Mathematic Modeling of Sulphur Adsorption by Calcium Hydroxide

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Abstract- **Sulphur compounds cause corrosion of petrochemical plants and especially if the gases are to be used as raw materials for chemical plants production, they often act either as poisons for catalysts or lead to coking in the pyrolysis process. The sulphur compounds present in the refinery gases are mainly hydrogen sulfide and mercaptans. To a lesser extent, carbonyl sulfide and carbon sulfide is detected. There is a wide variety of types of desulfurization plants. Gas desulfurization processes are based on either reactions or selective absorption or desorption. This paper presenting a mathematical modeling of adsorption by sulf dioxide in calcium hydroxide.**

Keywords – sulphur dioxide, desulfurization, adsorption mathematical model.

I. INTRODUCTION

For the reactive adsorption of sulphur dioxide from waste gases, the most used adsorbents are: limestone, dolomite, lime and dolomitic lime.

But the reactivity of these adsorbents is different, depending on their composition and chemical structure.

Chemical composition of limestone (the presence of magnesium and silicium) can be a factor that contributes significantly to its reactivity when used as an adsorbent [1].

Experimental observations have shown that a high iron content in the adsorbent can accelerate the reactivity, and sodium is an impurity that can cause the diffusivity to change through the reaction product layer ($CaSO_4$).

Also, the size of the pores (or contact particles) makes the removal of sulphur dioxide from chemical gases different.

In practice, it has been found that the use of fine adsorbent particles allows the advanced removal of sulphur dioxide (the costs of crushing the limestone imposes the value of the size of the adsorbent particle at an average diameter of about 5 µm).

Ishihara s.a. [2] considers the particle with a diameter of 1-2 µm as the lower limit below which the resistance due to diffusion inside the particle can be completely eliminated.

At the same time, in the sulfation process, the particle size is practically represented by the size of the agglomerated particle, which retains less sulphur dioxide.

In the absence of pore diffusion, the reactivity of calcium oxide increases exponentially with temperature, according to Arrhenius. The apparent activation energy for sulphur dioxide is approximately 154.7 KJ / mol.

The optimum temperature in the dry injection depends on the source adsorbent, particle size and reaction type, always required experimental determinations [3,4].

The experiment underlying the numerical modeling chose as working conditions the calcination temperature of calcium hydroxide of 700° C and the pressure of 0.35 bar [5,6].

In first stage of experiments obtained calcined CaO was further subjected to the sulfation reaction [7,8].

The concentration of sulfur dioxide in the gas mixture was chosen to be close the values of the concentration of sulfur dioxide in the refinery waste gases [9].

Chemical equation is (calcination and sulfation):

$$CaCO_3(s) = CaO\ (s) + CO_2(g) \qquad \Delta H_{r,\ 298} = 178,5\ \text{kcal/mol} \qquad (1)$$
$$CaO(s) + SO_2(g) + 1/2O2(g) = CaSO4(s) \qquad \Delta H_{r,\ 298} = -502,2\ \text{kcal/mol} \qquad (2)$$

II. MATERIAL AND METHODS

A. Materials

The experiment consisted in the heat treatment of a solid adsorbent used whose chemical composition was as follows: $CaCO_3$-97%; Fe_2O_3 - 1.5%; Al_2O_3 -0.5%, SiO_2 -0.1%.

The adsorbent was calcined for 40 minutes at a temperature of 100°C and a pressure of 0.35 bar, after which it was passed through the obtained powder (at a size of 0-50 μm of particles), a gas stream formed from a mixture SO_2 + N_2, pure O_2, pure N_2 and pure Ar (0,35 % vol. SO_2, 0,8 % vol SO_2, 25 % vol. O_2 , and 73,85 % vol. Ar).

In order to observe the absorption of SO_2 in CaO, we took from the experiment the variation of the weight of the calcined sample and treated with SO_2 depending on the contact time.

