

# Experimental Examination of Sulfur Dioxide Dry Removal from a Mixture of Gases by Calcium Oxide, Calcium Carbonate and Dolomite

**Đurić, Slavko\*<sup>†</sup>; Brankov, Saša**

*Faculty of Technical Sciences, 6, Trg Dositeja Obradovića, Novi Sad, SERBIA*

**Stanojević, Petko**

*Railways of Republika Srpska, 71, Svetog Save, Doboj, BOSNIA AND HERZEGOVINA*

**Božičković, Ranko**

*Faculty of Transport and Technical Sciences, 52, Vojvode Mišića, Doboj, BOSNIA AND HERZEGOVINA*

**ABSTRACT:** This paper refers to an experiment of  $SO_2$  absorption to the three different sorbents: calcium-oxide ( $CaO$ ), calcium-carbonate ( $CaCO_3$ ) and dolomite ( $CaMg(CO_3)_2$ ). In the reactor under the condition of oxidation atmosphere with the mass of sorbent (sample) of 100 g with fractional composition of 500-700 $\mu$ m, the gas temperature varied from 200°C and 400°C. The examinations indicated that the highest degree of sorbent utilization of 14 % was determined for dolomite ( $CaMg(CO_3)_2$ ) and the binding degree of  $SO_2$  from 65-80% and the lowest for calcium oxide ( $CaO$ ) of 4% and the binding degree of  $SO_2$  from 34-60% at the reaction temperature of 200°C. When the reaction temperature is 400°C the degree of sorbent utilization is a bit lower. The achieved results indicate the injection capability of powdered sorbents  $CaMg(CO_3)_2$ ,  $CaCO_3$  and  $CaO$  in the areas of lower temperatures as it is the convective part of the boiler or furnace flue of the thermo power plant.

**KEY WORDS:** Sorbent, Absorption degree of  $SO_2$ , Reaction temperature, Particle diameter.

## INTRODUCTION

During dry Flue Gas Desulfurisation (FGD) processes the dry particles of the reagent are injected into the stream of gases, which absorb  $SO_2$  through chemical reactions. Most often used reagents are calcium compounds  $CaCO_3$ ,  $CaO$  or  $Ca(OH)_2$ . The industrial examinations show that the binding degree of  $SO_2$  from

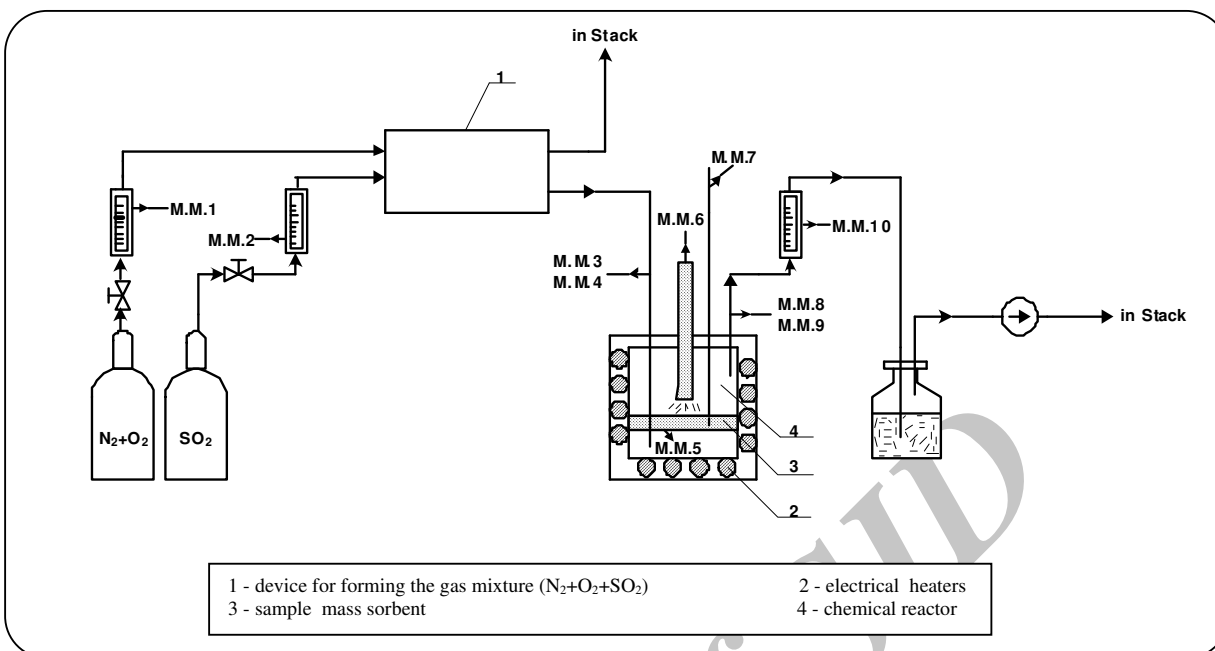
flue gases to the sorbent particles is usually function of stochiometric relation of calcium share in injected sorbent and sulfur share from coal and it is in a wide range of 30-70% utilizing  $CaCO_3$ , 35-45% utilizing  $Ca(OH)_2$ , 25-60% utilizing  $CaO$ , 60-70%, utilizing dolomite ( $CaMg(CO_3)_2$ ) in stochiometric relations  $Ca/S= 1-5$ . [1-3]. Theoretical

