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Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

KINETIC STUDY OF FLUE GAS DESULPHURIZATION WITH SODIUM CARBONATE AT LOW TEMPERATURE

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ABSTRACT. This paper presents the kinetic study of the dry desulphurization process at low temperature using solid adsorbents by thermogravimetric analysis technique. Experiments are performed in isothermal conditions, at three temperatures (373 K, 473 K and 573 K) with diameters of sodium carbonate granules of 31.5 μm and 900 μm and sulfur dioxide concentration of 0.5 % and 1.0 %. The particle size, temperature and gas flow rate show a dominant influence on the variation of carbonate conversion. The obtained activation energy values are in the range from 4.234 KJ/mol to 12.275 KJ/mol showing that the diffusion through the solid product layer is the determinate rate step of the process. The experimental results confirm that the shrinking Unreacted Core Model can be used to describe the sulfation of sodium carbonate at low temperature.

Keywords: *flue gas desulphurization, kinetic study, activation energy, sodium carbonate, unreacted core model, effective diffusion coefficient.*

INTRODUCTION

Problems concerning environmental protection are today very important, taking into consideration the big quantities of emissions (for example SO_2, SO_3, HF and HCl) evacuated in atmosphere [1, 2]. A particular case consists of the sulfur dioxide emissions. Sulfur dioxide is a harmful gas resulted in large quantities by fuel combustion with air excess, which in the atmosphere transforms itself into sulfuric acid – a major component of acidic rain, sulfuric acid being extremely soluble in water.

There are many processes used for the reduction of such emissions. The use of solid adsorbents to reduce SO_2 emissions from coal fired power plants has been investigated during the last twenty years [3-6].The adsorption phenomenon of sulfur dioxide on solid adsorbents can be: a physico-sorption process, characterized by weak bonds (on zeolites for example) or/and chemo-sorption characterized by strong bonds.

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Adsorption of SO_2 on the sodium carbonate is a chemo-sorption process in accordance with reaction scheme (1):

$$Na_2CO_{3[s]} + SO_{2[g]} \rightarrow Na_2SO_{3[s]} + CO_{2[g]} \qquad (1)$$

In the worldwide there are plants at pilot and industrial scale, which are using adsorption of sulfur dioxide on calcium oxide and soda ash or sodium carbonate with a smaller than 50 % adsorption degree [3, 4]. The investigations are oriented towards to the discovery of influence of some parameters such as: initial porosity of solid particles, their geometrical size, reaction temperature, concentration of sulfur dioxide in the gas mixture, as well as the contact time over the reaction [5].

The aim of the present study is the kinetic study of the desulphurization process at low temperature using sodium carbonate as solid adsorbent by thermogravimetric analysis.

RESULTS AND DISCUSSION

The primary thermogravimetric measurements have been converted into kinetic curves considering the transformation degree of sodium carbonate, as Equation 2 shows:

$$\eta_{Na2CO3} = \frac{53}{63} \cdot \frac{\Delta m_s}{\overline{x}^0_{Na2CO3} \cdot m^0_s} \qquad (2)$$

and presented in Figure 1.

The experimental data presented in Figure 1 and Figure 2 show a significant influence of temperature and granule size on the conversion of sodium carbonate. Thus, it can be observed a positive effect on sodium carbonate conversion obtained by increasing the temperature and a negative effect by increasing the particle size.

As Figure 2 shows, for granule size of 900 μm, it can be achieve only a conversion lower than 30 % after a reaction times of 60 minutes, probably due to the strong influence of the SO_2 diffusion through the solid product layer.

The influence of the gas concentration and gas flow rate on the conversion of solid particles is less important, as it can be seen in Figure 3 and Figure 4.

The lower influence of the gas flow rate may be the qualitative confirmation for a kinetic mass transfer regime. A more accurate and quantitatively interpretation of the experimental results is not possible without kinetic modeling.

