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FLUE-GAS CLEANING AFTER THERMAL WASTE UTILIZATION

The paper presents universal technology of cleaning flue gases from boilers, where municipal waste and dangerous waste (medical as well), coal, lignite, mazout are burned. This technology allows us to remove pollution from flue gases to any lower level. The use of oxidizer for NO oxidation to acid anhydride enables us to remove it in a reaction with $\text{Ca}(\text{OH})_2$, similarly to SO_2 , SO_3 and HCl . Removing dioxins, furans and heavy metals from flue gas is done by injection of active charcoal to flue gas before a fabric filter. The dose size of oxidizer and active charcoal affect the effectiveness of removing NO and dioxins, furans and heavy metals. The analysis of exploitation costs was made for efficiency of cleaning flue gases to the level of the emission of pollution that is in the Waste Act [1]. The technology was developed on the basis of research results from the pilot installation.

1. INTRODUCTION

According to the Waste Act [1], thermal waste utilization is waste combustion by oxidation and other thermal processes of waste utilization including pyrolysis, gasification and the plasma process, if substances made during those processes are burnt. It can be done in a waste incineration plant or a waste co-incineration plant that complies with the requirements of detailed regulations.

According to the Waste Act, thermal, municipal and dangerous waste utilization is a process for rendering waste harmless (D10 – waste thermal utilization in installations or a unit located on the land) including waste other than municipal or dangerous waste and municipal packaging wastes specified in the Waste Act (Art. 49a, items 1 and 3) – recovery process (R1 – used as a fuel or other way to be used in making energy).

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In the analysis of the possibilities of thermal waste utilization, the Ordinance of the Ministry of Economy of 21.03.2002 (Official Journal of Laws No. 37, item 339 as amended) is essential. It specifies the requirements of carrying out thermal waste utilization.

The regulatory provisions specify the conditions during thermal waste utilization in a combustion chamber, the following temperatures are the minimum values:

– 1100 °C for waste with the content of organic chlorine derivatives combination higher than 1% converted to chlorine,

– 850 °C for waste with the content of organic chlorine derivatives combination lower than 1% converted to chlorine.

Table
Allowable amount of emission to the air from a waste incineration plant

Name of substance	Unit (*)	Value
Dust	mg/m ³ _u	10
Organic gases and vapours (total organic carbon)	mg/m ³ _u	10
Hydrogen chloride (HCl)	mg/m ³ _u	10
Hydrogen fluoride (HF)	mg/m ³ _u	1
Sulphur dioxide (SO ₂)	mg/m ³ _u	50
Nitric oxide (NO) and nitrogen dioxide (NO ₂) as nitrogen dioxide for existing installations with nominal capacity of at least 6 Mg per hours, from new installations, i.e. working since January 1st, 2010	mg/m ³ _u	200
Nitric oxide (NO) and nitrogen dioxide (NO ₂) as nitrogen dioxide for older existing installation with nominal capacity less than 6 Mg per hour	mg/m ³ _u	400
Heavy metals and their metal compounds:		
Cadmium + thallium	mg/m ³ _u	0.05 (**)
Mercury	mg/m ³ _u	0.05 (**)
Antimony+arsenic+lead+ chromium+cobalt+copper+ manganese+ nickel+vanadium	mg/m ³ _u	0.5 (**)
Dioxins and furans	mg/m ³ _u	0.1 (***)

(*) Average day value in mg/m³_u with 11% content in flue gas.

(**) Average from test with time from 30 minutes to 8 hours.

(***) Average from test with time from 6 hours to 8 hours.

The time of detention of exhaust in the combustion chamber at the above temperatures cannot be shorter than 2 seconds. Other specified conditions refer to measuring appropriately the waste utilization level and the maximum content of non-oxidized organic compounds in slag and furnace ash. Concentration of pollutants in waste gases should not exceed the limits given in table.

New technologies of cleaning flue gases from heavy metals, mostly mercury, are being studied at the moment [7]. Multi-Pollution Control research is done on oxidation of nitric oxide [8]–[14].