The analysis of the data collected from the experiment shows the following:

a. The absorption rate is defined by a curve, with 80% by mass measured of CaO absorbed in the first 20 minutes,

b. After 20 minutes the absorption capacity is reduced, up to an hour being a maximum of 98%,

c. Figures 1 and 2 show the variation of the absorption process efficiency depending on the contact time and the maximum amount of SO_2 absorbed.

Table -1 Experiment Result

| Calcium oxide mass mCa [mg]	time contacts t [min]	Calcium oxide mass with gas compounds mCa-gas[mg]	Δm [mg]	adsortion capacity of CaO[%]
2.5	0	2.5	0	0
2.5	5	3.254	0.754	30.16
2.5	10	3.952	1.452	58.08
2.5	15	4.254	1.754	70.16
2.5	20	4.553	2.053	82.12
2.5	25	4.653	2.153	86.12
2.5	30	4.689	2.189	87.56
2.5	35	4.758	2.258	90.32
2.5	40	4.789	2.289	91.56
2.5	45	4.853	2.353	94.12
2.5	50	4.863	2.363	94.52
2.5	55	4.983	2.483	99.32
2.5	60	4.934	2.434	97.36
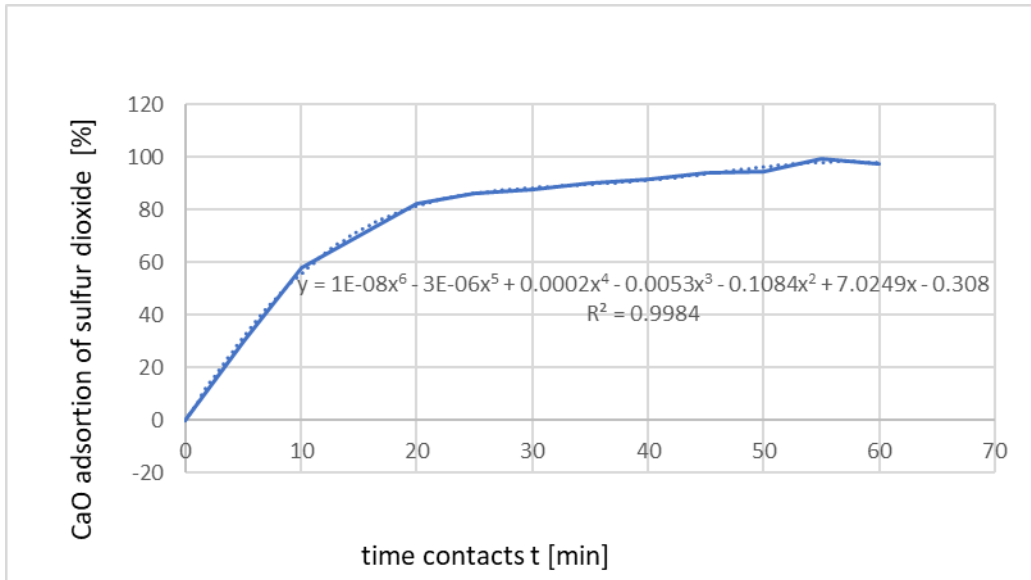
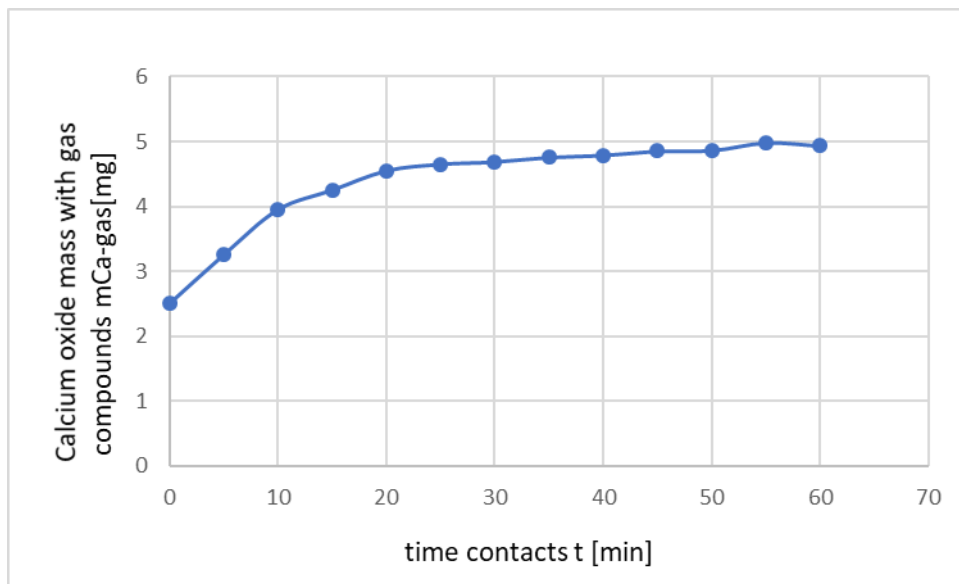Figure 1. Randaments of CaO adsorption of sulfur dioxide.