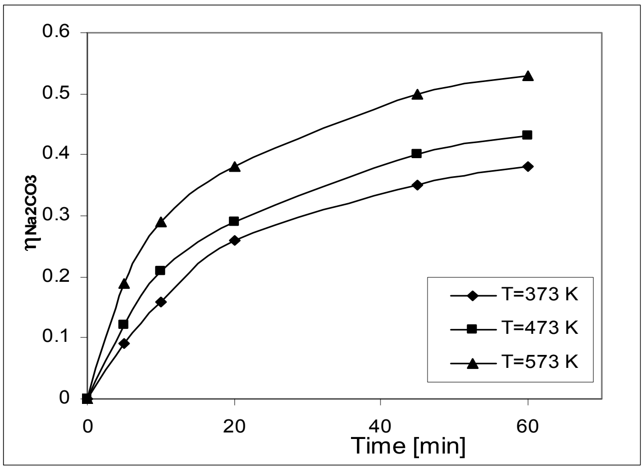

Figure 1. Kinetic curves conversion vs. time for d_{Na2CO3} = 31.5 µm, C_{SO2} = 0.5%, Gv = 1.55 x 10^{-4} m^3/s at different temperature.

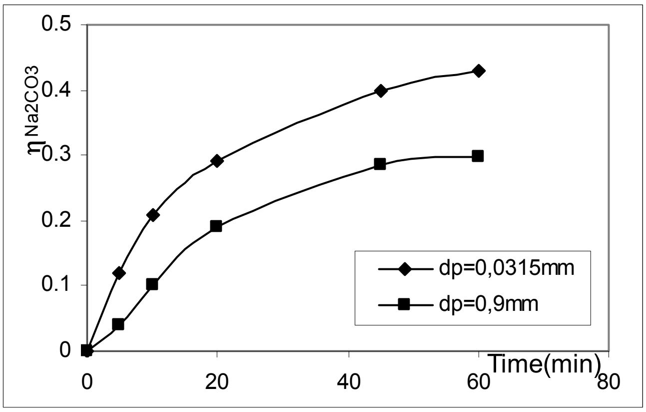

Figure 2. Kinetic curves conversion vs. time for different Na_2CO_3 diameters at C_{SO2}=0.5%, T=473 K and G_v=1.55 x 10^{-4} m^3/s.

To establish the mechanism of the desulphurization process the kinetic data presented in Figure 1 are processed using the *horizontal section method.* In accordance with this method for a constant conversion, the relative constant rate of the process k can be written as Equation (3) shows:

$$\bar{k} = \frac{1}{\tau} \tag{3}$$

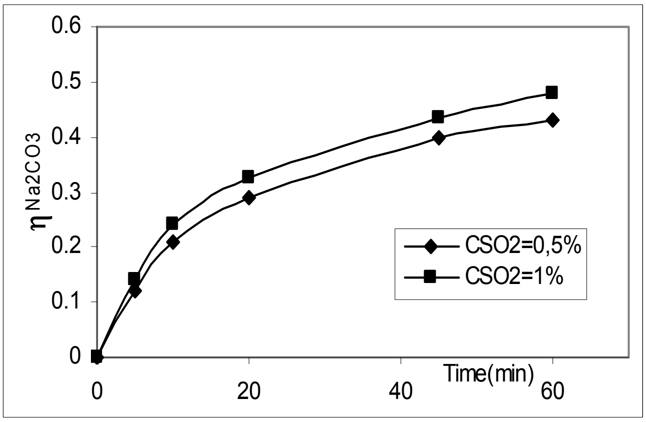

Figure 3. Kinetic curves conversion vs. time for d_{Na2CO3} = 31.5 µm at T=473 K, G_v=1.55 x 10^{-4} m^3/s and different SO_2 concentrations.

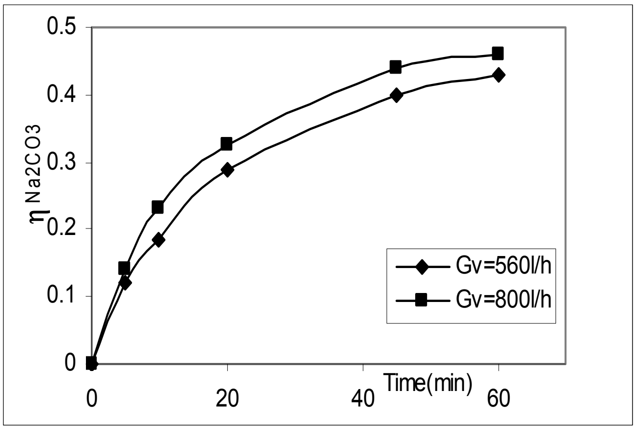

Figure 4. Kinetic curves conversion vs. time for d_{Na2CO3} = 31.5 µm at T=473 K, c_{SO2}=0,5% and different gas flow rates.

