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SIMULTANEOUS DESULPHURISATION AND DENITRIFICATION OF FLUE GASES

This paper deals with the possibility of simultaneous removing nitrogen oxides and sulfur dioxide in dry and semi-dry installations for flue gases desulfurization. It presents the results of the oxidation of NO to NO₂ and N₂O₃ and N₂O₅ in flue gases. The mixtures of calcium hypochlorite, sodium hypochlorite or hydrogen dioxide, all in the presence of powdered calcium hydroxide, are used as oxidants. The effectiveness of SO₂ and NO removal from flue gases is determined.

1. INTRODUCTION

Nowadays the necessity to reduce sulfur oxide and nitrogen oxides' emission into the atmosphere does not raise any doubts. However, the problem of choosing appropriate technologies of flue gases cleaning gives rise to discussion. It results mainly from different physicochemical characteristics of both pollutants and from their small quantities in huge streams of the gas that is cleaned. Additionally, the difficulty in the process of cleaning lies in the fact that the concentration of sulfur dioxide in flue gases depends mainly on the kind of the fuel burnt, and the amount of nitrogen oxides released in the combustion processes depends also on the combustion temperature, the contact time of reagents (nitrogen and oxide) during combustion (especially in the high temperature zone), the type of boilers, etc. [1].

Recently in international research, more attention is paid to the methods of simultaneous removal of sulfur oxide and nitrogen oxides from flue gases. Most often, the known methods of a separate removal of sulfur oxide and nitrogen oxides from flue gases are modified.

As a result of research, numerous methods allowing us to reduce the emissions of sulfur oxide and nitrogen oxides [2], [3] have been developed. Those methods can be divided into two main groups:

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- primary methods, which reduce the amount of sulfur dioxide and nitrogen oxides produced in the process of combustion,
- secondary methods, which remove sulfur dioxide and nitrogen oxides from flue gases.

The use of primary and secondary methods, directed at denitrification of flue gases, is connected with some negative consequences.

Primary methods are widely used because of the positive relation of the extent of flue gases denitrification to the costs. Their basic drawbacks are: the necessity of complex system of combustion controlling and monitoring as well as the possibility of increasing the emission from incomplete combustion (carbon oxide, hydrocarbons, carbon black). Therefore, the choice of a specific type of a primary method of flue gases denitrification should result from a deep analysis of the possibilities of modifying a boiler, which would take into account the quality of fuel combusted, the type of boiler and local conditions of the plant.

Secondary methods are not only reliable, but also highly effective in denitrification of flue gases. However, they have not been widely applied in Poland, mainly because of high investment and exploitation costs. The application of a specific method of flue gases denitrification should be preceded by detailed technical and economical analyses, which would take into account specific conditions of the plant.

The above comments lead to a conclusion that the choice of an appropriate technology depends on many factors, merging into a method that meets emission standards for sulfur dioxide, nitrogen oxides and other pollutants, at the lowest investment and exploitation costs.

2. SIMULTANEOUS DESULFURISATION AND DENITRIFICATION OF FLUE GASES

It is estimated that after 2016 the concentration of nitrogen oxides in flue gases emitted from energetic boilers (over 500 MW) will not be allowed to exceed $200 \text{ mg NO}_2/\text{m}_n^3$ [4]. Such a concentration of nitrogen oxides is already compulsory in flue gases emitted from waste incinerator.

Under domestic conditions, the process of simultaneous desulfurisation and denitrification of flue gases from energetic boilers will be successfully carried out through dry and semi-dry methods of flue gases desulfurisation [5]–[9], which allow us to meet the emission standards of sulfur dioxide, nitrogen oxide and other pollutants [10] at the lowest investment and exploitation costs [11].

