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Methods to Reduce Mercury and Nitrogen Oxides Emissions from Coal Combustion Processes

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Abstract

The chapter presents the issue of reducing mercury and nitrogen oxides emissions from the flue gas of coal-fired boilers. The issue is particularly relevant due to the stricter regulations regarding exhaust gas purity. A brief review of the methods for reducing Hg and NO_x emissions has been made, pointing out their pros and cons. Against this background, the results of the authors' own research on the injection of selected oxidants into flue gases to remove both of these pollutants are presented. The injection of sodium chlorite solution into the flue gas (400 MWe lignite fired unit) upstream the wet flue gas desulphurization (WFGD) absorber contributed to the oxidation of both metallic mercury and nitric oxide and enhanced their removal efficiency. The results of tests on lignite and hard coal flue gases indicate that in order to reduce the unfavorable phenomenon of mercury re-emission from WFGD absorbers, in some cases, it is necessary to add selected chemical compounds (e.g., sulfides) to the desulfurization system. The results of field tests for flue gas from lignite (400 MWe unit) and hard coal-fired boilers (195 and 220 MWe units) confirmed the usefulness of oxidizer injection technology to reduce mercury emissions below the level required by BAT conclusions.

Keywords: Hg emissions, NO_x emissions, combustion, industrial pollution, heavy metals

1. Introduction

In nature mercury is present in trace amounts only; due to its toxicity and the ability to join various natural cycles, it poses a threat to human health and life. Mercury exposure, even in small amounts, poses a threat to both people and the environment. A global study commissioned by United Nations Environment Programme (UNEP) confirmed the high environmental impact of mercury, entirely justifying the actions implemented to combat its spread on the international level. In recent years, the European Union has been systematically tightening standards for permissible mercury concentrations in atmospheric air.

According to UNEP data, in 2015 the global emissions from anthropogenic sources amounted to 2220 tons of mercury, accounting for almost 30% of the total atmospheric emissions of mercury. The remaining 70% comes from environmental processes and contemporary natural sources [1]. The technological processes with

the largest share in mercury emissions are gold production, 38%; coal combustion, 21%; nonferrous metallurgy, 15%; cement plants, 11%; waste incineration plants processing mercury-containing waste, 7%; and combustion of other fuels, including biomass, 3%. Analyzing data on mercury emissions in the respective continents, it can be stated that we find the highest ones in Asia, with about 1084 tons p.a.; in South America, about 409 tons p.a.; Sub-Saharan Africa, 360 tons p.a.; and in the European Union, with 77.2 tons p.a. [1]. Therefore, we can see that the processes of burning fossil fuels form one of the most significant sources of global atmospheric emissions of mercury.

Research on Polish coals [2] demonstrates that the average mercury content in hard coal ranges from 50 to 150 ppb and 120 to 370 ppb in the case of lignite. For comparison, the mercury content of American coals is about 30–670 ppb, with the average content for hard coal of 70 and 118 ppb for lignite. The mercury content in furnace waste indicates that it is mainly found in fly ash and only a small part of it in slag. Literature data indicates that in the result of burning coal, approximately 30–75% of the mercury, contained in the fuel, will be released into the atmosphere [3].

In the process of coal combustion, a number of chemical reactions occur that lead to the decomposition of all chemical compounds containing mercury. In the result of these processes, at a temperature above 600°C, only the metallic mercury Hg^0 in the form of vapor will be present in the exhaust gas [4]. As the exhaust gas is cooled below 540°C [5], this mercury can be oxidized by gas phase components such as NO_2 , HCl , SO_2 , H_2O , and fly ash, producing various compounds of mercury (**Table 1**).

It was noticed that when burning coals containing significant amounts of chlorine, bromine, or iodine, the concentration of oxidized mercury increases with simultaneous decrease in concentration of metallic mercury. In the process of burning carbons containing chlorine, bromine, or iodine, the process of mercury oxidation is such that during this combustion salts containing chlorine, iodine or bromine is decomposed into HCl , HI , and HBr , whereby $0.5 \div 9\%$ of these compounds are further decomposed to Cl_2 , I_2 , and Br_2 . These react with metallic mercury to form $HgCl_2$, $HgBr_2$, and HgI_2 salts, respectively, which are stable at high temperatures in vapor form. Oxidized mercury is removed from the flue gas both in dust collectors and in wet and semidry flue gas desulfurization units [6]. However, the efficiency of removal of metallic Hg^0 in the aforementioned devices is low.

No.	Name	Symbol	Boiling point
1.	Mercury	Hg	356.6°C
2.	Mercuric chloride	$HgCl_2$	302.0°C
3.	Mercuric bromide	$HgBr_2$	322.0°C
4.	Mercury(II) iodide	HgI_2	354.0°C
5.	Mercurous oxide	Hg_2O	Decomposes at >100°C
6.	Mercuric oxide	HgO	Decomposes at >500°C
7.	Mercury(I) carbonate	Hg_2CO_3	Decomposes at >130°C
8.	Mercury(II) nitrate	$Hg(NO_3)_2$	Melting point 79°C
9.	Mercury(II) sulfate	$HgSO_4$	Decomposes before reaching liquid phase

Table 1.
Mercury compounds in flue gases from coal combustion processes.

The degree of the removal of mercury and its compounds depends mainly on the degree of transition of metallic mercury to oxidized mercury, with HgCl_2 accounting for the main part of oxidized mercury. The value of Hg emissions depends on the combustion process and the method of exhaust gas purification; the mercury removal efficiency in an electrostatic precipitator is 30–40%, while in a wet desulfurization plant, as much as 80–90% of Hg^{2+} (divalent) mercury and mercury adsorbed by the solid phase will be removed, but in the case of elemental Hg^0 mercury, far less is removed, with a removal efficiency of just 26.6% [3].

The proportions between individual forms of mercury in the exhaust gas downstream the boiler depend mainly on the type of furnace and fuel characteristics (mercury, halides, and ash content of coal). The content of halides (fluorine, bromine, iodine, and chlorine) and mercury in fuel has the greatest impact on the amount of Hg^{2+} , while the ash content determines the amount of $\text{Hg}(\text{p})$ [7]. For example, the proportions between elemental mercury, oxidized mercury, and ash-bound mercury in flue gas downstream of a pulverized coal boiler are on average 56% (8–94%), 34% (5–82%), and 10% (1–28%), respectively [7]. The type of furnace is not without significance for the mercury speciation in the exhaust gas. Circulating fluidized bed boilers generate the highest amount of $\text{Hg}(\text{p})$ (up to 65% of the so-called total mercury Hg^{T} defined as $\text{Hg}^{\text{T}} = \text{Hg}^0 + \text{Hg}^{2+} + \text{Hg}(\text{p})$) due to the extended contact time between gaseous mercury and fly ash and the low temperature of the exhaust gas downstream of the boiler [7].

The European Commission (on July 31, 2017) established conclusions on the best available techniques (BAT) for large combustion plants (LCP). BAT conclusions tighten the regulations related to the emissions from combustion processes, including nitrogen and sulfur oxides, and introduce mercury emission limits (that were not present in the EU till that date). **Table 2** contains the permissible concentrations of mercury and nitrogen oxides in the exhaust gas, resulting from the BAT conclusions. BAT conclusions include ranges of emission limit values for mercury and nitrogen oxides in exhaust gases, with maximum concentration values that will apply from 2021 onwards. Permissible mercury concentrations in exhaust gases resulting from BAT conclusions [8] are referred to as total mercury Hg^{T} . These values vary depending on the status of the source. For existing sources with a capacity of $>300 \text{ MW}_t$, they are $1\text{--}4 \mu\text{g}/\text{m}^3_{\text{USR}}$ for hard coal and $1\text{--}7 \mu\text{g}/\text{m}^3_{\text{USR}}$ for lignite. For new sources with a capacity of $>300 \text{ MW}_t$, they are $1\text{--}2 \mu\text{g}/\text{m}^3_{\text{USR}}$ for hard coal and $1\text{--}4 \mu\text{g}/\text{m}^3_{\text{USR}}$ for lignite. Concentrations are converted to standard USR means conditions: (dry gas at a temperature of 273.15 K and a pressure of 101.3 kPa, calculated for oxygen content in the flue gas $\text{O}_2 = 6 \%$).

Oxidant	Oxidizing potential, V	Oxidizing potential relative to oxygen
Oxygen, O_2	0.695	1.00
Oxygen radical, O	1.229	1.77
Chlorine, Cl_2	1.360	1.96
Hydrogen peroxide, H_2O_2	1.760	2.53
Ozone, O_3	2.080	2.99
Chlorine (I) anion, ClO^-	0.890	1.28
Chlorate (III) anion, ClO_2^-	0.786	1.13
Hypochlorous acid, HClO	1.630	2.35

Table 2.
Oxidation potentials of oxidants used [31].

