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EQUILIBRIUM PARTIAL PRESSURE OF SO_2 OVER THE ABSORPTION SLURRY IN CASE OF PURIFICATION OF THE FLUE GAS FROM SULFUR DIOXIDE USING GYPSUM TECHNOLOGY

Ljutzkan A. Ljutzkanov, Elena N. Razkazova-Velkova, Nikolai N. Kolev,
Dimitar N. Kolev, Daniela B. Dzhonova-Atanasova
Institute of Chemical Engineering- Bulgarian Academy of Sciences,
"Acad. G. Bonchev" Str., Bl.103, 1113 Sofia, Bulgaria

Abstract

The most widely used process for purification of flue gases from SO_2 is its absorption with slurry containing $CaCO_3$. Up to now there are installations for carrying out of the SO_2 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 SO_2 are necessary. Up to now such data are available in the literature only for a temperature of 25°C. That is why experiments for obtaining of equilibrium data for the partial pressure of SO_2 over slurry containing $CaCO_3$, $CaSO_3$ and $CaSO_4$ at different temperatures are carried out. The results 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.

Key words: *SO_2, purification of flue gas, equilibrium partial pressure, absorption slurry, gypsum, absorption degree, experiment.*

1. INTRODUCTION

The most widely used process for purification of flue gases from SO_2 is its absorption with slurry containing $CaCO_3$ [1-17]. Even when $Ca(OH)_2$ slurry is used as an absorbent, as a result of its circulation in the absorber and saturation in CO_2 from the flue gas (CO_2 concentration about 12%), the absorbent is transformed into $CaCO_3$. Up to now there are installations for carrying out of the SO_2 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 SO_2 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 SO_2 concentration of about 150 ppm, requires a great height of the stack. That is why the National Science Fund of Bulgaria in partnership with Trade and technology joint-stock company – Bulgaria funded a project for creation of an installation proper for small and middle capacity boilers. For choosing the technological scheme and type of the absorbers and their calculation, data for the equilibrium partial pressure of SO_2 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 SO_2 are found only at a temperature of 20 °C [15] and 25°C, [16].

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There are no data at temperatures at which the industrial apparatuses for absorption of SO_2 from the flue gases operate. The aim of this paper is to obtain the necessary data.

2. CHEMICAL REACTIONS IN ABSORPTION OF SO_2 WITH $CaCO_3$ SLURRY

In the absorption of SO_2 with slurry of $CaCO_3$, the following chemical reactions take place in the liquid phase:

$$SO_2(aq) + H_20 = H_2SO_3 \quad (1)$$

$$H_2SO_3 = H^+ + HSO_3^- \quad (2)$$

$$HSO_3^- = H^+ + SO_3^{2-} \quad (3)$$

$$HSO_3^- + 0{,}5O_2 = HSO_4^- \quad (4)$$

$$HSO_4^- = H^+ + SO_4^{2-} \quad (5)$$

$$H_2O = H^+ + OH^- \quad (6)$$

$$CaCO_3 + H_2SO_3 = CaSO_3 + H_2CO_3 \quad (7)$$

$$H_2CO_3 = H^+ + HCO_3^- \quad (8)$$

$$HSO_4^- + CaCO_3 = CaSO_4 + HCO_3^- \quad (9)$$

$$CaSO_3 + SO_2 + H_2O = Ca(HSO_3)_2 \quad (10)$$

$$2HSO_4^{'} + Ca^{++} + 2H_2O = CaSO_4.2H_2O + H_2SO_4 \quad (11)$$

$$H_2SO_4 + CaCO_3 + H_2O = CaSO_4.2H_2O + CO_2 \quad (12)$$

Of all components which take place in the reactions, $CaCO_3$, $CaSO_3$ and $CaSO_4$ are badly soluble, and their concentrations in the slurry are quite greater than their solubility. That is why the concentration of the $SO_2(aq)$ in the liquid of the slurry, which directly determines the equilibrium partial pressure of SO_2 in the gas phase, is not dependent on the concentration of these three components in the slurry.

The concentrations of H^+, $HSO_3^-, H_2SO_3, SO_3^{2-}, SO_4^{2-}, HSO_4^+, H_2SO_4$ are connected definitely trough the dissociation constants by the corresponding equations:

$$K_{H_2SO_3} = \frac{C_{H^+}.C_{HSO_3^-}}{C_{H_2SO_3}} \quad (13)$$

$$K_{HSO_3^-} = \frac{C_{H_2}.C_{HSO_3^{2-}}}{C_{HSO_3^-}} \quad (14)$$

$$K_{H_2SO_4^-} = \frac{C_{H^+}.C_{SO_4^{2-}}}{C_{HSO_4^-}} \quad (15)$$

$$K_{H_2SO_3} = \frac{C_{H^+} C_{HSO_3^-}}{C_{H_2SO_3}}, \quad (16)$$

where K are the dissociation constants and C the concentrations. The indices denote the corresponding chemical compounds or ions.

