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

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I declare that this document is an original work of my own authorship and that it fulfils all the requirements of the Code of Conduct and Good Practices of the *Universidade de Lisboa*.

Resumo

À luz dos novos regulamentos Europeus no que diz respeito a Grandes Centrais de Combustão há uma ênfase crescente na redução de poluentes que são emitidos pelas centrais térmicas tradicionais de produção de energia. Esta tese tenta identificar caminhos para reduzir o impacto negativo do carvão nos processos dentro de uma certa Central Térmica de Energia e das respetivas emissões para o ar. O Capítulo 2 descreve as propriedades do carvão atualmente utilizado e que são requeridos pela nova legislação e discute a nova oportunidade. O Capítulo 3 contém um resumo do estado do conhecimento atual relativamente ao impacto de cada um dos processos envolvidos na geração de energia e no tratamento dos gases de escape no contexto de uma Central Térmica convencional localizada na Polónia. O último capítulo descreve uma experiência para prever as emissões de Óxido de Azoto (NO_x) pela central térmica usando a composição química do combustível segundo a metodologia de Toshihiko Nakata. Para os seis dias que foram analisados mostraram ser precisas.

Keywords

Thermal Power Generation, Pollutant emissions, Coal quality, Nitrogen Oxides, NO_x

Abstract

In the light of new European regulations regarding Large Combustion Plants there is an ever increasing emphasis on the reduction of pollutants from traditional thermal power plants. This thesis attempts to find ways of reducing negative impact of coal on processes within a certain Power Plant and emissions to air. Chapter 2 describes properties of coal currently researched and required by new laws and discusses new opportunities. Chapter 3 contains a summary of current state of knowledge about fuel impact at every process of energy generation and flue gas treatment within a conventional Power Plant located in Poland. The last chapter describes an experiment in predicting Nitrogen Oxide (NO_x) emissions from the power plant using chemical composition of fuel using methodology proposed by Toshihiko Nakata. For the six analysed days, the indicator has proven to be accurate.

Keywords

Thermal Power Generation, Pollutant emissions, Coal quality, Nitrogen Oxides, NO_x

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List of Acronyms

BAT	Best Available Technologies
BREF	BAT Reference Document
CCSEM	Computer Controlled Scanning Electron Microscopy
COD	Chemical Oxygen Demand
ESP	Electrostatic Precipitator
EU	European Union
FGD	Flue Gas Desulphurisation
HD	High Dust
IED	Industrial Emissions Directive
IMOS	See *WFGD*
IPCC	Intergovernmental Panel on Climate Change
LCA	Life Cycle Analysis
LCP	Large Combustion Plant
LHV	Lower Heating Value
LOI	Loss on ignition
NO_x	A generic term for Nitrogen Oxides produced during combustion
PLN	Polish Złoty
R&D	Research and Development
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction
TOC	Total Organic Carbon
TSS	Total Suspended Solids
UPS	Combustion side products
WFGD	Wet Flue Gas Desulfurisation
XRD	X-Ray Diffraction

List of Symbols

Latin letters

A	Ash Content [%mass]
a	Constants in Nakata's equation
AFI	Slagging tendency indicator
A_k	Alkali number
C_m / $R_{(b/a)}$	Fouling tendency indicator
CR	NO_x conversion ration
d	diameter
DT	Softening temperature in reducing atmosphere (Deformation Temperature) [°C]
e_e	Erosion indicator
EI	Erodibility index
EI	Erosion indicator
FC	Fixed Carbon
FR	Fuel Ratio
FT	Flow temperature in reducing atmosphere (Flow Temperature) [°C]
F_u	Ability of coal ash to form deposits
HGI	Hardgrove grindability index
HT	Melting temperature in reducing atmosphere (Hemisphere Temperature) [°C]
I	Inertinite [%mass]
L	Liptinite[%mass]
M	Mineral Content
$\dot{m}$	Mass flux [kg/s]
Pa	Transport susceptibility
Q	Heating value [Mj/kg]
RI	Sinterability
R_o	Rogi index
R_s	The Babcock Factor
Ry	Colour
SI	Free swelling index
S_R	Silica concentration
t	Temperature [°C]
V	Volatile compounds content [%mass]
v	Volume [m^3]

V_t	Vitrinite [%mass]
W	Moisture content [%mass]

Upper indexes

a	Analytical state
daf	Dry, ash free
i	Lower (in relation to heating value)
r	Working conditions
s	Higher (in relation to heating value

