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## DESULPHURIZATION OF BOILER FLUE GAS IN CIRCULATION FLUIDIZED BED – FOREIGN AND DOMESTIC EXPERIENCE

An outline is given of boiler flue gas desulphurization in the reactor with circulation fluidized bed of sorbent. Equations are given for desulphurization efficiency versus Ca/S molar ratio, the difference between final flue gas temperature and its adiabatic saturation temperature, the concentration of chlorides in flue gas fed to the reactor, specific surface of sorbent and its circulation multiplicity in the reactor.

### 1. INTRODUCTION

Semi-dry methods of flue gas desulphurization consist in injecting a sorbent, as a solution of suspension, into flue gas duct or to the process reactor, located downstream the boiler, where the sorbent reacts with sulphur dioxides ( $\text{SO}_2$ ,  $\text{SO}_3$ ) contained in the flue gas. Reaction products in the form of  $\text{CaSO}_3$  and  $\text{CaSO}_4$ , together with an unreacted sorbent surplus, are dried in the flue gas and, together with fly dust (if the flue gas has not been subjected to dedusting at an earlier stage), separated in the dust extractor – either an electrostatic precipitator or a fabric filter.

Semi-dry desulphurization methods differ in construction of the process reactor and its operating principle. It may be a spray dryer or a fluidized-bed reactor with circulation layer.

Pneumatic or rotary spargers (atomizers) are used to atomize the sorbent in spray dryers. The former ones are used in process reactors with active height-to-diameter ratio of ca. 0.8, while the latter – in reactors wherein this ratio is ca. 2.0 [2]. The flue gas flows through the reactor, independently of its design and sorbent atomizing method, for 10–12 s [3] (at present, reactors with flue gas retention times as long as 12–15 s are being designed). Pneumatic spargers are recommended for volumetric

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streams of flue gas whose flow rate is slower than 250,000 m<sup>3</sup>/h [1]. Should the flue gas flow capacity in a reactor be higher, rotary atomizers are more economical. They are less susceptible to clogging with solid particles than the pneumatic units and need not be operated at increased pressure. While atomizing the sorbent (at disc speed of the order of 10,000–12,000 rpm), they produce the droplets of the diameter ranging from 25 to 150 μm [1], whereas the droplets of the diameter range of 25–100 μm are produced by air-operated atomizers (at positive gauge pressure of 0.9–0.63 MPa).

In the case of desulphurization in the reactor with circulation fluidized bed, the sorbent is fed into the reactor from its bottom side (into the stream of contaminated flue gas), most often in the form of Ca(OH)<sub>2</sub> as a suspension or dry solid particles, which need to be wetted with water atomized above the fluidized bed of the sorbent being formed there. The sorbent is carried away by the stream of flue gas and raised within the reactor and, at the same time, it reacts with SO<sub>2</sub> and SO<sub>3</sub>, and also with other acid pollutants (HCl, HF), contained in the flue gas. In the course of flue gas desulphurization inside the reactor, water is being vaporized while desulphurization products and unreacted sorbent are dried. Dry product of flue gas treatment is fed into circulation cyclone, where its considerable portion is separated, and then returned into fluidized-bed reactor. Final dust removal from desulphurized flue gas takes place in an electrostatic precipitator or a fabric filter.

## 2. DEVELOPMENT OF FLUE GAS DESULPHURIZATION PROCESS IN CIRCULATION FLUIDIZED BED

In the 80-ties of the previous century, the Danish company, FLS Miljø, has developed an innovative semi-dry method of flue gas desulphurization, i.e. the Gas Suspension Absorption (GSA), which was tested at pilot plant in Copenhagen for flue gas being collected downstream a power boiler [4]. The method was commercially applied for the first time in Roskilde (Denmark) in 1988. It was the treatment plant to remove SO<sub>2</sub> and HCl from flue gas generated in municipal waste incineration process. In USA, the method was commercially tested at the power plant located close to Paducah locality (Kentucky) in 1992. In the mid 90-ties of the previous century, GSA method underwent commercial tests at iron ore sintering plant in Sweden where desulphurization was made for the flue gas generated in power boiler of the power rating of 135 MW<sub>e</sub> [4].