Figure 2. CaO mass with sulfur dioxide adsortion.

B. Methods –

To observe how the absorption capacity varies mathematically depending on the contact time, we tried to write two equations that offer:
a. The efficiency of the experiment,
b. Adsorption capacity.

This equation is:

$$y = 1E\text{-}08x^6 - 3E\text{-}06x^5 + 0.0002x^4 - 0.0053x^3 - 0.1084x^2 + 7.0249x - 0.308 \qquad (3)$$
$$R^2 = 0.9984$$

Where:
- y is randaments of process adsorption (experimental yelds CaO adsortion of sulfur dioxide [%])
- x is time contacts,

and a second equation:

$$y = 3E\text{-}10x^6 - 7E\text{-}08x^5 + 6E\text{-}06x^4 - 0.0001x^3 - 0.0027x^2 + 0.1756x + 2.4923 \qquad (4)$$
$$R^2 = 0.9984$$

Where:
- y is Calcium oxide mass with gas compounds mCa-gas (mg),
- x is time contacts (s),

III. RESULT AND DISCUTION

We compared the experimental data with the industrial data collected from a sulfur dioxide washing column with CaO solutions.

Table 2. Distillation column gas treated variation depending on the measurement time

| time	gas with sulfure dioxide quantity (Nm³/h)	gas treated quantity (Nm³/h)	Temperature to distillation columns, °C	randaments of instalations, % gas treated
0	139,947,041	135,843,623	19,76614189	97.06788
1	1,431,368,652	1,386,741,504	19,43262482	96.8822
2	1,417,509,277	1,365,031,836	19,12623215	96.29791
3	1,404,666,895	1,355,238,379	18,8857708	96.48112
4	1,429,369,824	1,387,003,125	18,72385216	97.03599
5	1,427,926,855	1,384,512,598	18,45790672	96.95963
6	1,437,133,691	1,388,610,938	18,19196129	96.62364
7	1,409,178,125	1,358,296,973	18,07437325	96.3893
8	142,240,166	138,646,650	17,98869705	97.47363
9	1,359,026,074	1,314,764,160	19,51935005	96.74312
10	141,039,873	134,695,898	22,23329926	95.502
11	142,962,002	136,557,568	24,73156357	95.52018
12	143,557,334	137,202,578	25,77627563	95.57337
13	1,421,307,324	1,374,792,090	25,83912468	96.72729
14	1,449,206,738	1,390,297,073	24,75012589	95.93504
15	1,446,141,797	1,386,478,809	23,66414642	95.87433
16	1,457,832,129	1,403,201,953	22,65464401	96.25264
17	1,454,849,902	1,402,334,277	21,55667686	96.39031
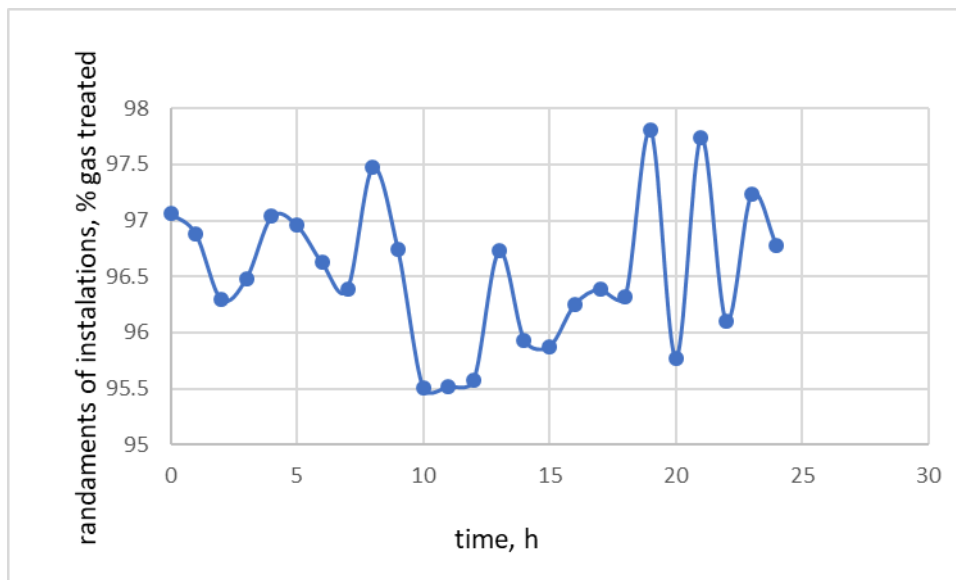