BAT conclusions include the range of mercury emission limit values for exhaust gases while specifying maximum concentration values that will apply from August 18, 2021 onwards. The lower values indicate levels that can be obtained using best available techniques, and as long as these values are not required now, it can be expected that existing and new coal units will have to achieve them in near future [8]. This means that users of combustion plants should seek for methods to achieve lower emission levels resulting from the BAT conclusions. The implementation of BAT conclusions thus forms a significant challenge for coal energy in Europe and in particular for the Polish energy sector. The introduction of emission limits also necessitates the addition of Hg^T measurement devices to the pollution monitoring system [8].

BAT conclusions also reduce the permissible levels of nitrogen oxides (NO_x) emissions. For existing sources, fired with hard coal and lignite, with a capacity of $>300 \text{ MW}_t$, these amount to 85 (65)–150 mg/m^3 , and for new sources with a capacity of $>300 \text{ MW}_t$ to 50 (65)–85 mg/m^3 in standard conditions.

The above provisions are associated with the need to implement *selective catalytic reduction* (SCR) and *selective non-catalytic reduction* (SNCR) techniques as well as other techniques, including integrated exhaust gas treatment (*multipollutant technologies*), in which a single device is applied to remove at least two pollutants. In this study, we would like to point to the possibility of such integrated flue gas treatment in absorbers of the wet flue gas desulfurization method. The wet limestone method is a common SO_2 removal technology used in power plants both in Europe and worldwide. The desulfurization efficiency of this method ranges from 90 to 95%. This technology is also very popular in Polish conditions, accounting for some 90% of the desulfurization installations.

2. Methods for reducing mercury emissions

2.1 Primary methods

Enrichment of coal prior to the combustion process, e.g., by removing pyrite, can significantly reduce mercury emissions. It is estimated that 65–70% of mercury in Polish coals occurs in combination with pyrite.

Coal enrichment methods are mainly based on physical separation of the mineral substance and involve the use of density differences (gravitational separation) or differences in the wettability of the components (flotation).

One of the methods that do apply dry gravitational separation is the removal of pyrite in purpose-modernized coal mills. The technology is offered by Hansom [9].

Primary methods also include changing the combustion process. For example fluidized bed furnaces to lower the exhaust gas temperature and ash grain composition or using of low emissions burners to lower exhaust gas temperature. Another solution is to replace the coal used for combustion and mixing high Hg and S content coals with those with lower contents of these elements [10]. What is also applied is the addition of halides, in the form of bromine, iodine, and chlorine salts, to the burning coal [11]. The oxidizing properties of these compounds contribute to the increase in the proportion of oxidized mercury in the exhaust gases, which in turn contributes to its more effective retention in existing aftertreatment devices. Unfortunately, these methods cannot guarantee the reduction of mercury to the level required by BAT conclusions.

2.2 Secondary methods

The degree of the removal of mercury and its compounds depends mainly on the degree of transition of metallic mercury to oxidized mercury. Secondary methods

consist mainly of removing oxidized mercury adsorbed on ash particles or other adsorbent, e.g., activated carbon, in its form bound with particulates—Hg(p).

An important group of secondary methods are the adsorptive mercury removal methods. They rely on binding of oxidized forms of mercury on the surface of adsorbents. What they use is the affinity of mercury vapors to various adsorbents. The most common adsorber is activated carbon in powdered form (powdered activated carbon). However, due to the limited efficiency of Hg⁰ reduction of this typical form of carbon, it is necessary to impregnate this medium with sulfur, iodine, chlorine, or bromine to improve the efficiency of mercury vapor retention. This increases the efficiency of mercury oxidation and its adsorption on PAC particles. Studies demonstrated that ordinary activated carbon can retain up to 80% of mercury in a higher oxidation state but only some 40–50% of elemental mercury. In contrast, carbon impregnated with sulfur, for example, adsorbs over 80% Hg⁰ and the iodine impregnated carbon virtually 100% [12].

2.2.1 Injection of activated carbon (PAC) in exhaust gases

Activated carbon is usually injected into the exhaust gas duct before the ESP or fabric filter (**Figure 1**). This technology is used in waste incineration facilities and coal-fired power plants. The effectiveness of this method depends primarily on the type and structure of PAC, the chemical properties of the sorbent surface, the amount of injected coal, and the temperature of the exhaust gas. The main disadvantage of this technology is the increase in the carbon content of ash, which significantly limits the possibilities of ash utilization. Sometimes it can also reduce dust collection efficiency, especially when particles of submicron scale are considered.

To tackle this issue, activated carbon injection downstream the ESP and further exhaust gas purification in the fabric filter are applied (**Figure 2**). However, this makes it necessary to dispose ash from two different locations [13].

Another solution for the injection of activated carbon into exhaust gases is the sorbent injection upstream the air preheater into the zone with a much higher temperature than in the solutions used so far downstream the air preheater or the electrostatic precipitator, i.e., the Alstom Mer-Cure™ technology [14] (**Figure 3**).

2.2.2 The use of systems for catalytic reduction of nitrogen oxides (SCR) for the oxidation of mercury

It was found, based on the research, that in flue gas denitrification installations based on the selective catalytic reduction method, the oxidation of Hg⁰ mercury

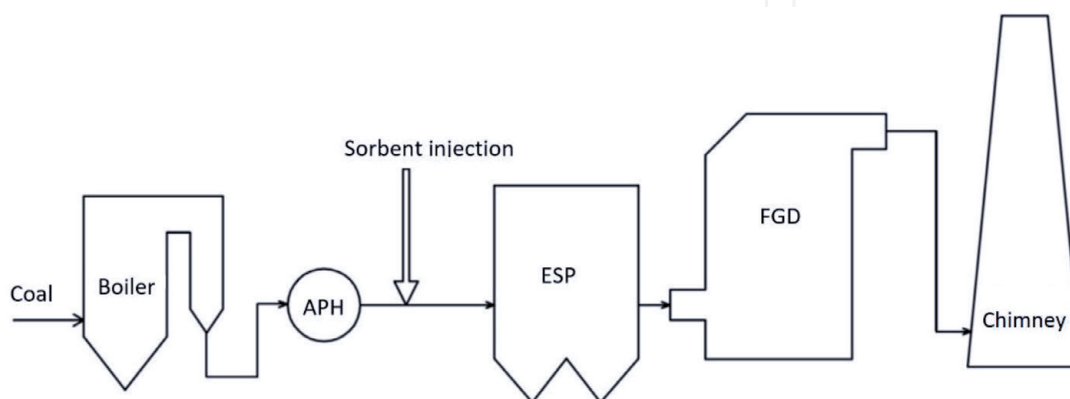


Figure 1.
Diagram of activated carbon injection technology upstream of the ESP; APH—air heater and FGD—flue gas desulfurization installation.

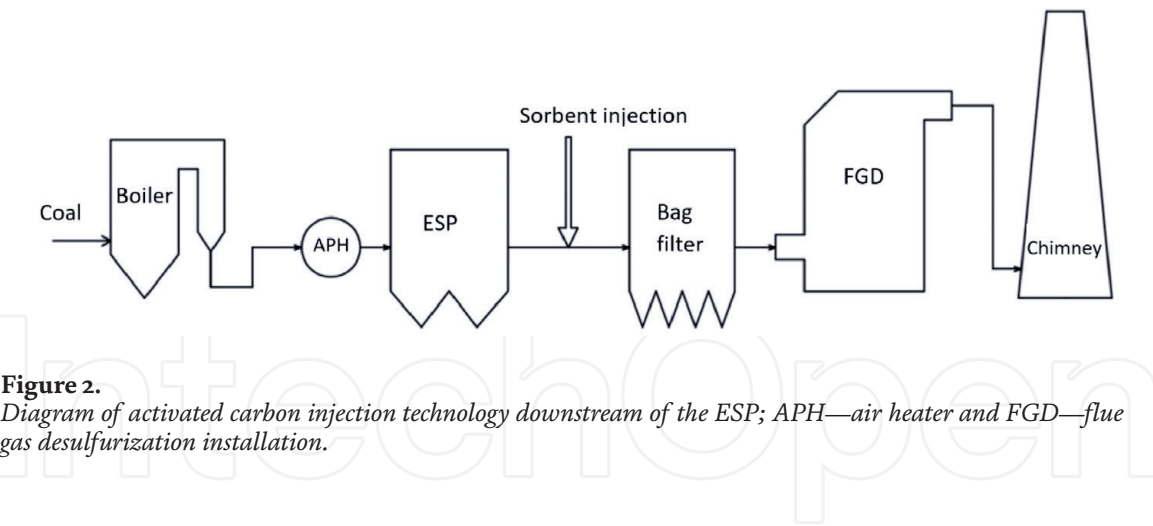


Figure 2. Diagram of activated carbon injection technology downstream of the ESP; APH—air heater and FGD—flue gas desulfurization installation.