In Poland, a semi-dry flue gas desulphurization method, similar to GSA Method in technology and equipment, was implemented in Fabryka Kotłów RAFAKO S.A. (Boiler Manufacturing Works) in co-operation with Silesian University of Technology at Heat and Power Plant No. 4 of Zespół Elektrociepłowni Łódzkich S.A. in 2004 [5]. The technical documentation for this installation was also worked out by Fabryka Kotłów RAFAKO S.A. in co-operation with Silesian University of Technology. The

installation is removing sulphur with the throughput of 550,000 m<sup>3</sup>/h of flue gas at the removal efficiency of over 87% [6].

### 3. OUTLINE OF FLUE GAS DESULPHURIZATION PROCESS IN CIRCULATION FLUIDIZED BED

The boiler flue gas desulphurization plant according to the GSA Method (Gas Suspension Absorption) [4] is composed of the following units (figure 1):

- an atomizer reactor, where lime water slurry is injected by a two-medium spray nozzle,
- a cyclone, which separates fly ash and flue gas treatment products from the reactor; these products are, in large measure, returned into the reactor,
- a system, which prepares slaked lime slurry out of limestone or directly of burnt lime, to feed the reactor,
- a dust extractor, where fly ash and desulphurization products are separated from flue gas stream.

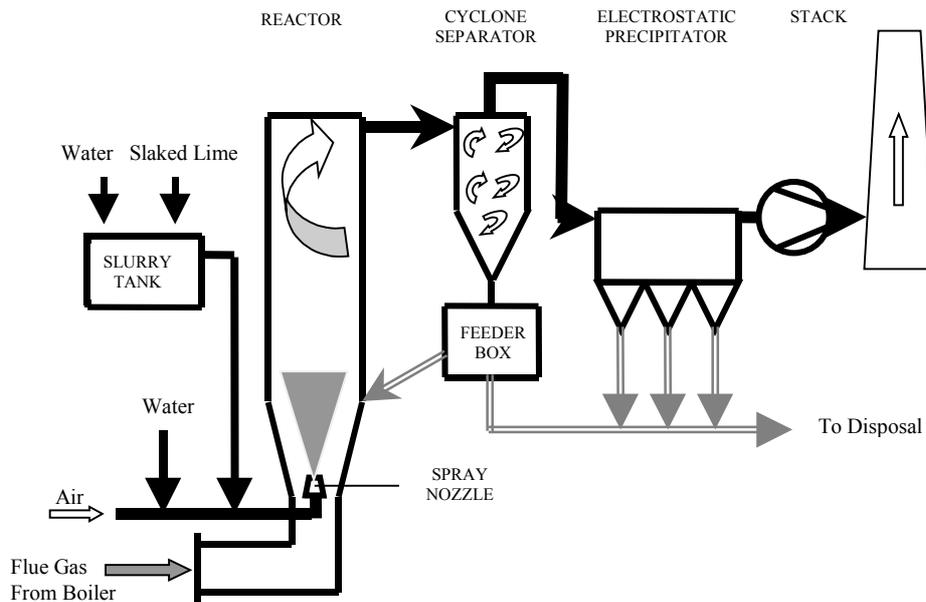


Fig. 1. Diagram of flue gas desulphurization technology in spray reactor with circulating fluid layer of post-reaction products

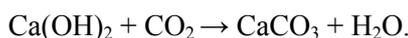
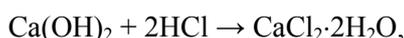
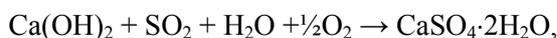
Fresh Ca(OH)<sub>2</sub> slurry is fed into the reactor by a single air-operated two-medium spray nozzle installed in the reactor axis. Heat contained in flue gas causes the lime

slurry water to evaporate and to moisten the flue gas. At the same time an absorption process between lime and  $\text{SO}_2$  contained in flue gas takes place. The droplets of atomized slurry collide with dry particles and are retained on their surface. As a result, the slurry is kept within the flue gas stream and does not reach the reactor wall and does not accumulate there as a solid deposit. The particles are suspended due to the flue gas flow; their retention time depends on the flow rate in the reactor. As a result of turbulence ensuring close contacting,  $\text{SO}_2$  is absorbed in lime slurry layer on the surface of solid particles. Purified flue gas, reaction products as solid particles (calcium salts) suspended in the flue gas stream and unprocessed lime flow upwards inside the reactor, then flow into a cyclone where they are mostly removed from flue gas as dry solid particles.