Figure 3. Industrial randaments of gas treated of petrochemical instalations.

Table 3. Equation of behavior of the gas treatement plant

Imput parameter X	Output parameter Y	equation	Relative error The diference between y is real and y is calculed	Absolute error= Relative error * 100
Measuretment time, h	Output pressure of gases treated , atm	$y = 1E-08x^6 - 9E-07x^5 + 2E-05x^4 - 0,0003x^3 + 0,0015x^2 - 0,0054x + 11,709$	0,005	0,5
Measuretment time, h	Pressure imput of gases untreated, atm	$y = -2E-05x^6 + 0,0014x^5 - 0,0411x^4 + 0,542x^3 - 3,2326x^2 + 7,6193x + 14,004$	0,002	0,2
Measuretment time, h	Output quantity of gases treated Nmc/h	$y = 0,0012x^6 - 0,0759x^5 + 1,6219x^4 - 13,823x^3 + 34,737x^2 + 48,544x + 14060$	0,2	2
Measuretment time, h	Input quantity of gases untreated Nmc/h	$y = 0,0016x^6 - 0,101x^5 + 2,3504x^4 - 23,433x^3 + 91,16x^2 - 78,037x + 13659$	0,3	3
Measuretment time, h	Distillation column °C	$y = -1E-05x^6 + 0,001x^5 - 0,0284x^4 + 0,3528x^3 - 1,8278x^2 + 2,936x + 19,008$	0,002	0,2

IV.CONCLUSION

To observe how the sulfur separation process works, we took the operating data for 24 hours and simulated the variation of the outlet and inlet pressure on the separation column, depending on the measurement time.

The resulting equations for simulating the process of separating sulfur dioxide per column are given in Table 1 and 3
We also simulated the variation of the processed gas outlet flow rate and the raw gas inlet flow rate (in Nm^3/h) depending on the measurement time.

In table 3 the equations of behavior of the gas treatment plant are presented together with the relative and the absolute error.

It can be seen that the errors are very small which makes the numerical model of the behavior of the installation in operation to be viable.

In figure 1 and 3 we presented the efficiency of the reaction of reduction of sulfur dioxide in calcium oxide and the efficiency of the technological installation for the treatment of sulfur gases.

The difference between the two equations is less than 0.02%, similar to everyone experiments [10].

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