Considering the influence of the temperature on the constant rate k (Arrhenius Equation 4), and processing the kinetic curves in ln k – 1/T coordinates, a linear Arrhenius dependence at different sulfation degree can be obtained (Figure 5). From the slope (-Ea/R), the activation energy Ea can be determined:

$$k = k_0 \cdot e^{-\frac{Ea}{RT}} \tag{4}$$

$$\ln k = \ln k_0 - \frac{E_a}{R} \cdot \frac{1}{T} \tag{5}$$

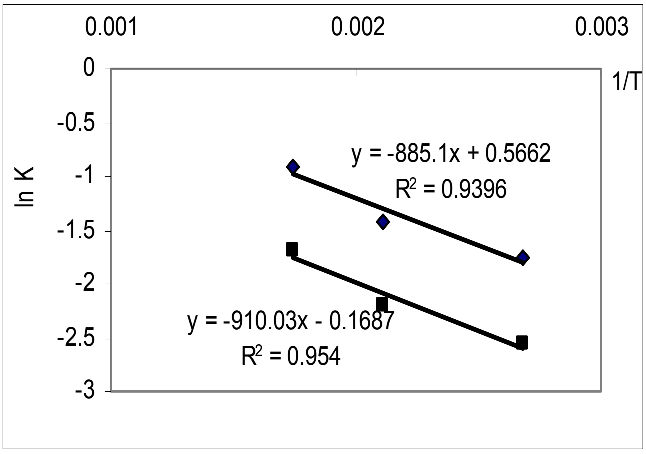

Figure 5. Determination of activation energy for particles of 31.5 µm at C_{SO2}=0.5 %, Gv=1.55 x 10^{-4} m^3/s at η_{Na2CO3}=0.1 and η_{Na2CO3}=0.2.

The activation energy values are in the range from 4.234 KJ/mol to 12.275 KJ/mol. These values indicate that mass transfer phenomena influenced the rate of the overall process, the diffusion through the solid product layer being the rate determining step [7].

Table 1. Activation energy values

d_p (mm)	w (m/s)	η_{Na2CO3}	E_a (KJ/mol)	$C_{SO2}*10^4$ (mol/l)
0.0315	0.5	0.1	7.325	
		0.2	7.531	2.23
	0.71	0.1	5.440	
		0.2	7.729	
0.0315	0.5	0.1	4.734	
		0.2	5.616	4.46
	0.71	0.1	6.565	
		0.2	12.275	
0.9	0.5	0.1	7.729	
		0.2	8.974	2.23
	0.71	0.1	5.082	
		0.2	7.169	
0.9	0.5	0.1	4.234	
		0.2	8.676	4.46
	0.71	0.1	4.346	
		0.2	5.178	

The kinetic equation which describes the sulfation process can be written as Equation 6 shows:

$$\frac{dn_{SO2}}{S\cdot d\tau}=-D_{ef_{SO2}}\cdot\frac{dc_{SO2}}{dr} \tag{6}$$

where S is the unreacted core surface of radius r:

$$S=4\pi\cdot r^2 \tag{7}$$

The apparent activation energies are centralized in Table 1.

Considering sodium carbonate to be of spherical and homogeneous solid particles, the shrinking unreacted core model may be applied for the kinetic modeling of desulphurization process.

