Evaluation of NOx formation indicators for hard coals selection to meet future environmental requirements

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I. INTRODUCTION

This research begun as a caste study for a certain Power Plant in southern Poland. Due to new legislation requiring the power generating facilities using solid fuels to monitor the chemical composition of fuel they use, research has been conducted to evaluate how these new parameters can be used to enhance Power Plant operation. First goals to achieve with this research was to summarize how fuel is procured and supplied to a Power Plant and what parameters are researched at each stage for this particular Power Plant. Another goal was to gather state of the art knowledge about impact of fuel quality on every process it influences both regarding power generation and pollutant emissions. Finally, as a part of a large scale experiment an indicator that predicts NO_x emissions resulting from coal nitrogen has been tested using data from the power plant.

II. DESCRIPTION OF A CASE STUDY POWER PLANT AND RELEVANT SYSTEMS

A. Boilers

Power Plant discussed in this paper is one of the largest energy generating facilities and pollutant emitters in central Europe. It is composed of eight power units fired by OP-650k boilers with wall-mounted burners produced by Rafako S.A. Each of the boiler is capable of combusting on average 95 tonnes of coal in an hour producing on average over 900000 (Nm^3) of wet flue gas each hour. There are several stages of cleansing the flue gas before emission to air in order to meet current environmental requirements

B. Denitrification installations

Originally, without any modifications, the boilers produced as much as 700 (mg/Nm^3) of nitrogen oxides. Over the years boilers has been retrofitted with primary methods of denitrification – low emission burners and air staging nozzles. As the amount of oxygen present near the burners is not enough to fully combust the coal there is no oxygen to react with nitrogen present in air due to high temperatures which in turn reduces NO_x production. As the air is fed later on higher within the boiler combustion is completed in temperature low enough to prevent so called "thermal" NO_x emergence. These modifications are overall beneficial for boiler operation as more uniform temperature distribution reduces thermal stresses on some parts extending their lifetime. Primary methods allow to decrease the NO_x concentration to around 400 (mg/Nm^3) which is still twice the current limits inflicted by law. To fulfil the requirements three of the boilers have been retrofitted with SNCR (*Selective Non-Catalytic Reduction)* allowing to decrease the NO_x concentration to below 200(mg/Nm^3) and two with SCR (*Selective Catalytic Reduction)* allowing to decrease the NO_x concentration to below 100 (mg/Nm^3) which is currently considered Best Available Technology for denitrification. Both methods use an ammonia solution that reacts with nitrogen oxides and reduces them to atomic nitrogen and water. SNCR uses 40% urea solution and SCR uses 24% solution of ammonia water. SNCR requires higher temperatures of operation in the range of 877–1077(°C) therefore it is installed as a part of the boiler to avoid reheating flue gas. SCR requires only the range of 320–390(°C) so it is installed after flue gases exit the boiler but before they enter electrostatic precipitators – this position is called "High Dust". SNCR not only is less efficient than SCR – it also causes new problems with boiler operation as the aqueous urea solution inside the incineration chamber increases humidity and propagates slagging and decreases combustion efficiency. It is also more susceptible to ammonia slip. To avoid such problems modern SNCR installations are paired with acoustic gas temperature measuring systems that enable efficient SNCR operation. SCR despite being more efficient and easier to operate is substantially more expensive, mainly due to presence of a catalyst that uses valuable, sometimes noble metals such as vanadium or tungsten. Although it uses less ammonia, the catalyst is prone to poisoning due to impurities in coal and regeneration or replacement cost can be overwhelming.

C. Dedusting installations

In this particular power plant electrostatic precipitators are the sole method of particulate matter removal from flue gases. An electrostatic precipitator uses an electric field to attract particles carrying an electrical load. Flue gas exiting the boiler contain fly ash particles. It is brought to electrostatic precipitator by flue gas ducts. Parameters that ought to be monitored in order to ensure proper dedusting process include:

- ash content of intake gases,
- chemical composition of fuel, especially mineral content,
- moisture content of intake gases,
- excess air during combustion.

Aforementioned variables are important because they influence the single most important parameter of fly ash regarding electrostatic precipitators performance – resistivity. Expressed in ($\Omega\cdot$cm) it should be contained for this particular plant within the range of $1\cdot10^9$-$1\cdot10^{11}$ ($\Omega\cdot$cm). Resistivity is affected by:

- temperature (resistivity increases along with temperature increase),
- moisture content in flue gases (resistivity increases along with moisture decrease),
- SiO_2 and Al_2O_3 content in fly ash (resistivity increases with increase of concentration),
- SO_3 concentration in flue gases (resistivity decreases with increase of concentration),
- Na_2O and Fe_2O_3 concentrations in fly ash (resistivity decreases with increase of concentration).

In addition to that, presence of Fe_2O_3 in fly ash catalyses oxidation of SO_2 to SO_3, which causes a synergy in decrease of resistivity. Except resistivity other important non-electric parameters important for correct electrostatic precipitator operation include keeping the underpressure not larger than the one assumed while designing the ESP equal to –4000 Pa as well as keeping the average input temperature of flue gas around 145($^\circ$C) (acceptable range from 115 to 170°C). It is vital to monitor CO concentration in flue gases, as carbon monoxide concentration above 0,3% should shut down the ESP because of the risk of explosion.

D. Desulfurisation installations

The sole method of mitigation of sulfur oxides emissions in this particular power plant is Wet flue gas desulfurisation (WFGD). It is indisputably the Best Available Technology for several reasons. First and foremost the efficiency of sulfur removal is extremely high – usually higher than 99%. The fact that a resulting product of flue gas cleansing is gypsum of a quality suitable for use as a building material makes WFGD profitable not only from environmental point of view but also from economical point of view. Inside a WFGD reactor, SO_2 present in flue gases react with a solvent – powdered limestone. Coal parameters vital for appropriate operation of WFGD are:

- sulfur content,
- ash content,
- moisture content,
- chlorine content.