Some 99% of solid particles separated in the cyclone are returned into the reactor. This way, most of unprocessed lime is re-introduced into sorbent fluid bed and fly dust being sprayed with atomized fresh lime slurry. This minimizes the lime consumption in flue gas desulphurization process. The time of retention of flue gas in the reactor and the cyclone is short and ranges from 3 to 5 s.

The remaining 1% of particles fed from the reactor into the cyclone leaves the cyclone with the flue gas moved to final dust removal in the dust extractor in the form of an electrostatic precipitator or a fabric filter.

Acid components of flue gas react with atomized sorbent and water inside the reactor. The reactions taking place there may be summarized as follows:



This way, solid products being the mixture of fly dust, calcium sulphite, sulphate, chloride, fluoride and carbonate, and also unreacted sorbent are generated. In the electrostatic precipitator, solid particles absorb 1–7%  $\text{SO}_2$  existing upstream the reactor, while in the case of filtration deduster, desulphurization due to absorption on generated cake is 3–5% more effective than that in the electrostatic precipitator [4].

Flue gas desulphurization of fly dust and sorbent in a form of lime slurry (the GSA system) in the spray dryer with circulation fluid bed requires automatic control and maintaining the  $\text{SO}_2$  on admissible emission-to-atmosphere level at minimum lime consumption. Such a system includes three control loops:

- Control of solid particle circulation from the cyclone to the reactor. A sensor located at the place, in which where flue gas enters the reactor, detects dynamic pressure

of flue gas and converts the latter into the volumetric stream. On the basis of this signal, a controller selects the screw feeder rotation speed to get the required stream of returned product fed to the reactor in proportion to the volumetric stream of flue gas.

- Flue gas temperature control. A temperature sensor, placed between cyclone and dust extractor, adjust the rotational speed of a pump delivering cold water to sorption slurry sparger; in this way, the volumetric stream of water atomized in the reactors is increased or decreased, depending on the flue gas temperature preset downstream the reactor.

- Control of  $\text{SO}_2$  emission. The  $\text{SO}_2$  emission-monitoring system, located in the stack, controls the rotary speed of the pump delivering lime slurry to the sparger to achieve the required capacity and efficiency of flue gas desulphurization.

The screw feeder of the product returned to the reactor, the cold water pump and the lime slurry pump are driven with electric motors provided with inverters to allow the accurate batching of the media. An exact liquid proportioning may be made by means of positive-displacement pumps (screw pumps, peristaltic pumps). The lime slurry sparger requires constant pressure, hence no impeller pumps shall be used to feed cold water and lime slurry as when such a pump changes its rate of delivery, the delivery head of this pump is changed as well.