\* To whom correspondence should be addressed.

+ E-mail: djuricnslavko@yahoo.de

1021-9986/12/2/

7/\$/2.70



**Fig. 1: The scheme of experimental facility (and measuring points) for  $SO_2$  separation from the gas mixture ( $N_2+O_2$ ) via dry processes by sorbent.**

and experimental researches of binding of  $SO_2$  to the sorbent particles on the base of calcium compound, confirmed the practical utilization of dry process of flue gases refinement from  $SO_2$  [4-14].

A significant number of theoretical and experimental studies examines indirect and direct sulfatization [4,10,11]. During the indirect sulfatization researchers conclude that the process of formation  $CaCO_4$  is enabled by formation of intermediate product  $CaSO_3$  which depending on the reaction temperature and  $O_2$  volume ratio in flue gas oxidizes in  $CaSO_4$  or  $CaS$ . According to some other researchers two mechanisms of  $CaSO_4$  synthesis are recommended. The first mechanism includes the formation of intermediate product  $CaSO_3$ , and the second mechanism the formation of  $SO_3$ . For the both mechanisms the reaction temperatures of around  $850\text{ }^\circ\text{C}$  are sufficient, but reaction temperatures over  $850\text{ }^\circ\text{C}$  favor the formation of  $CaSO_4$  only for the second mechanism.

The complex interaction of various resistances (diffusion over film gas, diffusion in the product layer and surface reaction of  $SO_2$ ), is the main cause of inconsistency between mechanisms and results which were given by various researchers.

## EXPERIMENTAL SECTION

### *The scheme and description of experimental facility for $SO_2$ separation from a mixture of gases*

The scheme of laboratory facility for  $SO_2$  separation from a mixture of gases in dry processes with lime ( $CaO$ ), limestone  $CaCO_3$ ), dolomite  $CaMg(CO_3)_2$  and the list of Measuring Points (M.P.) are shown in Fig. 1, and in Fig. 2 the schemes of thermal furnace and reactor container for  $SO_2$  separation are shown.

During the experiment of  $SO_2$  absorption process, sorbent mass (sample) in the reactor was 100 g and the sorbent particle size was  $500\text{-}700\text{ }\mu\text{m}$ . The heating process of the reactor and sorbent inside the reactor is achieved by electrical heaters. For each experiment the reaction temperature was adjusted to approximately firstly  $200\text{ }^\circ\text{C}$ , and secondly  $400\text{ }^\circ\text{C}$ . When the desired temperature was reached ( $\approx 200\text{ }^\circ\text{C}$  i.e.  $\approx 400\text{ }^\circ\text{C}$ ), the sorbent is mechanically injected into the reactor using the dispenser. Then the gas mixture  $N_2+O_2+SO_2$  is introduced into a reactor by vacuum pump in order to separate  $SO_2$ . A gas analyzer was continually used in measuring the concentration of  $SO_2$  and  $O_2$  in the inlet and gas outlet until the measured concentration