Apart from sulfur dioxide (SO_2) other combustion side products

are removed during the process such as:

- sulfur trioxide (SO_3)
- hydrogen chloride (HCl)

- hydrogen fluoride (HF)
- sulfuric acid VI (H_2SO_4)
- remains of fly ash remaining after electrostatic precipitation.

Chlorine in form of calcium chloride ($CaCl_2$) remains in the solution almost entirely which negatively affects solubility and dissolution rate of limestone, removal levels of SO_2 and process of gypsum formation.

III. ENVIRONMENTAL REQUIREMENTS REGARDING EMISSIONS AND COAL QUALITY MONITORING

The IED 2010/75/EU directive (Industrial Emissions Directive) is the document that European Commission has introduced to oblige the Member States to control and gradually reduce impact of pollutant emissions to the natural environment from industrial sources. It uses so called BAT (*Best Available Technologies)* described it BAT Reference documents (BREF) to assess full impact of any installation on the environment – including emissions of pollutants to water, air and earth, production of waste, usage of primary resources and energy efficiency among other factors. On 17th august 2021 large combustion plants such as one discussed in this case study will be obliged by new emission and coal quality control standards imposed by the aforementioned directive.

A. Fuel acquisition and testing processes

Nowadays the fuel procurement process is based on the contract between the Power Plant and another branch of the same company that is solely dedicated to fuel procurement. Employees responsible for procurement have little consciousness about the quality of the fuel they are buying and as long as initial parameters are satisfied the only criterion for evaluating the fuel is its price. Before contract for fuel supply is signed, the supplier provides a safety data sheet for the fuel in which one can find much more parameters than those included in the contract. Currently quality of fuel is only taken into account during calculation of price of coal per (GJ) of energy that can be produced using each fuel. Costs associated with incineration such as usage of reagents in flue gas treatment installations, cost of equipment renovation and downtime caused by failures are in no way taken into account. The BREF/BAT documents for large combustion plants oblige power suppliers to perform regular fuel quality control in order to check if it is consistent with initial characteristics and specification of construction of the object [1]. Research and coal characteristics can be done by the plant operator or fuel supplier in the form of product specification or supplier's warranty. For hard coals following characteristics will have to be researched:

- lower heating value in working conditions Q_i^r
- moisture content in working conditions W^r,
- volatile matter content in chosen conditions V
- ash content in working conditions A^r
- fixed carbon content,
- Elemental composition: C, H, N, O, S, Br, Cl, F,
- Metals and metalloids: As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Tl, V, Zn..

These requirements mean that there will have to be additional research undertaken for each fuel by the Power Plants own laboratory or by the fuel suppliers. Currently some parameters required are not researched at all, currently volatile compound contents are not researched by almost 30% of the Power Plants' suppliers, fixed carbon value is never provided, however it could be calculated based on currently available analysis, and elemental analysis is usually incomplete – e.g. bromium and thallium aren't checked by any supplier. At the stage of fuel

consumption four most important for the process parameters are being constantly monitored:

- lower heating value Q_i^r,
- moisture content W^r,
- ash content A^r,
- sulfur content S^r.

IV. CURRENT STATE OF KNOWLEDGE ABOUT COAL QUALITY INDEXES AND ITS IMPACT ON PROCESSES WITHIN THE POWER PLANT

A. Coal preparation – grinding

In a coal fired power plant the process of electricity generation begins in the moment of fuel preparation to be incinerated in a power boiler. The key of preparation is to pulverize the fuel to the appropriate fineness. The finer the coal dust supplied to combustion chamber, the faster it combusts and the firing loss (related to incomplete combustion), emission of NOx, sometimes even emission of fly ash [2] are lower. Simultaneously costs of fuel preparation increase related to: unitary energy use for pulverization, increased power consumption by ventilation fans and increased abrasion of coal mill elements. With increase of surface area of coal dust slagging risk also increases. Pulverized coal fired boilers are known to be the most economically profitable in incinerating hard coal 25–30% of grains is of size grade of 0–90 (µm) and 92% of grains is contained within the grade of 0–200 (µm) [3]. The quality of pulverization usually is defined as a function of fuel type, volatile compounds content V_{daf} and the type of furnace. In real life however, unitary cost of pulverization is more affected by ash content and lower heating value to larger extent than V_{daf}, along with other factors like moisture, erodibility, coal mill load degree and coal grindability. Along with the decrease of lower heating value of coal, usually the amount of so called ballast increases, most importantly – amount of fuel needed to incinerate in order to maintain appropriate dry steam parameters increases. In such a situation the coal mills load will increased what may result in worse pulverizing efficiency - – that means that there will be less coal particles of appropriate size in coal-air mixture supplied to the boiler. Too high moisture content of a fuel W^r is another parameter that negatively impacts the work of coal mills. It makes transportation of fuel into the mill more difficult as well as the pulverization process itself. Because of its erosive properties and hardness, content of pyrites FeS_2 in coal means faster abrasion of pulverizing elements in coal mills. Parameter often used to characterize the grindability of a coal, defined as energy consumption of process of pulverizing energetic blends of coal is Hardgrove's Index (HGI). Method of its determination is based on assumption that the energy expenditure for coal grinding is proportionate to the newly created surface area (accordingly to Rittinger's law). In Hardgrove's method change of surface area of researched coal sample is compared to the change of standard sample for which the HGI = 100 [4]. The higher the value of HGI index, the easier it is to pulverize the coal, and the energy expenditure is lower. The relation between the energy expenditure and HGI index is not linear and one cannot calculate total energy needed to pulverize the sample of coal based on it. Large value of HGI index is achievable for coals of high carbon content and medium or low volatile compound content and low moisture content. Empirical measurement of HGI index is necessary, because aforementioned values are not quantitative. It is agreed that Hardgrove's grindability index should exceed the value of HGI > 50 in order to sustain appropriate work conditions within a coal mill. Coal grindability has direct impact on costs associated with power plant's own needs as the mills are the larger consumers of electricity from all the auxiliary equipment. Therefore it can be concluded that low heating value and low HGI index are responsible for decreasing the profit of electricity generation and shortens the availability of the coal mills as they need to be renovated more often.

