first physically restrained and then is retained by the chemical reaction; the last process occurs with a lower speed and a greater time for reaction is needed.

*Effectiveness of SO<sub>2</sub> retentions in NaOH solutions of different concentrations at different temperatures*

Conversion level of SO<sub>2</sub> retention in solutions of NaOH is calculated on the basis of formulas:

$$\eta_{SO_2\ abs} = \frac{V_{SO_2\ abs}}{V_{gas}} \cdot 100 \quad (8)$$

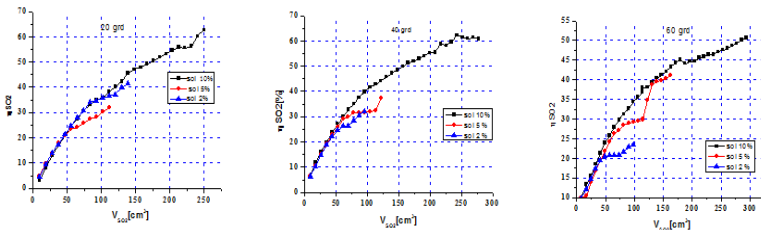


Figure 5. Effectiveness of SO<sub>2</sub> restraint in the NaOH solution at 20, 40 and 60 °C.

From the three graphs it is noted that the absorption process is identical up to a point, up to a certain volume of SO<sub>2</sub> injected, about 40-50 cm<sup>3</sup>, regardless of the reaction environment temperature, meaning the reaction goes first by physically absorption followed by chemical reaction of SO<sub>2</sub> retention into solutions, process that occurs with a different speed. The shape of curves plotted at constant temperature is similar to various concentrations of the solution.

It is noticed that the concentration increasement of the absorptive environment conduct to increases the SO<sub>2</sub> volume that is retained. For temperatures of 40 and 60 degrees there is a „ jump” of the restraint effectiveness, according to the beginning of the chemical absorption.

### Conclusions

Absorption is much better at high temperatures; in this case the sulphite conversion level is much higher.

At 20 °C temperature, SO<sub>2</sub> is physically absorbed, and SO<sub>2</sub> may be desorbed when removing the absorbent solution.

Temperatures of 40 and 60 °C lead to the chemical absorption of SO<sub>2</sub> with formation of sodium sulphite as for Version A if the solutions have concentrations of 5%. The chemical absorption reaction can follow Version B if the solutions are of 10% concentration, requiring a higher amount of NaOH to fix also the physically absorbed SO<sub>2</sub>.

The chemical absorption Version C with formation of Na<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>SO<sub>3</sub> can only occur in the case of solutions with 10% concentration at 40 °C temperature, the reactions being exothermic.

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### References

- Bekassy-Molnar, E, Marki, E & Majeed, JG 2005, ‘Sulphur dioxide absorption in air-lift-tube absorbers by sodium citrate buffer solution.’ *Chemical Engineering and Processing*, vol. 44, pp. 1039–1046.
- Cheng, CM, Amaya, M, Lin, S, Su, Q, Wu, MC, Butalia, T & Wolfe, W 2017, ‘Leaching characterization of dry flue gas desulfurization materials produced from different flue gas sources in China’, *Fuel*, vol. 204, pp. 195–205.
- Czyzewski, A, Kapica J, Moszynski D, Pietrzak R & Przepiórski J 2013, ‘On competitive uptake of SO<sub>2</sub> and CO<sub>2</sub> from air by porous carbon containing CaO and MgO’, *Chemical Engineering Journal*, vol. 226, pp. 348–356.
- Dagaonkar, MV, Beenackers, AACM & Pangarkar VG 2001a, ‘Absorption of sulfur dioxide into aqueous reactive slurries of calcium and magnesium hydroxide in a stirred cell’, *Chemical Engineering Science*, vol. 56, no. 3, pp. 1095–1101.
- Dagaonkar, MV, Beenackers, AACM & Pangarkar VG 2001b, ‘Enhancement of gas–liquid mass transfer by small reactive particles at realistically high mass transfer coefficients: absorption of sulfur dioxide into aqueous slurries of Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> particles’, *Chemical Engineering Journal*, vol. 81, no. 1–3, pp. 203–212.

