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Combined NO_x and NH_3 Slip Reduction in a Stoker Boiler Equipped with the Hybrid SNCR + SCR System FJBS+

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Abstract: The application of secondary NO_x control methods in medium to low-capacity furnaces is a relatively new topic on the energy market and thus requires further research. In this paper, the results of full-scale research of SNCR and hybrid SNCR + SCR methods applied into a 29 MW_{th} solid fuel fired stoker boiler is presented. The tests were performed for a full range of boiler loads, from 33% (12 MW_{th}) to 103% (30 MW_{th}) of nominal load. A novel SNCR + SCR hybrid process was demonstrated based on an enhanced in-furnace SNCR installation coupled with TiO_2-WO_3-V_2O_5 catalyst, which provides extra NO_x reduction and works as an excess NH_3 "catcher" as well. The performance of a brand-new catalyst was evaluated in comparison to a recovered one. The emission of NO_x was reduced below 180 mg NO_x/Nm^3 at 6% O_2, with ammonia slip in flue gas below 10 mg/Nm^3. Special attention was paid to the analysis of ammonia slip in combustion products: flue gas and fly ash. An innovative and cost-effective method of ammonia removal from fly ash was presented and tested. The main idea of this method is fly ash recirculation onto the grate. As a result, ammonia content in fly ash was reduced to a level below 6.1 mg/kg.

Keywords: selective non-catalytic reduction; selective catalytic reduction; NH_3 slip; catalyst regeneration; stoker boiler; fly ash

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1. Introduction

Nitrogen oxides NO and NO_2 (known together as NO_x) emitted from power units are claimed to significantly contribute to the formation of numerous environmental pollutants, such as acid rain, haze, or smog. The technologies of selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) are commonly implemented to reduce NO_x emissions in the power sector [1,2]. Their effectiveness is based on the reaction of nitrogen oxides with ammonia or urea compounds. In general, the reduction of nitrogen oxides takes place according to the following chemical reactions [3,4]:

$$4\,NH_3 + 4\,NO + O_2 \rightarrow 4\,N_2 + 6\,H_2O \tag{1}$$

$$(NH_2)_2CO + 2\,NO + \frac{1}{2}\,O_2 \rightarrow 2\,N_2 + CO_2 + 2\,H_2O \tag{2}$$

In fact, the reaction mechanism is very complex: 31 compounds and 173 reactions that occurred during the NO_x reduction process were identified [5]. The most efficient NO_x conversion in the non-catalytic process can be reached in a temperature range of 870–1100 °C [6,7] while in catalytic conversion in 180–450 °C, for most catalysts 300–350 °C [8,9]. SCR technology is possible to be applied in waste-to-energy units, including combustion of medical and hazardous waste [10,11]. It can be potentially used to reduce the NO_x emission not only from power plants and waste combustion units but other stationary sources as well (e.g., chemical and metallurgical industry) [12–14].

While large combustion plants were successfully confronted with the challenge of reducing pollutants, the small and medium-sized plants (<50 MW_{th}) became the subject of emission regulations quite recently. However, scaling the emission control technologies down from large to smaller plants has not been an easy task. Satisfactory NO_x reduction efficiency is particularly challenging in small furnaces of low-to-medium load power units, such as stoker boilers.

Stoker boilers are commonly used in heating plants all over Europe. They are easy to operate, can consume low-quality fuels such as RDF (Refuse Derived Fuel) or waste, and do not require advanced maintenance. In the past, there was not enough focus on developing flue gas cleaning methods for stoker boilers and frequently they have not been equipped with efficient systems to reduce nitrogen oxides emissions. Hence the application of secondary NO_x control methods is a relatively new topic in this energy sector. Therefore, selective catalytic and non-catalytic reduction methods and their hybrid installations still require research and improvement.

Compared to pulverized fuel boilers and fluidized bed boilers, the combustion process in a stoker furnace is characterized by different temperature and flue gas velocity distribution inside the combustion chamber. The following differences should be emphasized:

- Lower maximum flue gas temperature
- Significant fluctuations of flue gas temperature in the combustion chamber
- Greater flame diffusion in the combustion chamber
- Different flue gas flow profile.

These characteristics are vital for the design of flue gas cleaning systems, especially methods for nitrogen oxides reduction. Thus, common denitrification solutions may not be applicable in stoker boilers.

Usually, nitrogen oxides concentration in stoker boilers flue gas is in the range of 300–400 mg/Nm^3 at 6% O_2. Based on the authors' experience and previous research, NO_x concentration strongly depends on the stoker operating conditions: the operation of primary air zones, speed of grate movement and thickness of the fuel layer on the grate. There is very limited research concerning the application of denitrification systems in stoker boilers and usually SNCR is the only one investigated [15–18]. For most European technologies effectiveness of NO_x reduction is in the range of 50–65%. Most of those technologies are based on ammonium reagent dissolved in demineralized water, in contrast with the FJBS (Furnace Jet Boiler System) and FJBS+ technologies proposed in this article.

Presented FJBS+ technology for NO_x reduction combines SNCR and SCR methods. For typical SNCR installations, a stoichiometric excess of the reagent does not exceed 2.5 while SCR usually operates with an almost stoichiometric ratio of reducing compound what finally guarantees low NH_3 slip. The characteristics of both methods allow them to be combined into a so-called hybrid SNCR + SCR system. In this case, ammonia slip generated by the SNCR is used as a reducing compound at the catalyst surface. As a result, the effectiveness of NO_x reduction is enhanced together with the elimination of remaining NH_3 in the flue gas. Such installations may be attractive for facilities that already have been equipped with non-catalytic systems and for which emission limits became more restrictive so that independent operation of SNCR does not permit the fulfillment of current standards. Moreover, a catalyst may operate as NH_3 "catcher" to reduce excess ammonia slip in flue gas.

Increased ammonia concentration in flue gas rich in SO_3 and H_2SO_4 favor the formation of ammonium salts such as ammonium bisulfate NH_4HSO_4 (ABS) according to Equations (3) and (4). Other salts (e.g., ammonium chloride) can be also found but usually in minor amounts.

$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4 \tag{3}$$

$$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4 \tag{4}$$

Ammonium bisulfate is a sticky, corrosive substance prone to the deposition in the flue gas ducts. Forming ABS deposits is more likely in lower temperature zones

(<340 °C) [19,20]. ABS deposition is likely to occur on the SCR injection components, in the cold end areas of the rotary air heaters and on catalyst surfaces reducing catalyst reactivity [21]. The degradation of catalysts due to ammonium bisulfate deposition is an crucial issue that decreases the catalyst efficiency. ABS formation takes place in the gas phase by the nucleation of NH_3, SO_3 and H_2O. The substance then builds up onto the catalyst and blocks the access to its surface.

In order to minimize the risk of ABS formation, it is reasonable to pre-clean the flue gas of sulfur compounds before it enters the catalyst. Many effective technologies of wet, semi-dry and dry flue gas desulphurization have been developed for industrial implementations in power engineering and other sectors [22–25]. The main sorbents that enable high efficiency of SO_2 and other acidic pollutants removal are based on calcium ($Ca(OH)_2$, $CaCO_3$) and sodium ($NaHCO_3$) [24].

In addition to ABS the main factors influencing catalysts deactivation are alkali metals and arsenic [26,27]. The compounds of alkali metals tend to agglomerate on the interface of a catalyst. They affect the catalytic process by preventing NO and NH_3 from accessing the reaction zone [28]. Furthermore, a loss of activity is likely to occur by the reactions of alkali metals with acid sites [29,30]. The presence of arsenic may reduce the strength of acid sites, the catalytic surface area and the number density of active sites [26,31,32]. For these reasons the lifespan of the most commercial SCR is usually no longer than 24–36 months. As a result, the problem of safe disposal of catalysts after their depletion is growing. SCR catalysts contain various hazardous compounds, hence their proper utilization is a great challenge.

To minimize the production of hazardous waste and make the SCR technology more cost-effective some methods of catalyst regeneration have been investigated. Up to date, only limited research deals with the regeneration of industrial catalysts from full-scale power units. The procedures of regeneration are usually investigated under simulated, laboratory conditions, that may be inconsistent with field conditions [27,33,34]. The investigated regeneration methods may differ, however, some of them can be characterized by high efficiency. Deactivated SCR catalyst may reclaim 92% of its initial efficiency after being treated with 0.5 M H_2SO_4 solution [35] or 91.4% after in situ high-temperature regeneration with water vapor [36]. However, some methods, such as washing with sulfuric acid solution, may result in the corrosion of power equipment or destruction of active components [37].

The presence of NH_3 remaining after the denitrification process in flue gas and fly ash is unfavorable not only because it leads to ABS formation. It is also important in terms of its further use in the concrete industry. Fly ash may be used as a concrete additive if it meets the appropriate criteria of chemical and physical properties. In the process of concrete production, the pozzolanic properties of ash are initialized by the generation of highly alkaline free lime. In such alkaline conditions, ammonia is liberated from ash into the gas phase. The equilibrium of ammonium ion in solution is shifted to molecular ammonia in accordance with the equation:

$$NH^{+}_{4\ (aq)} + OH^{-}_{(aq)} \leftrightarrow NH_{3\ (aq)} + H_2O \tag{5}$$

The released molecular ammonia is characterized by a strong smell. The physical and mechanical properties of the concrete are not affected by the presence of ammonia, however, the smell is intolerable to the users and manufacturers [38,39]. Hence the ammonia content of 100–200 mg NH_3/kg is claimed to be the limit for concrete production [40]. Nevertheless, many industrial manufacturers accept only fly ash with no more than 50–100 mg NH_3/kg.

