TATIANA TRYBUŚ*

DRY PROCESSES
OF FLUE GAS DESULPHURIZATION

In this paper, the principles and advantages of dry methods of flue gas desulphurization are described. The following technologies are presented: LIMB, LIFAC, WAWO and COOLSIDE. Experiments were performed at the heat generation plant in Wrocław according to WAWO technology.

1. INTRODUCTION

1.1. FLUE GAS DESULPHURIZATION (FGD)

FGD, the method of reducing SO_2 emitted from power stations, is a well-known technology with a number of different processes. The installation of FGD system has, in general, been enforced by legislation. Countries have their own SO_2 emission limits, but they are not very enthusiastic about keeping them.

There are three categories of the methods allowing us to control SO_2 emissions:

1. Pre-combustion methods (fuel switching or cleaning).

2. Combustion zone technologies, where sorbent is injected into the burning fuel (LIMB, LIFAC, FBC, WAWO).

3. Post-combustion flue gas treatment:

dry sorbent injection, where both the sorbent and the residue are dry (COOLSIDE),

semi-dry systems,

wet-systems.

Modes of SO_2 removal by dry sorbent addition are shown in figure 1.

Due to specific applications the dry sorbent injection technologies offer advantages over the wet FGD systems, because they allow us to control the emissions of SO_2 produced during combustion of high-sulphur coal. These potential advantages

* Institute of Environment Protection Engineering, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.
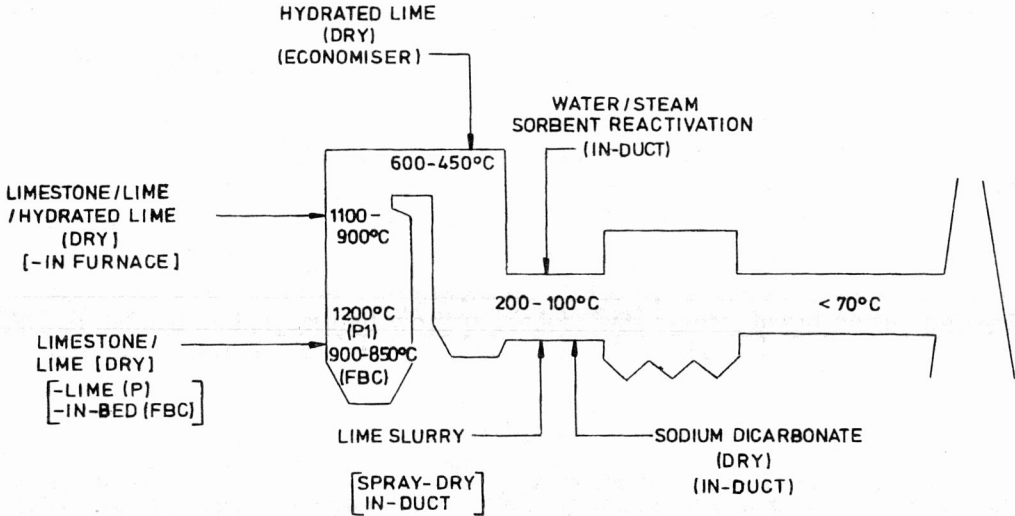
Fig. 1. Modes of SO$_2$ removal by dry sorbent addition

include ease of retrofit, dry waste and lower capital investment. The main factor that distinguishes the dry processes from the other processes is that a calcium-based sorbent is injected into various parts of a pulverized coal boiler unit or in-duct.

1.2. BRIEF OUTLINE OF DRY TECHNOLOGIES

LIMB (Lime Injection Multistage Burners). Limestone (CaCO$_3$) or hydrated lime (Ca(OH)$_2$) is injected into the upper furnace cavity, where temperature ranges from 900 to 1300 °C. The sorbent is rapidly calcined forming CaO which reacts with SO$_2$ to form CaSO$_4$. In the boiler economizer process, Ca(OH)$_2$ is injected between the superheater and air preheater where temperature is in the range of 300–800 °C. Typical SO$_2$ capture efficiencies under these conditions are about 35 and 55% for CaCO$_3$ and commercial Ca(OH)$_2$, respectively. Boiler construction should provide 1–2 second contact time.

