EXPERIMENTAL EXAMINATION OF SULPHUR DIOXIDE SEPARATION FROM MIXURE OF GAS IN DRY PROCEDURE WITH THE AID OF CALCIUM CARBONATE

by

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This paper refers to an experiment of SO_2 absorption to the particles of sorbent $CaCO_3$. Sample mass was 100 g with fractional composition of 500-700 μm and 1100-1300 μm. During the experiment the temperature varied from 200 to 400 °C. The aim of this experiment is to examine the influence of lower reaction temperature, the size of sorbent particles, and the reaction time to the degree of SO_2 absorption and determining the degree of $CaCO_3$ sorbent utilization. The results show that at the reaction temperature of approximately 200 °C and average diameter of sorbent particles 600 μm, the absorption degree of SO_2 absorption to the particles of sorbent is between 42-66%. Reaching temperature of 400 °C and with the same fractional composition of the sorbent, 600 μm, the absorption degree of SO_2 is slightly higher and it is somewhere around 45-78%. With greater diameters sorbent particle of 1200 μm, absorption degree of SO_2 is a bit lower. The determined degree of utilized sorbent $CaCO_3$ is considerably lower and it reaches up to 6.87%. The acquired results indicate that besides CaO, $Ca(OH)_2$, and $CaMg(CO_3)_2$ it is reasonable to inject the $CaCO_3$ sorbent, in the areas of lower temperatures i. e. in the flue channel of the thermal power plant.

Key words: *absorption degree of SO_2, sorbent $CaCO_3$, reaction temperature, fractional composition, reaction time*

Introduction

During dry flue gas desulphation procedures (FGD) the dry particles of the reagent are injected in the stream of gasses, which absorb SO_2 through chemical reactions. Most often used reagents are calcium compounds $CaCO_3$, CaO or $Ca(OH)_2$. The place where the reagents were injected in the stream of flue gasses (burning place of boiler, convective part of the boiler, and furnace flue of the thermo power plant), the contact time of the gas and hard phase, and the kinetic process of FGD still presents the subject of theoretical and experimental examination. The first extensive industrial examination of injecting the powder of limestone ($CaCO_3$), to the fur-

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nace of the boiler was performed back in 1970-1972 in the thermal power plant Dimitrov in Leipzig, Germany. The examinations indicated that the separation degree of SO_2, from flue gas is mainly a function of Ca/S molar ratio and it varies from 30-70 % at the stoichiometric relation Ca/S = l-5 mol/mol [1]. Further industrial surveys of SO_2 retention, for sorbent $CaCO_3$ confirmed practical applicability of dry limestone procedure of purifying the flue gas of SO_2 [2, 3].

A significant number of both theoretical and experimental studies examines the kinetic reaction system $CaCO_3$-SO_2-O_2 on the higher reaction temperature [4-11].

Two kinds of sulphurization mechanization were proposed [7]. The first mechanism involves the creation of intermediate product $CaSO_3$ and the second mechanism is creation of SO3. For both mechanisms reaction temperatures of about 850 °C are sufficient, but reaction temperatures which are above 850 °C create $CaSO_4$ only for the second mechanism.

Mechanism 1:

$$CaO + SO_2 \rightleftarrows CaSO_3 \tag{1}$$

$$CaSO_3 \ \frac{1}{2}O_2 \rightleftarrows CaSO_4 \tag{2}$$

Mechanism 2:

$$SO_2 \ \frac{1}{2}O_2 \rightleftarrows SO_3 \tag{3}$$

and

$$SO_3 + CaO \rightleftarrows CaSO_4 \tag{4}$$

During the direct sulphation, researchers [9, 10] regulate the reaction:

$$CaCO_3 \ SO_2 \ \frac{1}{2}O_2 \rightleftarrows CaSO_4 \ CO_2 \tag{5}$$

Complex interaction of various reactions (resistances) – diffusion over film gas, diffusion in the product layer, and surface reaction of SO_2 – is the main cause of mechanism inconsistency and the result which were given by various researchers.