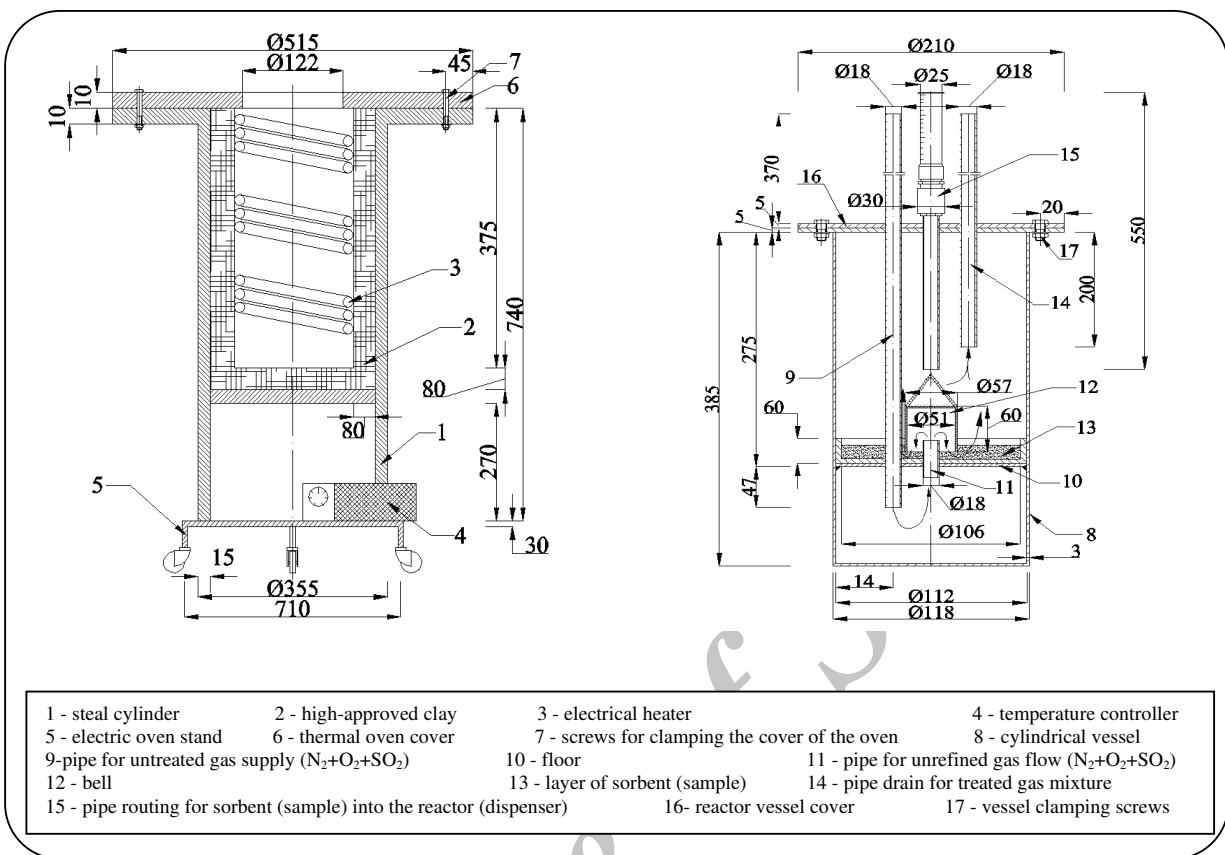


Fig. 2: The scheme of thermal furnace a) and reactor container b).

of SO<sub>2</sub> is stabilized in the gas outlet. The experiments last up to 50 min. The speed of the gas which flows through the reactor for SO<sub>2</sub> separation was between 0.13-0.14 m/s. The gas velocity provides constant sorbent mass in the reactor. The sorbent mass was measured before and after the process of SO<sub>2</sub> separation from the gas mixture. During the experiment the gas value flow rate through the reactor in order to separate SO<sub>2</sub> was between 1.97-2.03 m<sup>3</sup>/h.