This paper presents research concerning mercury removal from coal-fired power and incinerator plants using oxidizer and sorbent injections. In our research, chlorinated lime $\text{Ca}(\text{ClO})_2$ was used as an oxidizer and powdered calcium hydroxide $(\text{Ca}(\text{OH})_2)$ was used as a sorbent. In such technology, elemental mercury undergoes oxidation by oxidizer and then is removed on sorbents and a filter cake. Moreover, sulphur dioxide (SO_2), hydrogen chloride (HCl) and nitrogen oxides (NO_x) are removed as well. Calcium hydroxide removes HSO_2 , SO_3 , HCl , HF , HNO_2 , and HNO_3 .

2. METHODOLOGY

The research was carried out at a pilot plant called WAWO-2 located at the already mentioned Wrocław heat power plant [2], [12]. A gas stream was taken from OP-430 boiler and dedusted in an electrostatic precipitator, then it was sucked into the pilot plant. The pilot plant is equipped with three sequential, parallel columns followed by a fabric filter. The first one is the humidifier, where water or liquid solutions can be injected by a metering pump, and the next two ones are sorption columns where dry, powdered sorbents can be injected by a vacuum pump. The main goal of our research was to estimate mercury removal, with simultaneous control of SO_2 and NO_x from real flue gases in a process of oxidizer and sorbent injection. Moreover, the influence of flue gas temperature on mercury removal was also assessed. Our research was based on two important guidelines. Firstly, experiments must be conducted in a way that would make it possible to determine the relationship between mercury removal and flue gas temperature with all other parameters remaining constant. Secondly, a suitable excess of the oxidizer and sorbents must be used, that is $0.75 \text{ Ca}(\text{ClO})_2/\text{NO}$ and $1.1 \text{ Ca}(\text{OH})_2/\text{SO}_2$. The excess oxidizer guarantees elemental mercury oxidation, and excess sorbents guarantee the sorption of acid flue-gas components. Experiments were started when the installation was completely heated and then measurements of the concentrations of flue gas components at the inlet and outlet of the installation were carried out.

The concentrations of SO_2 , NO , O_2 were constantly measured in raw and cleaned flue gases by continuous analyzer MADUR GA-40. Total mercury concentrations were measured by continuous analyzer LUMEX RA-915, situated between the inlet and outlet of the installation. Cleaned and raw flue gases were alternately passed through the analyzer every ten minutes, we administered only one analyzer. Only six minutes in the middle of the measurements were taken into consideration; the first two and last minutes were rejected. Our experiments started when the mercury concentration at the inlet and outlet of the installation was almost constant ($+/- 5\%$).

Constant parameters:

- flue gas stream, 700 m³/h at a temperature of 150 °C,
- SO₂ concentration in flue gas, 1500 ± 30 mg/m³,
- NO concentration in flue gas, 320 ± 20 mg/m³,
- Hg concentration in flue gas, 10–11 µg/m³,
- amount of chlorinated lime (Ca(OCl)₂), 0.8 kg/h,
- amount of calcium hydroxide (Ca(OH)₂), 0.7 kg/h.

Changeable parameters:

- flue gas temperature, 141.9–62.7 °C,
- amount of water humidifier, 5, 10, 15, 20 dm³/h.

The amount of 5, 10, 15 and 20 dm³/h water was introduced into the humidifier. The weight ratio of sorbents to the concentration of SO₂ and NO was kept constant; only the concentration of Ca(OCl)₂ and Ca(OH)₂ were changeable, in order to achieve adequate temperature of cleaned flue gases. Powdered Ca(OH)₂ in quantities of 0.7 kg/h was introduced into the sorption column by the feeder. After stabilizing the temperature and SO₂, NO, O₂ concentrations of clean flue gases, the measurement of mercury concentration was commenced using the LUMEX analyzer. First, the mercury concentration in cleaned flue gases was measured and after ten minutes it was measured in raw flue gases. Experiments were done in this way because we had only one mercury analyzer. Five experiments were done; each of them lasted two hours.

3. RESULTS

The results are presented in figures 1 and 2.