As a remedy, numerous methods to eliminate ammonia from fly ash have been investigated last years. These methods can be divided into thermal and chemical ones. Thermal methods base on the high-temperature ammonia desorption process and usually take place at a temperature range of 300–450 °C. They are usually less complex than chemical methods, which makes them more cost-effective [41]. In the Energy Research Center Method fly ash is processed in a fluidized bed reactor where air is supplied as a fluidizing medium. This method allows removing up to 90% of ammonia, however, it has been tested for ash with 500–1000 mg NH_3/kg and its efficiency for low NH_3 concentrations has not been investigated [42]. The Carbon Burnout method requires a fluidized bed reactor as well to decompose ammonium compounds together with burning out an unburnt carbon. The process lasts for 45 min at a temperature of 700 °C. Ammonia content below 5 mg NH_3/kg can be reached with a simultaneous reduction of total organic carbon, which has a positive impact on the ash characteristics in terms of the use in civil engineering [43].

The basis of most chemical methods is the release of molecular ammonia from ammonium salts solutions with an alkaline pH. Such as in the STI method, where a mixture of water and alkaline compounds is introduced into the ash [44]. Similarly, the ASM Technology assumes the introduction of calcium hypochlorite. The efficiency of these processes is up to 95%. [45]. Simple wet methods are based on the water solubility of ammonium compounds only. According to the studies of Wang et al. [46] up to 85% of ammonia can be removed after 10 min of water extraction.

Another approach is ozone oxidation. This method assumes the use of ozone admixed to humid air, which is supplied to the fly ash as an oxidizing medium. The ozone concentration of 2% was found to be the most effective in ammonia removal at a temperature of 150 °C [47].

Moreover, catalytic methods have been investigated. Their principle is the reaction of selective catalytic oxidation of ammonia according to (6):

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \tag{6}$$

The best reported efficiency of ammonia conversion is 60% with nitrogen selectivity over 90% [48,49].

All those methods require high investment costs. In thermal methods, a dedicated reactor is needed, while in chemical methods ash becomes wet and requires drying. The undoubted disadvantage of catalytic methods is the necessity of assembling the catalyst and the danger of its degradation by SO_2 and heavy metals. Therefore, there is a strong need to develop a simple and cost-effective method for ammonia removal from fly ash.

The objectives of presented paper are:

(1) to examine the parameters of a novel SNCR installation called FJBS (Furnace Jet Boiler System) applied to a stoker boiler for the full range of boiler load: 12–30 MW_{th}, which corresponds to 33–103% of the nominal load.

(2) to investigate the effectiveness of a novel, hybrid FJBS+ installation (a combination of FJBS with a catalyst) applied to a stoker boiler, including a comparison of brand new and regenerated plate type TiO_2-WO_3-V_2O_5 catalyst,

(3) to determine the fate of NH_3 in combustion by-products (flue gas and fly ash) during the hybrid FJBS+ process,

(4) to test an innovative method of ammonium removal from fly ash by high-temperature desorption on boilers' grate.

2. Materials and Methods

The investigated object is a 29 MW_{th} solid-fuel-fired unit with a mechanically driven grate producing hot water for district heating purposes. The combustion chamber and the second pass are built with membrane wall technology. The flue gas composition at the boiler outlet is as follows: 6–11% O_2, 0–100 mg/Nm^3 CO, 12–15% CO_2, 1200–1500 mg/Nm^3 SO_2 and fly ash concentration below 50 mg/Nm^3. The flue gas flow on maximal boiler load is 59,000 Nm^3/h. Apart from the primary air under-the-grate distributing zones, the boiler is equipped with secondary air nozzles, that are assembled above the ignition zone. Combustion conditions specific to stoker boilers make the base concentration of NO_x to be relatively low. The right grate movement rate and fuel particles size make the flame temperature lower compared to PC boilers. Average NO_x emission without FJBS was determined to be 340 mg NO_x/Nm^3 at 6% O_2 with an upper value of approximately 380 mg NO_x/Nm^3.

During every test presented in this study the continuous measurement of flue gas composition (O_2, NO, NH_3, CO) was performed with infrared FTIR Gasmet DX-4000 (measuring accuracy at 0,1 mg/Nm^3) and Siemens Ultramat 23 (measuring accuracy at 1 ppm for NO_x, CO and 0,1% for O_2 sensor) online gas analyzers.

Presented Furnace Jet Boiler System (FJBS) is a non-catalytic technology that combines primary and secondary methods for reducing nitrogen oxides emissions. The NO_x formation in the combustion chamber is reduced by realizing the objectives of the secondary air nozzles. At the same time, the injection of 40% urea water solution is realized to meet the objectives of selective non-catalytic reduction. The combustion chamber is equipped with jet blowers (Figure 1) whose location was determined based on temperature measurements, numerical calculations [50] and previous experience [51]. The number of jet blowers and their arrangement on the boiler walls can vary depending on the boiler specification. In the investigated case, the combustion chamber is equipped with 8 jet blowers, installed on 4 levels. The FJBS blowers are distributed in two columns on the opposite sidewalls of the boiler. The system includes a vertical inclining mechanism that allows adjusting of the reagent injection.

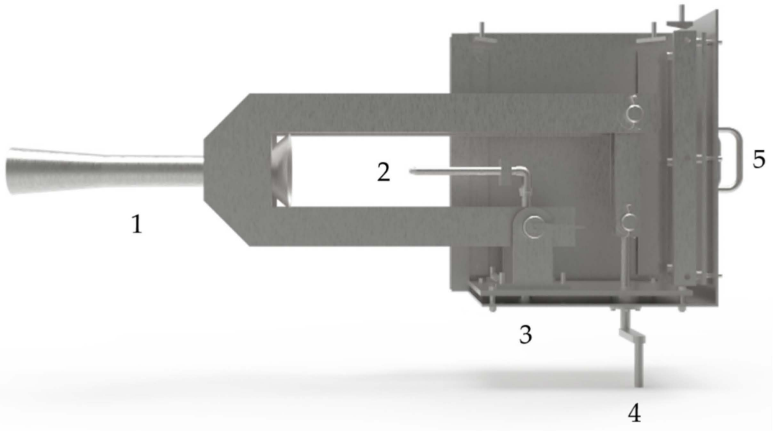

Figure 1. FJBS jet blower 1-jet blower, 2-motive medium nozzle, 3-location of nozzle supply, 4-tilting mechanism, 5-revision doors.

The FJBS technology favors flue gas mixing, which leads to the stabilization of temperature in the combustion zone and the homogenization of flue gas composition. A typical motive medium (MM) of a jet blower is air, but water vapor or recirculated flue gas may be used as well. The high-pressure MM works as OFA (Over Fire Air) nozzles and is simultaneously used to inject the chemical reagent for NO_x reduction. In the presented study, a 40% urea water solution was used as a reagent.

The hybrid system FJBS+ was created by the combination of SNCR and SCR methods. Ammonia slip, which is not desirable if the SNCR method is used as a stand-alone method, is the source of reducing compound for the catalytic method. A brand new and regenerated plate type TiO_2-WO_3-V_2O_5 catalysts were installed in the investigated object.

The catalyst was regenerated by two-stage flushing with demineralized water. The catalyst was placed in a stainless-steel tank filled with demineralized water at 50 °C. The tanks were aerated through air nozzles placed in the bottom. The initial stage of the cleaning process took 20 min and was followed by the second stage with the same duration time. After that, the baskets with catalysts were placed on the platform to dry and cool down to ambient temperature. Finally, the catalyst was dried with hot air.

A catalyst may be typically situated in two different locations in the technological structure of a boiler. In the High Dust system, it is placed before the de-dusting device, usually in the second or third boiler pass with the proper thermal conditions. An unquestionable disadvantage of this solution is the direct catalyst exposure to dust (fly ash) contamination resulting in its fast deactivation. The other solution is in the Tail End, where dust-free flue gas enters the catalyst. However, for this solution flue gas has needs reheating to reach the optimum SCR temperature. In presented research catalysts were placed in the space between the upper and lower coil of the second pass water heater (High Dust system) without interfering with the pressure section of the boiler. Both brand-new and regenerated catalysts are equipped with a measuring set which measures emissions directly before and after the reduction process. The overall layout of the FJBS+ technology is presented in Figure 2.