During the experimental process of SO<sub>2</sub> separation from the gas mixture, the following measuring instruments were used:

#### Measuring the temperature of the sample (sorbent) layer in the reactor

Instrument: Thermo element Ni-Cr-Ni with digital gauges Fluke 54 -N series

Measurement range: -200-300 °C

Measuring error: ±0.2%

#### Measuring the volume share of O<sub>2</sub> and concentration of SO<sub>2</sub> at the entrance and exit of the reactor

Instrument: Gas analyzer Testo 350 XL

Measurement range: 0-25%

0÷5000 ppm SO<sub>2</sub>

Measuring error: for SO<sub>2</sub> je ±5% for concentration range 100-2000 ppm and ±10%for concentration range 2001-5000 ppm ,

Measuring error: for O<sub>2</sub> is ±0.8% for the range of 0-25%

#### Measuring the sample (sorbent) mass

Instrument: Platform scale EMB 500-1

Measurement range: 0-500g

Measuring error: ±0.001g

#### Measuring the air volume flow

Instrument: Rotametar RAGK

Measurement range: 0.2-6300 l/h

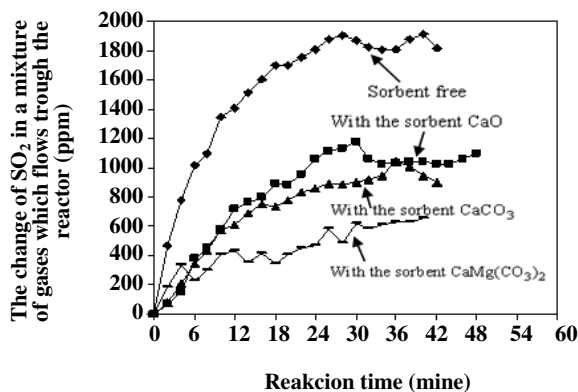


Fig. 3: The change of  $\text{SO}_2$  concentration in a mixture of gases which flows through the reactor without sorbent and adding sorbent depending on the reaction time ( $m(\text{sorbent}) = 100 \text{ g}$ ,  $t = 200 \text{ }^\circ\text{C}$ ,  $d_p = 600 \text{ }\mu\text{m}$ ).

Measuring error:  $\pm 4\%$

#### Measuring the $\text{SO}_2$ volume flow

Instrument: Rotametar RAGK  
Measurement range: 0.2-6300 l/h  
Measuring error:  $\pm 4\%$

#### Measuring the gas mixture volume flow

Instrument: Rotametar RAGK  
Measurement range: 0.2-6300 l/h  
Measuring error:  $\pm 4\%$

## RESULTS AND DISCUSSION

In Fig. 3 and 4 the  $\text{SO}_2$  concentration change in the flue gas which flows through the reactor for  $\text{SO}_2$  is shown, without the sorbent and adding the sorbent depending on the reaction time (time of flue gas flow through the reactor) and reaction temperature. As it was expected, the concentration of  $\text{SO}_2$  in the outlet gas is the lowest for  $\text{CaMg}(\text{CO}_3)_2$  sorbent particles.

Being at reaction temperature of approximately  $200 \text{ }^\circ\text{C}$  and mean diameter of sorbent particles  $\approx 600 \text{ }\mu\text{m}$ , the degree of  $\text{SO}_2$  absorption to the sample particles occurs in the interval of 65-80% with sorbent  $\text{CaMg}(\text{CO}_3)_2$ , 42-66% with sorbent  $\text{CaCO}_3$  and 34-60% with sorbent  $\text{CaO}$  (Fig. 5).