LIFAC. In this two-step process, the sorbent is injected into the boiler and flue gas undergoes humidification with a spray water in reactor. Unreacted sorbent is activated in reactor resulting in SO$_2$ removal which approaches 50–80%. All injected water evaporates and therefore the decrease in gas temperature is close to adiabatic saturation point, thus flue gas must be mixed with hot stream of gas.

WAWO. This technology is based on two-step process, the sorbent injection into the boiler where temperature ranges from 800 to 1200 °C and flue gas humidification in alkaline medium which increases the sorption capacity of this solution resulting in better performance of SO$_2$ removal. The temperatures of flue gas at the reactor inlet and outlet range from 135 to 165 °C and from 20 to 40 °C, respectively, and are higher than adiabatic saturation temperature.

COOLSIDE. The calcium-based sorbent injected into the flue gas duct within the temperature zone of 100–200 °C is activated by a spray water. Contact time is in the range of 1–4 seconds. Most often the water/gas ratio is 0.01 dm^3/m^3. The mechanism of SO$_2$ removal does not depend on thermodynamic process which is important in LIMB or LIFAC. Under well controlled conditions the efficiency of SO$_2$ removal reaches 80%.

In dry desulphurization technologies, the particulate removal system is necessary. If the flue gas is conditioned by a water spray to reduce dust resistivity and to prevent back corona, it is profitable to use electrostatic precipitator (ESP). Otherwise, the baghouse system should be fitted. The advantage of this mode is SO$_2$ removal by the dense sorbent bed in the fabric filter.

1.3. MAIN FACTORS INFLUENCING FLUE GAS DESULPHURIZATION AND SORPTION OF SO$_2$

The temperature and location of a sorbent injection are very important. Sulphur retention reaches its maximum in three narrow temperature ranges (figure 2) [1]. The efficiency of sulphur sorption increases with the increase in the Ca/S ratio. This parabolic function is shown in figure 3 [2].
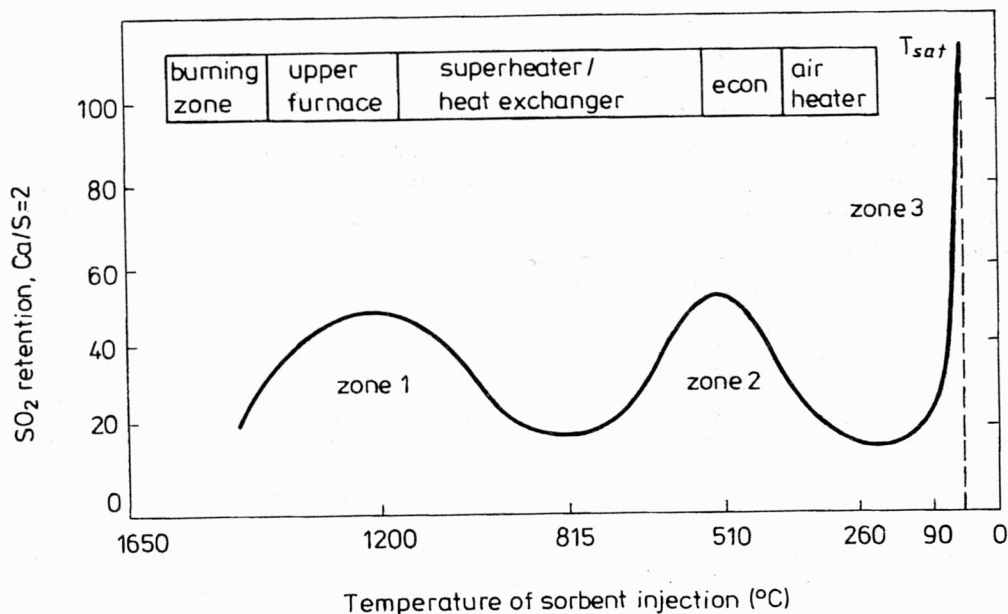

