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EXPERIMENTAL STUDY OF SULFUR DIOXIDE ABSORPTION INTO CALCIUM CARBONATE SUSPENSIONS

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ABSTRACT. This paper presents the experimental data obtained in absorption process of SO_2 into limestone suspensions. The absorption experiments have been performed in a 0.75 L reactor, fitted with mechanical stirring, at temperature of 293, 303 and 313 K. The consistency of limestone slurry expressed as solid-liquid ratio was: R1=1/30; R2= 1/15; R3=1/10 and R4= 1/7.5. The influence of the limestone content in the initial slurry and the operating temperatures on the total absorption capacity were determined and analyzed. The obtained results, absorption capacity between 0.49 - 2.14 mol SO_2/L slurry, are comparable with those reported by other authors.

Keywords: *absorption, wet desulphurization, calcium carbonate slurry*

INTRODUCTION

Atmospheric contamination with high quantities of noxes (CO_2, SO_2, SO_3, NO_x, HF, HCl, etc.) from the coal-fired power plants is a significant problem. This can lead to negative environmental impacts such as acidification of soil and global warming. Particularly notable are the programs on flue gas desulphurization (FGD) technologies that have been ongoing in a number of countries for several years [1-4].

Emissions of sulfur dioxide into the atmosphere have increased with industrial development and many countries have therefore adopted strict regulations regarding SO_2 emissions from fossil fired boilers which are one of the important sources of SO_2 emissions. The removal of SO_2 for various industrial sources has gained a considerable attention in the last years. Many processes for flue gas desulphurization (FGD) have been developed for reducing SO_2 emissions and were grouped into the following three major categories: wet, dry and semi-dry processes [1].

The dominating procedures employed to desulphurization for exhaust gases is based on wet scrubbing, especially slurry scrubbing [1,2]. In the last few decades, wet scrubbing with lime, limestone or dolomite slurry is the most applied method due to its high degree of SO_2 removal, low cost and widespread availability [3-7].

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The main factors that favor the use of limestone and dolomite slurry in the FGD processes are:

- limestone and dolomite are abundant minerals;
- the specific properties of the aqueous slurries facilitate an increase the absorption rate;
- the product of SO_2 removal is gypsum that is stable and reusable.

The major disadvantage of this limestone-gyp desulphurization process is the problem concerning the big amount of calcium sulfate obtained.

The aim of the present study is to investigate the absorption process of SO_2 into the natural limestone slurries containing calcium carbonate from Sănduleşti-Turda. The effect of temperature and the sorbets content of slurry on the total absorption capacities were determined.

RESULTS AND DISCUSSIONS

The overall reaction for FGD process can be written as:

$$SO_{2[g]} + CaCO_{3[s]} + 2H_2O_{[l]} + 0.5O_2 \rightarrow CaSO_4 \cdot 2H_2O_{[s]} + CO_{2[g]} \quad (1)$$

A simplified representation of mass transfer and reaction steps model for the absorption process of sulfur dioxide in calcium carbonate slurry is shown in figure 1.

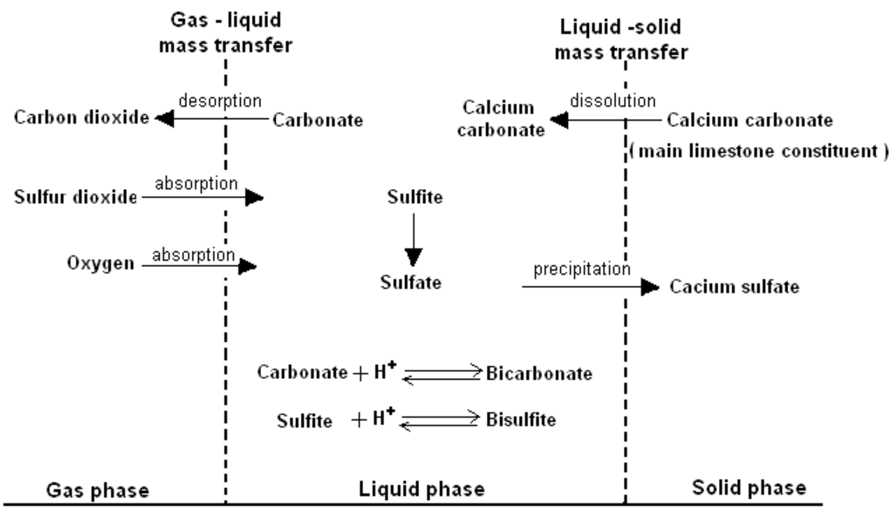

Figure 1. Schematic illustration of mass transfer and reaction steps for sulfur dioxide absorption in calcium carbonate slurry

