

Determination of the Equilibrium Partial Pressure of SO₂ over the Absorption Slurry in Case of Purification of Flue Gas From Sulfur Dioxide using Gypsum Technology

Elena Razkazova-Velkova, Ljutzkan Ljutzkanov, Nikolai Kolev, Dimitar Kolev, Daniela Dzhonova-Atanasova

Abstract: *The most widely used process for purification of flue gases from SO₂ is its absorption with slurry containing CaCO₃. Up to now there are installations for carrying out of the SO₂ absorption according to this process only for big capacity boilers because of the great height of the existing absorbers for this technology, about 20-30 m. To create new absorbers for small and middle capacity boilers, equilibrium data for the absorption of SO₂ are necessary. Up to now such data are available in the literature only for a temperature of 20 and 25°C.*

Key words: *SO₂, purification of flue gas, equilibrium partial pressure, absorption slurry, gypsum, absorption degree, experiment.*

INTRODUCTION

The most widely used process for purification of flue gases from SO₂ is its absorption with slurry containing CaCO₃ [1-14]. Even when Ca(OH)₂ slurry is used as an absorbent, as a result of its circulation in the absorber and saturation in CO₂ from the flue gas (CO₂ concentration about 12%), the absorbent is transformed into CaCO₃. Up to now there are installations for carrying out of the SO₂ absorption according to this process only for big capacity boilers. It is because the height of the existing absorbers for this technology is too great, about 20-30 m. Building of such installations for small and middle capacity boilers is too expensive and leads to unacceptably long pay back term. Another disadvantage of the existing installations is their low degree of absorption, about 95%. It means that about 5 % of the SO₂ entering the absorber goes out with the flue gases into the atmosphere. Because they are cooled in the installation, their distribution in the atmosphere, with an initial SO₂ concentration of about 150 ppm, requires a great height of the stack. For choosing the technological scheme and type of the absorbers and their calculation, data for the equilibrium partial pressure of SO₂ over the slurry at the temperature in the absorber are necessary. Although a great number of papers are published in the area of the considered technology, data for the equilibrium partial pressure of the SO₂ are found only at a temperature of 20 °C [4] and 25°C, [12]. There are no data at temperatures at which the industrial apparatuses for absorption of SO₂ from the flue gases operate. The aim of this paper is to obtain the necessary data. Due to the low solubility of the main solid components of the slurry circulating in the absorbers, the concentration of the SO₂ and its partial pressure in the gas phase at a given temperature is practically a function of pH.

EXPERIMENTAL

At first it was decided the experiment to be carried out by passing gas through a succession of thermostated absorption flasks. The SO₂ partial pressure was calculated from the pressure in the last flask and SO₂ concentration in the out gas, measured by a precise gas-analyzer. For analyzing of the SO₂ in the gas phase an infrared Hartman and Braun analyzer is used. The investigations are carried out at different temperatures and pH values. The equilibrium partial pressure (P_{SO_2}) in Pa was calculated according to Equation (1):

$$P_{SO_2} = 10^{-6} P_a \frac{P_a - P_{H_2O}}{P_a} C_{GSO_2}, \quad (1),$$

where P_a is the atmospheric pressure in Pa;

P_{H_2O} - the equilibrium partial pressure of the H_2O vapors at the temperature in the last vessel;

C_{GSO_2} - the concentration of the SO_2 in the gas phase in ppm in the gas analyzer.

The constant 10^{-6} is for transformation of C_{GSO_2} from ppm to mol/mol, and the expression

$$\frac{P_a - P_{H_2O}}{P_a}$$

for taking into account the ratio of the partial pressure of SO_2 in the vessel

to that in the analyzer, where the concentration C_{GSO_2} is determined.

The actual number of the needed flask was proved by changing them until their increasing does not change the measured outlet SO_2 concentration.

By measuring the pH in the subsequent flasks it was found that they differ too much. The last flask where the outlet concentration of SO_2 is measured has always lower pH. The difference in the pH in the flasks increases with the decrease of pH and the increase of the temperature. Due to this another experimental setup shown in Fig. 1 is used. The slurry is thermostated in the vessel (1) with magnetic agitator (2) and (3) and bubbler (13). The gas enters trough pipe (9) the bubbler (13) and contacts the slurry at intensive agitation. Then it goes out trough vertical cooler (6) in which the great part of the evaporated in the vessel (1) water vapor condenses and goes back in the vessel (1). The pipe (7) connects the cooler (6) with a gas pump, which is a part of the gas analyzer (8), and the analyzer. The analyzed gas comes back to the vessel and circulates trough it and the gas analyzer until the measured concentration becomes constant, that is until reaching the equilibrium. Position (4) and (5) are pipes connecting the thermostating jacket of the vessel (1) with the thermostat of the installation, not presented in the figure. Pos. (10) and (11) are thermometer and glass pH-electrode connected with a pH-meter not presented in the figure. Pos. (12) is a capillary connected with the atmosphere to ensure the pressure in the vessel (1) equal to the atmospheric pressure. The equilibrium partial pressure (P_{SO_2}) in P_a was calculated according to Equation (1).