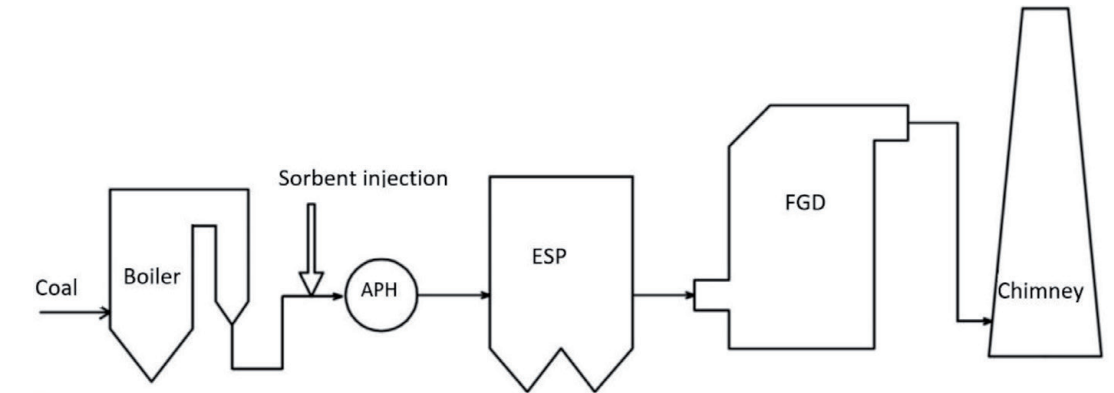


Figure 3. Diagram of the Mer-Cure™ technology for activated carbon injection; APH—air heater and FGD—flue gas desulphurization installation.

to Hg^{2+} form occurs. The condition for this process, however, is the appropriate chlorine content in the flue gas. Typically, for hard coal, this content proves sufficient to trigger the oxidation process. Important for this process is the fact that the denitrification and oxidation reactions of mercury cannot occur simultaneously, because they depend on the same active centers. Research in industrial conditions indicates that the achievable degree of mercury oxidation is up to 78% [15].

When lignite is burned, the absence of chlorine in the flue gas causes oxidation reactions not to occur. In this case, NH_4Cl injection upstream of the SCR catalyst is proposed to allow mercury oxidation in the catalyst (**Figure 4**). NH_4Cl or NH_4OH injection takes place in a zone with a temperature of about $370\text{--}420^\circ\text{C}$, and then activated carbon is added to the exhaust gas, after which the exhaust gas is directed

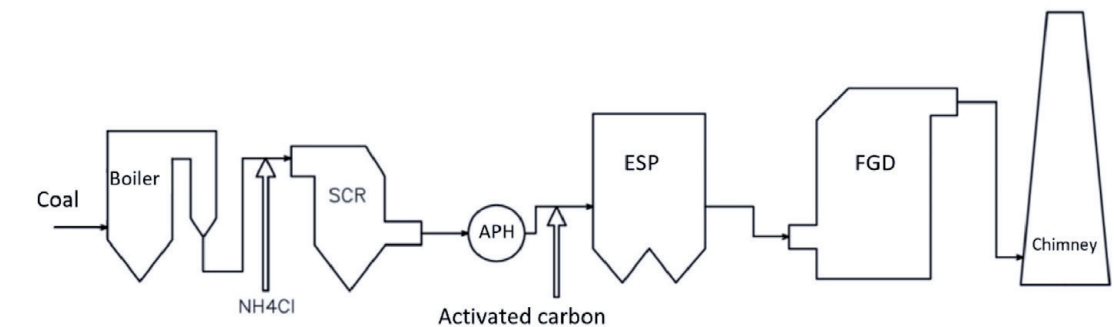


Figure 4. Diagram of mercury emission reduction technology for lignite-fired boilers: SCR—catalytic flue gas denitrification reactor; APH—air heater; and FGD—flue gas desulphurization installation.

to a dust collector (ESP or fabric filter), and finally to the absorber of the wet desulfurization method [16].

2.2.3 Injection of oxidizing additives and the use of fly ash as the adsorbent

Based on numerous studies [17–23], it was found that with use of chloride additives, it is possible to achieve high efficiency of mercury vapor adsorption on ordinary activated carbon or other sorbents (fly ash) [12, 24].

The proposed method involves the injection of aqueous additive solutions based on chlorite and/or potassium permanganate into the exhaust duct upstream the electrostatic precipitator [25] (**Figure 5**).

The degree of mercury oxidation in this technology depends on numerous parameters; the most important of them are flue gas temperature; flue gas composition, including the SO_2 , SO_3 , and NO concentrations; pH; and the chemical composition of fly ash. The main oxidized mercury compounds are HgO and $\text{Hg}(\text{NO}_3)_2$. Part of the oxidized mercury is adsorbed on fly ash particles and as $\text{Hg}(\text{p})$ is removed with dust in the ESP unit. The remaining Hg^{2+} mercury in gaseous form is retained in the WFGD absorber and is removed along with the wastewater.

2.3 Removal of oxidized mercury in flue gas purification devices

2.3.1 Removal of mercury in electrostatic precipitators

Tests of mercury content in fly ash upstream of the electrostatic precipitator demonstrate that it is several times higher than the mercury content of coal, which indicates a high sorption capacity of fly ash [26, 27]. The mechanism of mercury adsorption is as follows: in the boiler (temperature of above 1400°C), mercury is in the form of metallic mercury vapors, while the chlorine (HCl) contained in the flue gas activates carbon particles in the ash, and as the flue gas cools down, Hg^0 adsorbs in the chlorinated carbon pores and undergoes oxidation. If there is no HCl (HBr , HI) in the flue gas, there is also no Hg^0 sorption on the ash particles, and the sorption of oxidized HgCl_2 mercury is also low.

Research on mercury content in fly ash from hard coal combustion in both pulverized coal and grate boilers indicates a higher Hg content in fine grains. In **Figure 6** we present the results of mercury content testing in individual fractions of fly ash grains from a pulverized coal boiler.

The sorption of mercury and its compounds depends significantly on the flue gas temperature and the content of unburned carbon in fly ash particles. Thus,

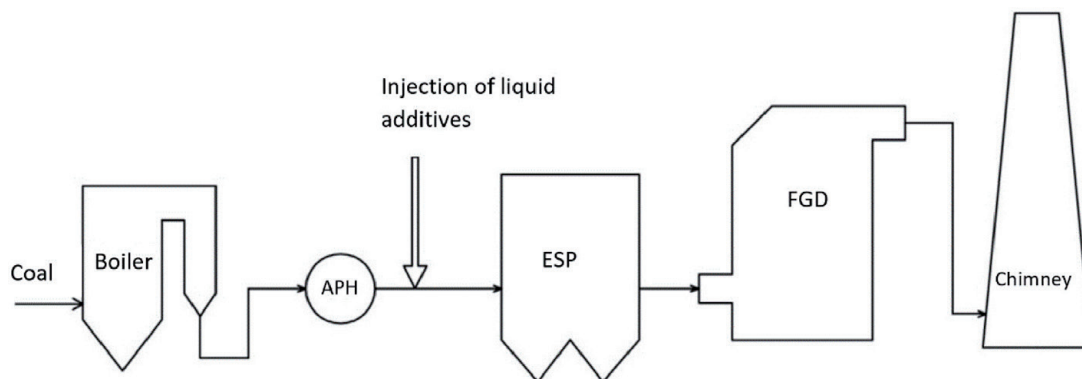


Figure 5.
Diagram of liquid additive injection technology upstream of the ESP: APH—air heater and FGD—flue gas desulphurization installation.

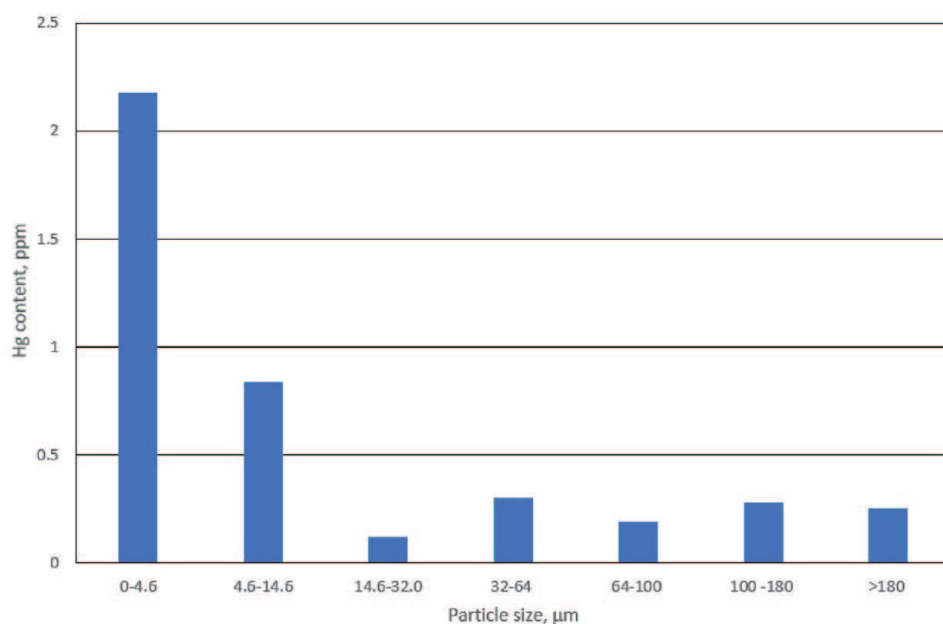


Figure 6.