Regarding the SO_2 absorption mechanism into calcium carbonate slurry, in the oxygen presence, the following processes can be considered [1, 3]:

– Transfer of SO_2 trough the gas-film near the gas-liquid interface:

$$N_{SO2} = k_g (p_{SO2} - p^*_{SO2}) \quad (2)$$

– SO_2 absorption in the liquid phase:

$$SO_{2[g]} \leftrightarrow SO_{2[aq]} \quad (3)$$

$$SO_{2[aq]} + H_2O \leftrightarrow H_2SO_3 \quad (4)$$

$$H_2SO_3 \leftrightarrow H^+ + HSO_3^- \quad (5)$$

$$HSO_3^- \leftrightarrow H^+ + SO_3^{2-} \quad (6)$$

A number of chemical reactions take place in the liquid phase. SO_2 is absorbed in the water and forms sulfite and sulfate ions.

– Calcium carbonate dissolution:

$$CaCO_{3[s]} \leftrightarrow CaCO_{3[aq]} \quad (7)$$

$$CaCO_{3[aq]} \leftrightarrow Ca^{2+} + CO_3^{2-} \quad (8)$$

$$CO_3^{2-} + H^+ \leftrightarrow HCO_3^- \quad (9)$$

Limestone dissolves into the slurry to form carbonate and bicarbonate species. The carbonate ion can react with the hydroxyl ion to increase the liquid pH.

– Oxidation:

$$HSO_3^- + 0.5O_2 \leftrightarrow SO_4^{2-} + H^+ \quad (10)$$

– Precipitation:

$$Ca^{2+} + SO_4^{2-} + 2H_2O \leftrightarrow CaSO_4 \cdot 2H_2O \quad (11)$$

$$Ca^{2+} + SO_3^{2-} + 0.5H_2O \leftrightarrow CaSO_3 \cdot 1/2H_2O \quad (12)$$

where: *g* is the gas phase, *s* - the solid phase, *aq* - the aqueous phase, HSO_3^- - the bisulfite ion, SO_3^{2-} - the sulfite ion, SO_4^{2-} - the sulfate ion, O_2 - oxygen, H^+ - the hydrogen ion and SO_2 - sulfur dioxide.

The dissolved calcium ions are free to react with the sulfite and sulfate ions to produce calcium sulfite and calcium sulfate. These materials begin to precipitate out of solution when they exceed their solubility limits.

The main factors influencing the dissolution of the calcium carbonate are: the size and origin of the limestone, the pH of liquid phase and the sulfite ions concentration in the suspension. Flue gas desulphurization process is dependent on the solid used in the preparation of absorbent suspension. It is very important to know how natural materials can interact with sulfur dioxide dissolved in suspension.

Chemical composition of the limestone used in the present study was determined by classical analytical methods and presented in table 1.

Experimental kinetic curves obtained at the sulfur dioxide absorption in calcium carbonate slurries with different ratio solid/liquid are shown in figures 2-9.

Table 1. Composition of limestone

Carbonate source	Composition			
	$CaCO_3$ [%]	Fe_2O_3 [%]	Al_2O_3 [%]	SiO_2 [%]
Limestone Săndulești - Turda	97	1,8	0,88	0,3