Fig. 2. Dependence of injection temperature on sulphur retention

Type of sorbent and its physical properties limit conversion from CaO to CaSO$_4$. Among standard calcium-based sorbents the most effective is hydrated lime, which is
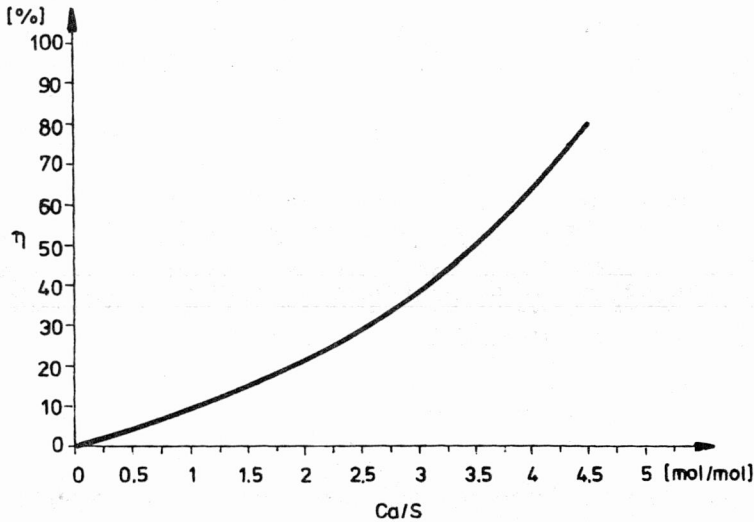
Fig. 3. Sulphur capture as a function of Ca/S molar ratio

also the most expensive. Satisfying results are achieved under the following conditions: porosity 60–80%, surface area 30–60 m^2/g, particle diameter 2–50 μm [5].

It is worth noting that CaSO$_4$ molar volume is 2.75 times bigger than that of CaO which can result in blocking and decreasing the CaO pore volume and the reaction is inhibited. The time of sorbent–SO$_2$ contact is usually determined by construction (1–2 s in boiler, 2–6 s in reactor or duct). Water droplet size sprayed by a nozzle system into reactor should be in the range of 20–50 μm to provide total evaporation before droplet falls down to the reactor chute resulting in ash concreting. If the temperature of outlet gas in reactor is closer to adiabatic saturation point, the process is more effective.

2. EXPERIMENTS PERFORMED IN THE HEAT GENERATION PLANT IN WROCŁAW ACCORDING TO WAWO TECHNOLOGY

2.1. DESCRIPTION OF THE INSTALLATION

Desulphurization of flue gas in WP-120 boiler (140 MW$_{th}$) is schematically shown in figure 4. The process consists of transport system, Ca(OH)$_2$ feed system, absorption unit and spray water system. Hydrated lime from the feed tank (4) is conveyed by feeding screw and pneumatic feeder (5) to retention tank (6); rotary feeders and blow-out apparatuses continuously supply Ca(OH)$_2$ to the boiler (1), depending on SO$_2$ concentration in flue-gas flowing from electrostatic precipitator (ESP, 3). The boiler exit duct is divided into two twin ducts where gas at 400–450 °C