Experimental and theoretical research of SO_2 separation process from admixture of gasses

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 procedure with $CaCO_3$ and the list of measuring points (MP) are demonstrated in fig. 1, and in fig. 2 the scheme of thermal furnace and reactor containers for SO_2 separation is shown. The laboratory facility is designed and constructed in the Institute for Energetics, Process Technique and Protection of Environment at the Faculty of Technical Sciences in Novi Sad. During the construction of experimental facility, materials resistant to high temperatures were used as well as materials resistant to corrosion. At the shown measuring points, the following processing variables are measured:

The volume gas flow

MP1   – air flow $N_2 + O_2$, [lh^{-1}]
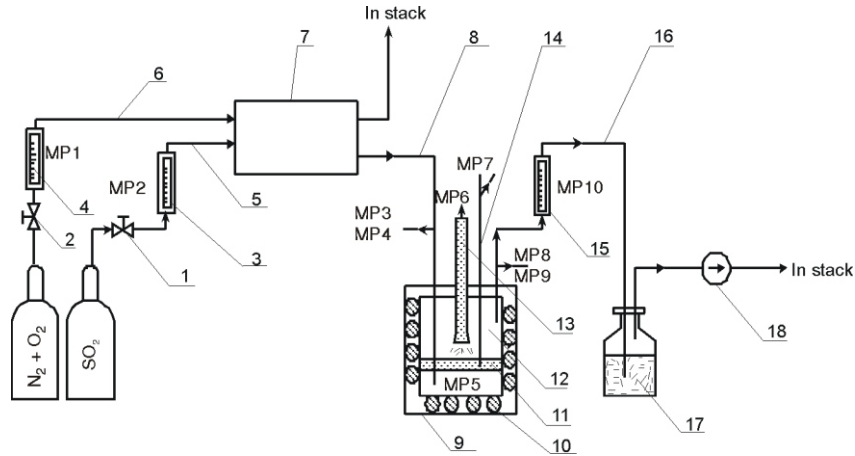MP2   – SO_2 flow, [lh^{-1}]

Figure 1. The scheme of experimental facility (and metering points) for SO$_2$ separation from the gas mixture (N$_2$ + O$_2$) via dry procedure by CaCO$_3$
(1) – valve at the exit of the bottle for SO$_2$, (2) – valve at the exit of the air bottle, (3) – flow meter of SO$_2$, (4) – flow meter of air, (5) – partial stream flow of SO$_2$, (6) – partial air stream flow of air, (7) – device for forming the gas mixture (N$_2$ + O$_2$ + SO$_2$), (8) – partial gas mixture duct at the chemical reactor entrance, (9) – thermal furnace, (10) – electrical heaters, (11) – chemical reactor, (12) – mass sample CaCO$_3$, (13) – dispenser of the CaCO$_3$ mass sample, (14) – vent for measuring the temperature of CaCO$_3$ mass sample, (15) – flow meter of gas mixture at the exit of chemical reactor, (16) – partial gas mixture flow from the chemical reactor, (17) – bottle for absorption of gas mixture (gas washing), (18) – vacuum pump
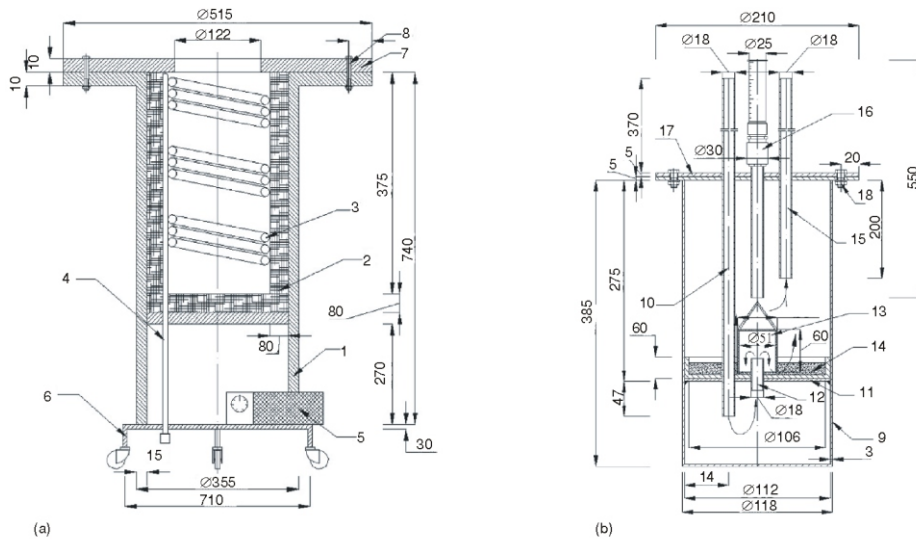