B. Combustion

Correct and efficient carrying out of the process of coal combustion is the basis of whole process of electricity production. Incomplete combustion results in increase of concentration of non-combusted carbon in ash called TOC (Total Organic Carbon) often measured as LOI (Loss on Ignition) which in turn has an impact on quality of combustion side products which are mostly ashes used as admixture to concrete or cement. Increased TOC or LOI makes the ash more difficult to sell.

The sum of thermal losses resulting from incomplete combustion (in %) caused by transfer of unburned fuel to solids: slag and fly ash and carrying them out with flue gases in form of volatile coke can be expressed with a following equation [5]:

$$S_n = \frac{100 W_k}{\dot{m}_b W_r} \sum \dot{m}_{Aj} c_{Aj} \qquad (1)$$

where: S_n – thermal loss due to incomplete combustion %, W_k – lower heating value of coke kJ/kg, W_r – lower heating value of fuel kJ/kg, $\dot{m}_b$ – mass flux of fuel kg/s, m_{Aj} – mass flux of products (fly ash and slag) kg/s, c_{Aj} – mass fraction of combustibles in fly ash and slag kg/kg.

Losses due to incomplete combustion can be a result of an insufficient amount of oxygen to complete the reaction or of due to a decrease of in the temperature within the boiler. In any of these cases, apart from CO_2, CO, soot and unburned hydrocarbons can be found among the products. Incomplete combustion losses can be described with an equation:

$$S_{CO} = v_s CO \frac{W_{CO}}{W_r} \qquad (2)$$

where: v_s – volume of flue gas obtained from 1 kg of fuel $\frac{m^3}{kg}$, W_{CO} – lower heating value of CO = 12760 $\frac{kJ}{m^3}$, CO – CO content in flue gas %

There are two parameters that can be distinguished that best describe fuel behaviour within an incineration chamber: volatile compounds content (usually researched in dry, ash free conditions) V^{daf} and sinterability index RI, determined by the Rogi method [6]. These two parameters are used to classify hard coals into types. It is widely accepted that the volatile compounds content V^{daf} should not be lower than 30% of fuel mass, however if a boiler is designed for a low V^{daf} values, it can be lower. The higher the volatile compounds content, the lower is the temperature in which degassing and incineration of coal happens, which means that the combustion process will be faster. However if the concentration of V^{daf} would be too high there is a risk of increasing the temperature in the beginning of incineration chamber, which in turn will mean an increased production of thermal NO_x and risk of steam superheaters fouling. In the case when V^{daf} is too low, there is a risk of incomplete combustion of coal due to increased reaction time and increased exhaust losses. An increase in concentration of volatile compounds in coal changes its combustion dynamics, namely the flame turns out longer which forces the boiler operator to adjust the distribution of air between nozzles at different heights.

C. Slagging and fouling risk

Hard coals are not 100% combustible. Except from the part that undergoes incineration there is also a part called a ballast, which includes moisture, mineral substances and ash that may account to as much as ⅓ of fuel's weight. Conditions within the power boiler namely high temperatures and interchanging reducing and oxidizing atmospheres cause ash to form deposits negatively affecting boiler performance. Formation of ash deposits casue following problems [2]:

- decrease in boiler efficiency due to temperature increase of exhaust gases,
- decrease in power plant efficiency due to a drop in steam temperatures below nominal levels,
- decrease of dust removal efficiency in an electrostatic precipitator due to increase of temperature and volumetric flow of flue gases on its intake,
- increased energy use due to need of pumping larger amounts of flue gas through the boiler,
- increased CO2 emissions in relation to each unit of useful heat produced.

. Generally, the deposits can be divided between:

- slags,
- ashes:
  - loose,
  - bound (sintered).

Another common division is based on temperature (high, mid, low). The process of sintering is caused by high temperatures, although not high enough to reach ash melting temperature. Ash fusion temperatures are characteristic temperatures which define the ability of ash to form deposits and are determined for both reducing and oxidizing conditions both present within modern boilers. According to the norm PN-82/G-04535 following characteristic temperatures of ash can be distinguished (in ascending order):

- sintering temperature t_S,
- initial deformation temperature t_A (according to PN ISO 540:2001 also known as DT),
- spherical temperature, also known as softening temperature ST according to PN ISO 540:2001 (no equivalent in PN-82/G-04535),
- melting temperature t_B (according to PN ISO 540:2001 in reducing atmosphere also known as hemispherical temperature HT),
- fluid temperature t_C (according to PN ISO 540:2001 in reducing atmosphere also noted as FT).

The slagging process takes places in the part of boiler in which the heat is mostly exchanged by radiation, so parts of boiler most susceptible to slagging are:

- burners,
- furnace water-cooled walls,
- slag hopper,
- first wall of superheater tubes,
- convection bundle in the rear wall of combustion chamber.

Slagging is dependent on the melting temperatures of ash components, it is therefore only fitting that most slagging indicators are based on content of respective chemical components of ash recalculated to their oxide shares. in fly ash alone is not enough to judge the coals fouling and slagging tendency.

First and primary factor that has to be taken into account when evaluating coal tendency towards fouling and slagging is simply ash content A^r – naturally if there is high ash content, problems with boiler fouling and erosion of pipes are to be expected. A parameter that defines the tendency towards slagging based on the characteristic temperatures is AFI – a parameter proposed by Gray and Moore in 1974 based on the characteristic temperatures of fly ash and defined by the following equation [2]:

$$AFI = \frac{4 \cdot DT + HT}{5} \tag{3}$$

where: HT – is the highest temperature for which half of base sample creates a hemisphere in the reducing or oxidizing conditions (hemisphere temperature = ash melting temperature), DT – is the lowest initial deformation temperature of fly ash in reducing or oxidizing temperature (deformation temperature = softening temperature).