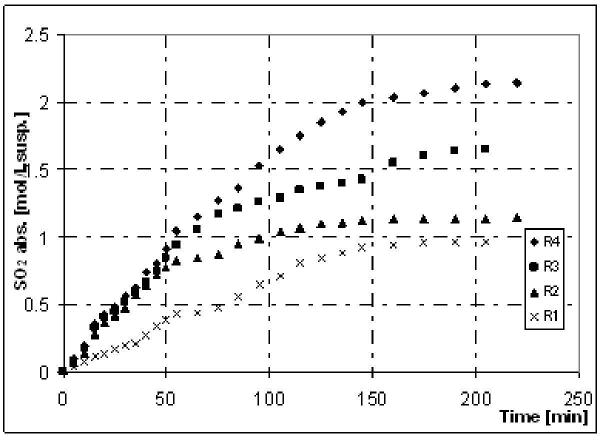

Figure 2. Kinetic curves of sulfur dioxide absorption in calcium carbonate suspensions with different concentration at T=293 K

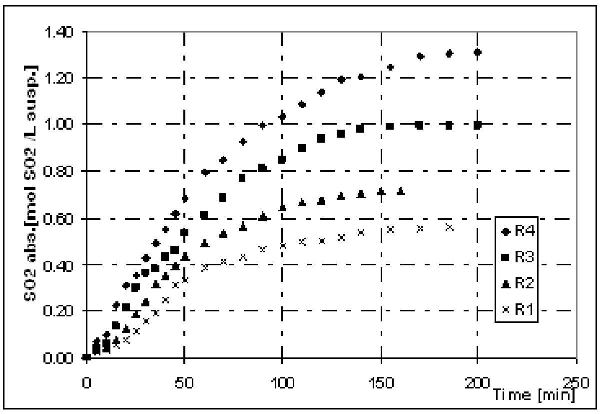

Figure 3. Kinetic curves of sulfur dioxide absorption in calcium carbonate suspensions with different concentration at T=303 K

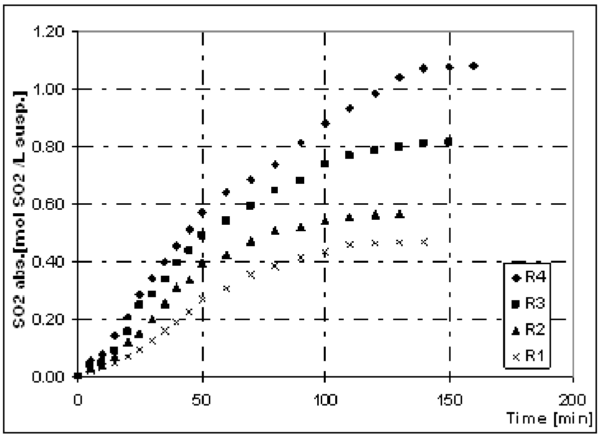

Figure 4. Kinetic curves of sulfur dioxide absorption in calcium carbonate suspensions with different concentration at T=313 K

From the plots shown in figures 2-4 it can be observed that the increase of the calcium carbonate content in the suspension, as refereed solid/liquid ration R, increases the sulfur dioxide absorption capacity. Experimental measurements of absorption process were made at four different rations: R: 1/30; 1/15; 1/10; and 1/7.5.

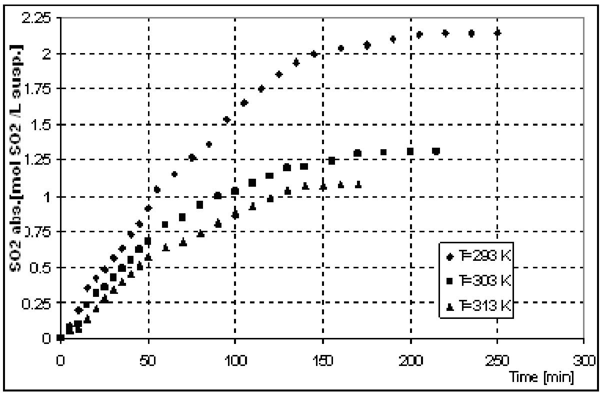

Figure 5. Temperature influence over sulfur dioxide absorption in calcium carbonate suspensions at R4

The absorption capacity increases from 0.9 mol SO_2/L slurry for ratio R1 = 1/30 to 2.14 mol SO_2/L slurry for R4 = 1/7.5, at a constant temperature of 293 K. The increase of absorption capacity with the increase of carbonate slurry content could be explained due to the higher concentration of Ca^{2+} in the slurries that leads to an increase in the internal Ca/S ratio and in the solid-liquid interface area.