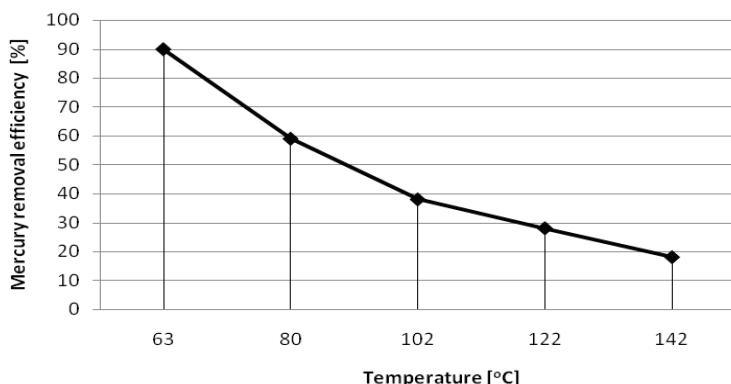


Fig. 1. Mercury removal efficiency vs. temperature at 5, 10, 15, 20 dm³/h water and 0.8 kg/h Ca(OCl)₂ and 0.7 kg/h Ca(OH)₂ injections

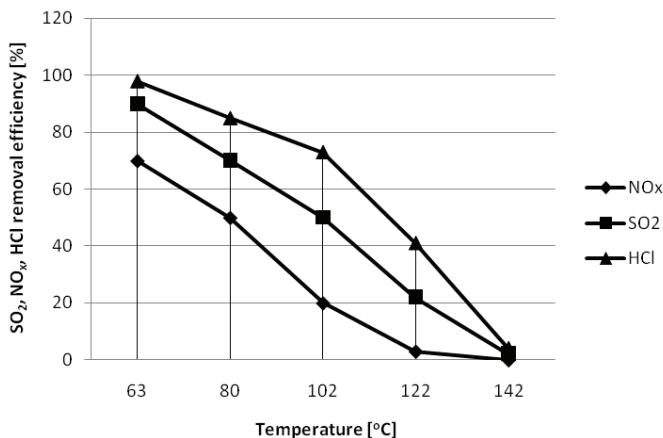


Fig. 2. SO₂, NO_x and HCl removal efficiency vs. temperature at 5, 10, 15, 20 dm³/h water and 0.8 kg/h Ca(OCl)₂ and 0.7 kg/h Ca(OH)₂ injections

Results presented in figure 2 show that the efficiency of pollution removal from flue gases (with the same level of injection of sorbent and oxidation) most of the time depends on temperature (stream dosage of water). The reactor can effectively remove HCl, SO₂, NO_x only if the temperature of flue gases is lower than 70 °C. At higher temperatures the removal effectiveness is much lower. The test was let through flue gases through the whole installation (temperature of 142 °C) and the registered slightly lower concentration of HCl and SO₂ probably has influence on the reaction of SO₂ and HCl with the ash collected on the filter cloth (stabilization of temperature was done after 2 hours of flowing flue gasses through installation). The concentration of NO and Hg did not change. This research was the basis for the development of the universal technology.

4. CHARACTERISTICS OF UNIVERSAL TECHNOLOGY

Similar technology of simultaneous reduction of NO_x and mercury emission is developed in the doctoral theses [3], [4] which are protected by patent applications [5], [6]. The essential characteristic of this technology is using oxidizer to oxidize NO to acid anhydrides, i.e. NO₂, N₂O₃ and N₂O₅, which are removed by reaction with Ca(OH)₂ similarly to SO₂, SO₃ and HCl.

The installation scheme which works according to this technology with extra active carbon dose system to remove dioxins, furans and heavy metals is shown in figure 3.

Waste gases from waste heat boiler (14) flow through flue gas-air heat exchanger (15), where they are chilled to 423 K (150 °C). Then flue gases flow into the reactor (7). Humidification and cooling of flue gases take place in the reactor (7) in water-

atomizing nozzles (16). The elimination of HCl, SO₂, NO_x gases and other acid gases is conducted by injecting powdered sorbent, containing a mixture of chlorinated lime and hydrated lime to reactor (7) through nozzles (17). Hydrated lime is stored in container (1), where it is provided to mixer (5) by feeder (3), where it is mixed with chlorinated lime in the right proportion. Chlorinated lime is moved from store container (2) to mixer (5) by feeder (4). The mix of sorbents (the proportion is provided for the actual concentration of SO₂, HCl and NO_x) from mixer (5) is periodically sent to intermediate container (6), where with help of compressed air it is pumped to reactor (7) all the time by nozzles (17). The products of the reaction carried by flue gases, unreacted sorbent and ash from waste burning are pumped to fabric filter (FF) (10), where they are cleaned by fan (11) are pumped to chimney (12).