Mercury content in individual fractions of fly ash from an OP-230 pulverized coal boiler.

the removal efficiency of mercury and its compounds increases with the mercury oxidation efficiency and the increased dust removal efficiency, especially of fine particles.

2.3.2 Removal of mercury in desulphurization installations

2.3.2.1 Mercury removal in absorbers of wet flue gas desulfurization installations

Oxidized mercury compounds contained in the flue gas (mainly the HgCl_2) are removed in FGD absorbers, whereas the Hg^{2+} reacts with the sulfides in the exhaust gas, e.g., with H_2S , to form mercury sulfide HgS , which is then precipitated. We also know the phenomenon of mercury re-emission from flue gas desulfurization absorbers. If the sulfide content in the suspension is too low, a chemical reduction of Hg^{2+} to Hg^0 may occur, resulting in higher concentration of metallic mercury downstream the absorber than upstream of it.

It is assumed that the efficiency of removing oxidized mercury in FGD absorbers reaches a value of up to 70%, while it can happen that almost all the oxidized mercury is removed in a dust collector, with only the metallic mercury reaching the absorber [6]. In this case, it is recommended to directly introduce oxidizing additive to the main FGD cycle [28].

2.3.2.2 Removal of mercury in semidry flue gas desulfurization installations

In semidry installations, the desulfurization process of the desulfurization reaction products (waste) remains dry. This process is implemented either by spraying lime milk in the upper part of the reactor (spray dryer) or using the so-called pneumatic reactor, where the sorbent and water are separately fed in its lower part. The resulting dry waste is most often recirculated, and the exhaust gases are dedusted in a fabric filter. The long residence time of sorbent particles in the reactor and the flow of exhaust gas through the filter cake in the bag filter allow for the additional benefit of removing quite a number of impurities, including mercury, provided that an appropriate sorbent is selected.

The semidry method using a pneumatic reactor integrated with a fabric filter for desulfurization of flue gas demonstrated a significant mercury removal efficiency of about 96%, when feeding additional activated carbon together with the primary sorbent (hydrated lime) [29].

3. Methods for reducing nitrogen oxides (NO_x)

Methods for reducing nitrogen oxides from coal combustion in power plants can be divided into two main groups, i.e., the primary and secondary methods. Primary methods rely on the organization of the combustion process in the chamber, primarily through the use of low-emission burners, air staging, exhaust gas recirculation, or reduction of the combustion temperature (fluidized bed boilers). The second group of methods is the secondary method, i.e., the selective catalytic and non-catalytic reduction and oxidative methods.

The latter group of secondary methods is applied in the integrated flue gas cleaning process. The basis for the operation of oxidative methods is the oxidation of sparingly soluble impurities in exhaust gases, i.e., nitric oxide and mercury to soluble forms, and their removal together with SO₂ by means of absorption or condensation [30]. There are many oxidants that are applied in oxidative methods. The most recommended oxidizing agents are ozone (O₃), hydrogen peroxide (H₂O₂), and numerous compounds of chlorine (NaClO, NaClO₂, Ca(ClO)₂, ClO₂) [31]. Whenever a gaseous oxidant is used, it may be fed directly to the flue gas duct; in the case of liquid oxidants, the conditions necessary for their evaporation should be provided, or, alternatively, they can be used as an additive to the sorption liquid in the absorber [18]. Comparison of the oxidizing potential of individual oxidants with respect to oxygen is presented in **Table 2**.

As you can see, ozone has the highest oxidation potential, and it has the valuable advantage in that it enables oxidation of NO and NO₂ to higher nitrogen oxides, while other oxidants oxidize it predominantly to NO₂ only [31]. The fact that oxidation occurs in the gas phase, which affects the increase in reaction rate, is also significant. Oxidation methods allow for the simultaneous removal of nitrogen oxides, sulfur dioxide, and mercury from flue gases in a single installation, with an efficiency exceeding 90%. Due to the lower operating and investment costs, they form an alternative to the commonly used combination of SCR and FGD. The presence of dust in the flue gas affects the amount of oxidizer used, and therefore a high-performance dust collector should be used upstream of the installation. In the case of commercial pollutant removal installations, ozone is the main oxidizer used for nitrogen oxides. Removal of the reaction products of nitrogen oxides with ozone takes place by means of absorption, for example, by the Lextran [32, 33] and LoTOx methods [34–36]. In Lextran method ozone is added to the flue gas before the absorber feed by mixture of water and catalyst. In LoTOx method, ozone is introduced before FGD absorber.

Another solution is to reduce pollution from flue gas with liquid oxidants. It involves their introduction into flue gas upstream of the wet or semidry flue gas desulfurization installations. Their task is to oxidize both the nitrogen oxide to NO₂ and the metallic mercury to Hg²⁺. In the case of wet flue gas desulfurization installations, liquid oxidants may also be added to the sorption liquid tank. Hydrogen peroxide [37] is a very popular oxidant used in industry, having the valuable advantage in that it is not as harmful to the environment as chlorine compounds and, at the same time, it is relatively cheap. Exhaust gas treatment with hydrogen peroxide is an extremely promising process. Many researchers around the world are working to improve its effectiveness in relation to the oxidation of nitrogen oxides. Works are carried out

on combining the dosing of hydrogen peroxide with metal oxides [38], activating hydrogen peroxide using ultraviolet rays [39], combining H_2O_2 injection with catalysts (Fe-Al, Fe_2O_3 , Fe-Ti) promoting the formation of OH^\bullet radicals [40], and using a combination of two oxidants, e.g., $\text{H}_2\text{O}_2/\text{NaClO}_2$ [41]. The results of these experiments are all very promising, and we can expect that future industrial flue gas cleaning installations will apply the presented processes. The achieved efficiency of NO_x and Hg removal from the carrier gas, at least in lab scale tests, is at the level of 90% [42]. Work on the use of sodium chlorite was also carried out on a laboratory and pilot scale [43]. It achieved a removal efficiency of 99% for SO_2 and Hg and 90% for NO_x .

4. Technologies for simultaneous removal of Hg^T and NO_x : authors' own research

As already mentioned, the efficiency of mercury removal in flue gas cleaning installations depends on the speciation of mercury, and the mercury present in the flue gas occurs in both the Hg^0 and the Hg^{2+} forms. Hg^{2+} oxidation increases with the increase in the content of halides (chlorides, bromides, and iodides) in carbon. In the absence of a natural oxidant, as is the case with lignite, liquid oxidative additive can be used for Hg^0 oxidation. Absorbers of the wet flue gas desulfurization plant capture mercury in the Hg^{2+} gas form. In the result of cooperation between the Wrocław University of Technology and Rafako S.A., we developed an Hg emission reduction technology dedicated for hard coal and lignite-fired units. The method involves the injection of sodium chlorite into the exhaust duct upstream the WFGD absorber. In the result of injection of the oxidant, Hg^0 is oxidized to Hg^{2+} and NO to NO_2 , and these oxidation products are captured from the flue gas together with SO_2 in the WFGD absorber. The technology has been tested on an industrial scale in a 400 MW_e lignite-fired unit.

4.1 Research on the impact of injection of oxidizer in exhaust gases on the efficiency of Hg and NO_x reduction

The tests were carried out using exhaust gases from a lignite-fired dust boiler (400 MW_e) equipped with a selective non-catalytic NO_x reduction installation, an electrostatic precipitator, and a wet flue gas desulfurization installation. The WFGD absorber is equipped with four levels of sprinkling and a system for feeding adipic acid into the suspension in order to increase the desulfurization efficiency. The test installation for injection of oxidizer (sodium chlorite) was built between the exhaust fan and the fan supporting the WFGD installation. The choice of the additive injection site upstream the booster fan guaranteed very good mixing of the additive with exhaust gases. The mercury content of the fuel during the tests varied between 0.215 and 0.701 mg/kg. A diagram of the installation, along with the location of the measuring points, is shown in **Figure 7** [44].