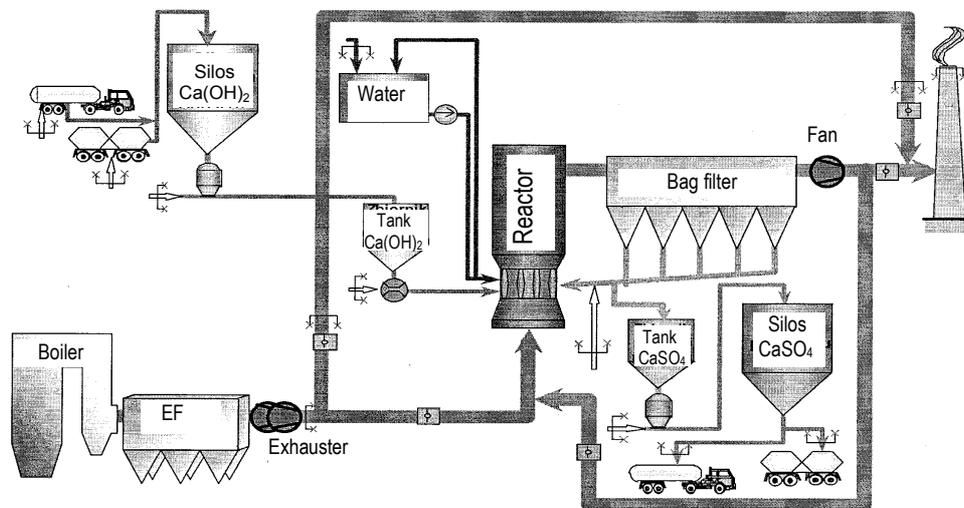


Fig. 2. Diagram of flue gas desulphurization system based on semi-dry method in a reactor with circulating fluid layer invented by Fabryka Kotłów RAFAKO for OP-430 boiler in Elektociepłownia 4 Łódź

The plant shown in figure 2 is used for flue gas desulphurization in the OP-430 Boiler (the power rating of the unit is  $100 \text{ MW}_e$ ). The rated wet flue gas flow rate in this installation is  $550,000 \text{ m}_n^3/\text{h}$ . The concentration of  $\text{SO}_2$  upstream the reactor is

3,100 mg/m<sub>n</sub><sup>3</sup> of dry flue gas, the desulphurization efficiency is higher than 87.2%, the flue gas temperature in the stack is above 365 K (92C °C), the sorbent (Ca(OH)<sub>2</sub>) consumption is 3 Mg/h, the water consumption is 20.5 m<sup>3</sup>/h, the mass flow of sub-process product is 4.9 Mg/h, the compressed air consumption is 1,864 m<sub>n</sub><sup>3</sup>/h, and the plant availability is 97%.

The RAFAKO S.A. applied the same process of desulphurization for the Bc-50 Boiler exhaust flue gas in Cogeneration Plant EC-4, in Łódź, with the power rating of 165 MW<sub>e</sub> (the volumetric flow of wet boiler flue gas is 380,000 m<sub>n</sub><sup>3</sup>/h, the SO<sub>2</sub> concentration at the reactor inlet is 3,536 mg/m<sub>n</sub><sup>3</sup> of dry flue gas, the desulphurization efficiency is above 88.7%, the sorbent consumption is 2.5 Mg/h, the water consumption is 10.2 m<sup>3</sup>/h, the mass flow of sub-process product is 3.8 Mg/h).

The same method was used to run flue gas desulphurization from the OP-120 Boiler with the power rating of 165 MW<sub>e</sub> in Skawina Power Plant (the volumetric flow of wet boiler flue gas is 615,000 m<sub>n</sub><sup>3</sup>/h, the SO<sub>2</sub> concentration at reactor inlet is 3,600 mg/m<sub>n</sub><sup>3</sup> of dry flue gas, the desulphurization efficiency higher than 92%, the sorbent consumption is 3.8 Mg/h, the water consumption is 14.2 m<sup>3</sup>/h, the mass flow of sub-process product is 6.0 Mg/h).

The measurement proved that the systems implemented are distinguished by excellent technical/economical features; desulphurization efficiency at the proper process temperature and Ca/S mole proportion reached 95% and that of SO<sub>3</sub>, HF and HCl removal exceeded 90%.

#### 4. FLUE GAS DESULPHURIZATION EFFICIENCY IN CIRCULATION FLUIDIZED BED

The efficiency of boiler flue gas desulphurization with GSA Method depends on many variable factors (the concentration of SO<sub>2</sub> in flue gas, the mass of the injected sorbent, the difference between the temperature of flue gas at the reactor outlet and the temperature of its adiabatic saturation, chloride contents in flue gas). They are preset and controlled, depending on the content of moisture, sulphur and chlorine compounds in coal as well as on the temperature of flue gas fed to the reactor.

Examinations proved that the efficiency of desulphurization also depends on the mass of the sorbent introduced into the process, which was expressed as the mole proportion of calcium in the sorbent to sulphur dioxide being converted to sulphur contained in flue gas. This relationship is shown in figure 3.