containing sorbent and ash flows into rotary air heaters (*2*), then at 145–165 °C enters reactors (R_1, R_2). Liquid-air spray is injected by GAJ-5 nozzle system. A pump (*8*) supplies spray water from compensation tank (*7*). The water comes from hydraulic ash transport, is taken from ponds, then passes through sludger and decanter.
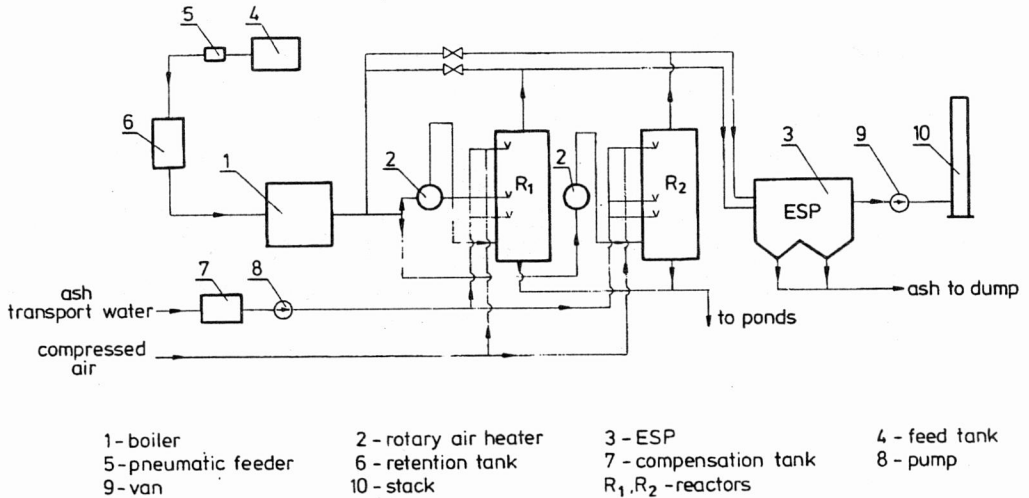

1- boiler	2 - rotary air heater	3 - ESP	4 - feed tank
5 - pneumatic feeder	6 - retention tank	7 - compensation tank	8 - pump
9 - van	10 - stack	R_1, R_2 - reactors	

Fig. 4. Desulphurization process at the Heat Generation Plant in Wrocław

Flue gas is humidified and cooled in reactors and SO_2 sorption on activated sorbent is enhanced. Ash is partly collected in reactor chute as well as absorption products and unreacted sorbent. The reject is hydraulically transported to ponds. The flue gas leaves reactors at 80 °C and is mixed with raw, hot gas flowing from the boiler, whose flow rate is controlled by by-pass throttle in order to maintain desired temperature before ESP. The volume of by-pass gas, which heats reactor gas, ranges from 5–10%. The reject collected in ESP is dumped. The gas undergoes precipitation and desulphurization, and thereafter passes through a van (*9*) and a stack (*10*).

2.2. EXPERIMENTAL METHODS

The experiments conducted in the Heat Generation Plant in Wrocław allowed the evaluation of the effectiveness of flue gas desulphurization installation fitted for WP-120 boiler.

SO_2 concentration in flue gas was measured at the reactor inlets and ESP outlet to determine the reduction of SO_2 as a difference between these two measurements.

Total operational efficiency of the installation was determined as a difference between working and not working desulphurization unit efficiencies.

The following flue gas parameters were analysed: flow rate, SO_2 concentration and humidity. The alkalinity and pH of spray water and humidity of the reject from reactors and ESP were measured as well.

2.3. RESULTS AND DISCUSSION

SO_2 emission was measured by means of two analysers (Westinghouse-Controlmatic and optical SO_2-CODEL-1021) and iodometric method. Gas samples were taken in three points: reactor inlet, top of reactor and ESP outlet. The reactor inlet and top allowed us to observe the process, while its outlet – to control the SO_2 sorption and sorbent feed rate. The results from the reactor inlets enabled evaluation of SO_2 background.

The results obtained by means of iodometric method and optical analyser are similar, with variation of 4–8%. Data obtained using the Westinghouse analyser is raised and error ranges from 20 to 30%. Comparison of the data based on these three methods of measurement is given in table 1.