Figure 2. Sheme of the thermal stove (a) and the reactor vessel (b)
(1) – steal cylinder, (2) – high-approved clay, (3) – electrical heater, (4) – electric probe, (5) – temperature controller, (6) – electric stove stand, (7) – thermal oven cover, (8) – screws for clamping the cover of the oven, (9) – cylindrical vessel, (10) – pipe for untreated gas supply (N$_2$ + O$_2$ + SO$_2$), (11) – floor, (12) – pipe for unrefined gas flow (N$_2$ + O$_2$ + SO$_2$), (13) – bell, (14) – layer of sorbent CaCO$_3$, (15) – pipe drain for treated gas mixture, (16) – pipe routing for sorbent into the reactor (dispenser), (17) – reactor vessel cover, (18) – vessel clamping screws

MP10 – flow of the gas mixture $N_2 + O_2 + SO_2$, [lh^{-1}]

Temperature of the CaCO₃ sample

MP7   – temperature of the $CaCO_3$ sample surface, [°C]

Analysis of the gas mixture

MP3   – volume ratio of O_2 at the entrance of the reactor (a unit for SO_2 separation), [%]

MP4   – concentration of SO_2 at the entrance of the reactor (a unit for SO_2 separation), [ppm]

MP8   – volume ratio of O_2 at the exit of the reactor (unit SO_2 separation), [%]

MP9   – concentration of SO_2 at the exit of the reactor (a unit SO_2 separation), [ppm]

The mass of the sample CaCO₃

MP5   – mass of the sorbent $CaCO_3$, [g]

MP6   – dispenser of the sorbent $CaCO_3$, [g].

During the experiment of SO_2 absorption process, sorbent mass (sample) in the reactor was 100 g and sorbent particle size was 500-700 μm and 1100-1300 μm. 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 °C and secondly 400 °C. When the desired temperature was reached (200 °C that is *i. e.*   400 °C), 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 capture SO_2. Gas analyzer is continually used in measuring the concentration of SO_2 and O_2 in the inlet and gas output until the measured concentration of SO_2 is stabilized in the gas output. The experiments last up to 50 minutes. The speed of the gas which flows through the reactor for SO_2 separation is 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_2 separation from the gas mixture. During the experiment the gas flow rate through the reactor in order to separate SO_2 is between 1.97–2.03 m³/h.

During the experimental process of SO_2 separation capturing from the gas mixture, the following instruments were used.

– *Measuring the temperature of the sample surface in the reactor CaCO₃*

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

Measurement range: for 200-300 °C

Measuring error: ±0,2%

– *Measuring the O₂ volume fraction and SO₂ volume share at the entrance and exit of the engine*

Instrument: Gas analyzer Testo 350 XL

Measurement range: 0-25% (O_2), 0-5000 ppm (SO_2)

Measuring error: for SO_2 is ±5% for share range 1000-2000 ppm and ±10% for share range 2001-5000 ppm

Measuring error: for O_2 is ±0,8% for range 0-25%

– *Measuring the sample CaSO₃ mass*

Instrument: Plaform scale EMB 500-1

Measurement range: 0-500 g

Measuring error: ± 0.001 g

– *Measuring the air volume flow*

Instrument: Rotametar RAGK

Measurement range: 0.2-6300 l/h

Measuring error: ±4%

– *Measuring the SO₂ volume flow*

Instrument: Rotametar RAGK
          Measurement range: 0.2-6300 l/h
          Measuring error: ±4%
          – Measuring the gas mixture volume flow
Instrument: Rotametar RAGK
          Measurement range: 0.2-6300 l/h
          Measuring error: ±4%

Results and analysis of the experiment

In figs. 3 and 4, a SO_2 concentration change is presented in the flue gas which flows through the reactor for capturing SO_2 in two ways without sorbent $CaCO_3$ and with the sorbent $CaCO_3$ depending on the reaction time (time of flue gas flow through the reactor), reaction temperatures, and the sorbent particles size. As it was expected, the concentration of SO_2 in the outlet gas is greater for the sorbent particles of greater diameter.