Increasing the reaction temperature from  $200 \text{ }^\circ\text{C}$  to  $400 \text{ }^\circ\text{C}$  the degree of  $\text{SO}_2$  absorption to sorbent particles has no greater influence and it is in the interval of

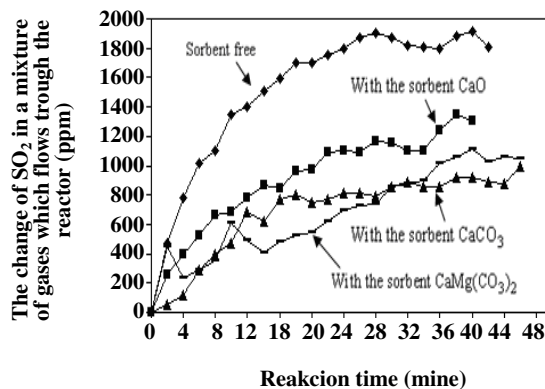


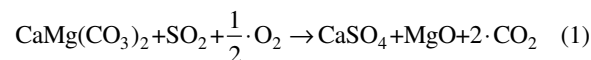
Fig. 4: The change of  $\text{SO}_2$  in a mixture of gases which flows through the reactor without sorbent and adding sorbent depending on the reaction time ( $m(\text{sorbent}) = 100 \text{ g}$ ,  $t = 400 \text{ }^\circ\text{C}$ ,  $d_p = 600 \text{ }\mu\text{m}$ ).

37-78% by  $\text{CaMg}(\text{CO}_3)_2$  sorbent utilization, 45-78% by  $\text{CaCO}_3$  sorbent utilization and 19-60% by  $\text{CaO}$  sorbent utilization (Fig. 6).

During the first 6 min of the process examination of  $\text{SO}_2$  absorption to sorbent particles, all sorbent samples quickly absorbed  $\text{SO}_2$  at the studied reaction temperatures. After 6 minutes  $\text{SO}_2$  absorption decreases, starts to stabilize and takes an approximately constant value (Fig. 5 and 6).

During the research, the value of stoichiometric relation of calcium in sorbent and sulfur in flue gases ( $\text{Ca}/\text{S}$ ) varied and it was above 5.

According to the data from the literature [4,8,11] following mechanisms of direct sulfatization can be recommended:



During the direct sulfatization of  $\text{CaMg}(\text{CO}_3)_2$ ,  $\text{CaCO}_3$  and  $\text{CaO}$  (reactions (1) - (3)) the degree of sorbent utilization can be determined with the expression:

$$\eta_{\text{sorbent}} = \frac{M_{\text{sorbent}}}{M_{\text{SO}_2}} \cdot \frac{m_{\text{SO}_2}}{m(\text{sorbent})} \cdot \eta_{\text{SO}_2}, (\%) \quad (4)$$

where:

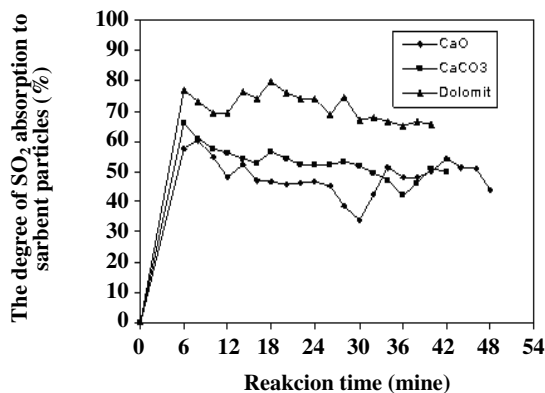


Fig. 5: The degree of  $SO_2$  absorption to sorbent particles ( $m(\text{sorbent}) = 100 \text{ g}$ ,  $t = 200 \text{ }^\circ\text{C}$ ,  $dp = 600 \text{ }\mu\text{m}$ ).