Lower indexes

1	Constant indicator
2	Constant indicator
A	Softening (in relation to temperature) or Ash Bound (In relation to Sulfur)
B	Melting (in relation to temperature)
C	Flow (in relation to temperature) or Combustible (in relation to Sulfur)
is	Slagging initiation (in relation to temperature)
O	Organic (In relation to Sulfur)
P	Pyritic (In relation to Sulfur)
S	Sintering (in relation to temperature)
t	Total

Greek letters

λ	Excess air coefficient
λ_z	Sintering tendency indicator

Chapter 1

Local conditions for a case-study Pulverized Coal Fired Power Plant located in Poland resulting from applicable law and operated devices

An introductory chapter describing the reasoning and rationale behind the need for such research and topic. As this work has been done with cooperation with a specific Power Plant, this chapter details on the Power Plant constitution and each installation that handles coal or its derivatives

1. Local conditions for a case study Pulverized Coal Fired Power Plant located in Poland resulting from applicable law and operated devices

1.1 Preface

The basis for the following thesis has been established during an internship at the Research & Development department for a leading energy company based in Poland. As a part of its assets this company operates several Coal Fired Power Plants across Poland that are subject to environmental regulations by European Commission, especially directive IED 2010/75/EU (Industrial Emissions Directive) that is further discussed in this work. In order to meet the requirements based on such restrictions, the company has to constantly broaden its knowledge about the chemistry and composition of the coal processed in its Power Plants. By better understanding phenomena that will be used to process the fuel and its remains after combustion it is possible to use the energy contained in it in a more efficient, clean and reliable manner. Nowadays more and more attention is focused on pollution control, and, in this context, the ability to predict the flue gas composition based on coal's chemical composition is of paramount importance. New laws will require Large Combustion Plants, such as the one discussed in the thesis, to monitor more coal properties than it is currently done, and this knowledge can be used to avoid excessive emissions and problems with Power Plant operation as early as the stage of coal procurement or selection. During the internship I have been asked to summarize the knowledge about currently used and soon to be required methods of measuring coal's chemical and physical properties prior to incineration both from internal documents and scientific press. As a next stage I have summarized the current stage of knowledge about impact if coal's chemical composition at each stage of fuel and flue gas treatment within a Power Plant, with the exception of waste water treatment. The Company has undertaken a rare experiment – to fuel one of boilers at a large power plant with only one type of coal with known detailed composition so that it was possible to use data from real-life large scale pulverized coal boiler to assess the usefulness of a NO_x conversion indicator that could be used to predict NO_x emission rates based on coal's chemical composition.

1.2 Warranty parameters of installations and devices operated within the Power Plant

1.2.1 Boilers

All eight power units are powered by OP-650k boilers with wall-mounted burners produced by Rafako S.A. To clarify the nomenclature within this thesis the boilers shall be referred to as K-*n*, *n* being the number of power unit fired by said boiler, i.e. K-2 will mean the boiler used in Power Unit 2. Juxtaposition of parameters used to design the OP-650k boilers and average values of same parameters in fuel nowadays are listed in Table 1.1.

Table 1.1 Fuel design parameters for the OP-650k boilers in contrast to the average fuel in 2015.

Parameter	Design	Current average (2015 r.)
Lower heating value [kJ/kg]	17 600	21 000
Total moisture content [%]	16	10
Ash content [%]	32	23
Sulfur [%]	1,4	0,8
Fuel consumption [t/h]	114	95

It is clearly visible that fuel has changed a lot over the years. The boilers have been designed to incinerate large amounts of coal of inferior quality what can be seen in geometry of the boilers. The incineration chamber is rectangular and unusually large. The current "fuel field" of acceptable coals for OP-650k is as displayed below on Figure 1.1.