Table 1

SO_2 concentration in flue gas.
Comparison of the results obtained by means
of CODEL-1021 optical analyser,
Westinghouse-Controlmatic analyser
and iodometric method

Iodometric method	CODEL	Westinghouse
	$[mg/m^3]$	
697	728	863
730	700	972
636	672	943
725	700	929
731	672	958

The main disadvantage of the technology presented is a high rate of utilized sorbent found in the reject from reactors. Unreacted sorbent partly dissolves itself in hydraulic ash transport water, which after treatment is used as spray water in reactors because of its high pH value (11.4–13.3), table 2.

Due to measurement of gas humidity it was possible to indicate lower limit of outlet temperature from reactors. Increase of gas humidity enhances SO_2 sorption, but exceeding safe range results in formation of acid droplets. According to experiments the maximum humidity did not exceed 30%. Control of the reactor and ESP reject moisture, at approximately 9–13% by w.t., respectively, helped to confirm right performance of the installation.

Table 2

Alkalinity of spray water

pH	F [mval/dm³]	M [mval/dm³]	Ca(OH)₂ [mg/dm³]	CaCO₃ [mg/dm³]
12.40	4.25	4.95	131.35	70.00
12.80	7.20	8.17	230.30	97.50
12.90	5.87	6.72	186.00	85.00
13.40	9.37	10.45	307.10	107.20
13.25	12.07	13.10	408.90	102.50*
13.35	25.30	26.40	895.40	110.00*
12.25	27.00	28.30	950.00	120.00*
12.25	24.30	25.60	850.00	130.00*
13.60	27.40	28.80	962.00	140.00*
12.90	18.00	19.10	625.30	110.00
12.50	10.85	12.10	355.20	125.00
12.50	8.12	9.35	255.30	122.50
12.55	7.80	8.70	255.30	90.00
12.50	5.05	6.00	151.70	95.00
12.70	7.50	9.00	222.00	150.00
12.65	15.30	16.18	510.60	150.00
11.87	12.80	13.80	436.60	100.00
13.08	13.70	14.80	466.20	110.00
13.10	8.15	8.85	275.00	70.00
11.41	2.35	3.30	51.80	100.00
12.19	3.50	4.75	83.25	125.00
11.86	6.25	7.30	192.40	105.00
12.92	7.20	9.00	199.80	180.00
12.80	11.10	12.50	358.90	140.00
12.34	5.60	6.70	166.50	110.00

F – alkalinity in the presence of phenolphtalein.
M – alkalinity in the presence of methyl orange.
* – sorbent: calcium oxide (CaO).

The flue-gas flow rates were measured (table 3). Based on these results figure 5 was plotted.

The influence of sorbent amount and gas temperature in reactor on total SO_2 removal is shown in figures 6 and 7.

A considerable increase in SO_2 capture was observed along with the decrease of gas temperature (close to adiabatic saturation point) and increase in Ca/S ratio. The efficiency of WAWO method as a function of Ca/S is plotted in figure 8.

Atomizing nozzles are of a great importance. They should provide the optimum conditions for SO_2 sorption process. Correlation between the gas temperature in reactors and flow rate of spray water is shown in figure 9 and table 4.

The experiments conducted gave the base to design the WAWO installation for BP-1150 boiler (360 MW).