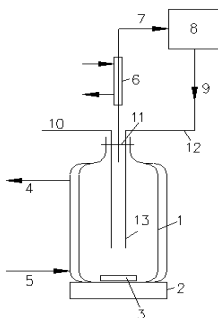


Fig. 1. Experimental installation:

- 1- Thermostated vessel; 2 and 3 – magnetic agitator; 4 and 5 pipes for connection with the thermostat; 6- vertical cooler; 7 – pipe; 8- gas analyzer; 9- pipe; 10- thermometer; 11- glass pH-electrode; 12- capillary tube; 13- bubbler.

RESULTS AND DISCUSSION

The results for the partial pressure of the SO_2 for both experimental setup as a function of the pH of the suspension are presented in Figs. 2,3 respectively.

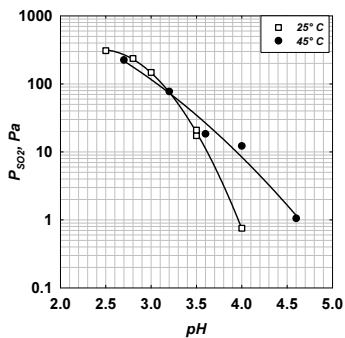


Fig.2. Partial pressure of the SO₂ for the experiment with absorption flasks.

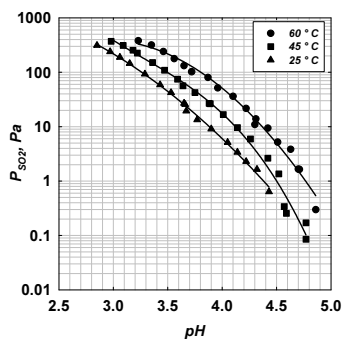


Fig. 3. Partial pressure of the SO₂ for the experiment with thermostated vessel.

Figs. 4,5 are comparison between the both methods for investigation for 25 and 45°C respectively.

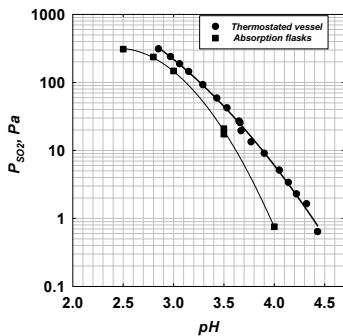


Fig 4. Comparison between the results with absorption flask and thermostated vessels for 25°C.

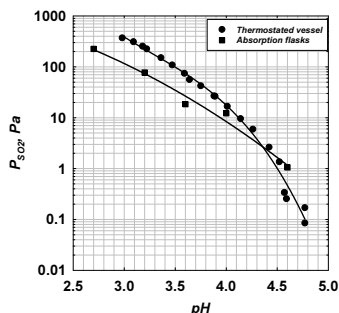


Fig 5. Comparison between the results with absorption flask and thermostated vessel 45°C

Fig. 6 . represents the influence of the concentration and the composition of the used suspension for 60°C using the method with thermostated vessel. Pure H_2SO_3 , suspension with concentration 22,5% of $CaSO_3$, two and four times diluted suspension with concentration 22,5% and nearly fully oxidized suspension with initial concentration of 22,5% and 5% of $CaSO_3$ at the time of the experiments are investigated.

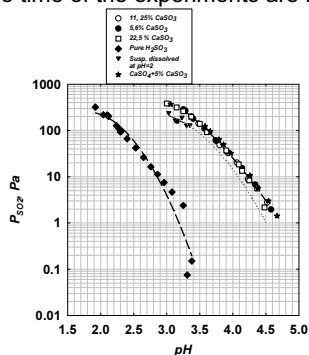


Fig. 6. Influence of the concentration and the composition of the used suspension for 60°C. Experiments with thermostated vessel

CONCLUSION

The results with thermostated vessel show that the increasing of the temperature from 25 to 45° C leads to about 3 times increasing of the partial pressure of SO_2 in the area of the lowest partial pressures. The respective increasing for the range of 25° to 60°C is about 10 times.

The method with thermostated vessel shows always higher results then these with absorption flasks. The latter is due to the redistribution of the SO_2 between the absorption flask. The actual concentration of the suspension does not reflect on the partial pressure. It depends probably only on the solubility product of the $CaSO_3$.