The value of C_{H^+} is also connected with the ionic product of water:

$$K = C_{OH^-}.C_{H^+} \quad (17)$$

The concentration of Ca^{2+} depends on the solubility products of $CaSO_3$ and of $CaCO_3$. The concentration of CO_2 at equilibrium depends only on its solubility. Thus all concentrations of the solution of the slurry are functions of the concentration of H^+, and of course of the temperature, on which the mentioned constants depend.

3. EXPERIMENTAL DETERMINATION OF THE EQUILIBRIUM PARTIAL PRESSURE OF SO_2 AS A FUNCTION OF PH AND THE TEMPERATURE.

The scheme of the experimental device is presented in Fig. 1. The slurry is thermostated in the vessel (1) with magnetic agitator (2) and (3) and bubbler (13). The inert 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. For analyzing of the SO_2 in the gas phase an infrared Hartman and Braun analyzer is used. To determine its "0", air circulating trough the analyzer, which was purified in the absorption vessel (1) with $NaOH$ solution, was used.

In Table 1 the obtained experimental data are presented.

The equilibrium partial pressure of SO_2 (P_{SO_2}) in Pa is calculated by the equation:

$$P_{SO_2} = 10^{-6} P_a \frac{P_a - P_{H_2O}}{P_a} C_{GSO_2}, \quad (18)$$

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 vessel (1);

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

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

for taking into account the ratio of the partial pressure of SO_2 in the vessel (1) to that in the analyzer, where the concentration C_{GSO_2} is determined.

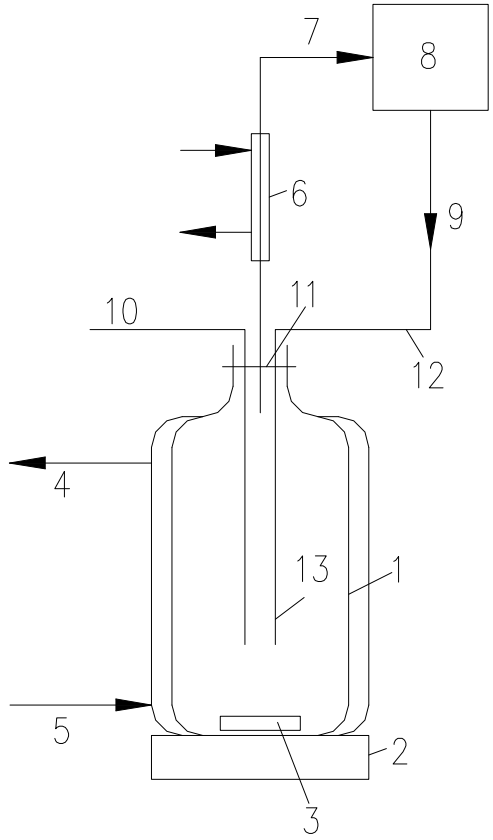

Fig. 1. Experimental installation: 1- thermostated vessel; 2 and 3 – magnetic agitator; 4 and 5 pipes for connection with the thermostat; 6- vertical cooler; 7 – pipe; 8- gas analyzer; 9- pipe; 10- thermometer; 11- glass pH-electrode; 12- capillary tube; 13- bubbler.

The values of the determined equilibrium partial pressure are also presented in Table 1.

Some of the data from Table 1 are presented in Fig. 2 in double logarithmic coordinates.

From the figure it can be seen that the increasing of the temperature from 25 ^{o}C to 45°C leads to about 3 times increasing of the partial pressure of SO_2 in the area of the lower partial pressures. The respective increasing corresponding to the change from 25 ^{o}C to 60°C is about 10 times.

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Table 1. Experimental results

Temperature ° C	pH	Atmospheric pressure, Pa	Concentration of sulphur dioxide, ppm	Sulphur dioxide partial pressure, Pa
60°C	3.23	95272.56	5047	380.2836
	3.35	95272.56	4216	317.6691
	3.46	95272.56	3197	240.889
	3.56	95272.56	2366	178.2744
	3.65	95272.56	1753	132.0858
	3.72	95272.56	1357	102.2478
	3.87	95272.56	1064	80.17075
	3.96	95272.56	686	51.68904
	4.10	95272.56	479	36.09191
	4.22	95272.56	288	21.70035
	4.31	95272.56	184	13.86411
	4.42	95272.56	125	9.418556
	4.51	95272.56	69	5.199043
	4.63	95272.56	51	3.842771
	4.70	95272.56	22	1.657666
	4.3	94429.44	147	10.95228
	4.71	94429.44	22	1.639117
	4.86	94429.44	4	0.298021
45°C	4.77	94804.16	2	0.17044
	4.77	94804.16	1	0.08522
	2.98	94804.16	4352	370.8765
	3.09	94804.16	3658	311.734
	3.18	94804.16	2983	254.2106
	3.22	94804.16	2648	225.662
	3.36	94804.16	1778	151.5208
	3.47	94804.16	1279	108.9961
	3.59	94523.12	878	74.57622
	3.64	94523.12	665	56.48427
	3.75	94523.12	500	42.46938
	3.88	94523.12	316	26.84065
	3.89	94523.12	311	26.41595
	4.01	94523.12	197	16.73293
	4.14	94523.12	113	9.598079
	4.26	94523.12	70	5.945713
	4.42	94523.12	31	2.633101
	4.52	94523.12	16	1.35902
	4.57	94523.12	4	0.339755
	4.59	94523.12	3	0.254816
25°C	2.85	94523.12	3415	311.9756
	2.97	94523.12	2620	239.3488
	3.06	94523.12	2061	188.2816
	3.15	94523.12	1589	145.1623
	3.29	94523.12	1016	92.81616
	3.43	94523.12	644	58.83229
	3.53	94523.12	463	42.29713
	3.65	94523.12	295	26.94957
	3.66	94523.12	280	25.57926
	3.67	94897.84	212	19.44659
	3.77	94897.84	146	13.39246
	3.9	94897.84	99	9.081192
	4.05	94897.84	56	5.136836
	4.14	94897.84	37	3.393981
	4.22	94897.84	25	2.29323