The figure presents the dependence of flue gas desulphurization on the difference between the flue gas temperature at the reactor outlet and the temperature of its adiabatic saturation ( $\Delta T$ ). The higher the molar ratio preset (Ca/S) and the lower the tem-

perature difference ( $\Delta T$ ), the better the efficiency of flue gas desulphurization. The lower the temperature difference ( $\Delta T$ ), the higher the relative humidity of flue gas downstream the reactor. The desulphurization also depends on the moisture contents in the flue gas generated in the coal burning process and on the temperature of the flue gas in the boiler. The value of  $\Delta T$  should not be too low as, due to slight cooling down the flue gas under such conditions, the steam in the flue gas may condensate, which leads to sorbent accumulation and desulphurization of products on the internal wall of the dust extractor, as well as to clogging and corrosion of flue gas ducts. The smallest safe value of temperature difference  $\Delta T$  is in the range of 8–10 K.

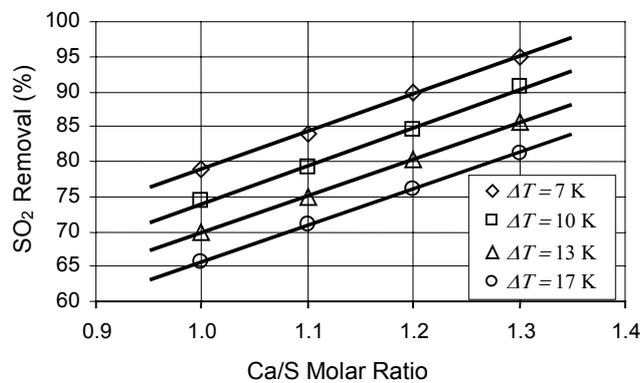


Fig. 3. Dependence of Ca/S molar ratio and temperature difference between flue gas temperature at reactor outlet and temperature of its adiabatic saturation (fly dust concentration of  $4.6 \text{ g/m}^3$  with no chlorides) on total flue gas desulphurization efficiency

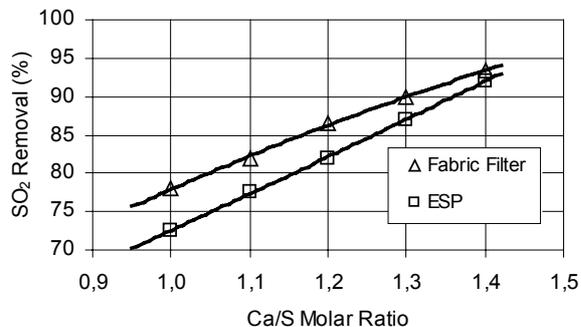


Fig. 4. Comparison of flue gas total desulphurization efficiency in a system with electrostatic precipitator and optionally fabric filter

When flue gas is subjected to the dust extraction in a fabric filter, the desulphurization efficiency is higher than that reached when electrostatic precipitator is used (figure 4). The lower the molar ratio (Ca/S), the higher the difference in the efficiency

in favour of the fabric filter. In the case of high values of Ca/S, no such a difference was observed.

Chlorides ( $\text{CaCl}_2$ ) in desulphurized flue gas are mainly created during HCl sorption, which improves the effectiveness of desulphurization process (figure 5). Their role is to reduce the water vapour pressure at the surface of absorbent droplets, thus to reduce the driving power of water evaporation process up to the moment when the water vapour pressure in the system reaches the state of equilibrium. Owing to that fact, the time of evaporating and drying the fluid bed, composed of droplets and solid particles (particles of  $\text{Ca}(\text{OH})_2$ , fly dust and products of removing  $\text{SO}_2$ , HCl and HF from flue gas), is longer.