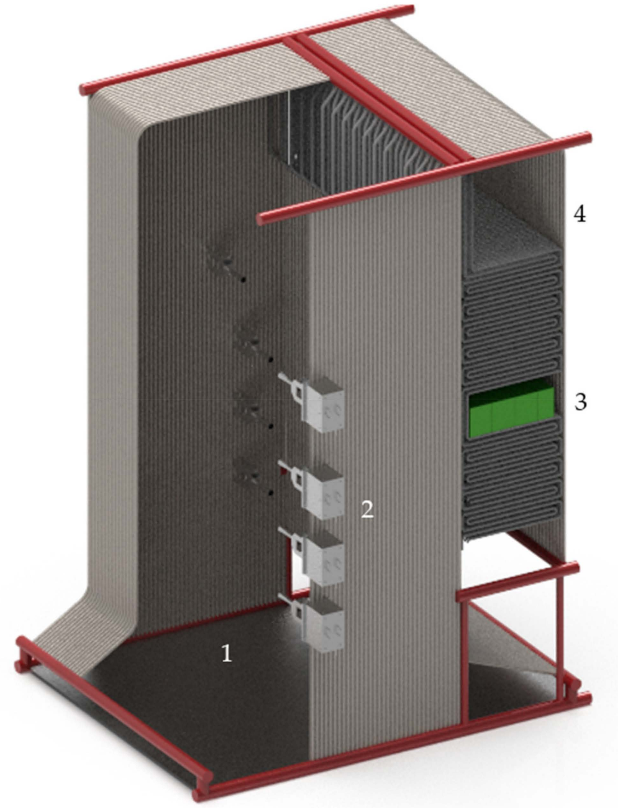

Figure 2. FJBS+ System: Arrangement of SNCR jet blowers in the combustion chamber and catalyst assembly in flue gas duct. 1-combustion chamber, 2-jet blowers, 3-catalyst, 4-flue gas duct.

Fly ash collected after the processes presented in this study may contain a considerable amount of ammonium compounds, reaching up to 3800 mg/kg. Moreover, denitrification processes may lead to an increased presence of unburned carbon (UBC) in the fly ash. To solve this problem an innovative study of fly ash cleaning method was carried out based on the fact, that high-temperature treatment leads to the decomposition of ammonium compounds. A simple and cost-effective idea of fly ash recirculation back to the furnace was proposed for that purpose. The presented process does not require the assembly of any dedicated reactor or the usage of any chemical compounds nor water.

The principle of the process is presented schematically in Figure 3. The main idea of this process is recirculation of the fly ash into the combustion chamber of the boiler (1) where thermal decomposition of ammonium compounds takes place on the grate (2). Fly ash separated from flue gas in the de-dusting system (4) or/and ash hoppers (3) is transported by the pneumatic conveyor (5) or by the mechanical feeder to the fuel feeder (6) or directly to the fuel tank (7) instead of being removed by the slag hopper (8) or slag removing system (9). After that, fly ash is placed onto the grate together with the fuel. The temperature of above 800 °C leads not only to the decomposition of ammonium compounds but the reduction of unburned carbon as well. At the end of this process, fly ash with slag is removed from the combustion chamber into the slag hopper (8).

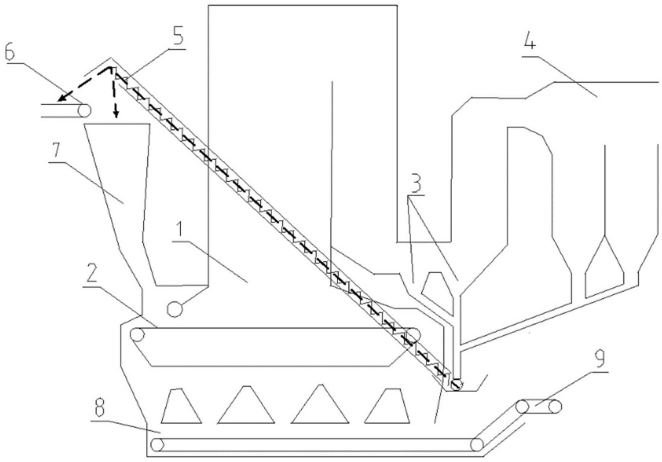

Figure 3. The principle of fly ash recirculation in a stoker furnace to reduce ammonia slip in fly ash. 1-combustion chamber, 2-grate, 3-ash hoppers, 4-de-dusting system, 5-pneumatic conveyor, 6-fuel feeder, 7-fuel tank, 8-slag hopper, 9-slag removing system.

NH_3 content in fly ash samples before and after every desorption test was determined according to VGB-B 401:1998 Blatt 4.4.2 standard. First, to assess the potential of high-temperature ammonia removal, a laboratory test was conducted. Ash samples with a mass of 50 g were placed in an electric furnace heated up to a temperature of 1050 °C for 25 min. Such parameters are a reflection of the typical conditions on a stoker grate. In presented research, the ammonia content in every sample was decreased below the detection limit.

After successful determination of process efficiency in a small scale a field test was carried out. The ash samples were placed in closed boxes made of fine-meshed heat-resistant steel mesh to maintain sample homogeneity and allow free flame access and flue gas outflow. Then samples were put into the furnace of the boiler through the inspection door and placed at the beginning of the moving grate. After approx. 25 min of residence time mesh boxes with ash samples were removed from the boiler at the end of the moving grate. NH_3 content in the samples was determined before and after the process. Presented method represents all the advantages of existing thermal methods, but investment costs are significantly reduced. Presented technology does not require the assembly of any external reactor hence the fly ash treatment takes place in the combustion chamber.

3. Results and Discussion

3.1. Selective Non-Catalytic Reduction FJBS

The first step of the research was to determine the effectiveness of non-catalytic FJBS technology in the wide range of boiler load.

The continuous flue gas composition measurement for 90 h is shown in Figure 4. For boiler load below 14.5 MW_{th} (50% of nominal capacity) the optimal temperature zone is located relatively close to the grate hence the lowest level of jet blowers was used to inject the urea solution. At a moderate boiler capacity of 18–27 MW_{th} (60–90% of nominal), the operation of second and third levels of jet blowers satisfied the emission limits. The most important condition is to provide a satisfactory NO_x reduction at nominal boiler load and during overload. In this case, the urea injection was carried out at the highest possible jet blowers level. The average NO_x emission without denitrification system depends on the boiler load and for investigated stoker is as follows: 320 mg NO_x/Nm^3 for low load, 340 mg NO_x/Nm^3 for moderate load and 375 mg NO_x/Nm^3 for maximum load, all expressed at 6% O_2.

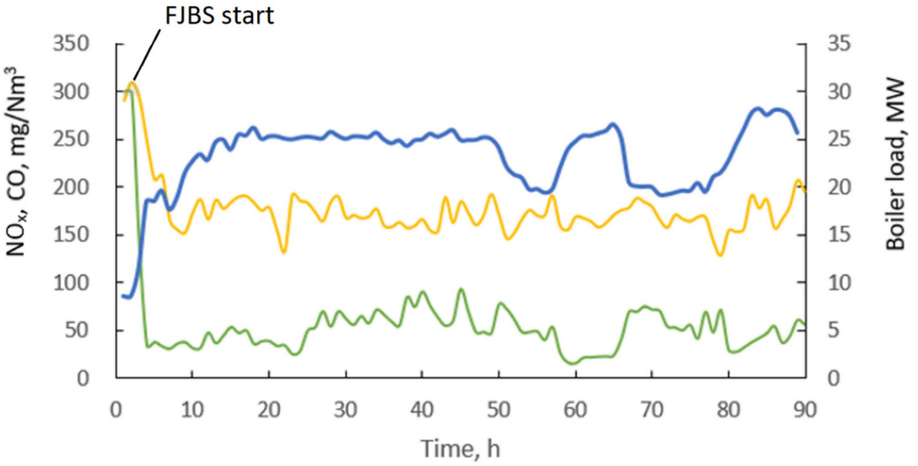

Figure 4. Stack emissions during the FJBS system test run.

For the load over 22 MW_{th} (75% of nominal), a significant effect of secondary air was found to support the reduction of NO_x. The air delivered from above the ignition arch lowers the flame temperature and moves it away from the boiler front wall, which is desired in terms of stable system operation. During the test, the NO_x emission below 180 mg NO_x/Nm^3 was continuously observed with an average emission of 169 mg NO_x/Nm^3.

The efficiency of NO_x reduction can be calculated as:

$$NO_x\text{reduction}(\%) = \frac{NO_x - NO_{x\ FJBS}}{NO_x} \quad (7)$$

where NO_x is the average NO_x emission without FJBS, and $NO_{x\ FJBS}$ is the average NO_x emission with FJBS expressed in mg NO_x/Nm^3 at 6% O_2.

For every boiler load, NO_x emission was reduced below 180 mg NO_x/Nm^3 with NO_x reduction of 48–53% as shown in Table 1.

Table 1. Average NO_x emissions and reductions during non-catalytic FJBS process.

Boiler Load MW_{th}	NO_x Emission without FJBS mg NO_x/Nm^3 at 6% O_2	NO_x Emission with FJBS mg NO_x/Nm^3 at 6% O_2	NO_x Reduction %
>14.5	320	168	48%
14.5–27	340	169	50%
29.5	375	174	53%

3.2. Hybrid SNCR + SCR System FJBS+

After successful determination of FJBS efficiency, the hybrid FJBS+ installation was tested. A single-layer catalyst was placed in the space between the upper and lower water heaters in the second flue gas pass. This location was selected based on the boiler design and on-site temperature measurements taken in the flue gas duct section, the results of which can be seen in Figure 5. The tests were divided into two parts: Part I: low to medium boiler load and Part II: high boiler load.

3.2.1. FJBS+ Part I: Low/Medium Boiler Load

The first part of the hybrid FJBS+ research was conducted in the summer. For most of the time the boiler load was 12.5 MW_{th} and therefore the temperature in the catalyst area was below 300 °C. At a low load, it may be necessary to transfer part of the heat output from the 2nd pass water heater to the one located in the 3rd pass. As a result, the temperature within the catalyst could be more favorable (300–400 °C). To avoid it, the study was conducted during the morning hours when the water consumption by the network user was high and a temporary increase in the boiler output was observed.