2.1. DESULFURISATION OF FLUE GASES

Searching for a simple and cheap way of reducing SO₂ emission has led to the invention of the simplest pattern of SO₂ removal from flue gases. This pattern is based on two assumptions [5]–[7]:

- An active dry sorbent should be introduced to flue gases flowing to dust collector in such a way as to avoid blocking the flue gas channel and to use efficiently the sorption capacity of sorbent (50 to 80%).
- The products of SO₂ reaction with sorbent and non-reacted sorbent in a highly efficient dust collector should be removed from flue gases. Such a process would be advantageous, because it allows us to prolong the contact time of non-reacted sorbent with SO₂ in dust collector, so that a further sorption of SO₂ can follow, for example during its flow through the layer of the products and sorbents formed on the fabric filter.

The attempts to follow the above-mentioned pattern make it possible to fully learn the process of flue gases desulfurisation and to define indispensable technical and economical conditions to be performed in practice (methods: Coolside [12], Turbosorb [13], NID [14]).

In general, one can distinguish two methods. The first one, in which dry sorbent is injected into the flue gases polluted in front of an efficient dust collector, is very cheap. Another one, in which dry sorbent is injected into cleaned flue gases, has considerably higher investments costs, because it needs a second dust collector (fabric filter), but ensures higher effectiveness of flue gases desulfurisation and smaller sorbent consumption. The combined option means using the second level, in which sorbent carried by flue gases (CaO, Ca(OH)₂) is activated by water or sorption mixtures. Water increases the humidity of flue gases, decreases the resistance of dust and reduces sulfur dioxide emission as a result of increasing sorbent's reactivity [7].

2.2. DENITRIFICATION OF FLUE GASES

Attempts to solve the problem of raising the level of oxidation of nitrogen oxides were made as early as in the 70-ties and 80-ties of the last century. This goal was achieved by applying absorption with simultaneous oxidizing nitrogen oxides with compounds of strongly oxidizing capacities in liquid phase [15]–[21], e.g. sodium hypochlorite, sodium chlorite, calcium hypochlorite, potassium permanganate, potassium dichromate, salts of iron, copper, nickel and cobalt, and hydrogen dioxide solution. The author's research [17] has led to the technology of removing nitrogen oxides from industrial flue gases. However, the problem of intensification of simultaneous removal of nitrogen oxides and sulfur dioxide from flue gases in energetic boiler remains unsolved.

Currently, due to the necessity of finding cheap and effective methods of reducing nitrogen oxides' emission to the level of 200 mg NO₂/m³, the research on oxidizing NO in gaseous phase with simultaneous sorption of NO₂ and SO₂ in suspensions or on

dry alkaline sorbents has been undertaken [9], [21], [22]. It is known that due to simultaneous NO oxidation and SO₂ removal, the temperature before the fabric filter should amount to 338 K, and the excess of SO₂ sorbent is expressed by the Ca/S = 2 ratio [9]. These tests have proved that Ca(OCl)₂ is an effective oxidant of NO.

An additional stimulus to such tests is the necessity of reducing the emission of nitrogen oxides from waste incinerators to the similar level of 200 mg NO₂/m_n³, whereas due to the content of hydrogen chloride in these flue gases (up to 1000 mg/m_n³), there are no obstacles for applying chloric oxidants.

3. EXPERIMENT CONDITIONS

The tests were carried out on real flue gases in the tests installation WAWO-2 in KOGENERACJA SA., described in works [8]–[10] and presented in the figure. The installation consisted of three columns (1 – moistener, 4, 5 – absorption towers), which formed a reactor closed with a cloth filter (6). The proportioning system of oxidative mixtures (9) consisted of a mixture tank, a proportioning pump, a rotameter and a nozzle, whereas the proportioning system of a dry sorbent (8) consisted of a sorbent tank, compressed air and balance.