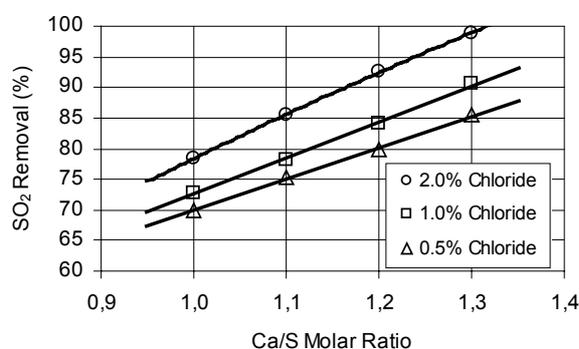


Fig. 5. Influence of chlorides in combusted coal and  $\text{Ca}(\text{OH})_2$  dosed to reactor on flue gas desulphurization efficiency

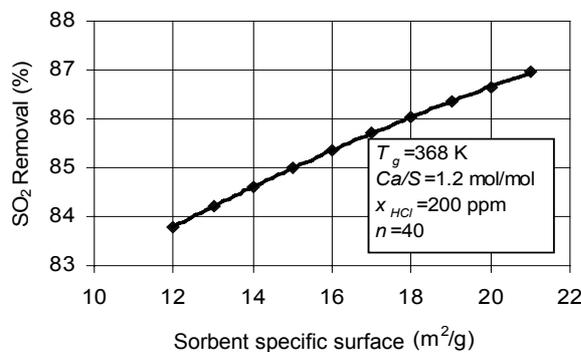


Fig. 6. Effect of  $\text{Ca}(\text{OH})_2$  specific surface on flue gas desulphurization efficiency

Flue gas desulphurization efficiency is greater when post-treatment product circulation multiplicity in the reactor-cyclone circuit is higher (figure. 7) and when a sorbent with a larger specific surface is used (figure 6) [9].

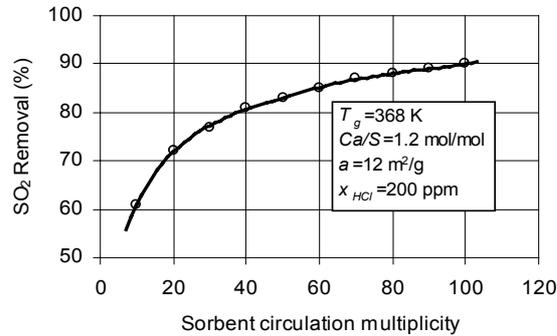


Fig. 7. Effect of sorbent circulation multiplicity on flue gas desulphurization efficiency in a reactor–dust collector system

Based on the results given in [4], it is possible to derive equation providing relation between the flue gas desulphurization efficiency in fluidized reactor with circulation sorbent layer such as  $\text{Ca}(\text{OH})_2$  and the content of chlorides in coal, the difference between the temperature of flue gas at the reactor outlet and the temperature of its adiabatic saturation, and the molar ratio ( $\text{Ca}/\text{S}$ ). This equation is as follows:

$$\eta_{\text{SO}_2} = 111.4 [\text{Cl}]^{0.0146} \cdot \Delta T^{-0.181} \cdot (\text{Ca}/\text{S})^{0.789}, \quad (1)$$

where:

$\Delta T$  – the difference between a final temperature of flue gas in the reactor and the temperature of its adiabatic saturation (K),

$\text{Ca}/\text{S}$  – the molar ratio of the reagents related to  $\text{SO}_2$  stream, at the reactor inlet (mole/mole),

$[\text{Cl}]$  – the chloride content in coal burnt out (%).

During desulphurization of boiler flue gas in the reactor and the cyclone, almost 100% of HCl and 99% of HF are removed simultaneously; if the installation is equipped with electrostatic precipitator, over 98% or most trace metals are removed (such as arsenic, barium, chromium, cadmium, cobalt, lead, vanadium) [4].

On the grounds of the tests carried out on pilot installations and full-scale system, MOKROSZ [9] derived empirical equations for desulphurization efficiency versus various variables. In his research, he examined the effects of the following variables on the desulphurization efficiency: flue gas humidity, multiplicity of sorbent circulation in the reactor,  $\text{Ca}/\text{S}$  molar ratio, specific surface of reagent,  $\text{SO}_2$  concentration, hydrogen chloride and fly dust content in flue gas at the reactor inlet.