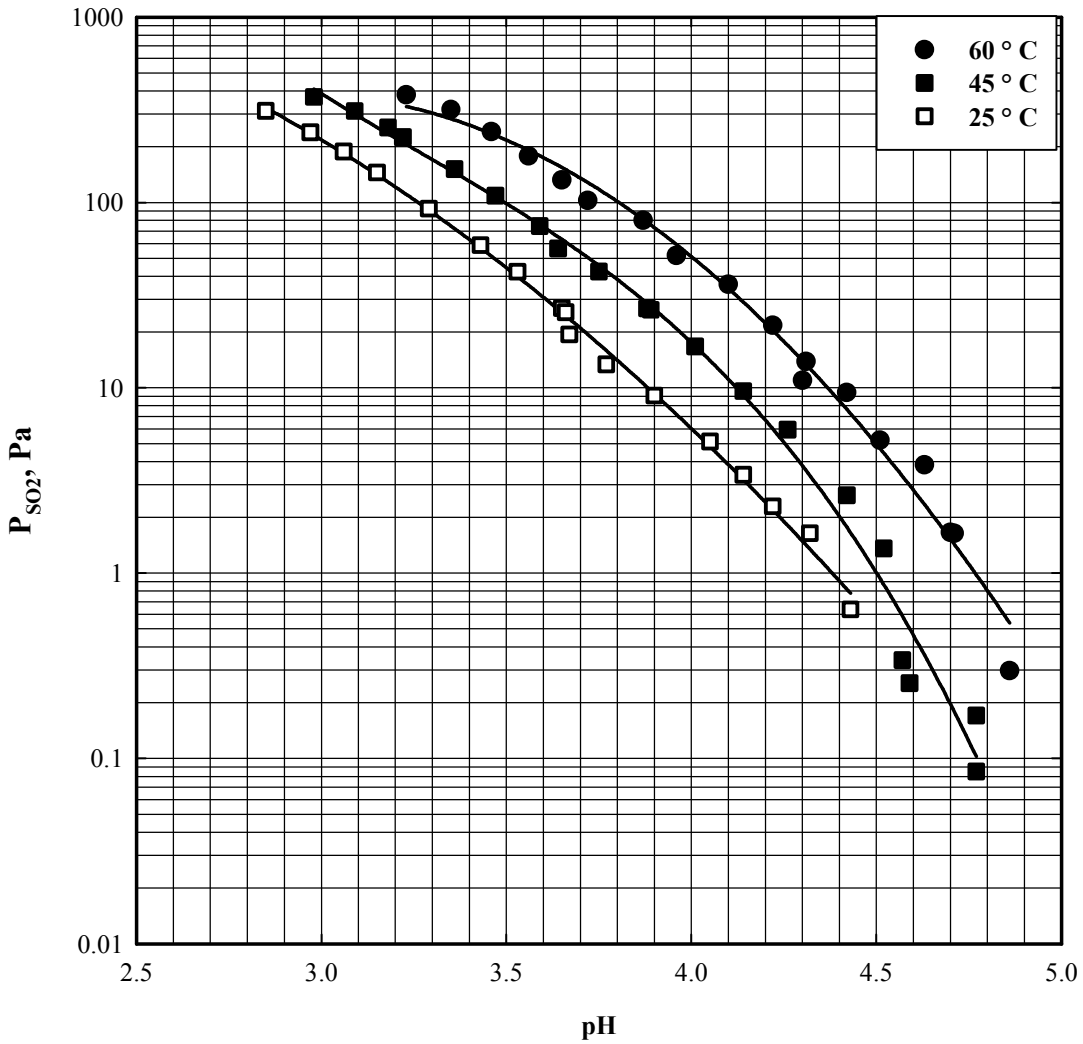

Fig. 2. Equilibrium partial pressure of SO_2 over the absorption slurry versus its pH.

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