As part of the research, we performed continuous measurements of mercury concentration in exhaust gases (using two Gasmet mercury emission monitoring systems) in measuring cross sections located upstream the injection site (A) and in the chimney (C); we carried additional measurements of mercury speciation by the manual method (Ontario-Hydro) at the chimney (C), upstream the WFGD absorber (B), and upstream the oxidative additive injection site (A). Based on the continuous measurements of mercury concentration in the exhaust gas upstream of the absorber and in the chimney, the efficiency of removing mercury from the exhaust gas in the WFGD absorber was calculated with the following formula:

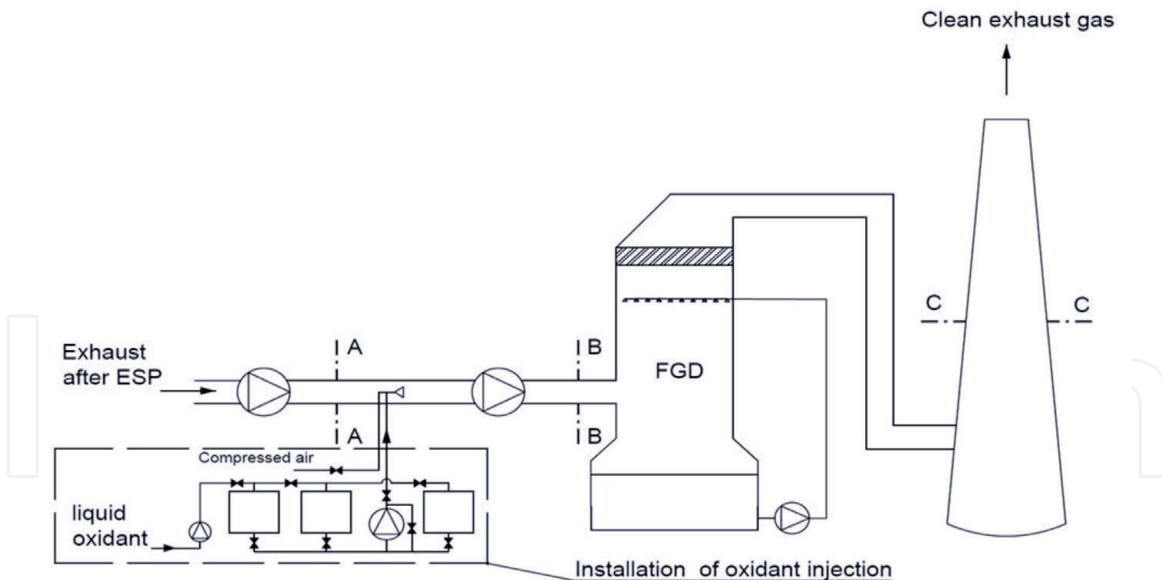


Figure 7.
Diagram of the research installation during tests on lignite flue gas. (A) Measuring cross section before oxidant injection. (B) Measuring cross section downstream the injection site. (C) Measuring cross section in the chimney.

$$\eta_{\text{Hg}} = \left(1 - (\text{Hg}^{\text{T}}_{\text{C}}/\text{Hg}^{\text{T}}_{\text{A}})\right) \cdot 100\% \quad (1)$$

where $\text{Hg}^{\text{T}}_{\text{C}}$ is the mean total mercury concentration in the flue gas in the chimney (C), $\mu\text{g}/\text{m}^3_{\text{USR}}$; and $\text{Hg}^{\text{T}}_{\text{A}}$ is the mean total mercury concentration in the exhaust gas upstream of the absorber (A), $\mu\text{g}/\text{m}^3_{\text{USR}}$.

To determine the NO to NO₂ oxidation degree in a given measurement cross section, the volumetric share of NO₂ in the flue gas in relation to the sum of nitric oxide and nitrogen dioxide (NO_x) was determined. The NO to NO₂ oxidation degree was calculated by means of the relations:

$$\eta^{\text{B}}_{\text{NO} \rightarrow \text{NO}_2} = (\text{NO}_2^{\text{B}}/\text{NO}_x^{\text{B}}) \cdot 100, \% \quad (2)$$

where NO₂^B is the NO₂ concentration in the flue gas in the measurement cross section (B), ppm; and NO_x^B is the NO_x concentration in the flue gas in the measurement cross section (B), ppm.

The effectiveness of NO_x removal from the flue gas in the FGD absorber was determined based on the measurement of NO_x concentration (sum of NO and NO₂ calculated as NO₂ [45]) in the cross section located in the chimney (C) and upstream the FGD absorber (A). The NO_x removal efficiency was determined by means of the relation:

$$\eta_{\text{NO}_x} = \left(1 - (\text{NO}_x^{\text{C}}/\text{NO}_x^{\text{A}})\right) \cdot 100\% \quad (3)$$

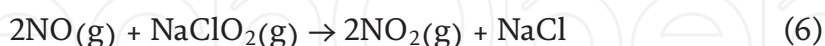
where NO_x^A is the average NO_x concentration in the flue gas upstream the absorber (A), $\text{mg}/\text{m}^3_{\text{USR}}$; and NO_x^C is the average NO_x concentration in flue gas in the chimney (C), $\text{mg}/\text{m}^3_{\text{USR}}$.

To specify the number of moles of the oxidant to be applied in relation to the moles of nitrogen oxide in the flue gas, a molar ratio x was introduced:

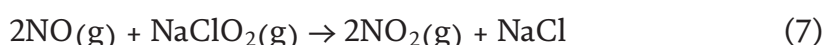
$$X = \text{NaClO}_2/\text{NO}, \text{mol}_{\text{NaClO}_2}/\text{mol}_{\text{NO}} \quad (4)$$

Calculation of the molar ratio X was made for the concentration of NO in the flue gas measured in the chimney (C) in the period immediately prior to the oxidant injection.

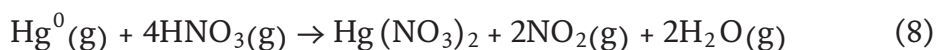
When the aqueous solution of sodium chlorite is sprayed in the flue gas upstream the absorber, first it evaporates (the temperature of the flue gas during the tests at the oxidant injection site (A) varies from 165 to 170°C) as a result of the reaction of gaseous sodium chlorite (initial pH of sodium chlorite solution was 11.5) with nitric oxide, nitrogen dioxide, and sodium chloride being formed [46]:



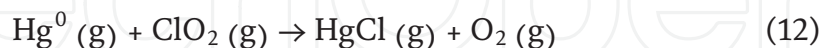
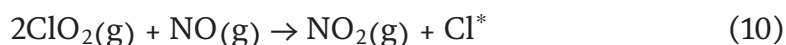
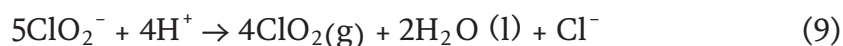
Due to the significant share of moisture in the flue gas (from 28 to 29%), there were very good conditions for the formation of nitric and nitrous acids [47]:



The nitric acid formed in the flue gas reacted with the metallic mercury and oxidized it to the form Hg^{2+} (mercury(II) nitrate), which increases Hg^{T} removal efficiency from flue gas [43, 46]:



Because flue gas contains acidic gases such as SO_2 , HCl , and HF , they can be absorbed by oxidant droplet and drop its pH before evaporation which caused the release of ClO_2 [48]. Chlorine dioxide can directly oxidized NO and Hg^0 ; additionally emission of chlorine radical is possible, which enhanced Hg^0 oxidation [15, 19]:



In such a complicated gas mixture as flue gases from lignite combustion, the presented mechanism can occur simultaneously. For example, the efficiency of NO to NO_2 oxidation and the removal of Hg^{T} and SO_2 during the tests carried out in a lignite-fired power plant (sodium chlorite fed to the exhaust gas prior to the FGD absorber) are shown in **Figure 8**.

The efficiency of Hg^{T} removal and oxidation of nitrogen oxides in exhaust gases depend on the stream of injected sodium chlorite to exhaust gases, which is illustrated by the molar ratio X . Changes in total mercury concentration in exhaust gases in the chimney (C) and NO , NO_2 , and NO_x downstream the sodium chlorite injection site (B) are illustrated in **Figure 9**. The undoubted advantage of the presented method is the almost immediate reaction of the entire system to the injected sodium chlorite. An increase in the amount of injected additive (series I < series II) causes an immediate decrease in the Hg^{T} concentration in the chimney and an increase in the NO_2 concentration in the exhaust gas downstream the injection site. The

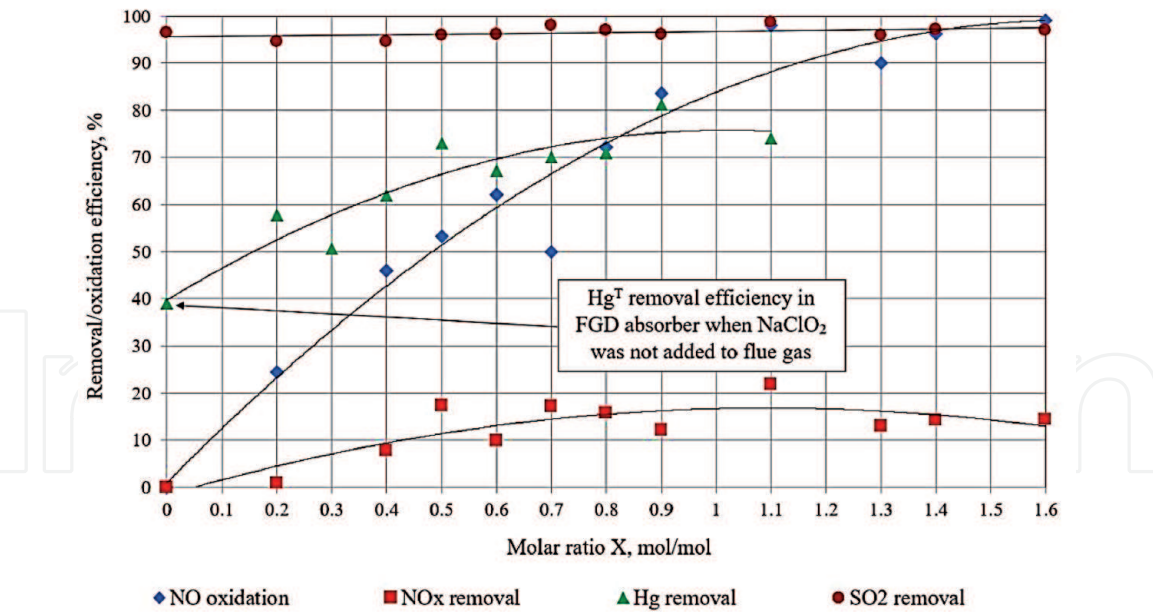


Figure 8.
Oxidation NO to NO₂, NO_x, SO₂, and Hg^T removal efficiency in function of molar ratio X.