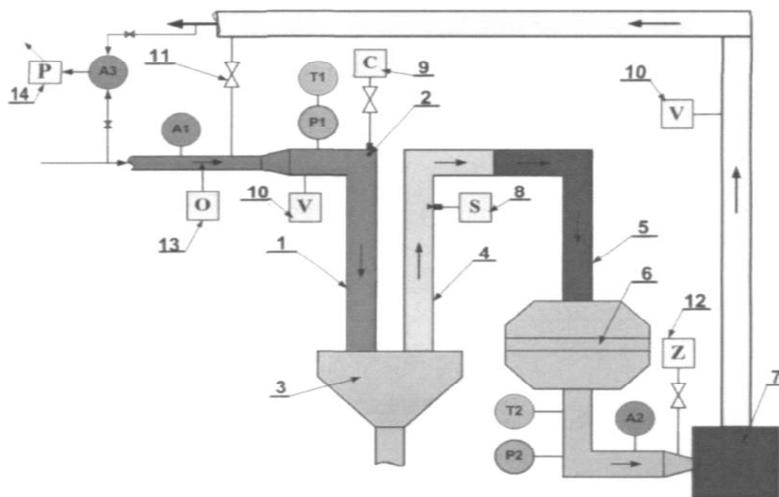


Fig. 1. Scheme of test installation WAWO-2:

- 1 – moistener, 2 – water nozzle, 3 – funnel, 4 – absorption tower I, 5 – absorption tower II, 6 – fabric filter, 7 – fan, 8 – proportioning system of dry sorbent, 9 – proportioning system of liquid oxidant, 10 – anemometer, 11 – gate valve for regulating SO₂ concentration, 12 – gate valve for regulating the stream of flue gases, 13 – proportioning system of ozone, 14 – draw-lift pump, A1, A2 – flue gases analysers Madur GA-40, T1, T2 – measurement of temperature and humidity of flue gases, P1, P2 – measurement of flow resistance

The research aimed at defining the extent of removing NO from flue gases in OP-430 boiler in the process of simultaneous removal of SO₂ and NO_x by simultaneous injection of the mixture of powdered caustic lime (Ca(OH)₂) either with sodium hypochlorite (NaOCl) or with hydrogen dioxide as an oxidant into the reactor before the fabric filter. Simultaneous measurements of the effectiveness of NO_x and SO₂ removal from flue gases were made.

The parameters of the research were as follows:

the stream of flue gases,	500 m ³ /h ± 20 m ³ /h ,
the concentration of SO ₂ in flue gases,	1580 mg /m ³ ± 20 mg /m ³ ,
the concentration of NO in flue gases,	510 mg /m ³ ± 10mg /m ³ ,
the mass stream of Ca(OH) ₂ ,	2000 g/h ± 100 g/h,
the mass stream of Ca(OCl) ₂ ,	389 g/h ± 20 g/h,
the mass stream of NaOCl,	405 g/h ± 10 g/h,
the mass stream of H ₂ O ₂ ,	185 g/h ± 5 g/h,
the volumetric stream of oxidant,	7.3 dm ³ /h,
the molar ratio of oxidant / NO,	1.0,
the time of contact between flue gases and reagent,	6.6 s,
the temperature of flue gases during injection,	338 K.

The flow rate of 2000 g/h of a dosed Ca(OH)₂ dust was estimated on the basis of preliminary tests, which aimed at checking the system and establishing the influence of desulphurization on NO concentration during the flow of flue gases without oxidant. It was established that the highest effectiveness of SO₂ removal from flue gases (over 80%, as economically profitable) was reached at the flue gases temperature of 338 K and molar ratio of Ca(OH)₂/SO₂ = 2, whereas Ca(OH)₂ dust injection into flue gases did not affect NO removal (average effectiveness equalled 3.5%). In the tests with the addition of oxidant, its planned amount was to make the concentration of active oxide equal to 88 g O/h, which at the average NO concentration of 510 mg/m³ and 6% O₂ in flue gases gave the molar ratio of oxidant/NO of 1.0.

After balancing the temperature on the inlet and outlet of the installation, the analysers of the constant measurement of SO₂, NO and O₂ in raw and cleaned flue gases were switched on. At first they measured the cleaned flue gases, and after 10 minutes – raw flue gases. The experiment was carried for 8 hours, the results were levelled after every hour.