T. TRYBUŚ

Table 3

Mean values of flue-gas flow rates

Boiler capacity [MW]	Flow rates × 10³	
	[m³/h]	[Nm³/h]
80	331	238
85	347	248
90	362	260
95	377	270
100	392	280
105	407	290
110	423	301
115	438	311
120	454	322
125	469	333
130	484	343
135	498	352
140	512	365
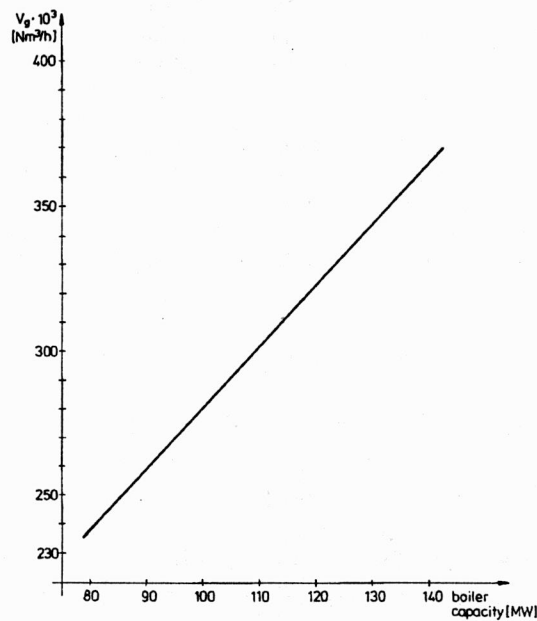
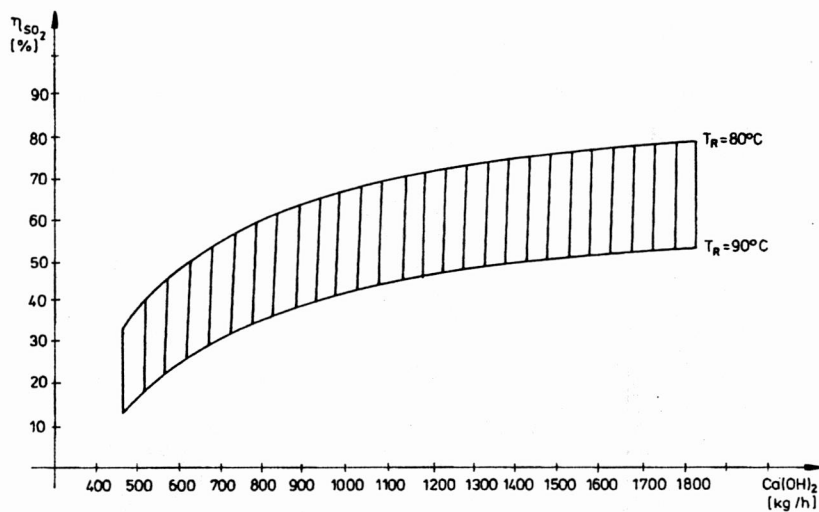Fig. 5. Flue gas flow rate versus boiler capacity

Fig. 6. Dependence of sorbent flow rate and gas temperature
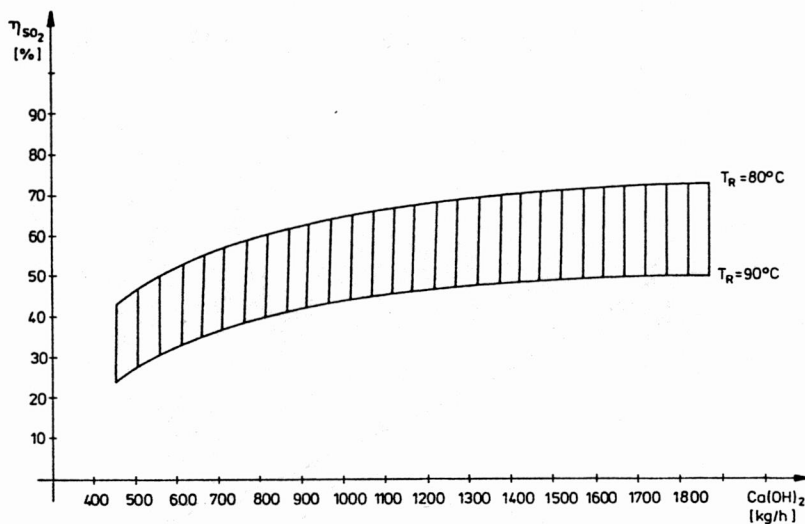on desulphurization efficiency in the left reactor