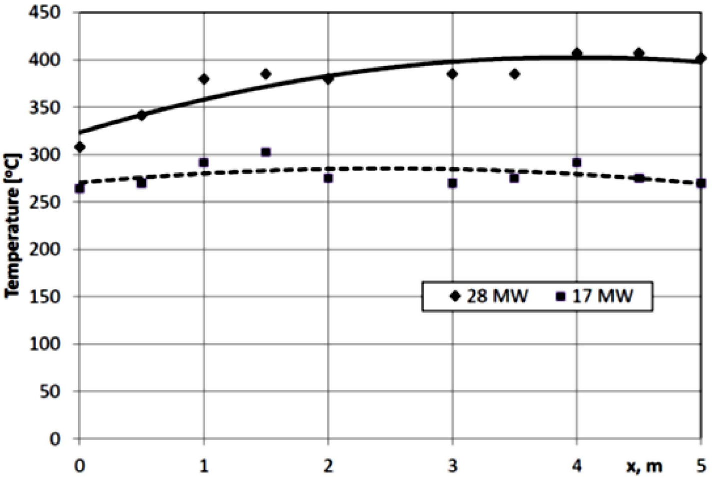

Figure 5. Temperature measurement in the space between the tube bank of the 2nd pass water heater for two boiler loads of 17 MW and 28 MW.

The efficiency of the catalysts was measured for two boiler loads: 12.5 MW_{th} and 18.5 MW_{th}, which corresponds to 43% and 63% of nominal capacity, respectively. According to in-furnace temperature measurement, both lower and middle nozzles levels were used and the urea solution was injected into a temperature zone of approximately 750 °C. To retain the NH_3 slip needed for the SCR catalyst, various overstoichiometric ratios of urea were used: $NSR_1 = 1.35$ and $NSR_2 = 1.8$. The stoichiometric ratio NSR (8) is defined as a ratio of urea actually introduced to its stoichiometric demand:

$$\mathrm{NSR} = \frac{\dot{m}_{\mathrm{CO(NH2)2\ actual}}}{\dot{m}_{\mathrm{CO(NH2)2\ stoichiometric}}} \tag{8}$$

As a result, the high efficiency of SNCR was observed, together with extra catalytic reduction. This resulted in a low final NH_3 slip determined at the outlet of the catalyst. Figure 6 presents a collective graph from on-stack continuous emission measurement system. The NO_x emission was reduced by 50 to 70%, from an average level of 380 mg/Nm^3 down to 156 mg/Nm^3. The transition stage is a time needed for stabilization of the FJBS+ parameters after changing the stoichiometric ratio from NSR = 1.35 to NSR = 1.8. An increase in CO emissions is observed as NSR is increased, with a direct correlation to the urea decomposition process.

Figures 7 and 8 present the effectiveness of a brand new (CN) and regenerated (CR) catalyst at the boiler load of 18.5 MW_{th}. The concentrations of NO_x and NH_3 were determined at the inlet and outlet of both catalysts. The brand new catalyst is characterized by an average NO_x conversion of 80% while for regenerated one conversion reached 57% (Table 2). The NH_3 slip at the catalysts outlets was reduced to relatively low levels: below 10 mg/Nm^3 for the new catalyst and below 20 mg/Nm^3 for the regenerated one. It should be emphasized, that the measurement was performed within a boiler operation that does not provide optimal temperature conditions for the SCR process. Thus, results may be considered unexpectedly satisfactory. The effectiveness of the catalytic layer is strongly affected by the distribution of the reducing compound, which may not be optimal in this case. A catalytic reduction can be attractive for units where ammonia slip is a major problem. A single or multi-layer catalyst can work as an effective NH_3 slip catcher.

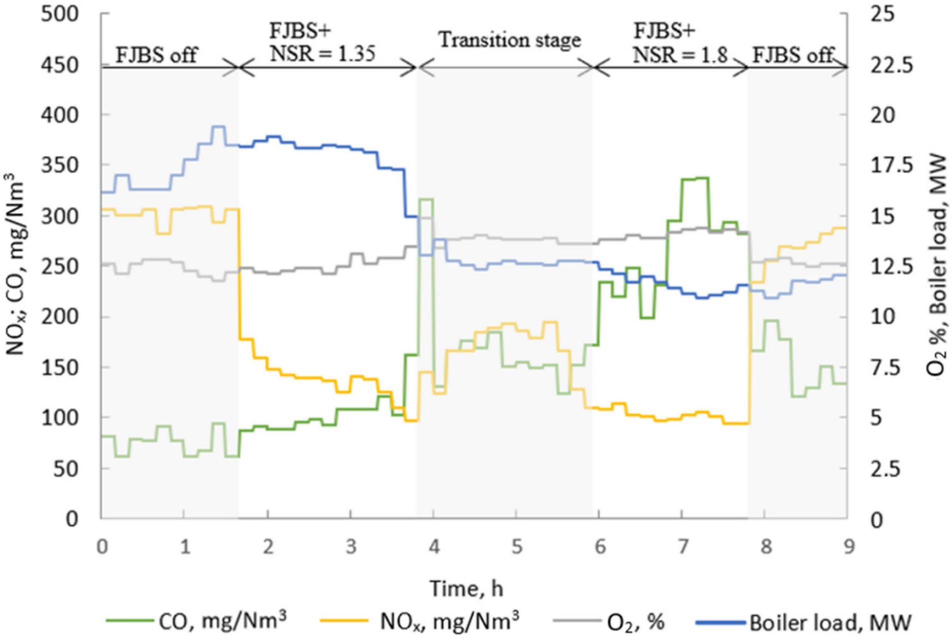

Figure 6. Stack emissions during the hybrid SNCR + SCR system operation at low/medium boiler load.

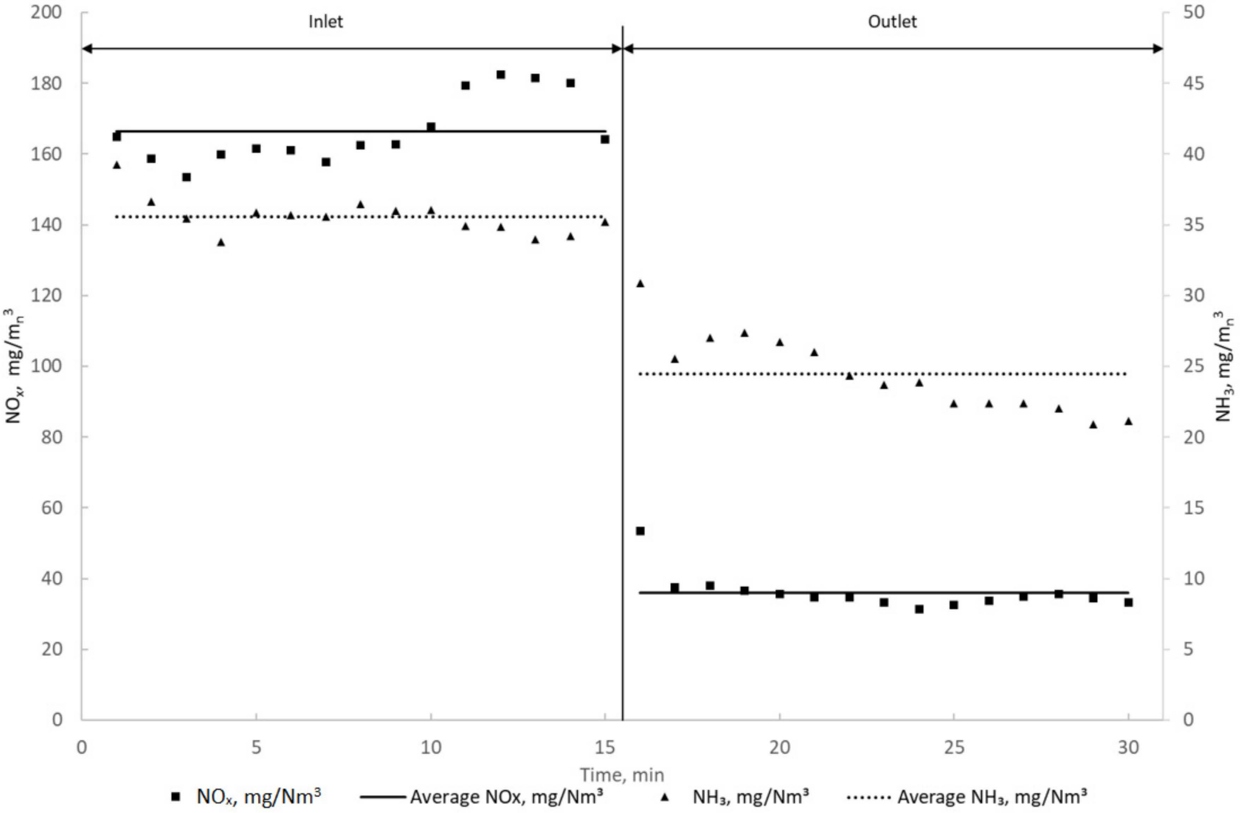

Figure 7. Emissions measured at the inlet and outlet of the new catalyst CN at an average power of 18.5 MW_{th}-flue gas temperature approx. 300 °C.