Combining Equation (6) and (7), as Equation (8) shows, and integrating in two steps, on the grain model theory:

$$\frac{-dn_{SO2}}{d\tau}=-4\pi r^2\cdot D_{ef_{SO2}}\cdot\frac{dc_{SO2}}{dr} \tag{8}$$

$$\frac{-dn_{SO2}}{d\tau}\left(\frac{1}{r}-\frac{1}{R}\right)=4\pi D_{ef_{SO2}}\cdot c_{SO2} \tag{9}$$

$$dn_{SO2}=\frac{\rho_{[]_s}\cdot\bar{X}_{Na2CO3}}{M_{Na2CO3}}\cdot 4\pi r^2 dr \tag{10}$$

$$dn_{SO2}=\rho^*\cdot 4\pi r^2 dr \tag{11}$$

Equation (9) becomes:

$$-\rho^*\left(\frac{1}{r}-\frac{1}{R}\right)\cdot r^2\cdot\frac{dr}{d\tau}=D_{ef_{SO2}}\cdot c_{SO2} \tag{12}$$

or as function of Na_2CO_3-conversion (η_{Na2CO3}):

$$\left[\frac{1}{\left(1-\eta_{Na2CO3}\right)^{1/3}}-1\right]\frac{d\eta_{Na2CO3}}{d\tau}=3\cdot\frac{D_{ef_{SO2}}}{\rho^*\cdot R^2}\cdot c_{SO2} \tag{12'}$$

The integration of Equation (12) at constant concentration of SO_2, Equation (13) is obtained:

$$\tau=\frac{1}{6}\cdot\frac{\rho^*\cdot R^2}{D_{ef_{SO2}}\cdot c_{SO2}}\left[1-3\left(\frac{r}{R}\right)^2+2\left(\frac{r}{R}\right)^3\right] \tag{13}$$

or as function of Na_2CO_3-conversion (η_{Na2CO3}):

$$\tau = \frac{1}{6}\frac{\rho^{*}\cdot R^{2}}{D_{ef_{SO2}}\cdot c_{SO2}}\left[1-3\left(1-\eta_{Na2CO3}\right)^{2/3}+2\left(1-\eta_{Na2CO3}\right)\right] = \frac{1}{6}\frac{\rho^{*}\cdot R^{2}}{D_{ef_{SO2}}\cdot c_{SO2}}F\left(\eta_{Na2CO3}\right) \tag{13'}$$

Equation (13') represents the mathematical model equation for sulfur dioxide diffusion through product layer.

For the validation of the proposed model the function $\tau = F(\eta)$ is shown for d_p=31.5 μm and C_{SO2}=0.5 % in Figure 6.

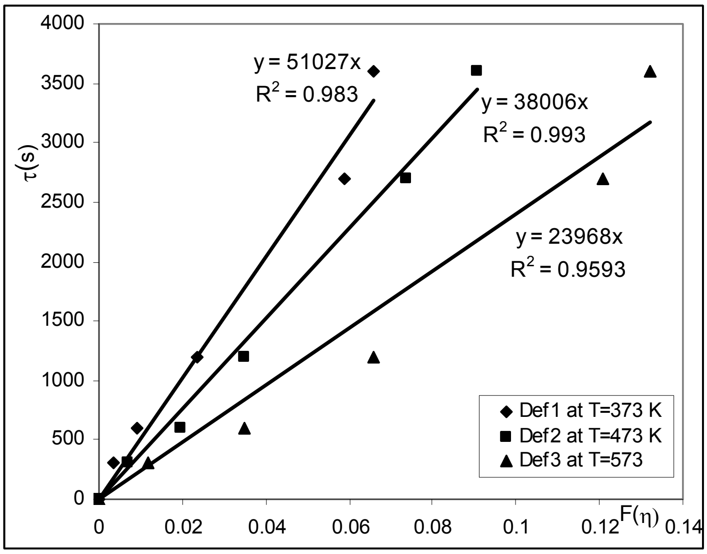

Figure 6. Dependence τ –F (η).