Acknowledgements: This participation is funded under contract № BG051PO001-3.3.04/ 30 /28.08.2009 by the Operational Programme “Human Resources Development” and the European Social Fund.

REFERENCES:

1. Binlin Dou, Weiguo Pan, Qiang Jin, Wenhuan Wang, Yu Li, (2009), Prediction of SO_2 removal efficiency for wet flue gas desulfurization, Energy Conversion and Management 50, pp.2547–2553.

2. Bravo, R.V., Camacho, R. F., Moya, V. M., García, L. A. I. (2002) Desulphurization of SO₂-N₂ mixtures by limestone slurries, *Chemical Engineering Science* 57, pp.2047 – 2058
3. Frandsen, J. B. W., Kiil, S., Johnsson, J. E. (2001) Optimisation of a wet FGD pilot plant using fine limestone and organic acids, *Chemical Engineering Science* 56, pp. 3275–3287.
4. Gerard, P., Segantini, G., Vanderschuren, J. (1996), Modeling of dilute sulfur dioxide absorption into calcium sulfite slurries; *Chemical Engineering Science*, Vol. 51, No. 12, pp. 3349-3358,
5. Gómez, A., Fueyo, N., Tomás, A. (2007) Detailed modelling of a flue-gas desulfurisation plant, *Computers and Chemical Engineering* 31, pp. 1419–1431.
6. Hrastel, I., Gerbec, M., Stergaršek, A. (2007), Technology optimization of wet flue gas desulfurization process, *Chem. Eng. Technol.*, 30, pp.220–233.
7. He S, Xiang G, Li D, Li Y, Yao Q, Xu X. (2002), Technology optimization of wet flue gas desulfurization process, *Environ. Prog.*, 21, pp.1311–1316.
8. Jannelli, E., Minutillo, M., (2007) Simulation of the flue gas cleaning system of an RDF incineration power plant; *Waste Management* 27, pp.684–690.
9. Keskinen, K. I, Alopaeus, V., Koskinen, J., Kinnunen, T., Pitkänen, H., Mojaner, J, Wärnström, U. (2002) CFD Simulation of the oxidation tank reactor of a wet flue gas desulphurization process, Prepared for presentation at 2002 AIChE Annual Meeting, Indianapolis, IN, Nov. 3-8, Copyright © Karli I Keskinen. Neste Engineering Oy, Finland.
10. Kiil, S., Michelsen, M. L., and Dam-Johansen, K. (1998). Investigation and Modeling of a Wet Flue Gas Desulfurization Pilot Plant, *Ind. Eng. Chem. Res.* 37 (7), pp. 2792–2806.
11. Özyüçüran, A., Ersoy-Meriçboyu A. (2010) Flue gas desulfurization by limestone and hydrated lime slurries, *Chemical and Metallurgical Engineering Faculty, Istanbul Technical University, 34469 Maslak-Istanbul-Turkey*,
12. Recej, T., Golob, J. (2004), Equilibrium and mass transfer in the Ca²⁺-SO₂-H₂O system for the analysis of the flue gas desulphurization process, *Institution of Chemical Engineers, Trans. IChemE, Part B, September, Process Safety and Environmental Protection*, 82(B5), pp.371–380
13. Zheng, Y., Kiil, S., Johnsson, J. E., Zhong, Q. (2002) Use of spray dry absorption product in wet flue gas desulphurization plants: pilot-scale experiments, *Fuel* 81 pp. 1899–1905
14. Zheng, Y., Kiil, S., Johnsson, J. E. (2003) Experimental investigation of a pilot-scale jet bubbling reactor for wet flue gas desulphurization, *Chemical Engineering Science*, 58 pp.4695 – 4703.

About the authors:

Люцкан Атанасов Люцканов- доцент; Институт по инженерна химия-БАН, ljutzkanov@bas.bg; тел.: (02) 979 32 73;

Елена Николаева Разказова-Велкова- гл. ас.; Институт по инженерна химия-БАН, razkazova_velkova@bas.bg; тел.: (02) 979 32 85;

Николай Николаев Колев- проф. Институт по инженерна химия-БАН, kolev@bas.bg; тел.: (02) 979 32 81;

Димитър Николаев Колев инж. д-р Институт по инженерна химия-БАН, kolev@bas.bg; тел.: (02) 979 32 81;

Даниела Боянова Джонова-Атанасова-гл.ас.; Институт по инженерна химия-БАН, dzhonova@bas.bg; тел.: (02) 979 32 85;

Докладът е рецензиран