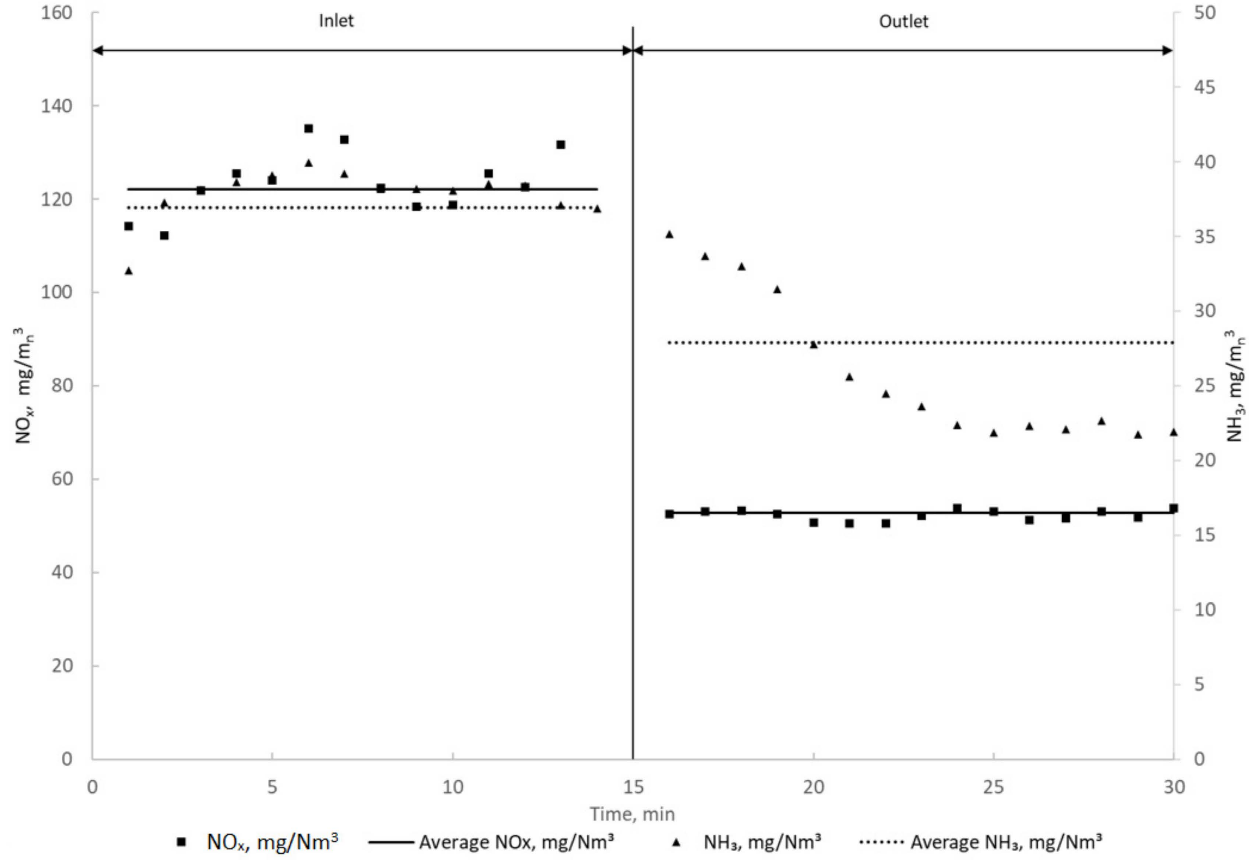

Figure 8. Emissions at the inlet and outlet of the regenerated catalyst CR at an average power of 18.5 MW_{th}-flue gas temperature approx. 300 °C.

Table 2. Average NO_x emissions and conversion for low and medium boiler load.

Boiler Load MW_{th}	NO_x Emission Inlet of New Catalyst CN mg NO_x/Nm^3	NO_x Emission Outlet of New Catalyst CN mg NO_x/Nm^3	NO_x Conversion!on New Catalyst CN %	NO_x Emission Inlet of Regenerated Catalyst CR mg NO_x/Nm^3	NO_x Emission Outlet of Regenerated Catalyst CR mg NO_x/Nm^3	NO_x Conversion on Regenerated Catalyst CR %
12.5	185	82	55	130	67	48
18.5	167	34	80	124	53	57

3.2.2. FJBS+ Part II: High Boiler Load

Part II of the research took place in the winter season with a high boiler output of 28 MW_{th}. In this case, a suitable temperature for effective NO_x reduction was provided. However, because of the high temperature in the furnace, it was not easy to produce sufficient ammonia slip. I this case, the FJBS nozzles located on the highest, 4th level were used and a high stoichiometric excess of urea NSR = 3 was used to ensure the presence of NH_3 in the flue gas exiting the combustion chamber. The overall emission measurement is shown in Figure 9. The concentration of nitrogen oxide at the catalyst inlet ranged from 160 to 220 mg/Nm^3. The use of catalyst allowed local reduction of NO_x emission to 30 mg/Nm^3 with stack emission ranging from 150 to 180 mg/Nm^3 in most points. The FJBS+ was switched off after 3 h of operation, which can be seen in Figure 9 as an instant peak in NO_x emission.

The direct effect of the catalysts can be seen in Figures 10 and 11. The efficiency of the new and regenerated catalyst was 63% and 50%, respectively (Table 3). This indicates the lower SCR efficiency compared to Part I. The temperature range was considered optimal;

however, it should be emphasized that the concentration of NH_3 in the flue gas at the catalyst inlet was much lower than expected, ranging from 5 mg/Nm^3 for CN to 6 mg/Nm^3 for CR. Catalyst outlet emission for NH_3 resulted in at least halving the inlet value.

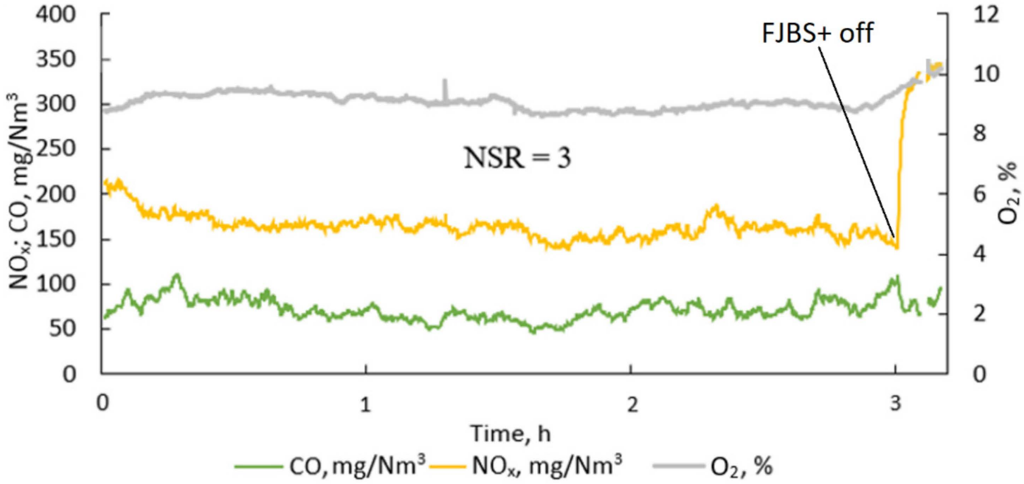

Figure 9. Stack emissions during the hybrid SNCR + SCR system operation at high boiler load of 28 MW_{th}.