4. RESULTS

The results of the experiments on the pilot installation with the injection of the mixture of calcium hypochlorite and powdered calcium hydroxide are shown in table 1. Table 2 presents the results of the research with the use of the mixture of

sodium hypochlorite with calcium hydroxide. Table 3 shows the results of the tests with the mixture of calcium hydroxide with hydrogen dioxide as an oxidant of nitrogen oxide.

Table 1

Concentrations of sulfur dioxide and nitrogen oxides at the inlet and outlet of the installation and the effectiveness of their removal as a result of the injection of the mixture of $\text{Ca}(\text{OCl})_2$ with $\text{Ca}(\text{OH})_2$ dust into flue gases at the temperature of 338 K, for 6% O_2

Sulfur dioxide (mg/m_n^3)		ηSO_2 (%)	Nitrogen oxides (mg/m_n^3)		ηNO_x (%)
Inlet	Outlet		Inlet	Outlet	
1607	153	90.5	503	182	63.8
1723	164	90.5	495	177	64.2
1601	148	90.8	509	185	63.7
1582	142	91.0	515	183	64.5
1542	137	91.1	517	194	62.5
1613	148	90.8	576	198	65.6
1541	131	91.5	502	165	67.1
1572	132	91.6	521	179	65.6
Average value		91.0	Average value		64.6

The results of the research (table 1) show that $\text{Ca}(\text{OCl})_2$ is a strong oxidant of NO. The average effectiveness of NO removal reached 64.6% with the average NO concentration in cleaned flue gases equal to $183 \text{ mg NO}_2/\text{m}_n^3$ and 6% O_2 , which gave the results below $200 \text{ mg NO}_2/\text{m}_n^3$ for 6% O_2 . Relatively lower effectiveness of NO removal results from the rule, according to which only $200 \text{ mg NO}_2/\text{m}_n^3$ of NO concentration should be reached at the installation outlet due to the cost of the oxidant. In the monitoring research, the achieved concentration equalled $10 \text{ mg NO}_2/\text{m}_n^3$ in the excess of the oxidant. The effectiveness of SO_2 removal under conditions of the experiment reached 91.0% in the average SO_2 concentration in cleaned flue gases reaching $144 \text{ mg SO}_2/\text{m}_n^3$ for 6% O_2 .

Those results confirm the possibility of simultaneous SO_2 and NO removal to the level below the assumed values of emission ($200 \text{ mg SO}_2/\text{m}_n^3$, $200 \text{ mg NO}_2/\text{m}_n^3$) in the processes of dry or semi-dry flue gases desulfurisation with the use of $\text{Ca}(\text{OCl})_2$ as an oxidant.

Calcium hypochlorite ($\text{Ca}(\text{OCl})_2$) in the form of the mixture of $\text{Ca}(\text{OCl})_2$, $\text{Ca}(\text{OH})_2$ and CaCl_2 is widely available on the market and commonly used for water chlorination, etc.

Table 2

Concentrations of sulfur dioxide and nitrogen oxides at the inlet and outlet of the installation and the necessity of their removal due to injection of the mixture of NaOCl oxidant with Ca(OH)₂ dust into flue gases of the temperature of 338 K, for 6% O₂

Sulfur dioxide (mg/m _n ³)		η SO ₂ (%)	Nitrogen oxides (mg/m _n ³)		η NO _x (%)
Inlet	Outlet		Inlet	Outlet	
1362	118	91.3	507	195	61.5
1584	131	91.7	504	193	61.7
1654	128	92.3	513	192	62.6
1596	122	92.4	501	187	62.7
1509	119	92.1	517	185	64.2
1602	117	92.7	492	176	64.2
1647	115	93.0	511	178	65.2
1672	113	93.2	506	171	66.2
Average value		92.4	Average value		63.5

As a result of the research with the mixture of sodium hypochlorite (table 2) a very high effectiveness of NO removal from flue gases was reached (on average 63.5%), with the average concentration of NO at the installation outlet equal to 185 mg/m_n³ for 6% O₂. The average effectiveness of SO₂ removal equalled 92.5% and the average SO₂ concentration at the installation outlet was 120 mg/m_n³ for 6% O₂. The outlet concentrations achieved were below the assumed values of emission (200 mg NO₂/m_n³, 200 mg SO₂/m_n³).