Fig. 7. Dependence of sorbent flow rate and gas temperature
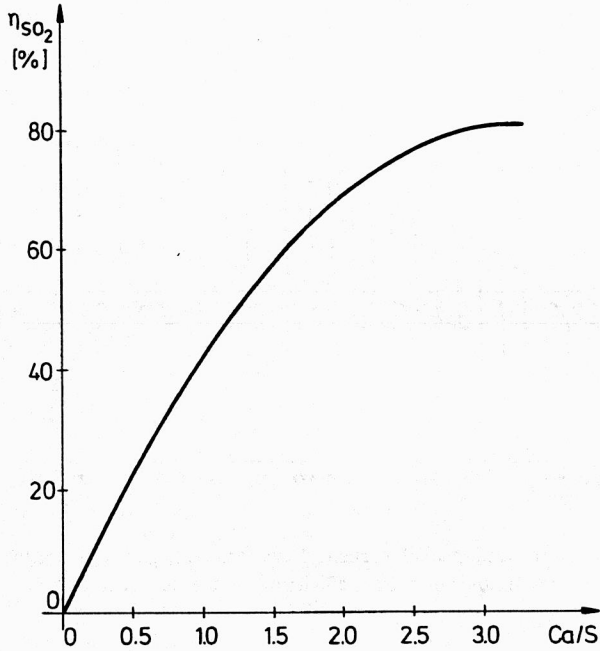on desulphurization efficiency in the right reactor

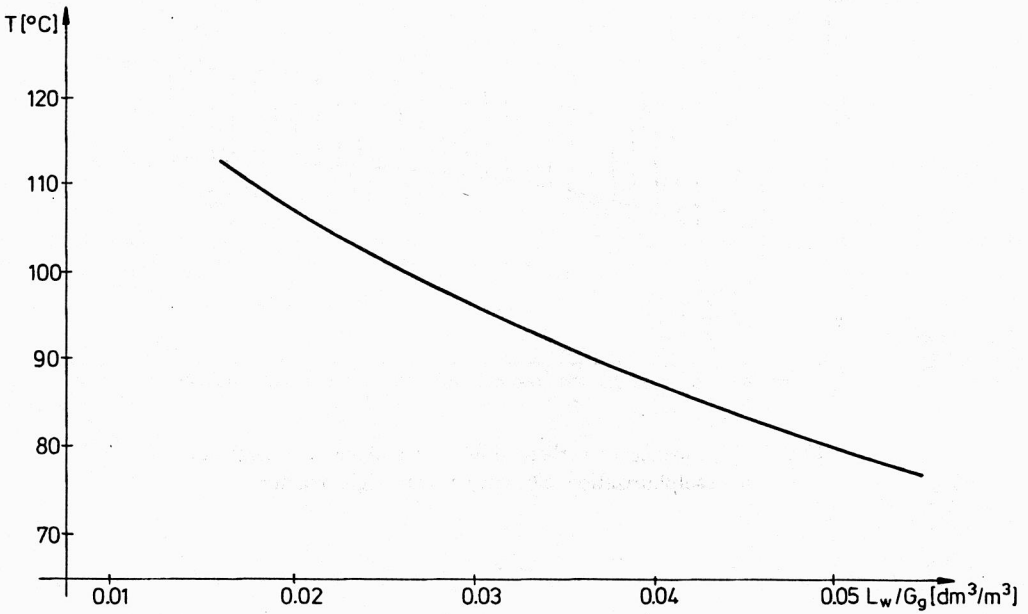Fig. 8. Desulphurization efficiency in the WAWO method