Table 2. D_{efSO2} through the product layer in our work conditions

T (K)	R (m)	Def (m²/s)	C_{SO2} *10⁴ (mol/l)	ρ^{*}_{Na2CO3} (mol/l)
373 473 573	15.75 x 10^{-6}	2.73 x 10^{-11} 3.67 x 10^{-11} 5.82 x 10^{-11}	2.23	7.53
373 473 573	45 x 10^{-5}	7.0 x 10^{-10} 11 x 10^{-10} 17 x 10^{-10}	2.23	7.53
373 473 573	15.75 x 10^{-6}	1.42 x 10^{-11} 1.98 x 10^{-11} 3.13 x 10^{-11}	4.46	7.53
373 473 573	45 x 10^{-5}	3.0 x 10^{-10} 6 x 10^{-10} 8 x 10^{-10}	4.46	7.53

The obtained values of D_{efSO2} in solid layer with the magnitude of 10^{-11}- 10^{-10} m^2/s are comparable with those founded in the literature [5, 6].

With the obtained slope's lines, the effective diffusion coefficient of SO_2 can be calculated with Equation (14):

$$D_{ef_{SO2}} = \frac{1}{6} \frac{\rho^* \cdot R^2}{c_{SO2} \cdot tg\alpha} \tag{14}$$

The values of the effective diffusion coefficients are centralized in Table 2.

CONCLUSIONS

The kinetic study of the gas desulphurization process with sodium carbonate at low temperature has shown a significant influence of temperature and granule size. A positive effect on sodium carbonate conversion was obtained by increasing the temperature and decreasing the particle size.

The apparent activation energy values evaluated from experimental data are in the range from 4.234 KJ/mol to 12.275 KJ/mol and have shown that the sulphur dioxide diffusion through the solid product layer is rate determining step of the overall process.

The kinetic data were quantitatively analyzed on the basis of the unreacted core model integrated in the general form. The macro kinetic SO_2 diffusion through the solid product layer model was validated and the obtained values of the SO_2 effective diffusion coefficients are comparable with those founded in the literature.

EXPERIMENTAL SECTION

In order to determine the effect of the temperature, grain size and gas flow rate on desulphurization process, the isothermal gravimetric method was used. The experiments were carried out on experimental equipment presented in Figure 7.

The installation contains a hand-made thermo balance, having a 20 mm diameter tubular reactor placed in a tubular electric furnace, with possibilities to operate in temperature range of 373 - 1473 K. The solid reactant, sodium carbonate placed in thin layer on a ceramic nacelle, was introduced in the tubular reactor and the experiments were carried out isothermally at three temperatures (373, 473, 573 K), with diameter of sodium carbonate granules of 31.5 µm and 900 µm and SO_2 concentration of 0.5 % and 1.0 %. The size distribution of solid particles was obtained by sieving of sodium carbonate on a Retzsch set of sieves, mesh between 0 - 1000 µm. Each sample was sulfated in a gas-air mixture containing 0.5 % and 1.0 % (vol.) SO_2, at constant flow rate of $G_v = 560$ l/h and $G_v = 800$ l/h.

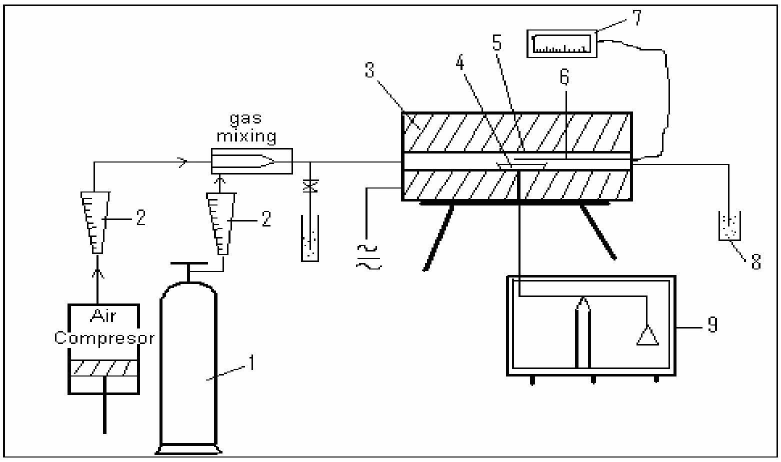

Figure 7. Experimental equipment.

1 - Gas cylinder with SO_2; 2 - Gas flow meter; 3 - Electric Furnace; 4 - Nacelle with solid sample; 5 - Tubular reactor; 6 - Thermocouple; 7 - Temperature controller; 8 - Absorbing vessel for gas; 9 - Thermo balance.

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