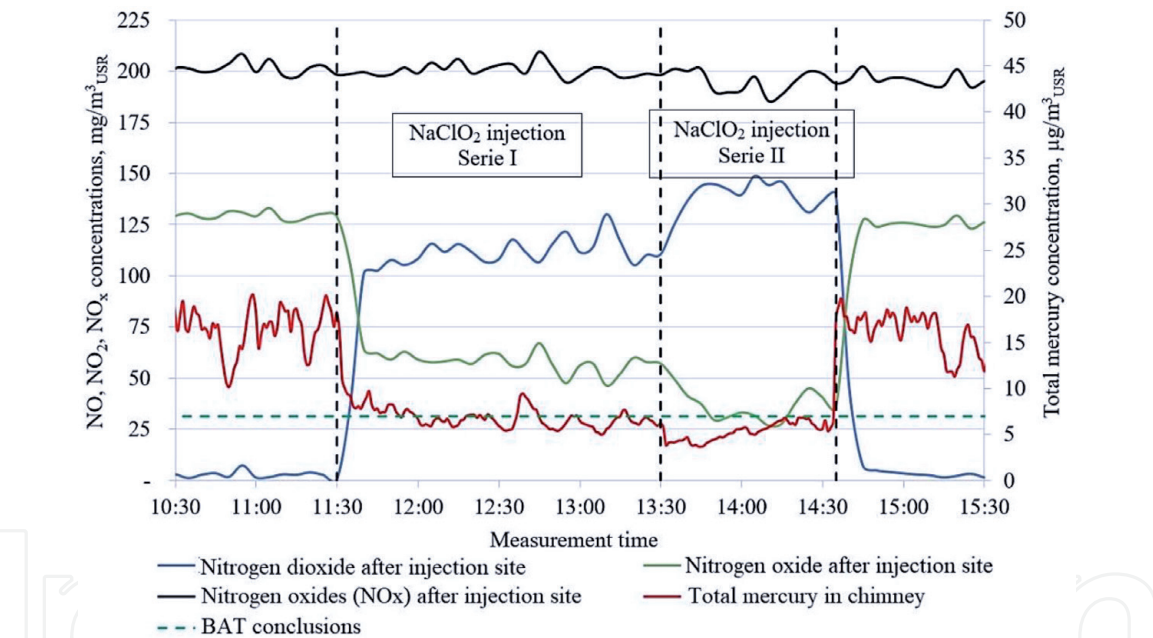


Figure 9.
NO, NO₂, and NO_x concentrations in the flue gas downstream the injection site (B) and Hg^T concentration in the chimney (C).

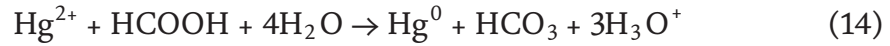
Hg^T concentration in the chimney during the presented tests was below the level required by the BAT conclusions, i.e., <7 µg/m³_{USR}.

Sodium chlorite injection into flue gas upstream of the WFGD absorber caused an increase in Hg²⁺ concentration in the flue gas, which translated into the efficiency of mercury removal. Unfortunately, in some cases, the increase in Hg²⁺ concentration in the exhaust gas intensified the phenomenon of re-emission [44].

4.2 Increased Hg removal efficiency by limiting re-emissions

The phenomenon of re-emission consists in chemical reduction of the Hg²⁺ absorbed in the suspension to the elemental Hg⁰ mercury emitted back into the

atmosphere [49]. Sulfite ions (SO_3^{2-}), acting as a reducing agent, are responsible for this phenomenon [50]:



In FGD installations, where the addition of organic acids (formic, adipic and other) serves increasing the SO_2 removal efficiency, the following reaction takes place (14) [50]. Dosing organic acids increases the concentration of Ca^{2+} , which improves the efficiency of SO_2 removal from the exhaust gases. Many researchers also reported the clear effect of sulfite concentration in the suspension on Hg^0 re-emission. Generally, an increase in SO_3^{2-} concentration increases the re-emission [51–53].

The re-emission phenomenon is assessed on the basis of measurements of mercury concentration in exhaust gas both upstream and downstream the WFGD absorber. In order to find out the nature of the re-emission phenomenon, research was carried out on a lignite-fired unit. We assumed that the concentration of total mercury in the cross section (C) was higher than in the cross section (B) the phenomenon of mercury re-emission from the FGD absorber was present, and the intensity of this phenomenon was described using re-emission rate:

$$\eta_{\text{re-emission}} = ((\text{Hg}^T_{\text{C}} - \text{Hg}^T_{\text{B}}) / \text{Hg}^T_{\text{B}}) \cdot 100\% \quad (15)$$

An example of variations in total mercury concentration in exhaust gases in the period when re-emission occurred is presented in **Figure 10**.

The observed phenomenon of mercury re-emission from the absorber lasted for approx. 4 h. Based on the analysis of the presented graphs, we calculated the degree of mercury re-emission according to Eq. (5); the calculation results are presented in **Figure 11**.

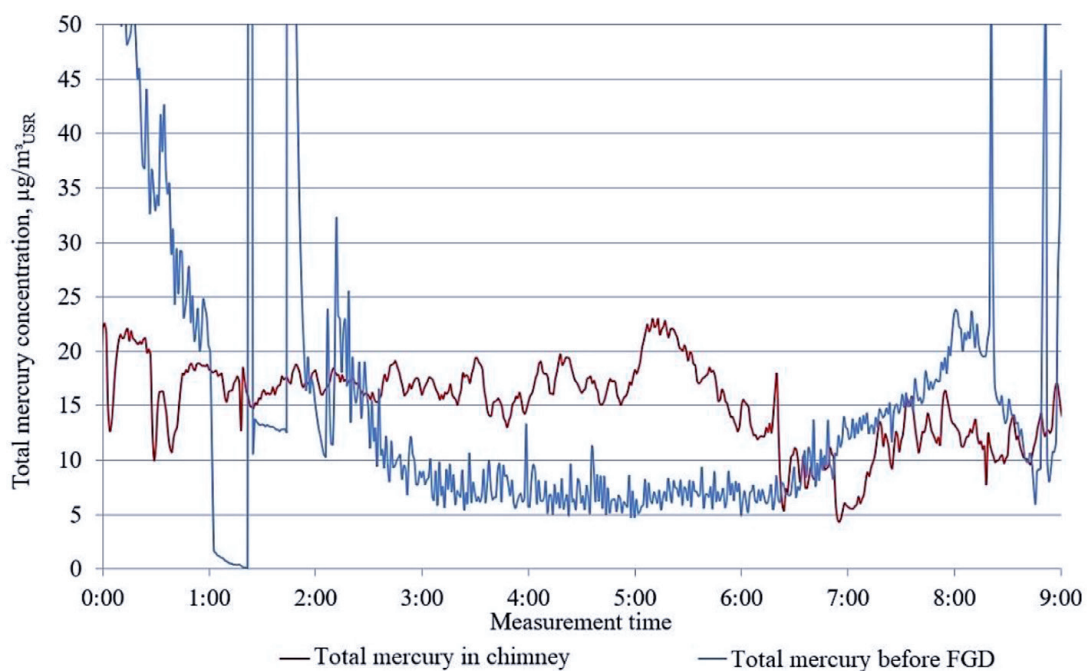


Figure 10.

Total mercury concentrations in flue gas upstream the WFGD absorber (B) and in the chimney (C).

The observed degree of re-emission from the WFGD absorber reached 220%. In order to explain the mechanisms of this phenomenon, the results of the re-emission degree were compared with the operating parameters of the unit and the WFGD (**Figure 12**). Mercury re-emission occurred when the absorber operating parameters changed, and the pH and ORP proved to be the most significant of them. A detailed description of the parameters affecting the intensity of the phenomenon of re-emission from the WFGD absorber is presented in the publication [44].