- Dupart, MS, Bacon, TR & Edwards, DJ 1993, 'Understanding corrosion in alkanolamine gas treating plants', Part 1 & 2, *Hydrocarbon Processing*, pp. 75-80.
- Gaudin, P, Michelin, L, Josien, L, Nouali, H, Dorge, S, Brillhac, JF, Fiani, E, Vierling, M, Molière, M & Patarin, J 2016, 'Highly dispersed copper species supported on SBA-15 mesoporous materials for SO<sub>x</sub> removal: Influence of the CuO loading and of the support', *Fuel Processing Technology*, vol. 148, pp. 1–11.
- Gómez, A, Fueyo, N & Tomás, A 2007, 'Detailed modelling of a flue-gas desulfurization plant', *Computers & Chemical Engineering*, vol. 31, pp. 1419–1431.
- [http://www.europarl.europa.eu/RegData/etudes/STUD/2016/578986/IPOL\\_STU\(2016\)578986\\_EN.pdf](http://www.europarl.europa.eu/RegData/etudes/STUD/2016/578986/IPOL_STU(2016)578986_EN.pdf). [27 July 2018].
- <https://www.eea.europa.eu/data-and-maps/indicators/emission-trends-of-sulphur-dioxide-so2/emission-trends-of-sulfur-dioxide-so2>. [27 July 2018].
- Irabein, A, Cortabitarte, F & Ortiz, I 1992, 'Kinetics of flue gas desulfurization at low temperatures: Nonideal surface Adsorption Model', *Chemical Engineering Science*, vol. 47, no. 7, pp. 1533-1543.
- Jannelli, E & Minutillo, M 2007, 'Simulation of the flue gas cleaning system of an RDF incineration power plant', *Waste Management*, vol. 27, pp. 684–690.
- Kilicarslana, A & Qatu, M 2017, 'Exhaust gas analysis of an eight-cylinder gasoline engine based on engine speed', *Energy Procedia*, vol. 110, pp. 459 – 464.
- Kohl, AL & Riesenfeld, FC 1985, 'Gas Purification', 4th ed., *Gulf Publishing Co.*, Houston, pp. 1–356.
- Ladwig, KJ & Blythe, GM 2017, 'Flue-gas desulfurization products and other air emissions controls - Coal Combustion Products (CCP's) Characteristics', *Utilization and Beneficiation*, pp. 67-95.
- Osaka, Y, Kito, T, Kobayashi, N, Kurahara, S, Huang, H, Yuan, H & He, Z 2015, 'Removal of sulfur dioxide from diesel exhaust gases by using dry desulfurization MnO<sub>2</sub> filter', *Separation and Purification Technology*, vol. 150, pp. 80–85.
- Przepiórski, J, Czyzewski, A, Kapica, J, Moszynski, D, Grzmil, B, Tryba, B, Mozia, S & Morawski, AW 2012, 'Low temperature removal of SO<sub>2</sub> traces from air by MgO-loaded porous carbons', *Chemical Engineering Journal*, vol. 191, pp. 147–153.
- Spörl, R, Maier, J & Scheffknecht, G 2013, 'Sulphur Oxide Emissions from Dust-Fired Oxy-Fuel Combustion of Coal', *Energy Procedia*, vol. 37, pp. 1435 – 1447.
- Srivastava, RK 2000, 'Controlling SO<sub>2</sub> emissions: a review of technologies', Report, U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Research Triangle Park NC 27711, pp. 1–100.
- Wang, WZ, Yang, CG & Zhang, JR 2011, 'Absorption of Sulphur Dioxide from Flue Gas with Sodium Alkali Solution in Packed Columns', *Advanced Materials Research*, vols. 383-390, pp. 6409-6415.
- Wei, CH, Zhuang, Z, Xin, Q, Al-Shamma'a, AI & Shaw, A 2011, 'Sensing of Diesel Vehicle Exhaust Gases under Vibration Condition', *Procedia Environmental Sciences*, vol. 11, pp. 1100 – 1107.



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- Yan, L, Lu, X, Wang, Q, Kang, Y, Xu, J & Chen, Y 2014, 'Research on sulphur recovery from the by-products of magnesia wet flue gas desulfurization', *Applied Thermal Engineering*, vol. 65, no. 1-2, pp. 487-494.
- Zhu, JL, Wang, YH, Zhang, JC & Ma, RY 2005, 'Experimental investigation of adsorption of NO and SO<sub>2</sub> on modified activated carbon sorbent from flue gases', *Energy Convers Manage*, vol. 46, pp. 2173-2184.