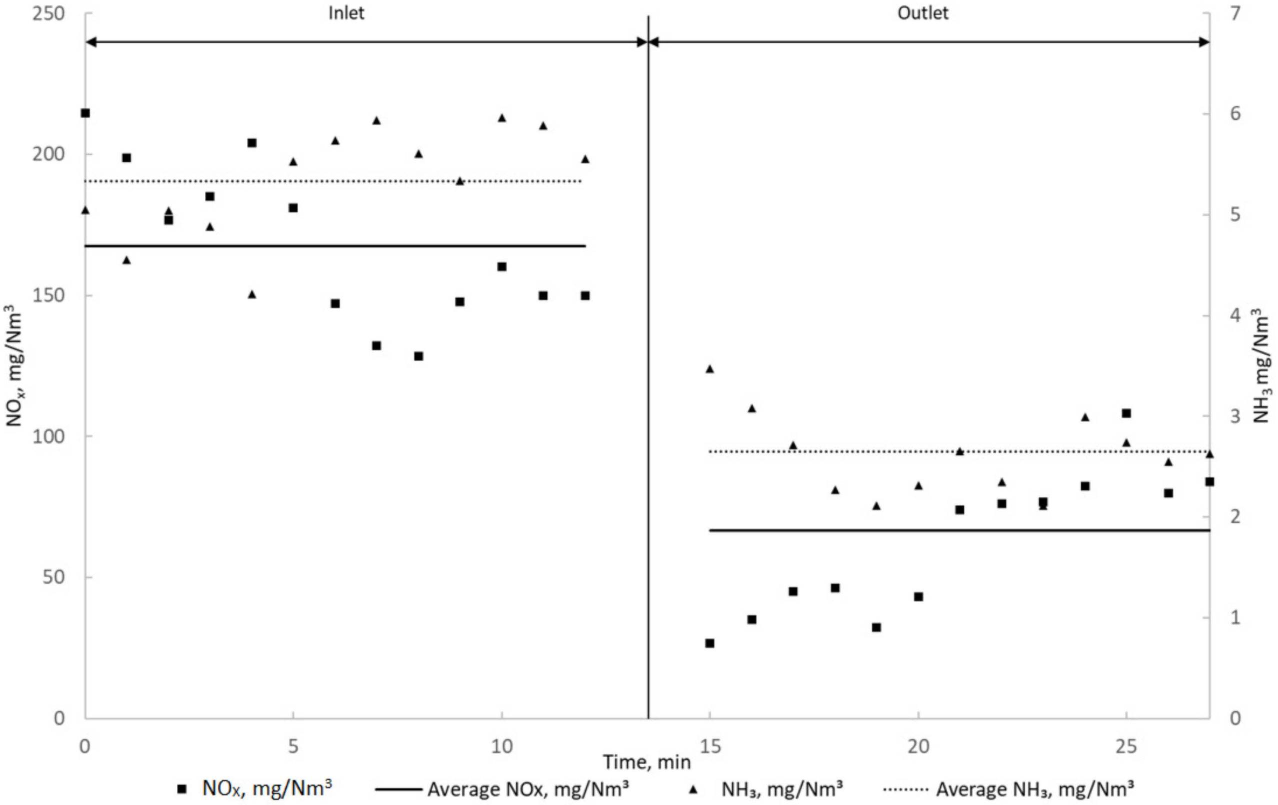

Figure 10. Emissions measured at the inlet and outlet of the new catalyst CN at an average power of 28 MW_{th}-flue gas temperature approx. 400 °C.

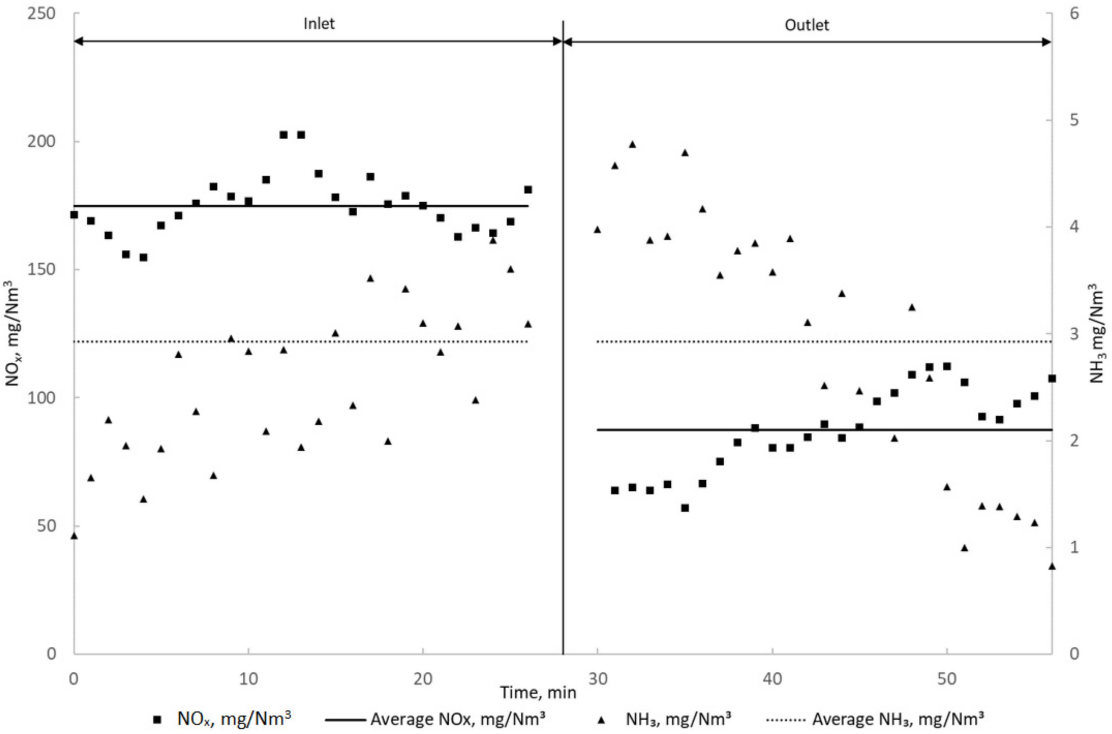

Figure 11. Emissions measured at the inlet and outlet of the regenerated catalyst CR at an average power of 28 MW_{th}-flue gas temperature approx. 400 °C.

Table 3. Average NO_x emissions and conversion for high boiler load.

Boiler Load MW_{th}	**NO_x Emission at the Inlet of New Catalyst CN mg NO_x/Nm^3**	**NO_x Emission at the Outlet of New Catalyst CN mg NO_x/Nm^3**	**NO_x Conversion on New Catalyst CN %**	**NO_x Emission at the Inlet of Regenerated Catalyst CR mg NO_x/Nm^3**	**NO_x Emission at the Outlet of Regenerated Catalyst CR mg NO_x/Nm^3**	**NO_x Conversion on Regenerated Catalyst CR %**
28	170	63	63	185	93	50

The measurement methodology did not allow the simultaneous emission measurement on the inlet and outlet of the catalyst. The measurement was conducted firstly as the catalyst inlet and then at the outlet. The characteristics of the FTIR measurements, the length of the measurement pipe and the response time affected the offset final NH_3 values. This can be observed at Figure 11, showing the efficiency of the regenerated catalyst, Figure 11.

3.3. The Fate of NH_3 in Combustion By-Products

For the FJBS+ process, an ammonia balance was determined taking into account mass fractions of urea and ammonia. As an input, a dose of 40% urea water solution was considered. The output was ammonia slip in fly ash, ammonia slip in flue gas and urea involved in stoichiometric NO_x reduction. Balance incorrectness δ was defined as a variance between total urea input and output.

As a urea input, a dose of urea was calculated taking into account the mass flow and composition of urea solution used as a reagent (Table 4).

According to the reaction of urea decomposition

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2\,NH_3 \tag{9}$$

2 kmols of ammonia are formed from 1 kmol of urea. The mass ratio of urea/ammonia γ can be determined as:

$$\gamma = \frac{M_{CO(NH2)2}}{2\ M_{NH3}} = 1.764706 \tag{10}$$

Hence 1 kg of NH_3 is a result of the decomposition of 1.765 kg of $CO(NH_2)_2$. Thus, ammonia stream flow can be recalculated out of the urea stream. Ammonia output as a sum of ammonia in ash, flue gas slip and urea stream for NO_x reduction is presented in Table 5.

Table 4. Parameters of incoming urea solution stream.

Parameter	Symbol	Value	Unit
Urea solution volumetric flow	$\dot{V}_u$	24	l/h
Solution density	ρ	1132	kg/m^3
Urea concentration in solution		40	%
Urea dose	$\dot{m}_{u\ in}$	0.003019	kg/s

Table 5. Parameters of outcoming ammonia compounds.

Parameter	Symbol	Value	Unit
Ammonia in fly ash (ash output)			
Fly ash mass flow	$\dot{m}_{ash}$	0.194	kg/s
Ammonia content in fly ash		2517	mg/kg
Ammonia stream in ash	$\dot{m}_{ash}$	0.0004883	kg/s
Urea stream equivalent	$\dot{m}_{u\ ash}$	0.0008617	kg/s
Ammonia in flue gas (slip)			
Flue gas volume flow	$\dot{V}_{fg}$	10.5	$m^3{}_n/s$
Flue gas ammonia content		9	$mg/m^3{}_n$
Ammonia stream in flue gas	$\dot{m}_a$	0.0000945	kg/s
Urea stream equivalent	$\dot{m}_{u\ fg}$	0.0001668	kg/s
NO_x reduction			
Avg. NO_x concentration in flue gas without reduction		310	mg/mn^3
Avg. NO_x concentration in flue gas with the reduction system		125	mg/mn^3
Avg. NO_x reduction		185	mg/mn^3
Urea stream for NO_x reduction	$\dot{m}_{u\ red}$	0.0019425	kg/s

Balance incorrectness δ was determined as a variance between total ammonia input and output:

$$\delta = \frac{\dot{m}_{u\ in} - \dot{m}_{u\ out}}{\dot{m}_{u\ in}} = \frac{\dot{m}_{u\ in} - \left(\dot{m}_{u\ ash} + \dot{m}_{u\ fg} + \dot{m}_{u\ red}\right)}{\dot{m}_{u\ in}} 100\% = 1.58\% \tag{11}$$

Finally, the mass balance of the FJBS+ process is summarized in Table 6 and presented in Figure 12.

As can be seen, 64.35% of ammonium compounds used in the denitrification process take part in stoichiometric NO_x reduction, 28.55% migrates into fly ash and 5.52% appears in flue gas as ammonia slip. The total value of ammonia output is almost equal to ammonia input. This difference is defined as balance incorrectness and for considered process parameters equals 1.58%. Some reasons for balance inaccuracy can be defined, such as the possible formation of ammonia-rich ash deposits inside the boiler ducts and migration of ammonia compounds into bottom ash.

Table 6. Mass balance of ammonium compounds in the FJBS+ process.