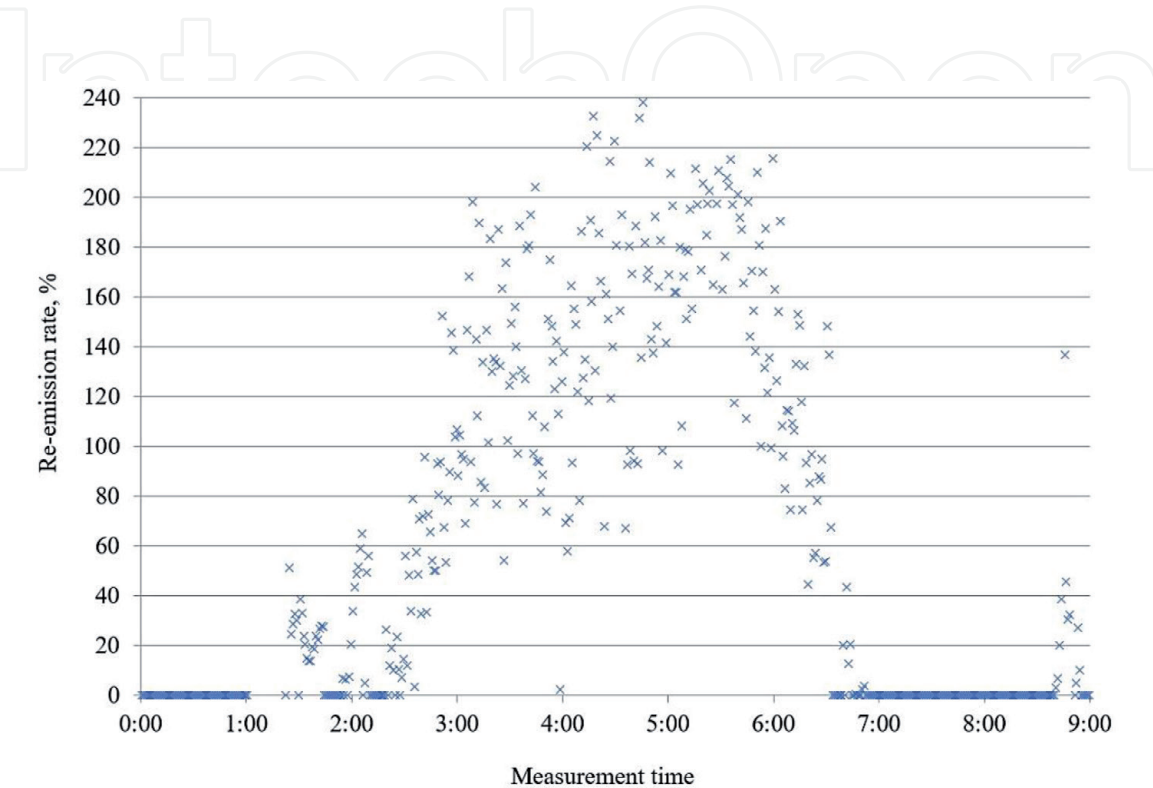


Figure 11.
The degree of mercury re-emission from the WFGD absorber during measurements for a lignite-fired unit.

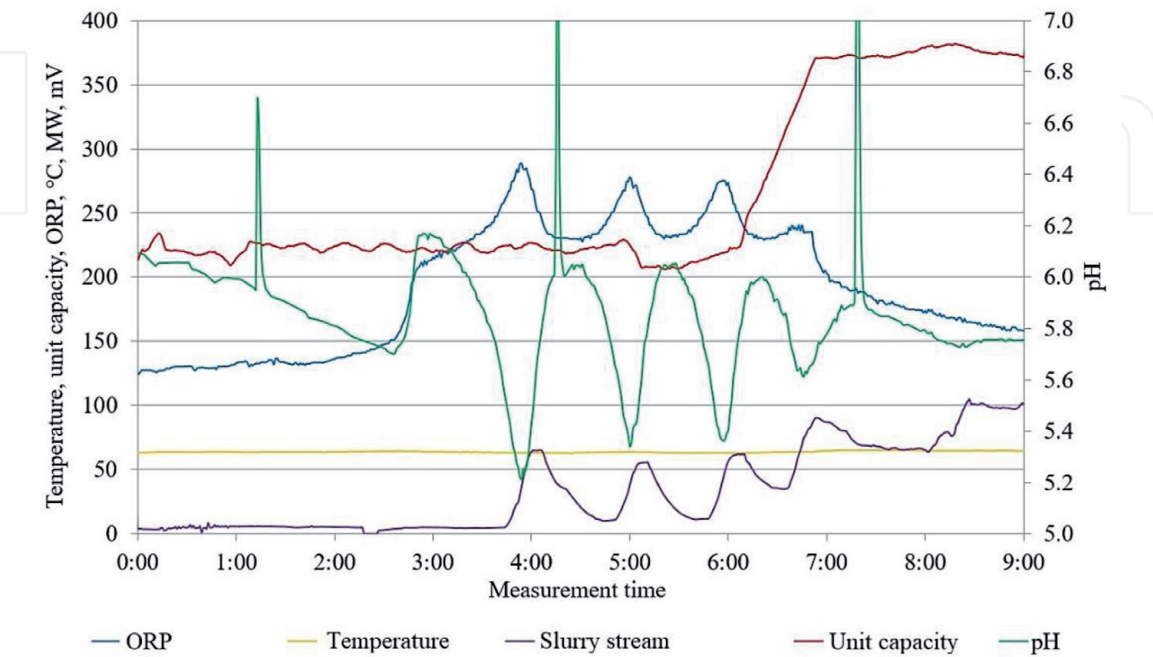


Figure 12.
Parameters of unit and WFGD absorber operation during measurements for a lignite-fired unit.

Research demonstrated that re-emission can be reduced by changing the absorber's operating parameters. We noticed that an increase in suspension temperature and pH increased re-emission, while the increase in chloride concentration in the suspension and the intensity of air flow through the suspension reduced it [54]. At the same time, numerous studies indicate that significant reductions of Hg^0 re-emission can be obtained by adding various additives [53–55]. The most common are simple additions of NaHS and Na_2S organic sulfides with a more complex structure. The goal is always the same, i.e., to remove from the solution (suspension) Hg^{2+} by formation HgS , which prevents re-emission. The effect of adding sodium sulfide (Na_2S) to the suspension circulation in the WFGD absorber was studied for a lignite-fired unit, and the results are presented in **Figure 13**. 4 m³ of 10% solution of sodium sulfide were pumped directly into the tank under the absorber. In this way, the mercury concentration in the exhaust gas was reduced below the level required by the BAT conclusions (7 µg/m³_{USR}) for a period of approx. 4 h.

The phenomenon of mercury re-emission from the WFGD absorber is not always identifiable on the basis of measurements of total mercury concentration in exhaust gases. Hard coal tests were carried out for the WFGD absorber, purifying flue gas from two units with a capacity of 195 and 220 MW_e. During the tests, both boilers operated at maximum power. Prior to the tests, measurements were performed with the Ontario-Hydro method revealing that the absorber is experiencing metallic mercury re-emission. The results of these measurements are presented in **Figure 14**.

The total mercury removal efficiency in the flue gas treatment installation (electrostatic precipitator and WFGD) was 72.4%. Mercury bound with the ash was virtually completely removed in the ESP. The flue gas downstream of the boiler contained a small amount of metallic mercury only (1.73 µg/m³_{USR}), which was a result of the high concentrations of halides in the fuel (Cl (0.110 ÷ 0.211%), Br (0.008 ÷ 0.011%), F (0.002 ÷ 0.004%)). The concentration of metallic mercury in the exhaust gas upstream of the absorber was lower than downstream the absorber, which meant that the absorber was the source of mercury re-emission. The total mercury removal efficiency in the ESP was 56.2% and another 36.9% in the WFGD absorber. Due to

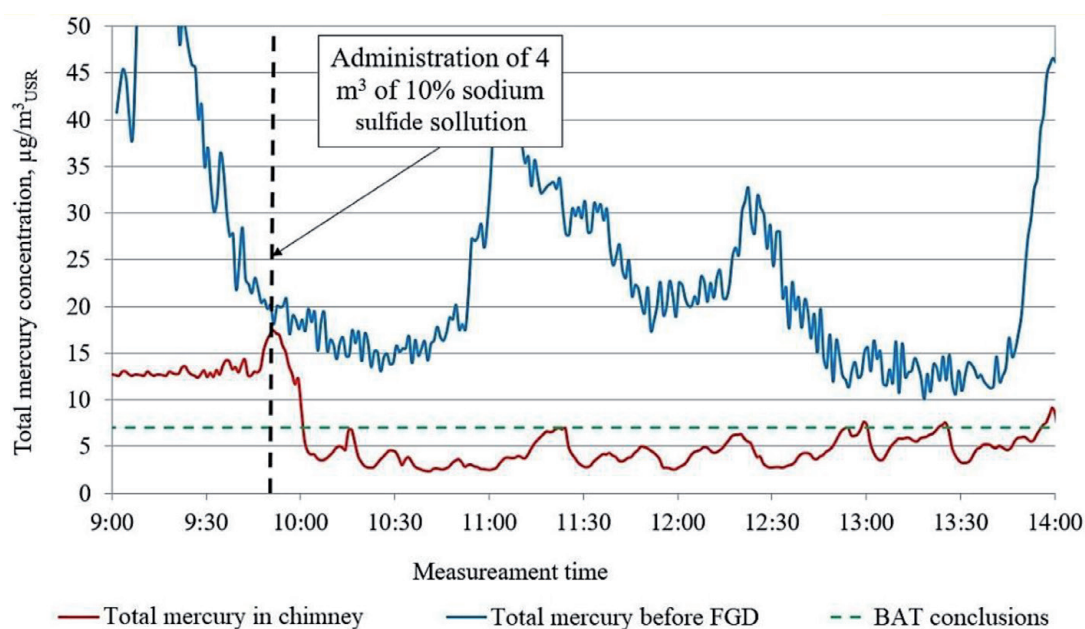


Figure 13.