Figure 3. The change of SO_2 concentration in the gas mixture which flows through the reactor without adding sorbent and with adding sorbent $CaCO_3$ depending on the reaction time and particle diameter of the sorbent
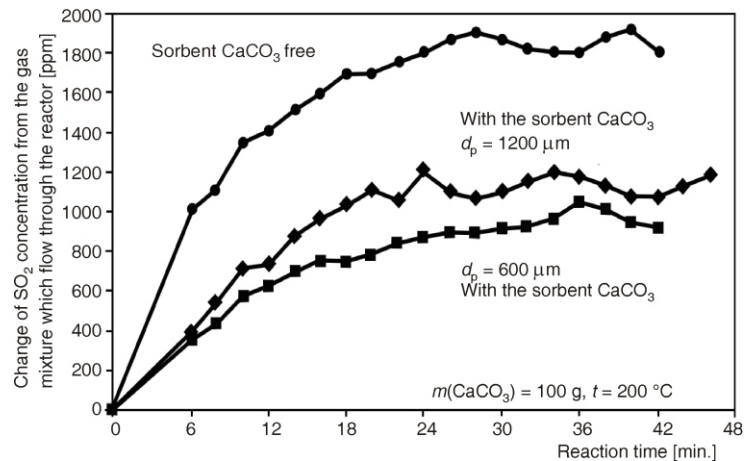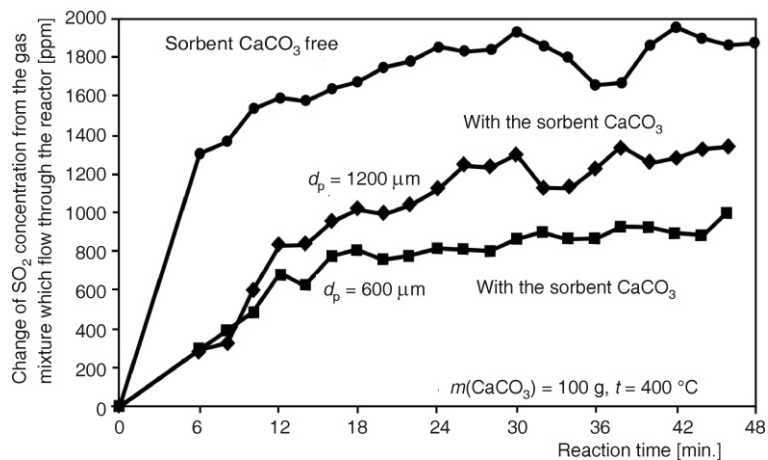

Figure 4. The change of SO_2 concentration in the gas mixture which flows through the reactor without adding sorbent and with adding sorbent $CaCO_3$ depending on the reaction time and particle diameter of the sorbent

Being at reaction temperature of approximately 200 °C and mean diameter of sorbent particles 600 µm degree of the sorbent particles SO_2 absorption occurs in the interval of 42-66%. Being at reaction temperature of approximately 400 °C and same fraction mixture of sorbent 600 µm, the absorption degree of SO_2 is a bit higher and it is in the interval of 45-78%. When greater diameters of sorbent particles of 1200 µm are used, the absorption degree of SO_2 is a bit lower and during the reaction temperature is around 200 °C in the interval of 33-61% and during the reaction temperature of 400 °C is in the interval of 20-78%. The first 6 minutes of experiment, the SO_2 absorption process for the sorbent particles for all samples of sorbent quickly absorbed SO_2, throughout the studied temperatures. After 6 minutes the absorption of SO_2 starts to stabilize and gains the approximate constant value (figs. 5 and 6).
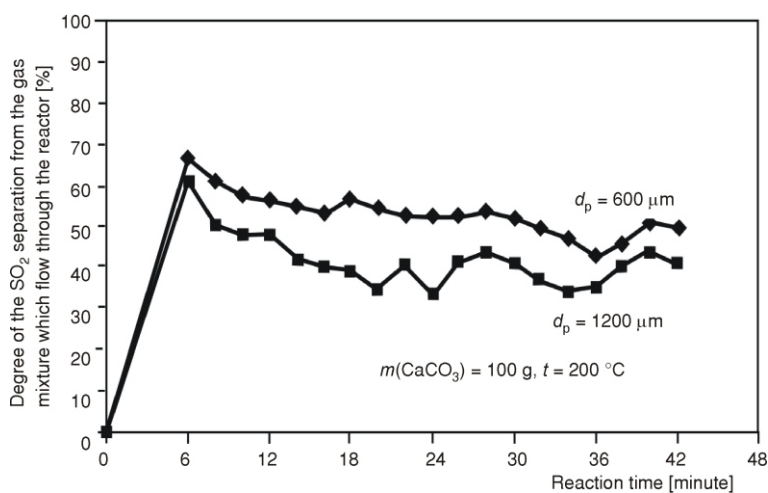