	Name	Symbol	Value	Unit
Input	Urea dose	$\dot{m}_{\text{u in}}$	0.003019	kg/s
			100	%
Output	Ammonia in fly ash	$\dot{m}_{\text{u ash}}$	0.000862	kg/s
			28.55	%
	Ammonia in flue gas	$\dot{m}_{\text{u fg}}$	0.0001668	kg/s
			5.52	%
	NO_x reduction	$\dot{m}_{\text{u red}}$	0.001943	kg/s
			64.35	%
	Output total		0.002971	kg/s
			89.20	%
	Balance incorrectness δ		1.58	%

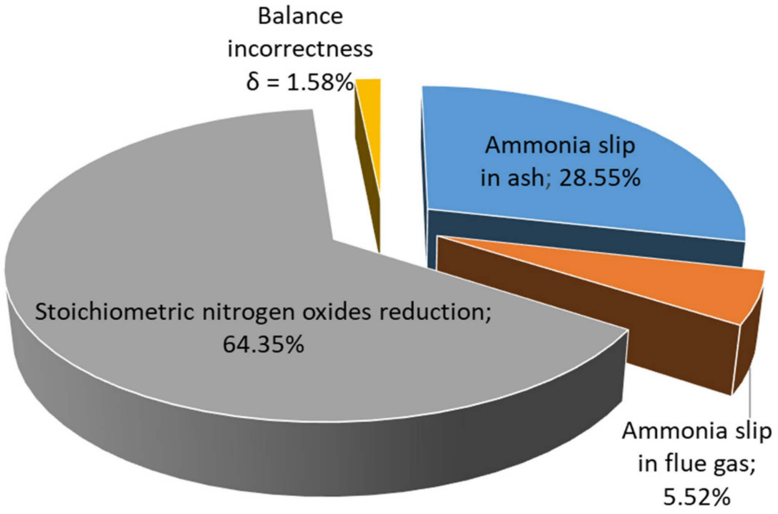

Figure 12. Ammonia mass balance for the FJBS+ process.

3.4. Reduction of Ammonia in Fly Ash

Fly ash collected after the process was tested due to the potential of ammonia removal in both laboratory and full scale. The results are presented in Table 7. Three samples of fly ash were chosen to be tested in terms of diversified ammonia contents: 479, 1326 and 3796 mg NH_3/kg. As a result of the laboratory test, the ammonia content in every sample was decreased below 6.1 mg NH_3/kg (below detection limit). After successful determination of process efficiency in the laboratory scale a full-scale (field) test was carried out. Ash samples were placed onto a grate in steel-mesh boxes. Figure 13 presents samples before and after thermal decomposition on a grate. For the field test, ammonia content was significantly reduced as well to a level up to 32.3 mg/kg. Presented demonstration proves the potential for industrial use of this innovative and cost-effective method.

Table 7. NH_3 content in fly ash before and after thermal treatment in the laboratory and field scale.

Parameter / Sample Number	Initial NH_3 Content in Fly Ash mg/kg	NH_3 Content after Laboratory Desorption mg/kg	NH_3 Content after Full-Scale Desorption mg/kg
1	479	<6.1	7.3
2	1326	<6.1	32.3
3	3796	<6.1	<6.1

(**a**) (**b**)

Figure 13. Fly ash sample before (**a**) and after decomposition on the grate (**b**).

4. Conclusions

The full-scale investigation of non-catalytic (FJBS) and hybrid SNCR + SCR (FJBS+) denitrification processes was successfully performed in a stoker boiler for the full range of power output. In every case, a stable NO_x reduction was achieved. The NO_x emission was reduced down to a level below 180 mg NO_x/Nm^3 at 6% O_2 with NO_x reduction rate reaching 53%. The FJBS installation was combined with the TiO_2-WO_3-V_2O_5 catalyst to create the hybrid SNCR + SCR system FJBS+. This solution reduces problems with proper injection and mixing of reducing compound and flue gas before entering the catalyst. The catalyst application in high dust area resulted in achieving the reduction efficiency of up to 80% for new catalyst and 57% for regenerated catalyst. The result can be considered very satisfactory, taking into account that only one catalyst layer was used and for the low/medium boiler load the temperature in the catalyst section cannot be considered optimal. The catalytic reduction can solve problems with elevated ammonia slip since the catalyst works as an effective NH_3 slip catcher. The use of regenerated catalyst allows reducing operating costs, hazardous waste disposal and environmental danger. Stokers are characterized by a small amount of fly ash compared to pulverized coal boilers, thus a long service life of the catalyst is expected. Presented technology can be applied in waste-to-energy units, including the combustion of medical and hazardous waste.

As follows from a balance 64.35% of ammonium compounds used in the denitrification process take part in stoichiometric NOx reduction, 28.55% migrates into fly ash and 5.52% appears in flue gas as ammonia slip. Ammonia content in fly ash is vital in terms of its possible use in civil engineering, thus an innovative and cost-effective method of ammonia removal from fly ash was presented and tested. Fly ash was recirculated into the combustion chamber, where ammonium compounds were thermally decomposed in a temperature of above 800 °C. The process was initially tested in the laboratory conditions and after that, the successful results were obtained in the full scale. In most cases the NH_3 content in fly ash was reduced below the detection limit of 6.1 mg/kg. In contrast with other methods, presented method does not require an external reactor nor any chemical compounds, which makes it competitive and prospective.

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References

1. Busca, G.; Lietti, L.; Ramis, G.; Berti, F. Chemical and mechanistic aspects of the selective catalytic reduction of NO by ammonia over oxide catalysts: A Review. *Appl. Catal. B Environ.* **1998**, *18*, 1–36. [CrossRef]
2. Bendrich, M.; Scheuer, A.; Hayes, R.E.; Votsmeier, M. Unified mechanistic model for standard SCR, Fast SCR, and NO_2 SCR over a copper chabazite catalyst. *Appl. Catal. B Environ.* **2018**, *222*, 76–87. [CrossRef]
3. Rosenberg, H.S.; Curran, L.M.; Slack, A.V.; Ando, J.; Oxley, J.H. Post combustion methods for control of NO_x emissions. *Prog. Energy Combust. Sci.* **1980**, *6*, 287–302. [CrossRef]
4. Muzio, L.J.; Quartucy, G.C.; Cichanowiczy, J.E. Overview and status of post-combustion NO_x control: SNCR, SCR and hybrid technologies. *Int. J. Environ. Poll.* **2002**, *17*, 4. [CrossRef]
5. Rota, R.; Antos, D.; Zanoelo, É.F.; Morbidelli, M. Experimental and modeling analysis of the NO_xOUT process. *Chem. Eng. Sci.* **2002**, *57*, 27–38. [CrossRef]
6. Daood, S.S.; Javed, M.T.; Gibbs, B.M.; Nimmo, W. NO_x control in coal combustion by combining biomass Co-firing, oxygen enrichment and SNCR. *Fuel* **2013**, *105*, 283–292. [CrossRef]
7. Lee, S.J.; Yun, J.G.; Lee, H.M.; Kim, J.Y.; Yun, J.H.; Hong, J.G. Dependence of N_2O/NO decomposition and formation on temperature and residence time in thermal reactor. *Energies* **2021**, *14*, 1153. [CrossRef]
8. Li, J.; Chang, H.; Ma, L.; Hao, J.; Yang, R.T. Low-temperature selective catalytic reduction of NO_x with NH_3 over metal oxide and zeolite catalysts—A Review. *Catal. Today* **2011**, *175*, 147–156. [CrossRef]
9. Forzatti, P. Present status and perspectives in De-NO_x SCR catalysis. *Appl. Catal. A Gen.* **2001**, *222*, 221–236. [CrossRef]
10. Van Caneghem, J.; de Greef, J.; Block, C.; Vandecasteele, C. NO_x reduction in waste incinerators by Selective Catalytic Reduction (SCR) Instead of Selective Non Catalytic Reduction (SNCR) compared from a life cycle perspective: A case study. *J. Clean. Prod.* **2016**, *112*, 4452–4460. [CrossRef]
11. Gohlke, O.; Weber, T.; Seguin, P.; Laborel, Y. A New Process for NO_x reduction in combustion systems for the generation of energy from waste. *Waste Manag.* **2010**, *30*, 1348–1354. [CrossRef]
12. Lai, J.-K.; Wachs, I.E. A Perspective on the Selective Catalytic Reduction (SCR) of NO with NH_3 by Supported $V_2O_5WO_3TiO_2$ Catalysts. *ACS Catal.* **2018**, *8*, 6537–6551. [CrossRef]
13. Keobel, M.; Elsener, M.; Marti, T. NO_x-Reduction in Diesel Exhaust Gas with Urea and Selective Catalytic Reduction. *Comb. Sci. Technol.* **1996**, *121*, 85–102. [CrossRef]
14. Boningari, T.; Koirala, R.; Smirniotis, P.G. Low-temperature catalytic reduction of NO by NH_3 over vanadia-based nanoparticles prepared by flame-assisted spray pyrolysis: Influence of various supports. *Appl. Catal. B Environ.* **2013**, *140–141*, 289–298. [CrossRef]
15. Więckowski, Ł.; Krawczyk, P.; Badyda, K. Numerical investigation of temperature distribution in the furnace of a coal fired grate boiler in part load conditions. *J. Power Technol.* **2018**, *97*, 359–365.