If:

- $1232 < AFI < 1342°C$ – coal poses a low risk of slagging,
- $1052 < AFI < 1232°C$ – coal poses a high risk of slagging,
- $AFI < 1052°C$ – coal poses an extremely high risk of slagging.

According to [7] an experimental indicator of slagging potential is sulfur content in working conditions $-S^r_t > 1,5\%$ jointly with Fe_2O_3 content in fly ash $> 7–8\%$, when both of these parameters are exceeded at once, intense slagging is to be expected.

Among the indicators based on oxide analysis one of most often recognised is C_m (also found in literature as $R_{(b/a)}$) which is ratio of basic to acid oxides in the fly ash which can be defined by the equation [2]:

$$C_m = \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O + P_2O_5}{SiO_2 + Al_2O_3 + TiO_2} \tag{4}$$

The C_m parameter has an indirect relation with ash melting temperatures. Oxides of iron, calcium and magnesium tend to decrease the ash melting temperature, and oxides of aluminium and silicon increase it, these relations are however by no means simple and linear. Sediment density directly affects its own thermal conductivity – and following that – its sinterability [2]. Hard sediments, friable and therefore sintered will have higher values of λ_z. In case of non-sintering sediments, they will work as insulation and accumulate the threat within the pipe causing it to overheat. As the sediments are sintering its heat conductivity rapidly increases and reaches 5–6 times higher values than λ_z in powdered state. The relation between λ_z and C_m can be defined by following equation [2]:

$$\lambda_z = 0,773 lg C_m + 0,673 \left[\frac{W}{mK}\right] \tag{5}$$

A parameter that takes into account both the alkalinity of fly ash and ash load within the boiler is A_K – The Alkali Number. It defines the ability of fly ash to form ash deposits taking into account the amount of fly ash. For boilers used in this particular Power Plant results of calculation of this parameter correlate particularly well with factual conditions within a boiler

$$A_K = (Na_2O + 0,9659 K_2O) \frac{A^d}{100} \tag{6}$$

If:

- $A_K < 0,3$ – coal with a low tendency to form deposits,
- $0,3 < A_K < 0,45$ – coal with a mediocre tendency to form deposits,
- $0,45 < A_K < 0,6$ – coal with a high tendency to form deposits,
- $A_K > 0,6$ – coal with a very high tendency to form deposits

Please note that these are just some of indicators related to slagging, fouling and ash deposits – for more please see the full version of the thesis.

D. Corrosion of pipes

Two main, most common mechanisms of corrosion occur in power boilers [8]:

- high-temperature sulfate-sulfite fireside corrosion, caused by reducing atmosphere and direct contact of flame containing blazing particles on the pipe; main participant in this process is sulfur and its compounds,
- high-temperature chloride fireside corrosion, gas corrosion induced by chlorine and its compounds.

-Evaporators and superheaters are boiler parts that are most susceptible to corrosion. High-temperature corrosion is a significant problem in industrial power generations for following reasons:

- usage of low-emission combustion techniques in order to decrease emission of NO_x means that in initial part of combustion chamber has to be in reducing conditions which accelerate the corrosion process [2],
- incineration of fuels with high content of chlorine and alkali elements – biomass, waste, coals with chlorine content Cl > 0,2% [9],
- raising of steam temperatures in order to increase the efficiency of power unit.

Corrosion rate and type generally depend on [2]:

- the degree of aggressiveness of the environment determined by composition of fuel, flue gases and ashes and combustion conditions (low emission combustion),
- working temperatures of pipe material and flue gas temperatures; therefore indirectly from boiler design and rate of deposits formed,
- pipe material properties – its chemical and phase composition, structure and degradation rate.

Sulfur trioxide SO_3 is responsible for sulfate-sulfite corrosion. However its concentration in flue gas is usually very low (below 35 ppm) [2], it is higher in direct proximity to pipes due to catalytic influence of iron oxides that promote oxidation of SO_2 to SO_3. It has been observed that corrosion occurs faster near deposits containing around 0.5-1% of lithium [2]. Chlorine corrosion is caused by presence of gaseous chlorine in combustion chamber and therefore this mechanism is most prevalent in waste to energy plants and biomass boilers fired by high chlorine fuels such as straw. It also happens in coal fired boilers, it has been noted in [2] that concentrations of chlorine as low as 0.15% in fuel are enough to trigger this mechanism. In reducing conditions it is possible that HCl and CO will in a way cooperate while attacking the protective layer [8]. Activity of chlorine is neutralized by presence of sulfur in fuel, which may be justified when corrosion is caused by chloride deposits (i.e. on superheaters) [10], [11] if the S^r/Cl^r ratio in fuel falls below 2. It is also possible that in parts of combustion chamber where reducing conditions occur, where corrosion is mainly induced by agents in gas phase, both high temperature mechanisms – sulfide and chloride – may mutually enhance each other and happen simultaneously. It is therefore ideal if not only the ratio of S^r/Cl^r in fuel is lower than 2, but also concentration of both elements is relatively low.

E. Erosion of pipes

Pulverized coal boilers are a subject to erosive processes, such as abrasion of the elements of coal mills and boilers due to influence of ground coal, and material losses of pipes in the convection draft of flue gases in boiler due to the presence of fly ash within the flue gas stream. The amount of material lost due to erosion is dependent on a number of factors, among which following can be distinguished [3.25]:

- average flue gas velocity in an empty duct at the inlet to the heat exchanger pipe bundle,
- velocity distribution of flue gases,
- concentration of fly ash in flue gases,
- fly ash distribution in boiler cross-section,
- working temperature,
- grade of steel,
- distribution of pipes (transverse graduation),
- probability of a particle impact on a pipe,
- erodibility indicator, that indicates the erosive properties of fly ash,
- degree of flat surface development of fly ash/dust.