SO₂ removal proved to be extremely effective, which was caused, among others, by the presence of additional quantity of NaOH (approx. 20 g/dm³), which is a very effective sorbent of SO₂ in the proportioned mixture of NaOCl.

Sodium hypochlorite (NaOCl) is a disinfection agent, widely available on market. It is a by-product in the production of chlorine, NaOH and NaCl.

The results obtained with the use of hydrogen dioxide (H₂O₂) have shown that it is a weaker oxidant in relation to NO than sodium hypochlorite. The effectiveness of NO removal reached on average 55.2%, which gave the outlet concentration of NO equal to 224 mg/m_n³ for 6% O₂, which slightly exceeds the assumed value (below 200 mg/m_n³ for 6% O₂). The average effectiveness of SO₂ removal from flue gases reached 88.1%, with the outlet concentration – on average 199 mg SO₂/m_n³ for 6% O₂.

Hydrogen dioxide (H₂O₂), the so-called peroxide, is available on market as a 35% mixture and used as an oxidant in the chemical, cosmetic and pharmaceutical industry.

Taking account of environment protection, oxidizing NO with the use of H₂O₂ is far more profitable than with chloral oxidants. However, under comparable conditions

of tests on the pilot installation, the effectiveness of NO removal from flue gases with the use of H₂O₂ was on average by 8% lower.

Table 3

Concentrations of sulfur dioxide and nitrogen oxides at the inlet and outlet of the installation and the necessity of their removal due to injection of the mixture of H₂O₂ oxidant with Ca(OH)₂ dust into flue gases of the temperature of 338 K, for 6% O₂

Sulfur dioxide (mg/m ³)		η SO ₂ (%)	Nitrogen oxides (mg/m ³)		η NO _x (%)
Inlet	Outlet		Inlet	Outlet	
1821	234	87.1	505	237	53.1
1485	187	87.4	504	226	55.2
1635	195	88.1	476	217	54.4
1552	185	88.1	506	234	53.8
1704	192	88.7	502	221	56.0
1612	184	88.6	512	217	57.6
1535	177	88.5	501	224	55.3
1387	163	88.2	492	216	56.1
Average value		88.1	Average value		55.2

5. SUMMARY

On the basis of the results obtained it can be inferred that it is possible to meet emission standards for sulfur dioxide and nitrogen oxides in flue gases on the level of 200 mg/m³:

- through the injection of the mixture of oxidant and sorbent into flue gases in the systems of dry or semi-dry flue gases desulfurization,
- at relatively small investment costs (for example, through adding injection system of the oxidant),
- the streams of oxidant and sorbent can be corrected during the work of the installation based on the current concentrations of SO₂ and NO in cleaned flue gases and on the amount of recirculated waste from fabric filter.

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JEDNOCZESNE ODSIARCZANIE I ODAZOTOWANIE SPALIN

Wskazano na możliwość jednoczesnego usuwania tlenków azotu i dwutlenku siarki w suchych i pół-suchych instalacjach odsiarczania spalin. Przedstawiono wyniki badań procesu utleniania NO do NO₂, a także N₂O₃ i N₂O₅ w spalinach. Jako utleniacz stosowano roztwór podchlorynu wapniowego lub podchlorynu sodowego oraz roztworu nadtlenu wodoru w obecności pyłu wodorotlenku wapniowego. Określono skuteczność usuwania SO₂ i NO ze spalin.