Figure 5. Degree of SO_2 separation from the gas mixture which flow through the reactor depending on the particle diameter of the sorbent and reaction time
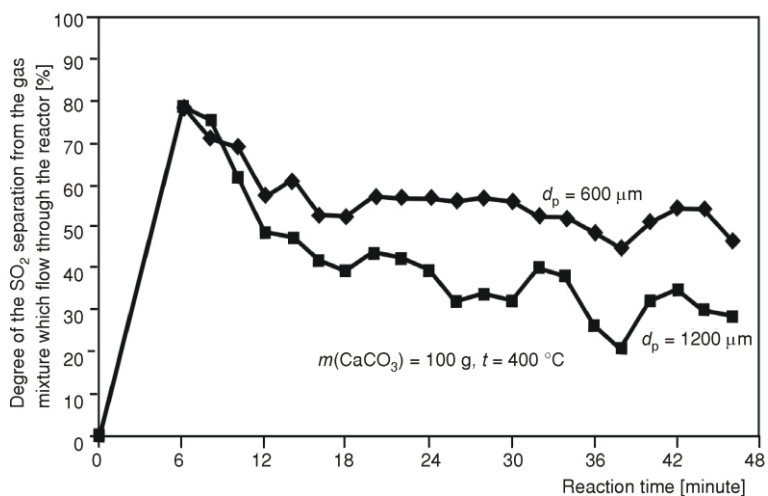

Figure 6. Degree of SO_2 separation from the gas mixture which flow through the reactor depending on the particle diameter of the sorbent and reaction time

Thermodynamic reaction $CaCO_3 + SO_2 + 0.5O_2 \rightleftarrows CaSO_4 + SO_2$

Using thermochemical data from the literature [12], the calculation of the thermodynamic functions was done: ΔH, ΔS, and ΔG of the taken reaction according to the reaction temperature and the pressure of 1.013 ⁵ Pa. The reaction of the exothermic ($\Delta H < 0$) with the negative change of entropy within temperature range of 298-1200 K, it means that the sign of ΔG is determined by relative proportion between enthalpy and element shown in Gibbs-Helmholtz equation $\Delta G = \Delta H - T\Delta S$. Reaction area of conduction of considered reaction is lower reaction temperatures (fig. 7).

Figure 7. Determination of the reactive area of the exothermic reaction $CaSO_3 + SO_2 + 0.5O_2 \rightleftarrows CaSO_4 + CO_2$
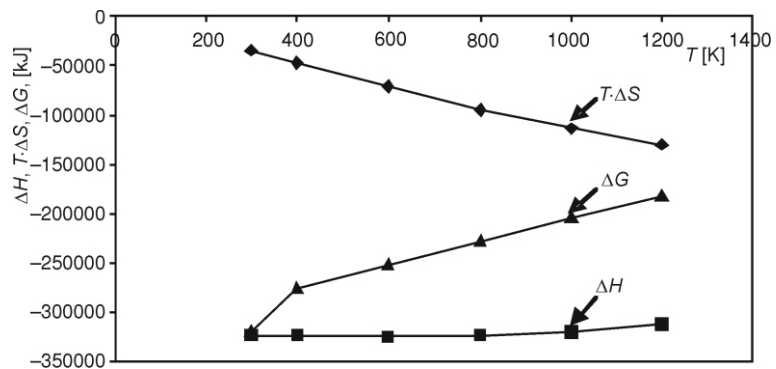
The equilibrium constant of the reaction is significantly higher than one ($K_p' \gg 1$) at lower reaction temperature. It means that there is more reaction products than reactants *i. e.* the purpose of the reaction is to produce reaction products. By increasing the reactive temperatures equilibrium constant is decreasing as a consequence of equilibrium movement in the direction of reaction reactants (fig. 8).