It is clear that most of the parameters are not dependent on fuel quality. It has been conducted by research described in [12] that the simplified form of c_m indicator mentioned before has the biggest influence on erosive properties of fly ash e_e and can be described by an equation:

$$c_m" = \frac{Fe_2O_3}{SiO_2 + Al_2O_3} \qquad (7)$$

The results of research described in [12] have been developed by the method of regression as a following function:

$$e_e = 4,78(c_m")^{-0,421} \qquad \text{-(8)}$$

e_e = indicator of erodibility characterizing the erosive properties of fly ash

A conclusion can be drawn that the increase of silica and aluminium in fly ash leads to the increase of erodibility indicator. Selection of coal with low ash content and high lower heating value is the best optimisation of boiler operation aimed for decrease of erosion risk that can be done at the stage of fuel selection. Far more possibilities to optimise the operation to avoid excessive erosion of pipes lay in modification of the flue gas aerodynamics, the distribution of flue gases within the boiler and washing the heating surfaces and use of erosion-proof overlays on the heating surfaces most susceptible to erosion. Unlike corrosion, the introduction of low-emission burners has been profitable for erosion of surfaces, since low-emission burners force a finer milling of fuel, which in turn decrease probability of a particle to hit the pipe, so in general decrease the material loss.

F. Efectivity of denitrification installations

Throughout the literature one may find fuel parameters that potentially have impact on the creation of fuel-derived nitrogen oxides. Three most important are featured below [13]:

- Nitrogen content in fuel,
- fuel ratio (mass ratio of solid carbon to volatile matter in dry state),
- mass ratio of -carbon to hydrogen C/H in dry state.

Controlling these parameters can contribute to reducing the formation NO_x as early as the stage of selection and purchase of fuel. What differs nitrogen from i.e. sulfur compounds formation is that there is more than one possible product that nitrogen may form during coal combustion. Atomic nitrogen, N_2, is one of them, but there are also oxides, most importantly: NO, N_2O, NO_2. Coal composition and other combustion products (i.e. SO_2), stoichiometric excess of air and temperatures are other factors that determine what route will nitrogen undergo during combustion. For that reason, it is

currently deemed almost impossible to foresee actual concentrations of NO_x [14]. The only parameter that in numerous studies have shown satisfactory correlation with the amount of formed nitrogen oxides is the difference of nitrogen content with a specific *fuel ratio* [15]. That parameter represents the amount of nitrogen that is present in volatile matter in relation to its amount present in solid residues, what has an impact on the mechanism of formation of NO_x, with increasing values of *fuel ratio* emission of NO_x is also growing [13]. With higher nitrogen content in volatile mater comes lower NO_x emissions which can be accounted to [13]:

- faster release of nitrogen from fuel in the near-burner zone in reduction conditions, which promotes formation of N_2 instead of NO_x,
- smaller amount of nitrogen present in coke undergoing afterburning further within the boiler, which contributes to lowering the amount of formed NO_x in oxidising conditions

etsts have been conducted by Nakata [16] where fuel ratio has been divided by nitrogen content in the fuel. Nakata has obtained a linear dependence between his parameters and suggests fuel ratio divided by nitrogen content is a potentially reliable indicator of amounts of NO_x formed during combustion of a particular fuel. According to [14] the ratio of fuel ratio to the nitrogen content is best suited to predict nitrogen conversion to NO_x for boilers with wall-mounted burners. It is therefore very plausible that it could be used to describe the processes of NO_x formation in this particular Power Plant.

1) Efficiency of SCR, risk of catalyst poisoning

Usage of SCR technology requires careful monitoring of sulfur content within the fuel as well as the composition of mineral substance within the fuel. . The process of degradation of catalytic abilities starts right from the first contact of flue gases with the catalyst, and is associated with emergence of undesired side products of reaction on the surface of catalyst. As the time passes, catalysts undergo deactivation due to several factors. Following mechanisms of catalyst deactivation may be distinguished:

- chemical poisoning of catalysts due to reaction of chemical substances present in flue gases (so called catalyst poisons) with the active substances on the catalyst surface (i.e. V, Ti, Pt). Catalyst poisons show affinity towards active centres of catalysts equal to or greater than NO_x or ammonia, and for that reason they decrease the efficiency of NO_x removal. Following substances can be considered SCR catalyst poisons [17]:
  - alkali metal oxides (Cs, Rb, K, Na, Li, Zn) – these are parts of ash particles that reacts with active substances of catalysts,
  - arsenic – in the form of arsenic oxide (III) it can be found in fly ash, reacting with vanadium it creates stable vanadium-arsenic compounds, which irreversibly poison the catalysts (with no chance of regeneration); the presence of arsenic in coal is relatively small, however it becomes a significant problem within boilers with flue gas recirculation (as their concentration increases in that case),
  - lead –as a part of fly ash particles, elemental lead, lead oxides and lead chlorides reacts with active substances of catalysts,
  - chlorine – in the form of hydrofluoric acid reacts with ammonia or vanadium,
  - phosphorus – its compounds (mainly oxides) are present in fly ash particles and react with active substances of catalysts,
  - sulfur – the influence of sulfur compounds is not unequivocal and can be both positive and negative; the mechanism of interaction has been discussed further within this chapter. It is accepted that SCR installations are designed for coals with sulfur content below 2%.

Deactivation of a catalyst causes the increase in concentration of unreacted reagent, therefore – contributes to ammonia slip. It is assumed, that in order to avoid fouling of air reheater and to minimize the contamination in fly ash the ammonia slip after the catalyst should not exceed 2–3 ppm.

- plugging

Fly ash particles of low diameters (d < 10 μm) and ammonium salts formed in the flue gas (d < 10 μm) may be a cause of plugging of catalysts pores, which results in decrease of its active surface. It is often the case that smaller particles agglomerating in pores are create larger particles (conglomerates) with a highly developed active surface – so called popcorn ash, that blocks the monoliths of catalysts. It is the most common cause of decrease of catalyst efficiency. The blocking of channels, besides catalyst deactivation causes the increase of flow resistance and significant flue gas pressure drops.