Fig. 9. Dependence of spray water/gas flow ratio on reactor gas temperature

Table 4

Temperature of reactor gas and spray water/gas ratio (L_w/G_g)

t_r [°C]	Boiler capacity [MW]	L_w [dm³/h]	G_g [Nm³/h · 10⁻³]	L_w/G_g [dm³/Nm³]
112.0	120.0	5100	316	0.016
112.0	99.6	4600	280	0.016
111.0	102.2	4900	290	0.017
111.0	79.7	3900	238	0.017
110.0	82.3	4300	243	0.018
104.0	110.6	6700	303	0.022
104.0	103.1	6200	286	0.022
102.0	121.5	7700	325	0.024
102.0	110.0	7100	300	0.024
100.0	86.5	6600	252	0.026
96.0	90.0	9000	260	0.032
96.0	100.8	9100	282	0.032
94.0	100.2	9500	280	0.034
92.0	108.0	10400	297	0.035
91.0	90.0	9000	260	0.035
90.0	90.6	9100	261	0.035
90.0	108.3	10900	282	0.037
90.0	103.9	10700	288	0.037
89.0	107.0	10900	294	0.037
89.0	100.0	10700	280	0.038
88.0	90.0	10300	260	0.039
82.0	100.8	13600	282	0.048
80.0	93.4	13000	266	0.049
80.0	128.1	17100	337	0.051
80.0	122.5	18400	331	0.051
79.0	118.8	16400	318	0.052
78.0	128.1	17700	337	0.053

L_w – spray-water flow rate.
G_g – flue-gas flow rate.

2.4. CONCLUSIONS

Based on the experiments carried out in Wrocław it was stated that the only disadvantage of the desulphurization process was reactor clogging influenced by:

location of nozzles, their blocking and lack of air flow resulting in increase in water droplet size,

phenomenon of incomplete fuel burning in furnace resulting in rapid increase in ash carried by flue-gas stream,

length of spray lances.

It was proved that nozzle blocking took place after long standstill of the installation. During the time of operation the air clogging of "upper" level of nozzles was observed, while spray water decayed. It occurs if water level in compensation

tank reaches minimum (probably the result of sludgers clogging or too low spray-water pressure). Satisfying nozzle operation is achieved by changing and maintaining the desired spray water–compressed air pressure ratio. Therefore the increased load of lower nozzle levels is observed and compressed air only flows through "upper" nozzle levels. Disturbance in spray-water system results in scrubbing the reactor inner walls causing its clogging. To avoid this problem it is necessary to control combustion process and to regulate automatically the operation parameters: water and compressed air pressure before nozzle, inlet and outlet reactor and ESP gas temperature, compressed air pressure and flow rate, by-pass gas flow rate, spray-water flow rate, compressed air flow rate and velocity of rotary feeders.

REFERENCES

[1] Zmuda J. T., Smith P. Y., *Retroit Acid Gas Emission Controls for Municipal Waste Incineration. Impact of New Regulations*, paper not published, manuscript.
[2] Gostomczyk M. A., *Ochrona powietrza przed zanieczyszczeniem*, Metody i Urządzenia do Ograniczania Emisji Zanieczyszczeń Gazowych, Debe 1991.
[3] Simons G. A., *Parameters Limiting Sulfation by CaO*, Physical Sciences Inc.-1000, SR-315.
[4] Harriott P., Ruether J., Sudhoff F., *Prediction of SO_2 Removal for Power Plants Using Duct Injection of Lime Slurry*, Energy & Fuels 1991, Vol. 5, No. 2.

SUCHE METODY ODSIARCZANIA GAZÓW ODLOTOWYCH

Omówiono zasady i zalety suchych metod odsiarczania gazów odlotowych. Przedstawiono następujące technologie: LIMB, LIFAC, WAWO i COOLSIDE. Technologię WAWO zaprezentowano opierając się na badaniach przeprowadzonych w elektrociepłowni we Wrocławiu.

СУХИЕ МЕТОДЫ ОБЕССЕРЕНИЯ ОТХОДЯЩИХ ГАЗОВ

Обсуждены принципы и приметы сухих методов обессерения отходящих газов. Представлены следующие технологии: LIMB, LIFAC, WAWO и COOLSIDE. Технология WAWO представлена на базе исследований, проведенных в теплоэлектростанции во Вроцлаве.