Figure 8. Dependency between equilibrium constant of the reaction $CaCO_3 + SO_2 + 0.5O_2 \rightleftarrows CaSO_4 + CO_2$ and reactive temperature
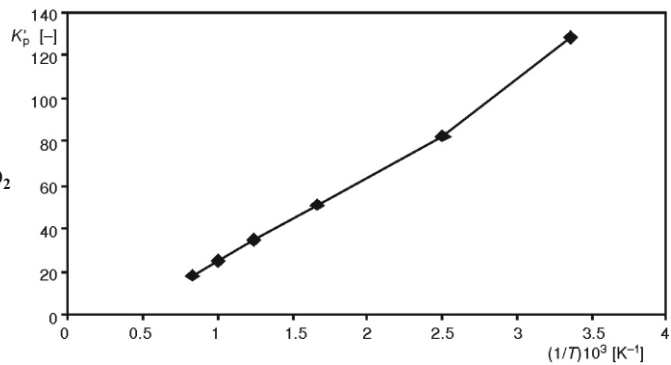
During the direct sulphuration:

$$CaCO_3 \quad SO_2 \quad \frac{1}{2}O_2 \quad CaSO_4 \quad CO_2 \tag{6}$$

the degree of sorbent utilization $CaCO_3$ can be determined with the expression:

$$\eta_{CaCO_3} \quad \frac{M_{CaCO_3}}{M_{SO_2}} \frac{mSO_2}{m_{CaCO_3}} \eta_{SO_2}, [\%] \tag{7}$$

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where M_{CaCO_3} is the $CaCO_3$ sorbent molar mass, $[gmol^{-1}]$, M_{SO_2} – the SO_2 molar mass, $[gmol^{-1}]$, m_{SO_2} – the SO_2 mass in the flue gas at the entrance of the reactor, [g], m_{CaCO_3} – the $CaCO_3$ sorbents (samples) mass, [g], η_{SO_2} $[(\varphi_{SO_{2,in}} \quad \varphi_{SO_{2,out}})/\varphi_{SO_{2,in}}]$ 100 – the absorption degree for particle sorbent of SO_2, [%], $\varphi_{SO_{2,in}}$ – the gas flue SO_2 volume ratio in flue gas at the entrance of the reactor, [ppm], and $\varphi_{SO_{2,out}}$ – the gas flue SO_2 volume ratio in flue gas at the outlet of the reactor, [ppm].

The usage of number data gained by measurements (figs. 3-8) and the usage of expression (7), the achieved values of the degree of utilization of $CaCO_3$ sorbent are considerably lower and are up to 6.87% at the reaction temperature of 400 °C and at the sorbent particle diameter of ≈600 μm. Throughout other examined conditions, the degree of sorbent utilization is considerably lower (figs. 9 and 10). The low degree of sorbent utilization is a consequence of consumption of greater mass of sorbent than the mass of the SO_2 in flue gas entering the reactor.
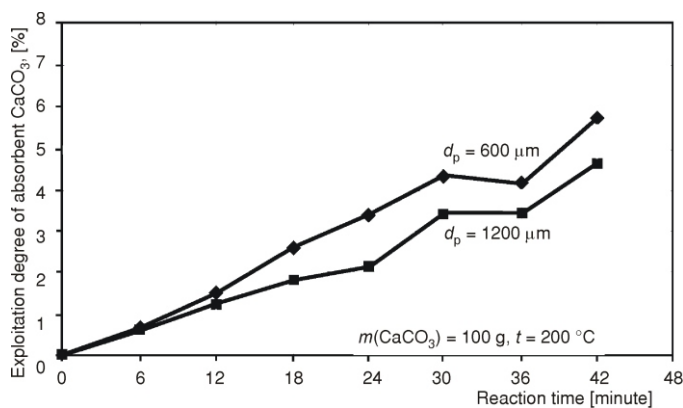

Figure 9. The exploitation degree of sorbent (sample) CaCO₃ depending on he flow time of flue gas through reactors for SO₂ separation
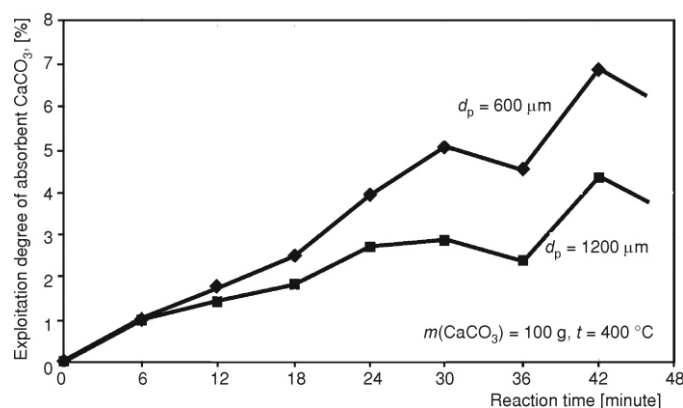