- fouling

Fouling of the catalyst surface is often considered a next stage of plugging. The surface of catalyst is covered by a layer of ash or other substances, i.e. $CaSO_4$, which is formed due to reaction of CaO present in fly ash with SO_3. Such a layer is not only a physical barrier that reduces the access of NO_x to the catalyst surface but also poisons the active substance of the catalyst.

- erosion

Deactivation due to erosion is a result of mechanical impact of fly ash particles on the surface of catalyst. The catalyst is particularly susceptible to erosion when the whole combustion process and SCR reactor are badly designed. The intensity of erosion depends on the mineral substance composition in coal and has been discussed in chapter 3.5.

Other factors influence the work of a catalyst include:

- temperature

SCR catalysts can work in the range of temperatures between 180 and 650°C, however the highest efficiency is achieved within the range of 350 to 430°C. Too high temperature of flue gases flowing through the catalyst may lead to its sintering, therefore a persistent decrease of activity due to changes in pore structure. This phenomenon might occur at temperatures as low as 230°C, but the rate of catalyst sintering is dependent on its composition and structure. New catalysts, currently available on the market are less susceptible to sintering.

- Sulfur oxides

The impact of sulfur oxides can be both positive and negative [17]. The positive impact of sulfur dioxide (SO_2) is that it increases the area of active centres within the catalyst. This phenomenon probably has to do with protection of the catalyst surface from the negative impact of alkali oxides, however it is not sufficiently researched to be sure. The negative impact of SO_2 in flue gases is derived from the fact that it oxidizes to sulfur trioxide (SO_3) while in contact with flue gas components and the catalyst surface that deactivates the catalyst [17]. The components which catalyse the conversion of

SO₂ to SO₃ are i.e. vanadium oxide that is present both in the mineral content of the coal and in the catalyst. SO_3 may react with ammonium compounds or alkali elements in temperatures lower than standard for typical reactions in the SCR process. The products of such reactions will plug the catalysts pores. Except from aforementioned substances the formation of ammonium sulfates as a product of a reaction with ammonia which is necessary in the denitrification reaction on the catalyst. In [18] the author suggests that presence of SO_3 influences the catalyst deactivation by formation of aluminum sulfate $Al_2(SO_4)_3$ which decreases the catalytic activity of vanadium, and causes sintering of deposits on the surface of the catalyst. Nowadays the most often identified SCR catalyst poisons in literature are alkali metals, alkaline-earth metals and their compounds. Negative influence of potassium ions is a very often recurring topic. Negative impact of sodium and potassium salts on the activity of SCR catalysts can be graduated according to following order: $Na_2CO_3 < K_2CO_3 < Na_2SO_4 < K_2SO_4 < NaCl < KCl$. As can be seen most impactful forms of potassium and sodium salts are chlorides and sulfates which can lead to the conclusion that low sulfur and chlorine content in fuel is desired.

In [19] it has been noted that activity of catalyst is disrupted by the same factors that cause fly ash deposition.

G. Efficiency of electrostatic precipitation

Parameters of fly ash that influence the efficiency if its capture within electrostatic precipitators are as follows:
- electrical resistivity,
- chemical composition,
- amount,
- size and distribution of particles.

The most important of said parameters is resistivity. It is accepted that for optimal operation of electrostatic precipitator it should be within the range of 10^9–10^{11} Ω·cm. Too low resistivity of fly ash will result in tendency of particles to raise back to flue gas stream during its precipitation from collection plates, too high resistivity will lead to the back corona phenomenon and decrease in electrostatic precipitator operation. Fuel parameters that impact fly ash resistivity are:
- unburnt carbon content in fly ash,
- moisture content,
- calcium, potassium and sodium salts content.

A fundamental compound that influences ESP operation is the concentration of SO_3 in flue gas, that is dependent on the amount of sulfur in fuel and the form of sulfur in which it is present. Other factors influencing emergence of SO_3 is the presence of compounds catalysing oxidation of SO_2 such as iron or vanadium compounds. Usage of the SCR installation practically always mean higher concentration of SO_3 in flue gas. Too high SO_3 concentration may induce condensation of sulfuric acid and damage the precipitator, too low concentration may cause increase in fly ash resistivity and complicate dust removal. If the ash forming in the boiler is too fine, it will negatively affect ESP operation. It has been proven in [20] that size distribution of ash particles is directly connected with size distribution of pulverized coal, therefore dependant on the operation of coal mills.

H. Desulfurisation efficiency

After the literature research it can be conducted, that the requirements given by the manufacturer of WFGD are complete and comprehensive. The influence of fuel on the installation is indirect, the final composition of flue gas entering the FGD is crucial. Among things that influence final flue gas composition one can distinguish: how the combustion has been conducted (presence of unburnt carbon, expressed as LOI), operation of SCR/SNCR installation (presence of ammonia, SO_3 concentration) and appropriate operation of electrostatic precipitators (amount of fly ash introduced with flue gas). Regarding fuel quality, adherence to parameters currently required by contracts with fuel suppliers to the Power Plant should ensure no problems with wet FGD operation.

I. Quality of combustion side products – fly ash and gypsum

Most important side products of combustion produced in a power plant are gypsum, slag, furnace ashes, fly ashes and waste from water and sewage treatment such as slime and sediments. It is accepted that about 15% of mineral substance contained in coal leaves the boiler in the form of slag and 85% in the form of fly ash. Ashes from coal fired power plants may be used for [21]:
- production of solidified ash slimes in the technology of curing (stabilization) of soils, embankments, dumping grounds,
- road construction,
- production of cementless binders,
- production of Portland clinker,
- as an active additive to cement,
- production of concrete,
- production of lightweight aggregates,
- used in agriculture and gardening,
- production of self-solidifying floors in mining.