16. Krawczyk, P. Experimental investigation of N_2O formation in selective non-catalytic NO_x reduction processes performed in stoker boiler. *Pol. J. Chem. Technol.* **2016**, *18*, 104–109. [CrossRef]
17. Krawczyk, P. *The Designing Method of NOx Reduction Installation for Coal Stocker-Fired Boilers Using SNCR Technology*; Oficyna Wydawnicza Politechniki Warszawskiej: Warsaw, Poland, 2019. (In Polish)
18. Wejkowski, R.; Kalisz, S.; Tymoszuk, M.; Ciukaj, S.; Maj, I. Full-scale investigation of dry sorbent injection for NO_x emission control and mercury retention. *Energies* **2021**, *14*, 7787. [CrossRef]
19. Hjuler, K.; Dam-Johansen, K. Mechanism and kinetics of the reaction between sulfur dioxide and ammonia in flue gas. *Ind. Eng. Chem. Res.* **1992**, *31*, 2110–2118. [CrossRef]
20. Bai, H.; Biswas, P.; Keener, T.C. Particle formation by ammonia-sulfur dioxide reactions at trace water conditions. *Ind. Eng. Chem. Res.* **1992**, *31*, 88–94. [CrossRef]
21. Muzio, L.; Bogseth, S.; Himes, R.; Chien, Y.-C.; Dunn-Rankin, D. Ammonium bisulfate formation and reduced load SCR operation. *Fuel* **2017**, *206*, 180–189. [CrossRef]
22. Flagiello, D.; di Natale, F.; Erto, A.; Lancia, A. Wet Oxidation Scrubbing (WOS) for flue-gas desulphurization using sodium chlorite seawater solutions. *Fuel* **2020**, *277*, 118055. [CrossRef]
23. Flagiello, D.; di Natale, F.; Lancia, A.; Salo, K. Effect of seawater alkalinity on the performances of a marine diesel engine desulphurization scrubber. *Chem. Eng. Trans.* **2021**, *86*, 505–510.
24. Poullikkas, A. Review of design, operating, and financial considerations in flue gas desulfurization systems. *Energy Technol. Pol.* **2015**, *2*, 92–103. [CrossRef]
25. Flagiello, D.; Esposito, M.; di Natale, F.; Salo, K. A novel approach to reduce the environmental footprint of maritime shipping. *J. Mar. Sci. Appl.* **2021**, *20*, 229–247. [CrossRef]
26. Peng, Y.; Li, J.; Si, W.; Luo, J.; Dai, Q.; Luo, X.; Liu, X.; Hao, J. Insight into deactivation of commercial SCR catalyst by arsenic: An Experiment and DFT Study. *Environ. Sci. Technol.* **2014**, *48*, 13895–13900. [CrossRef] [PubMed]
27. Jiang, Y.; Gao, X.; Zhang, Y.; Wu, W.; Song, H.; Luo, Z.; Cen, K. Effects of PbCl2 on selective catalytic reduction of NO with NH_3 over vanadia-based catalysts. *J. Hazard. Mater.* **2014**, *274*, 270–278. [CrossRef]
28. Zheng, Y.; Jensen, A.D.; Johnsson, J.E. Laboratory investigation of selective catalytic reduction catalysts: Deactivation by potassium compounds and catalyst regeneration. *Ind. Eng. Chem. Res.* **2004**, *43*, 941–947. [CrossRef]
29. Guo, Y.; Xu, X.; Gao, H.; Zheng, Y.; Luo, L.; Zhu, T. Ca-Poisoning effect on V_2O_5-WO_3/TiO_2 and V_2O_5-WO_3-CeO_2/TiO_2 catalysts with different vanadium loading. *Catalysts* **2021**, *11*, 445. [CrossRef]
30. Tang, F.; Xu, B.; Shi, H.; Qiu, J.; Fan, Y. The poisoning effect of Na+ and Ca_2+ Ions Doped on the V_2O_5/TiO_2 catalysts for selective catalytic reduction of NO by NH_3. *Appl. Catal. B Environ.* **2010**, *94*, 71–76. [CrossRef]
31. Li, X.; Li, J.; Peng, Y.; Si, W.; He, X.; Hao, J. Regeneration of commercial SCR catalysts: Probing the existing forms of arsenic oxide. *Environ. Sci. Technol.* **2015**, *49*, 9971–9978. [CrossRef]
32. Lange, F. Infrared-spectroscopic investigations of selective catalytic reduction catalysts poisoned with arsenic oxide. *Appl. Catal. B Environ.* **1996**, *8*, 245–265. [CrossRef]
33. Peng, Y.; Li, J.; Si, W.; Luo, J.; Wang, Y.; Fu, J.; Li, X.; Crittenden, J.; Hao, J. Deactivation and regeneration of a commercial SCR catalyst: Comparison with alkali metals and arsenic. *Appl. Catal. B Environ.* **2015**, *168–169*, 195–202. [CrossRef]
34. Kröcher, O.; Elsener, M. Chemical deactivation of V_2O_5/WO_3–TiO_2 SCR catalysts by additives and impurities from fuels, lubrication oils, and urea solution. *Appl. Catal. B Environ.* **2008**, *77*, 215–227. [CrossRef]
35. Khodayari, R.; Odenbrand, C.U.I. Regeneration of commercial TiO_2-V_2O_5-WO_3 SCR catalysts used in bio fuel plants. *Appl. Catal. B Environ.* **2001**, *30*, 87–99. [CrossRef]
36. Shi, Y.; Zhang, P.; Fang, T.; Gao, E.; Xi, F.; Shou, T.; Tao, M.; Wu, S.; Bernards, M.T.; He, Y.; et al. In situ regeneration of commercial NH_3-SCR catalysts with high-temperature water vapor. *Catal. Commun.* **2018**, *116*, 57–61. [CrossRef]
37. Yu, Y.; Meng, X.; Chen, J.; Yin, L.; Qiu, T.; He, C. Deactivation mechanism and feasible regeneration approaches for the used commercial NH_3-SCR Catalysts. *Environ. Technol.* **2016**, *37*, 828–836. [CrossRef]
38. Chyliński, F.; Goljan, A.; Michalik, A. Fly ash with ammonia: Properties and emission of ammonia from cement composites. *Materials* **2021**, *14*, 707. [CrossRef] [PubMed]
39. Michalik, A.; Babińska, J.; Chyliński, F.; Piekarczuk, A. Ammonia in fly ashes from flue gas denitrification process and its impact on the properties of cement composites. *Buildings* **2019**, *9*, 225. [CrossRef]
40. Bittner, J.; Gasiorowski, S.; Hrach, F. Removing Ammonia from Fly Ash. Presented at the International Ash Utilization Symposium, Lexington, KY, USA, 22–24 October 2001; Paper #15.
41. Mazur, M.; Janda, T.; Żukowski, W. Chemical and thermal methods for removing ammonia from fly ashes. *Czasopismo Techniczne* **2017**, *6*, 31–50. [CrossRef]
42. Conn, R.; Sarubac, N.; Levy, E. Removing ammonia from fly ash. *Lehigh Energy Update* **2001**, *19*, 1–2. Available online: https://www.lehigh.edu/~{}inenr/leu/leu_28.pdf (accessed on 30 September 2021).
43. Carbon Burn-Out Process. Available online: https://Flyash.Com/Products-and-Technologies/Carbon-Burn-out/ (accessed on 30 September 2021).
44. Gąsiorowski, S.; Hrach, F. Method for Removing Ammonia from Ammonia Contaminated Fly Ash. U.S. Patent No. 6,077,494, 20 June 2000.

45. O'Connor, D. *Ammonia Removal from Fly Ash: Process Review, Headwaters Ammonia Slip Mitigation (ASM^{TM}) Technology*; EPRI: Palo Alto, CA, USA, 2005.
46. Wang, H.; Ban, H.; Golden, D.; Ladwig, K. Ammonia release characteristic from coal combustion fly ash. *Fuel Chem. Div. Preprints* **2002**, *47*, 836–838.
47. Kastner, J.R.; Miller, J.; Kolar, P.; Das, K.C. Catalytic ozonation of ammonia using biomass char and wood fly ash. *Chemosphere* **2009**, *75*, 739–744. [CrossRef] [PubMed]
48. Shrestha, S.; Harold, M.P.; Kamasamudram, K.; Kumar, A.; Olsson, L.; Leistner, K. Selective oxidation of ammonia to nitrogen on Bi-Functional Cu–SSZ-13 and Pt/Al_2O_3 monolith catalyst. *Catal. Today* **2016**, *267*, 130–144. [CrossRef]
49. Chmielarz, L.; Węgrzyn, A.; Wojciechowska, M.; Witkowski, S.; Michalik, M. Selective Catalytic Oxidation (SCO) of ammonia to nitrogen over hydrotalcite originated Mg–Cu–Fe Mixed Metal Oxides. *Catal. Lett.* **2011**, *141*, 1345–1354. [CrossRef]
50. Garbacz, P.; Wejkowski, R. Numerical research on the SNCR method in a grate boiler equipped with the innovative FJBS system. *Energy* **2020**, *207*, 118240. [CrossRef]
51. Hernik, B. Numerical calculations of the WR-40 boiler with a furnace jet boiler system. *Energy* **2015**, *92*, 54–66. [CrossRef]