Figure 10. The exploitation degree of sorbent (sample) CaCO₃ depending on he flow time of flue gas through reactors SO₂ separation

Conclusions

The aim of the SO_2 separation experiment from the flue gas with dry procedure and using reagent $CaCO_3$, which is demonstrated in this paper, was to determine the influence of: the reaction temperatures, the reaction time in the reactor, the size of sorbent particles, and the degree of sorbent utilization on the SO_2 separation degree from the flue gas. The temperatures varied from

200 to 400 °C and the size of the sorbent particles varied from 600 to 1200 µm. The sample mass of the sorbent $CaCO_3$ within the reactor was 100 g. During the examination the following conclusions were made.

(1) It was acknowledged that the increase of the reaction temperature from 200 to 400 °C has higher degree on SO_2 retention to the sorbent particles. When the reaction temperature is somewhere around 200 °C and the mean diameter of sorbent particles is   600 µm, the degree of SO_2 retention is in the interval of 42-66%. When the reaction temperature is somewhere around 400 °C and it has the same fractional sorbent content (600 µm) the degree of SO_2 retention is somewhat lower and it is in the interval of 45-78%.

(2) When the sorbent particle diameter is   1200   m, the degree of SO_2 retention is somewhat lower and during the reaction temperature it is around 200 °C in the interval of 33-61% and when the reaction temperature is somewhere around 400 °C in the interval of 20-78%. These results were expected.

(3) The first 6 minutes of examination of SO_2 absorption process for the sorbent particles, all the sorbent particles quickly absorbed SO_2 during the given reaction temperatures. This leads to a conclusion that the first 6 minutes of the process is completely controlled by the chemical reaction on the pore surface of the sorbent. After 6 minutes, the SO_2 retention decreases and starts to stabilize, SO_2 takes approximate constant value (figs. 7 and 8) and leads us to a conclusion that the diffusion resistance becomes significant due the layer creation which is in accordance with the given results in [8-10].

(4) Low $CaCO_3$ sorbent degree of utilization is determined of only 6.87% during the reaction temperature of 400 °C and where the sorbent particle diameter is 600   m. Under the different examination conditions the utilization degree of sorbent is lower.

The attained results of the experiment described in this paper indicate the capability of injecting limestone $CaCO_3$ in the areas with lower temperatures as it is the convective part of the furnace and the flue canal of thermal power plant and whose aim was to reduce the SO_2 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

ΔG – reaction Gibbs free enthalpy, [kJ]
d_p – particle sorbent diameter, [µm]
ΔH – reaction enthalpy, [kJ]
K_p – reaction equilibrium constant, [Pa], for the reaction $CaCO_3 + SO_2 + 0.5O_2$ $CaSO_4 + CO_2$
K_p – reaction equilibrium constant reduction to the referent pressure, $p_0 = 1.013 \cdot 10^5$ Pa
M – molar mass, $[gmol^{-1}]$
m – sorbent mass, [g]
P – pressure, [Pa]
S – reaction entropy, $[kJK^{-1}]$
T – absolute temperature, [K]
t – reaction temperature, [°C]

Greek letters

$\varphi_{SO_2,in}$ – gas flue SO_2 volume ratio in flue gas at the entrance of the reactor, [ppm]
$\varphi_{SO_2,out}$ – gas flue SO_2 volume ratio in flue gas at the outlet of the reactor, [ppm]
η_{SO_2} – retention degree of SO_2 for particle sorbent, [%]
η_{CaCO_3} – exploitation degree, [%]

Simbols

$CaCO_3$ – calcium carbonate
$CaMg(CO_3)_2$ – dolomite
CaO – calcium oxide
$Ca(OH)_2$ – calcium hydroxide

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CaS   – calcium sufide
$CaSO_3$ – calcium sulphite
$CaSO_4$ – calcium sulfate
CO_2 – carbon dioxide
N_2 – nitrogen
O_2 – oxigen

SO_2 – sulphur dioxide
SO_3 – sulfphur trioxide

Acronyms

FGD – flue gas desulphation
MP – measuring point

    The values of SO_2 separation from fuel gas attained in these experimental examinations correspond to the degree of SO_2 separation taken from the listed literature.

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