Two crucial parameters determining usefulness of fly ash for concrete production are its fineness and content of LOI (Loss on ignition) which is a measure of unburnt carbon in fly ash (TOC). It directly impacts puzzolanic properties of fly ash and therefore if it can be sold with profit. The main factor influencing quality of fly ash and amount of unburnt carbon is the composition and quality of fuel [22]. It is however not the only factor, in report [23] one may find information that introduction of low emission burners lead to change in:
- particle size – fly ash after combustion in reduction burners is usually larger than during uncontrolled combustion,
- particle shape – they are usually more angular and irregular than spherical as usually is during uncontrolled combustion
- unburnt carbon content is usually higher than before the modification.

Another economically significant combustion side product is gypsum produced in wet FGD process. In order to carry out the crystallization process appropriately it is crucial to monitor concentration of SO_2 in flue gas on the inlet to the wet FGD absorber as well as pH of the suspension (in the range of 5-5,1). Other parameters that influence the quality of gypsum include ash content, HCl and HF in flue gas on the absorber inlet, concentration of combustibles in fly ash, presence of carbonates and sulphites and appropriate operation of hydrocyclones and gypsum centrifuges.

V. EVALUATION OF NOₓ FORMATION INDICATOR

During six days of an experiment a boiler at the case study power plant was fuelled by coal from a known source and known composition so it was possible to assess whether the indicator designed in laboratory conditions could be used to

predict emissions a real, large scale boiler. The indicator has the

Figure 1 NOx measured to calculated ratio in case 1

following form[16]:

$$NO_x = \frac{160.0}{V_{dry}} \cdot (a_1 \cdot FR + a_2 \cdot FN) \tag{9}$$

NO_x: NOx concentration (PPM)
V_{dry}: Volume of flue gas (Nm³/kg)
a_1, a_2 : Constants equal to $a_1=10.94$ and $a_2=6.77$ for wall-mounted burners
FR: fuel ratio (fixed carbon/volatile matter wt%/wt%)
FN: fuel nitrogen (air dried basis)

From the data available from the boiler sensors 10 periods with constant power and coal have been selected. During these period the SNCR installation that this particular boiler is equipped with has been turned off for more than an hour so it is assumed that all ammonia has been washed out and does not affect the NO_x measurements. Two factors used by Nakata in his equation are troublesome for this research, and because of that four cases have been considered. First of all volumetric stream of dry flue gas V^{daf} is not known, as only total, not standardized flue gas stream is measured. In case one, NO_x concentration has been calculated using unstandardized volumetric flow available from the sensors and using constants provided by Nakata's work equal to $a_1 = 10,94$ and $a_2 = 6,77$ [16]. In case 2 there has been an attempt to assume the amount of water entering the boiler with fuel, air and produced by combustion of hydrogen present in coal. The moisture present in coal is monitored in real time so values for each day are known along with coal stream entering the boiler and its hydrogen content. The amount of water entering with air is calculated based on online weather archive. Both values have been decreased by 50% to account for the drying that happens during coal pulverisation and air heating. Resulting stream of water vapour present in flue gas has been subtracted from total flue gas stream assuming its density at 140°C and V^{daf} has been calculated this way. In case 3, unstandardized flue gas volume has been used again, but this time a_1 and a_2 constants that have been proposed for laboratory scale burners have been set as variables. An attempt was made to optimise the average relative error and lower it as much as possible with use of GRG non-linear mathematical solver available in Microsoft Excel. Case 4 represents the same attempt for V^{daf}. Results for each attempt are also represented on graphs In case 3 adjusted constants have values as follows: $a_1 = 11,338$, $a_2 = 6,390$. In case 4 adjusted constants have values as follows: $a_1 = 10,820$,
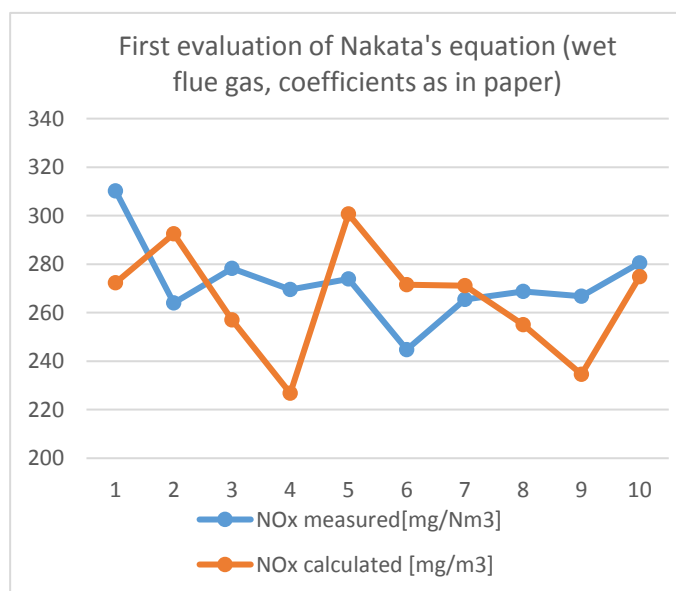
$a_2 = 5,720$. The results can be seen in Table 1. Comparison of NO_x measured to calculated in case 1 can also be seen on Figure 1.