The effect of essential parameters on the flue gas desulphurization with  $\text{Ca}(\text{OH})_2$  sorbent was described by equations valid in two ranges of final flue gas temperature [7]. The following equation was derived for the final temperature of flue gas  $T \leq 373$  K:

$$\eta_{\text{SO}_2} = 1 - \exp \left[ -1.5 \cdot \Delta T^{-0.5} \cdot a^{0.4} \cdot x_{\text{HCl}}^{0.04} \cdot \left( \frac{\text{Ca}}{\text{S}} \cdot n \right)^{0.34} \right], \quad (2)$$

whereas for the final temperature of flue gas  $T \geq 373$  K, the following equation is valid

$$\eta_{\text{SO}_2} = 1 - \exp \left[ -0.07 \cdot \Delta T^{0.3} \left( \frac{\text{Ca}}{\text{S}} \cdot n \right)^{0.4} \right], \quad (3)$$

where:

- $a$  – the specific surface of sorbent ( $\text{m}^2/\text{g}$ ),
- $x_{\text{HCl}}$  – the HCl concentration in flue gas at the reactor inlet (ppm),
- $\text{Ca}/\text{S}$  – the molar ratio of reagents related to  $\text{SO}_2$  stream at the reactor inlet (mole/mole),
- $n$  – the circulation multiplicity of solid particles in the reactor–dust extractor system,
- $\Delta T$  – the difference between the final temperature of flue gas in the reactor and the temperature of its adiabatic saturation (K).

Equation (2) comes true in the following ranges of variables:  $\Delta T$ , 10–45 K;  $a$ , 10–21  $\text{m}^2/\text{g}$ ;  $x_{\text{HCl}}$ , 1–250 ppm;  $n$ , 5–100;  $\text{Ca}/\text{S}$ , 1.0–1.25 mole/mole, while equation (3) in the following ranges:  $\Delta T$ , 45–250 K;  $n$ , 5–100;  $\text{Ca}/\text{S}$ , 1.0–1.25 mole/mole. The relative error of correlation given by equation (2) is  $\pm 15\%$ , while that given by equation (3) is  $\pm 5\%$ . Due to a considerable error in calculating the flue gas desulphurization efficiency according to equations (2) and (3), they cannot be used in the engineering design of flue gas desulphurization process.

## 5. CONCLUSIONS

The survey and analysis of research, available in domestic and foreign bibliography, on boiler flue gas desulphurization in circulation fluid bed reactor allow the following conclusions to be drawn:

- desulphurization process may be run with 95% efficiency at the molar ratio of  $\text{Ca}/\text{S} = 1.25$  mole/mole, provided that the other essential variables of the process are kept within proper ranges,
- desulphurization efficiency depends on the  $\text{Ca}/\text{S}$  molar ratio, flue gas temperature at reactor outlet, flue gas moistening ratio in reactor, reagent circulation multiplicity in reactor–dust extractor circuit (cyclone separator, filter or electrostatic precipitator), specific surface of reagent ( $\text{Ca}(\text{OH})_2$ ) and chloride content in flue gas (in coal being burnt out),

• further works in order to implement GSA technology and to examine the processes occurring in circulation fluidized bed create conditions for improving this method of boiler flue gas desulphurization in process and equipment domains, for increasing the installation availability and decreasing the capital investments and operating costs.

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ODSIARCZANIE SPALIN KOTŁOWYCH W CYRKULACYJNYM ZŁOŻU FLUIDALNYM  
– DOŚWIADCZENIA ZAGRANICZNE I KRAJOWE

Omówiono proces odsiarczania spalin kotłowych w reaktorze z cyrkulacyjną warstwą fluidalną sorbentu. Podano równania opisujące zależność skuteczności odsiarczania od stosunku molowego Ca/S, różnicy temperatur pomiędzy temperaturą końcową spalin w reaktorze i temperaturą ich adiabatycznego nasycenia, stężenia chlorków w spalinach kierowanych do reaktora, powierzchni właściwej sorbentu i krotności cyrkulacji sorbentu w reaktorze.