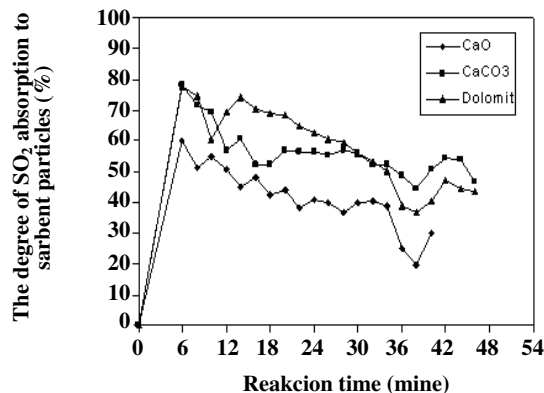


Fig. 6: The degree of  $SO_2$  absorption to sorbent particles ( $m(\text{sorbent}) = 100 \text{ g}$ ,  $t = 400 \text{ }^\circ\text{C}$ ,  $dp = 600 \text{ }\mu\text{m}$ ).

$$M_{\text{sorbent}} - \text{sorbent molar mass, } \left( \frac{\text{g}}{\text{mol}} \right),$$

$$M_{\text{SO}_2} - \text{SO}_2 \text{ molar mass } \left( \frac{\text{g}}{\text{mol}} \right),$$

$m_{\text{SO}_2}$  - sulfur dioxide mass in flue gases at the entrance of the reactor (g),

$M(\text{sorbent})$  - sorbent mass (sample), (g),

$$\eta_{\text{SO}_2} = \frac{\varphi_{\text{SO}_2, \text{in}} - \varphi_{\text{SO}_2, \text{out}}}{\varphi_{\text{SO}_2, \text{in}}} \cdot 100, (\%), - \text{ the degree of}$$

$SO_2$  absorption to sorbent particles

$\varphi_{\text{SO}_2, \text{in}}$  -  $SO_2$  volume ratio in flue gas at the entrance of the reactor, (ppm),

$\varphi_{\text{SO}_2, \text{out}}$  -  $SO_2$  -  $SO_2$  volume ratio in flue gas at the exiting of the reactor, (ppm).

Using the numerical data gained by measurements (Fig. 3-6) and using the Eq. (4), the achieved values of the degree of sorbent utilization at the reaction temperature of  $200 \text{ }^\circ\text{C}$  are low and are up to 14 % for sorbent dolomite, 6 % for sorbent  $CaCO_3$  and 4 % for sorbent  $CaO$ . At the reaction temperature of  $400 \text{ }^\circ\text{C}$  the degree of sorbent utilization is slightly lower. The low degree of sorbent utilization is a consequence of consumption of greater mass of sorbent than the mass of  $SO_2$  in flue gases entering the reactor. (Fig. 7 and 8).

## CONCLUSIONS

The aim of the  $SO_2$  separation experiment from a mixture of flue gases, which is demonstrated in this paper, was to determine the dependability of  $SO_2$

separation degree from flue gas using different sorbents: dolomite ( $CaMg(CO_3)_2$ ), calcium carbonate ( $CaCO_3$ ) and calcium oxide ( $CaO$ ), the influence of reaction temperature in the reactor and degree determination of sorbent utilization. Because of the previously said the temperatures varied from 200 and  $400 \text{ }^\circ\text{C}$ . The sample mass within the reactor was 100 g and the mean diameter of sorbent particles was  $\approx 600 \text{ }\mu\text{m}$ . During the examination the following conclusions were made:

(1) It was acknowledged that the increase of the reaction temperature from 200 to  $400 \text{ }^\circ\text{C}$  has no greater impact on  $SO_2$  absorption to  $CaMg(CO_3)_2$  and  $CaO$  sorbent particles. When the reaction temperature is somewhere around  $200 \text{ }^\circ\text{C}$  and the mean diameter of sorbent particles is  $\approx 600 \text{ }\mu\text{m}$ , the degree of  $SO_2$  absorption is in the interval of 65-80% by  $CaMg(CO_3)_2$  sorbent utilization, 42-66% by  $CaCO_3$  sorbent utilization and 34-60% by  $CaO$  sorbent utilization. When the reaction temperature is somewhere around  $400 \text{ }^\circ\text{C}$  and it has the same diameter of sorbent particles, the degree of  $SO_2$  absorption is in the interval of 37-78% by  $CaMg(CO_3)_2$  sorbent utilization, 45-78% by  $CaCO_3$  sorbent utilization and 19-60% by  $CaO$  sorbent utilization.