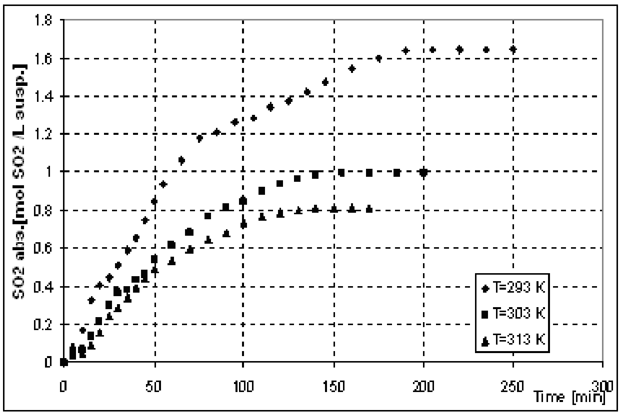

Figure 6. Temperature influence over sulfur dioxide absorption in calcium carbonate suspensions at R3

From figures 5-8 it can be observed that the influence of temperature is significantly on the total absorption capacity. With the increase of temperature, the solubility of SO_2 in water decreases, and as result the absorption capacity decreases. In the same time the solubility of $CaCO_3$ increase only slightly with the temperature increase.

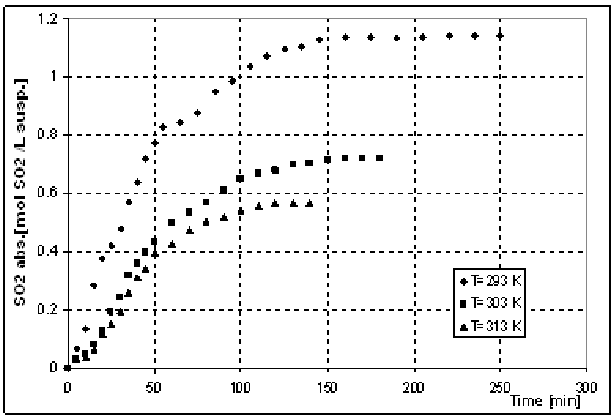

Figure 7. Temperature influence over sulfur dioxide absorption in calcium carbonate suspensions at R2

Thus, at the highest content of carbonate slurry, R4 = 1/7. 5, the total absorption capacity is reduced from 2.14 mol SO_2/L slurry, at a temperature of 293 K, to 1.1 mol SO_2/L slurry, at 313 K.

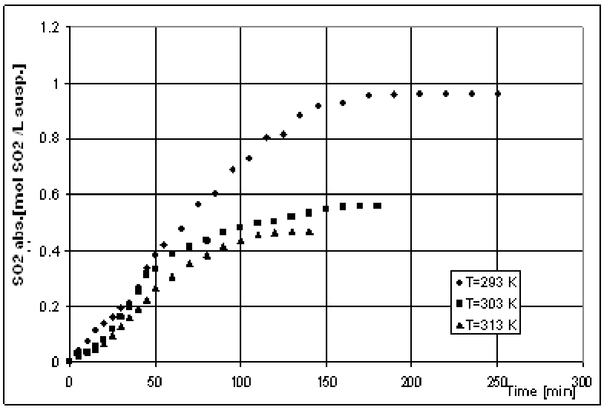

Figure 8. Temperature influence over sulfur dioxide absorption in calcium carbonate suspensions at R1

By diluted suspensions, R1 = 1/30, the absorption capacity reduces from 0.9 mol SO_2/L slurry, at 293 K, to 0.46 mol SO_2/L suspension, at 313 K.

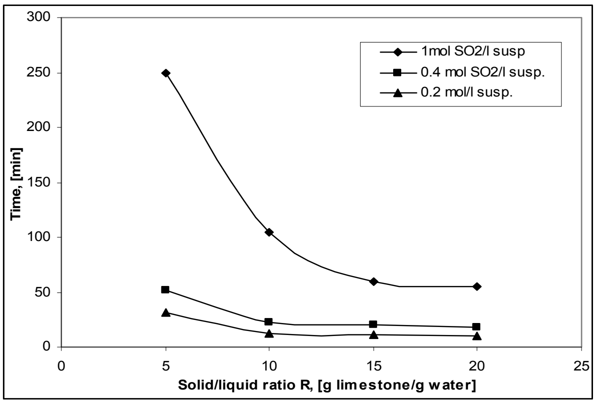

Figure 9. Influence of the solid/liquid ratio over the time necessary to achieve the sulfur dioxide concentration in reaction mass at T=273 K

From the figure 9 it can be observed that the increase of solid/liquid ration in the suspension, diminishes substantially the time needed to achieve the same concentration of sulfur dioxide in the reaction mass.