In conclusion, while trying to calculate with equation proposed by Nakata and using wet flue gas stream as measured by the Power Plant sensors the results are surprisingly satisfactionary. Average error of prediction is as low as 3,16% with maximum deviation equal to 18,86%. -With a minor change of constants to $a_1 = 11,338$, $a_2 = 6,390$ this average error can be brought down to 0 with maximum deviation of 15,23%, however there are not enough sample periods available to confirm these values as universally better for the boiler. It seems that the equation

Table 1 Juxtaposition of NOx concentration levels measured on site and calculated in 4 different cases

Period	NOx measured by a sensor [mg/Nm³]	NOx calculated in case 1 [mg/Nm³]	Error in case 1 [%]	NOx calculated in case 2 [mg/m3]	Error in case 2 [%]	NOx calculated in case 3 [mg/m3]	Error in case 3	NOx calculated -in case 4[mg/m3]	Error in case 4
1	310,23	272,32	-13,92%	278,87	-11,24%	281,16	-10,34%	256,08	-21,14%
2	264,02	292,50	9,74%	300,08	12,02%	302,00	12,57%	275,56	4,19%
3	278,31	257,05	-8,27%	284,54	2,19%	265,22	-4,93%	261,29	-6,51%
4	269,52	226,80	-18,84%	262,80	-2,56%	233,91	-15,23%	241,33	-11,68%
5	273,86	300,65	8,91%	318,65	14,06%	310,33	11,75%	292,61	6,41%
6	244,80	271,53	9,85%	320,33	23,58%	280,01	12,57%	294,16	16,78%
7	265,42	271,12	2,10%	319,82	17,01%	279,58	5,07%	293,69	9,63%
8	268,72	255,01	-5,38%	300,33	10,52%	262,97	-2,19%	275,79	2,56%
9	266,77	234,55	-13,74%	275,01	3,00%	241,87	-10,29%	252,54	-5,63%
10	280,50	274,80	-2,08%	323,56	13,31%	283,38	1,02%	297,12	5,59%
Average:			-3,16%		8,19%		0,00%		0,02%

First evaluation of Nakata's equation (wet flue gas, coefficients as in paper)

— NOx measured[mg/Nm3]
— NOx calculated [mg/m3]

proposed by Mr. Nakata for laboratory scale wall-mounted burners and volumetric values of dry flue gas, also works fine for large scale wall-mounted burners with same constants values and volumetric values for wet gas measured by sensors. Recalculating the value of flue gas to exclude water causes average error within the period to raise to the value of 8,19% with maximum deviation of 23,58%. For such conditions a change in constant values to $a_1 = 10,820$, $a_2 = 5,720$ would be beneficial for the average results bringing them down to 0%, with 21,14% maximum deviation, however for the sake of practical use unchanged equation seem more appropriate and do not produce such high deviations from the norm.

VI. Conclusions

There are numerous processes within a conventional thermal power plant influenced by chemical composition of fuel and flue gas. Some of relations between fuel quality and problems with plant operation are known for years now, i.e. many of slagging and fouling indices have been discovered several decades ago. Due to lack of appropriate laboratory measurements of each fuel shipment this knowledge has yet to be put to use in the industry for live mixing of different types of coal to achieve certain results. In depth analysis usually has been only undertaken when a certain fuel was causing significant damage e.g. pipe failure due to intensive erosion. With the IED 2010/75/EU directive this will change. With much more frequent and in depth analysis of fuels it will be possible to avoid problems with power plant operation and decrease emissions as early as the stage of fuel procurement. In order to do so personnel responsible for coal procurement should be supplied with a new set of indicators that would help them evaluate coal quality based on chemical composition that will be supplied to them. As each power unit varies, evaluation of indicators should be performed individually for each type of boiler, ideally for each power plant. First step that should be undertaken in such evaluation is to ask questions to people that have been operating the plant for a long time. Such conversations with boiler operators of this case study Power Plant resulted in identifying parameters and shipments of coal that were linked to problems occurring in the past that led to breaks in power plant operation. Having this initial knowledge it was easier for R&D experts to identify slagging and fouling indicators that were accurate or to come up with new indicators dedicated for a certain power unit. This approach however will not help with emission issues. Some, seemingly crucial pollutants such as sulfur oxides and particulate matter have been appropriately dealt with and are being removed with enormous efficiency. This is partly due to the possibility of obtaining marketable side product as a result of flue gas treatment that provides economic incentive for any power company to fund research in this topic.

Some pollutants such as NO_x cannot be turned into marketable product, therefore incentive for their removal is solely imposed by lawmakers. No method of NO_x removal is as yet optimal, because either it decreases combustion efficiency, contributes to global warming and causes problems with corrosion and ammonia slip to combustion side products (SNCR) or it is simply is very expensive and causes side effects such as oxidizing SO_2 that would be efficiently removed in WFGD to aggressive SO_3 that is not as easily removed. For this reason experiments such as the one described in this thesis are conducted to try and decrease time during which such installations are turned on and save some money on reagents. As *thermal* and *prompt* NO_x are already dealt with by using primary methods of denitrification most NO_x remaining should come from nitrogen present in coal. An indicator evaluated in this work has been published in 1988 by Toshihiko Nakata and his team. It has taken three decades until the subject has been given enough importance and sufficient data to even attempt to predict NO_x emissions based on coal quality. Even though the indicator has been proposed for laboratory scale boiler and uses normalized and dry flue gas flux instead of wet un-normalized that is available from boilers' sensor system it has proven surprisingly well suited for prediction of emission. 10 periods have been found during which the fuel quality is known, conditions in combustion chamber are stable and denitrification has been turned off for more than an hour. Nakata's indicator has been first tested for flue gas volume "as is" from sensor system and recalculated to a dry flue gas stream using known data about fuel and moisture present in air. Average error in first case ("as is") was as little as 3,16% and with recalculated flue gas stream error reached 8,19%. In both cases a non-linear solver available in Microsoft Excel has been used to try and optimize the constants in the equation to decrease the error even further. With only 10 data samples however it is recommended to simply use the equation proposed by mr. Nakata with flue gas streams available from the boiler and the indicator is satisfyingly accurate and can be used to predict NO_x emissions. This accuracy perhaps could be even higher if the value for atomic nitrogen content was known each time – value from safety data sheet has been used, though it can be assumed that nitrogen content is rather constant in coal from the same deposit and mine. This could be used by SNCR and SCR operators to be able to adjust the amount of reagent injected in the flue gas stream earlier.

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