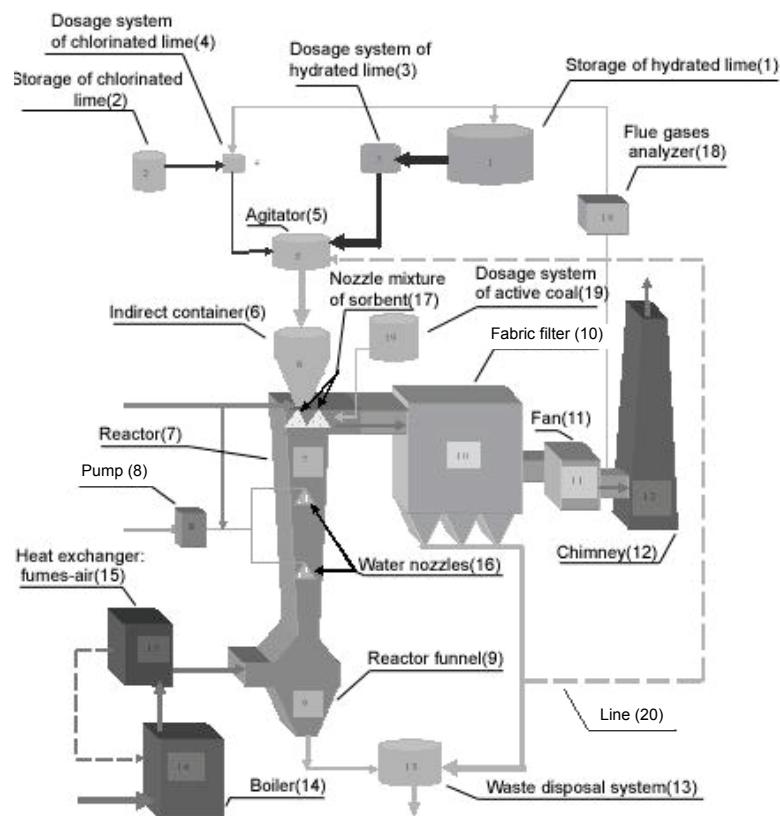


Fig. 3. Technology scheme of flue-gas cleaning in an incineration plant

50% of waste is sent to storage (13) and from there it is delivered to a sealed landfill. The residual ash from the filter is delivered to mixer (5) by line (20). Data from analyzer (18) (concentration of NO_x) in cleaned flue gases make the increase

or decrease of the stream of chlorinated lime possible, it is delivered to the system by feeder (4). The data from analyzer (18) show the current concentration of SO₂ in cleaned flue gases and make the increase or decrease of the stream of hydrated lime possible, it is delivered to mixer (5). Removing dioxins, furans and heavy metals can be done by the injection of activated charcoal from system (19) to flue gases before fabric filter (10). In the funnel under reactor (9), bigger ash particles are collected and then they are periodically or permanently removed to waste disposal system (13).

Cost analysis of the installation for municipal waste incineration to clean around 150 000 m³/h of flue gases evolving during the combustion of 15 Mg/h municipal waste is as follows:

Initial data:

- Calorific value of wastes = 7 MJ/kg.
- Time of incinerator work = 7000 h/a.
- Mineral substances = 26%.
- Boiler with step grate and turbine.
- Emission: SO₂ = 2.35 kg, NO = 1.22 kg, HCl = 3.76 kg, ash = 23.5 kg [per 1 Mg of waste] (before installation of flue-gas cleaning).
- Exploitation cost = 6 million PLN/a.
- Electric power generation = 61 250 MWhe (for our needs = 8400 MWhe) = Eel = 52 850 MWhe*160 PLN/Mwhe = 8 456 000 PLN/a.
- Heat power generation = 112 292 MWhth = Eth*72 PLN/MWhth = 8 085 024 PLN/a.
- Yearly income is about 16.5 million PLN/a.
- Investment cost for installation of flue-gas cleaning = 6 000 000 PLN.

5. CONCLUSIONS

The technology presented allows us to remove pollutant from flue gases to lower its level (it depends on the amount of provided oxidizer and active charcoal). The analysis of exploitation cost was made for the efficiency of cleaning flue gases to level of pollutant emission which is acceptable for waste combustion installation (table).

This technology is universal and can be used to clean flue gases from boilers, municipal waste and dangerous waste, coal, lignite and mazout.

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