The differences between the total absorption capacities, considering the slurry content or/and temperature, imposes the setting of the macrokinetic mechanism and the developing of the mathematical model witch can describe the sulfur dioxide absorption process in calcium carbonate slurries.

EXPERIMENTAL SETUP

The experiments were carried out on a laboratory equipment. A schematic diagram of the experimental setup is shown in figure 2, with the essential element the absorber, a 0.75 L glass reactor with mechanical stirring. The supply system for sulfur dioxide and final gas neutralization system complet the experimentally setup.

To eliminate the possibility that the sulfur dioxide transfer through the gas phase becomes a limitative step of rate in the overall process, experimental measurements were made with pure sulfur dioxide from SO_2 cylinder. Stirring the suspension was adjusted so that the separating contact surface between aqueous suspension carbonate and gas phase was smooth, without waves generated by the moving slurry. Interface surface remained flat and steady. The gas which was not absorbed was continuously exhausted and neutralized in the hydroxide solution. The temperature has been controlled using an ultrathermostat. The absorption experiments have been performed at 293, 303 and 313 K with a constant rotation of the mechanical stirring (100 rot/min).

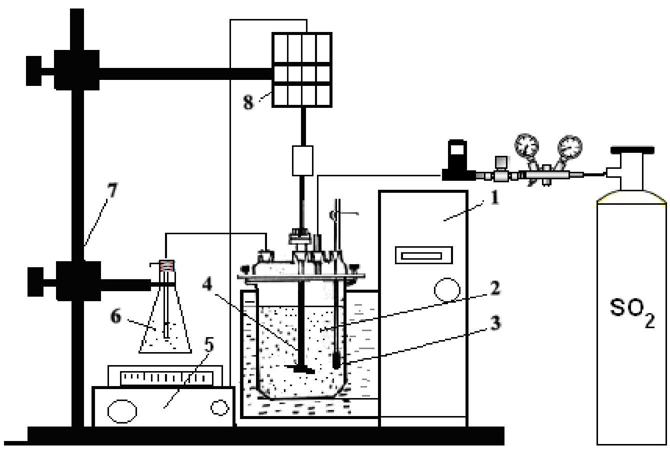

Figure 10. Schematic diagram of the experimental set-up
1 - ultrathermostat, 2 - absorber reactor with stirring, 3 - thermometer, 4 - stirrer, 5 - tachometer, 6 - vessel gas neutralization final, 7 - fixing support, 8 - mixer motor

Calcium carbonate powder with particle size d_p<0.25 mm was mixed in distilled water: 5, 10, 15 and 20 g $CaCO_3$/150 g water which corresponds to the ratio: R_1=1/30; R_2= 1/15; R_3=1/10 and R_4= 1/7.5.

The evolution of absorption process has been expressed by variation of the content of sulfur dioxide absorbed into the reaction volume, using iodometrical method.

CONCLUSIONS

New experimental data were obtained for the total absorption capacity of SO_2 in four limestone suspensions with different consistency.

The present study has been performed with limestone having a content of 97% $CaCO_3$, chemical reactivity being the main parameter to validate or not the use of the suspension carbonate in this process.

The experimental results demonstrate that the absorption capacity is influenced strongly by the slurry consistency. The total absorption capacity increases from 0.9 mol SO_2 /L slurry for ratio R1 = 1/30 to 2.14 mol SO_2 /L slurry for R4 = 1/7.5, at a temperature of 293 K.

The total absorption capacity is significantly influenced by temperature. With increase of temperature from 293 K to 313 K, the solubility of SO_2 decreases and the final absorption capacity in suspension is reduced to half.

The experimental research shows that the natural limestone having more than 97% $CaCO_3$ can be successfully used in the FGD processes.

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