(2) During the first 6 min of examination of  $SO_2$  absorption process to the sorbent particles, all sorbent samples quickly absorbed  $SO_2$  at the studied reaction temperatures. This leads to a conclusion that the first 6 min of the process is completely controlled by the chemical reaction on the solid surface of the sorbent. After 6 min, the  $SO_2$  absorption starts to stabilize and takes an approximate constant value (Fig. 5 and 6) and

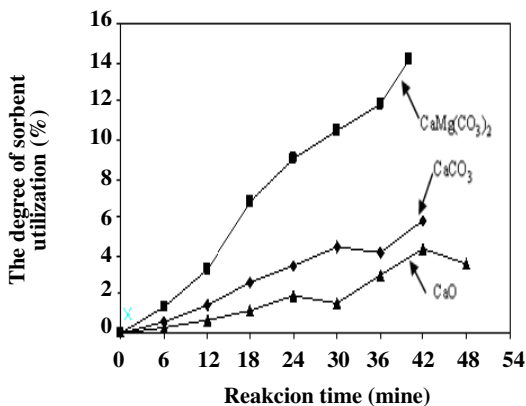


Fig. 7: The degree of sorbent (sample) utilization depending on the time of flue gas flow through the reactor for SO<sub>2</sub> separation ( $m(\text{sorbent}) = 100 \text{ g}$ ,  $t = 200 \text{ }^\circ\text{C}$ ,  $d_p = 600 \text{ }\mu\text{m}$ ).

leads to a conclusion that the diffusion resistance becomes significant due the thickness of product layer.

(3) Low degree of sorbent utilization is determined: 14 % by dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) utilization, 6 % by calcium carbonate (CaCO<sub>3</sub>) utilization and 4 % by calcium oxide (CaO) utilization at the reaction temperature somewhere around 200 °C. When the reaction temperature is somewhere around 400 °C only higher degree of sorbent utilization for calcium carbonate CaCO<sub>3</sub> is marked and it is of 7 %. Low degree of sorbent utilization is due the utilization of great mass of sorbents (samples) in relation to the SO<sub>2</sub> mass entering the reactor.

The attained results of the experiment described in this paper indicate the capability of injecting powdered sorbents CaMg(CO<sub>3</sub>)<sub>2</sub>, CaCO<sub>3</sub> and CaO in the areas with lower temperatures as it is the convective part of the furnace and the flue canal of thermal power plant and which aim was to reduce the SO<sub>2</sub> emission in flue gas. The achieved results can also represent the starting point in the phase of equipment designing for FGD as well as the equipment for separation the solid particle, whose practical utilization would improve the energetic and ecological efficiency of thermal-energetic power plants.

#### Nomenclature

$d_p$	Sorbent particle diameter, $\mu\text{m}$
$m$	The mass of sorbent, g
$t$	Reaction temperature, $^\circ\text{C}$
$\varphi_{\text{SO}_2, \text{in}}$	Gas flue SO <sub>2</sub> volume ratio in flue gas at the entrance of the reactor, ppm

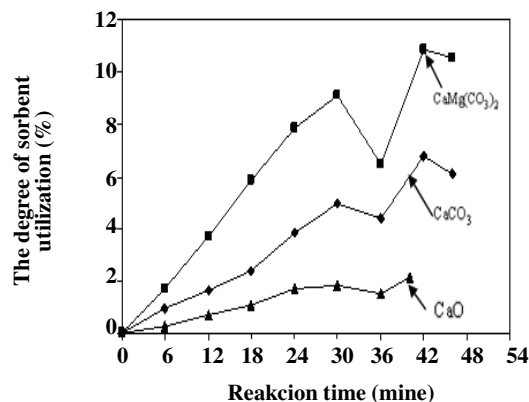


Fig. 8: The degree of sorbent (sample) utilization depending on the time of flue gas flow through the reactor for SO<sub>2</sub> separation ( $m(\text{sorbent}) = 100 \text{ g}$ ,  $t = 400 \text{ }^\circ\text{C}$ ,  $d_p = 600 \text{ }\mu\text{m}$ ).