Total mercury concentration in the chimney and upstream the WFGD absorber after a one-time injection of 4 m³ of sodium sulfide (10%).

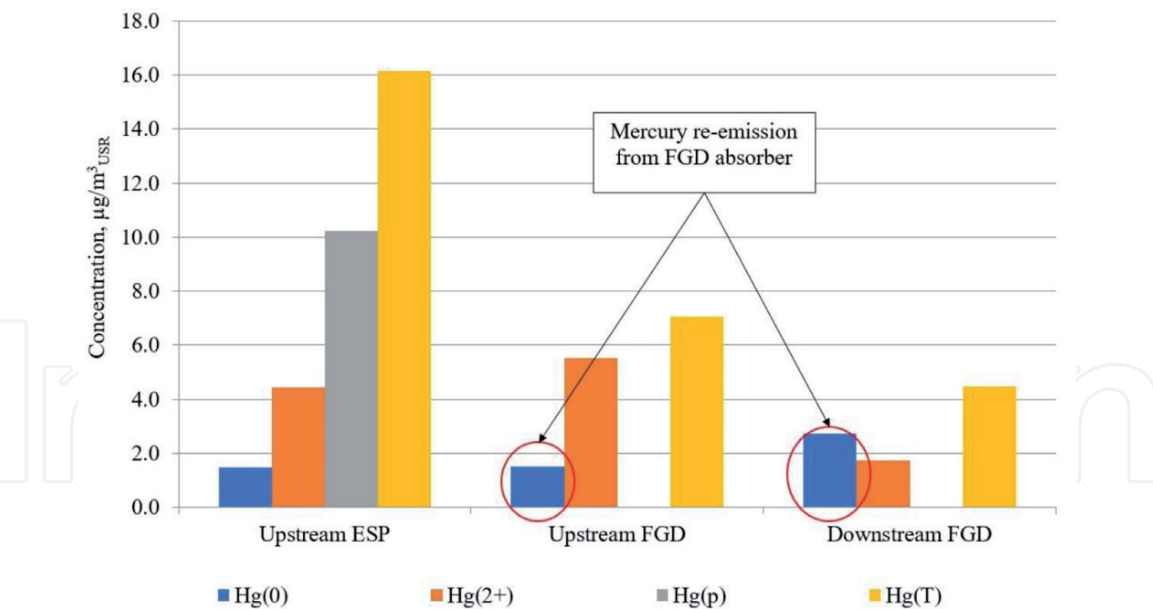


Figure 14.
Comparison of mercury concentration in flue gas for hard coal tests.

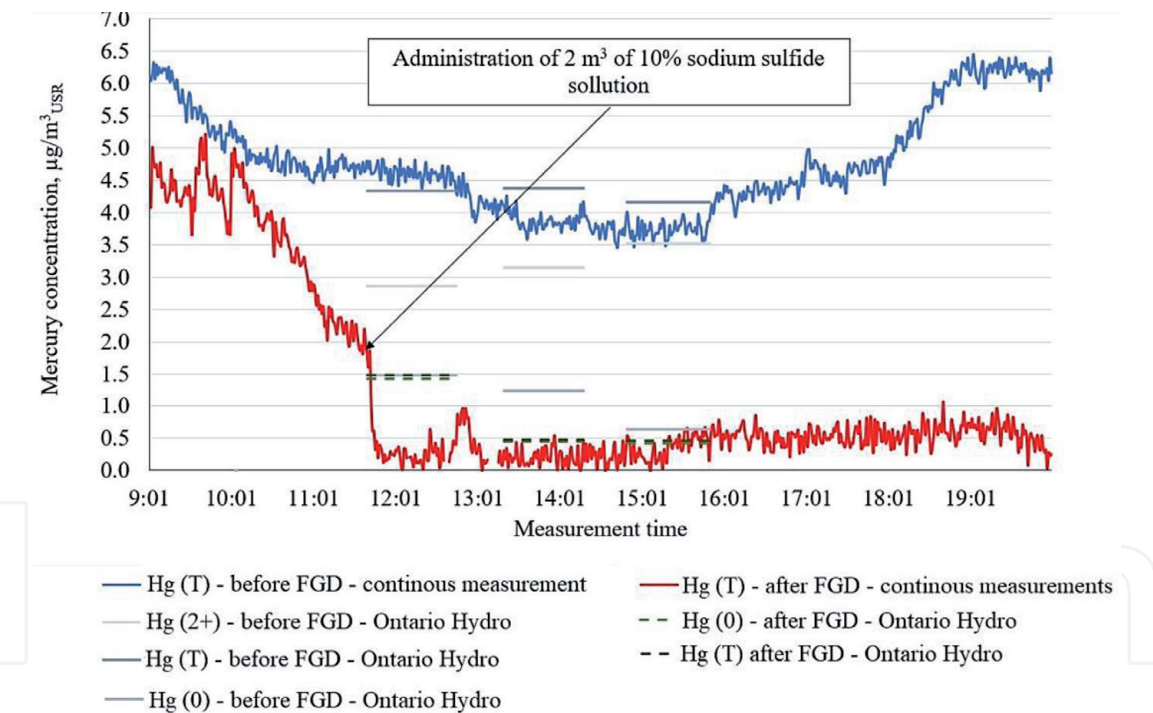


Figure 15.
Measurement results of mercury concentration in flue gas upstream and downstream the WFGD absorber (continuous and Ontario-Hydro measurements) during the addition of Na₂S.

the fact that the proportion of oxidized mercury upstream the WFGD absorber is significant, sodium sulfide was fed to the absorber to reduce mercury emissions in the flue gas in the chimney. In **Figure 15**, we present the results of measurements of mercury concentration in exhaust gas upstream and downstream the WFGD absorber, during dosing of sodium sulfide. Measurements were carried out with two continuous emission monitoring systems and the Ontario-Hydro method.

The total mercury concentration in the exhaust gas before the administration of sodium sulfide was $4.3 \mu\text{g}/\text{m}^3_{\text{USR}}$, and after the addition of sodium sulfide, the

concentration of total mercury in the exhaust gas dropped to $0.45 \mu\text{g}/\text{m}^3_{\text{USR}}$. The mercury removal efficiency for the exhaust gas in the WFGD absorber amounted to 25.5% without the addition of sulfide and increased to 90.5% after applying the additive. To sum up, due to the content of halides in coal, a considerable amount of Hg^{2+} is present in hard coal exhaust gas, which can be effectively removed in WFGD, as long as the phenomenon of re-emission is controlled.

5. Summary

The chapter presents selected issues related to Hg and NO_x emissions from coal combustion processes, in the aspect of regulations related to limiting permissible emissions of pollutants, as contained in the BAT conclusions. The review of methods applied to reduce mercury emissions demonstrates that the specific technology should be selected individually for each facility considered. There is no single, universal, cost-effective solution. In order to choose an effective method for reducing mercury emissions, it is first and foremost necessary to hold the knowledge of the speciation of mercury in the exhaust gas downstream the boiler. In the case of low concentration of oxidized mercury, there are no devices that can be installed in order to secure sufficient limiting of mercury emissions. In such a case, one should first consider the solutions that consist in supplementing the exhaust gas with additives to oxidize the metallic mercury first.

Among the methods used for denitrification of exhaust gases, attention has been given to oxidative methods, which form an opportunity to simultaneously reduce NO_x and Hg emissions. The results of the author's own research in industrial conditions confirmed the usefulness of injection of the oxidant (sodium chlorite) to the exhaust gas upstream the WFGD absorber to reduce mercury emission. Under favorable conditions for lignite flue gases, up to 70% Hg removal efficiency was achieved, coupled with 17% NO_x removal efficiency and an unchanged SO_2 removal efficiency. Whenever there is the phenomenon of re-emission of mercury from the WFGD absorber, appropriate measures must be undertaken to limit it. Again, test results on lignite and hard coal exhaust gas indicate that it is possible to reduce re-emissions to such an extent, as to ensure compliance with emission standards in line with BAT conclusions.

By using mercury oxidation technologies with simultaneous application of flue gas purification devices (DeNO_x , DeSO_x , and dedusting) and effectively combating re-emissions, we can achieve total mercury concentrations at the level required by BAT conclusions, i.e., in the order of $1\text{--}7 (4) \mu\text{g}/\text{m}^3_{\text{USR}}$.

List of abbreviations

APH	air (pre)heater
BAT	best available techniques
ESP	electrostatic precipitator
FGD	flue gas desulphurization
PAC	powdered activated carbon
SCR	selective catalytic reduction
WFGD	wet flue gas desulphurization

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