$\varphi_{\text{SO}_2, \text{out}}$	Gas flue SO <sub>2</sub> volume ratio in flue gas at the outlet of the reactor, ppm
$\eta_{\text{SO}_2}$	Retention degree of SO <sub>2</sub> for particle sorbent, %
$\eta_{\text{sorbent}}$	Exploitation degree, %

Received : Aug. 19, 2010 ; Accepted : July 4, 2011

#### REFERENCES

- [1] LIFAC Sorbent Injection Desulfurization Demonstration Project, U.S. Department of Energy, Assistant Secretary for Fossil Energy, Washington , DC 20585, Project Performance Summary Clean Coal Technology Demonstration Program, 6-7, (2004).
- [2] Sorbent Injection SO<sub>x</sub> Control Combustion Optimization Generation Optimization, U.S.- China NO<sub>x</sub> and SO<sub>2</sub> Control Workshops Shenyang, Liaoning Province, P.R. China 3-7 November, (2003).
- [3] Klingspor J., Cope D.R., FDG handbook, "Flue Gas Desulphurisation Systems", IEA Coal Research, London, (1987).
- [4] Hallaj R., Nikazar M., Dabir B., Thermogravimetric Study and Modeling of Direct Sulfation of Limestone by Sulfur Dioxide, *Chem. Eng.*, **12**, p. 566 (2004).
- [5] Nikazar M., Hallaj R., Rahmani M., Dabir B., Hajaligol M.R., Direct Sulfation of Limestone by Sulfur Dioxide, *Pakistan J. App. Sci.*, **2**, p. 158 (2002).

- [6] Manović V., Anthony J.E., Sequential SO<sub>2</sub>/CO<sub>2</sub> Capture Enhanced Bysteam Reactivation of a CaO - Based Sorbent, *Fuel*, **87**, p. 1564 (2008).
- [7] Tambe S., Gauri K.L., Li S., Cobourn G., Kinetic Study of SO<sub>2</sub> Reaction with Dolomite, *Environ. Sci. Technol.*, **25**, p. 2071 (1991).
- [8] Mahesh V.I., Himanshu G., Bartev B.S., Liang S.F., Multicyclic Study on the Simultaneous Carbonation and Sulfation of High-Reactivity CaO, *Ind. Eng. Chem.*, **43**, p. 3939 (2004).
- [9] Stanmore, B. R., Gilot, P., Review - Calcination and Carbonation of Limestone During Thermal Cycling for CO<sub>2</sub> Sequestration, *Fuel Processing Technology*, **86**, p. 1707 (2005).
- [10] Sima A., Rouein H., Manouchehr N., Study and Kinetic Modeling of the Direct Sulfation of Iranian Limestones by Sulfur Dioxide at High CO<sub>2</sub> Partial Pressures, *Iranian Journal of Chemistry and Chemical Engineering*, **27**, p. 45 (2008).
- [11] Fuertes A.B., Velasco G., Fuente E., Alvarez T., Study of the Direct Sulfation of Limestone Particles at High CO<sub>2</sub> Partial Pressures, *Fuel Processing Technology*, **38**, p. 181 (1994).
- [12] Bruce K.R., Gullett B.K., Beach L.O., Comparative SO<sub>2</sub> Reactivity of CaO Derived From CaCO<sub>3</sub> and Ca(OH)<sub>2</sub>, *AIChE J.*, **35**(1), p. 37 (1989).
- [13] Pisani R., Moraes D., Removal SO<sub>2</sub> with Particles of Dolomite Limestone Powder in a Binary Fluidized Bed Reactor with Bubbling Fluidization, *Braz. J. Chem. Eng.* **20**(2), (2003).
- [14] Yrjas P., Kristiina Iisa K., Hupa M., Comparison of SO<sub>2</sub> Capture Capacities of Limestones and Dolomites under Pressure, *Fuel*, **4**(3), p. 395 (1995).