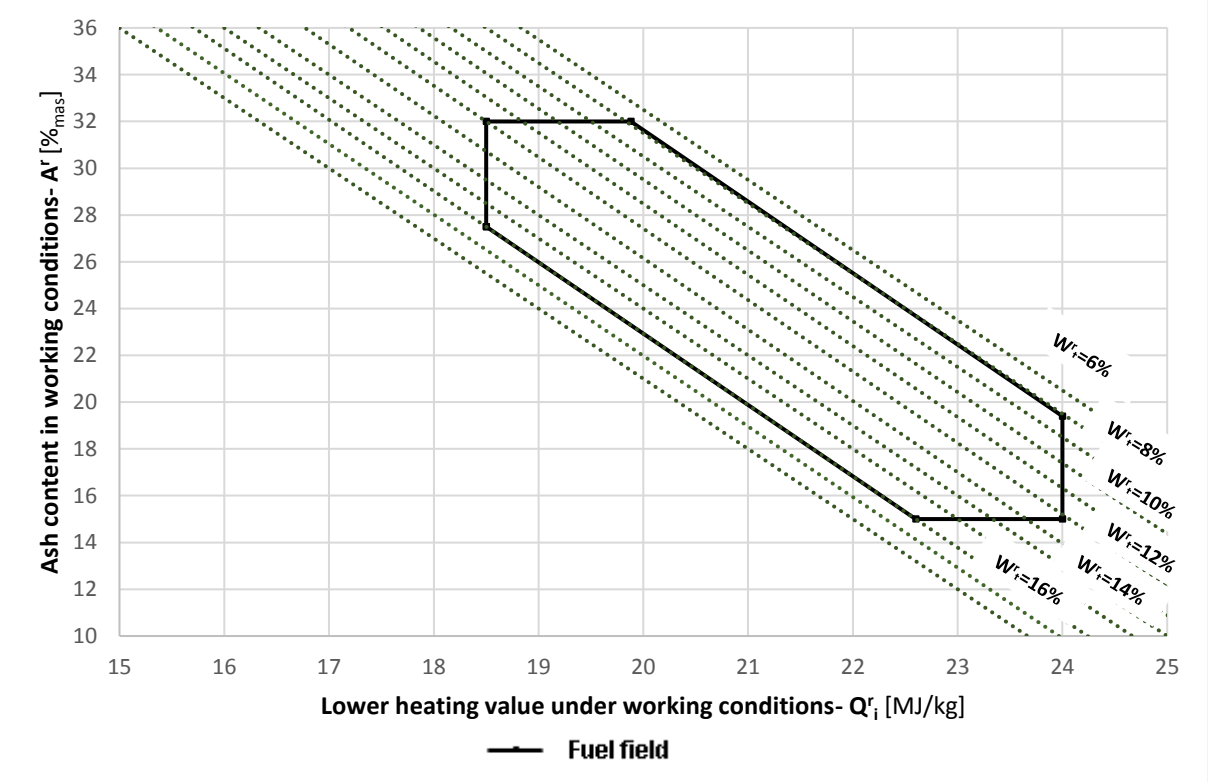


Figure 1.1 Current fuel field for OP-650k boilers

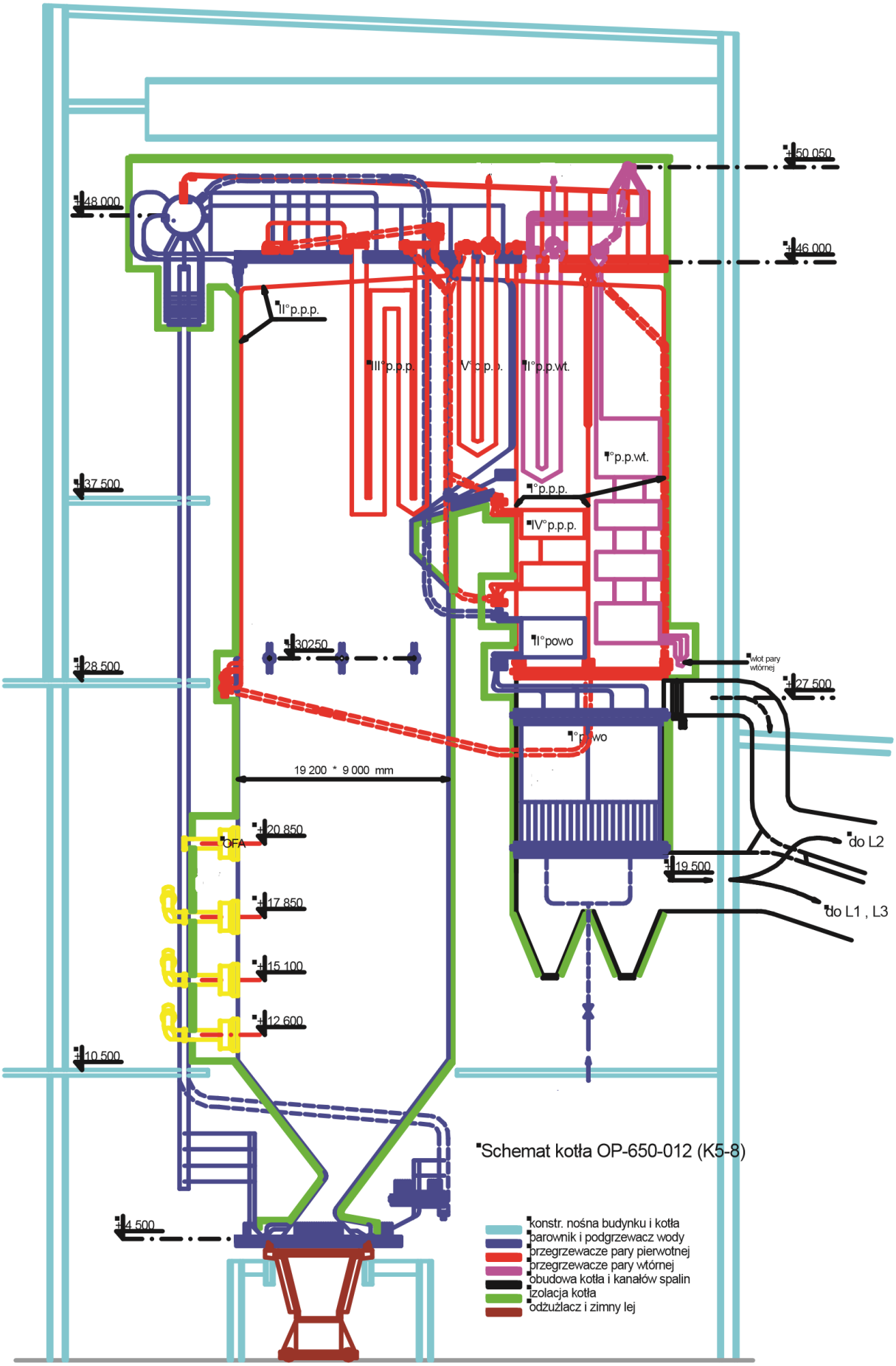


Figure 1.2 Silhouette of OP-650k Boiler

The simplified boiler silhouette can be seen on Figure 1.2. Colour scheme of the boiler drawing is as follows:

- light blue – supporting structure of the boiler and the building,
- dark blue – evaporator and water heater,
- red – primary steam superheater,
- purple – secondary steam superheater,
- black – boiler and flue gas shafts casing
- green – insulation
- brown – cold slag hopper.

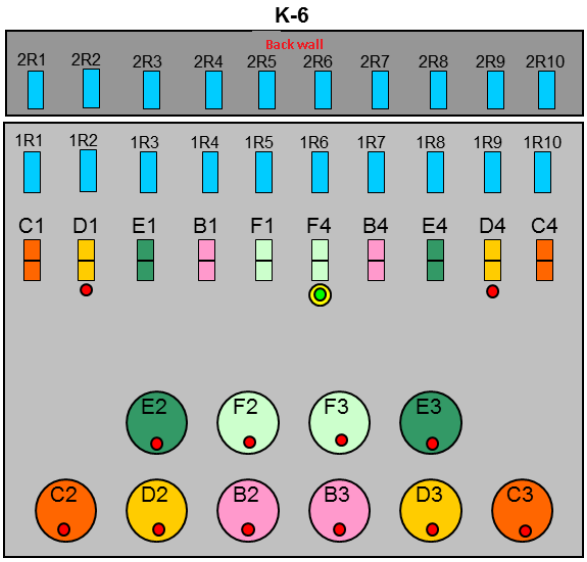
1.2.2 Denitrification installations

As a response to exacerbating NO_x emission standards The Company has introduced a number of modifications to their boilers aiming to reduce NO_x concentration in flue gases. In order to decrease the emissions it is necessary to reduce the concentration from its primary value after combustion, 700 mg/Nm^3 or sometimes more, by a mix of primary and secondary methods has been used, including:

- Low emission burners,
- Air staging,
- Catalytic and non-catalytic reduction methods.

In the Power Plant, each boiler excluding K-1 and K-2 has been modified with primary reduction methods including low emission burners and air staging.

In practice, fuel and air staging can be seen on Figure1.3 on which burners and over fire air nozzles are displayed:



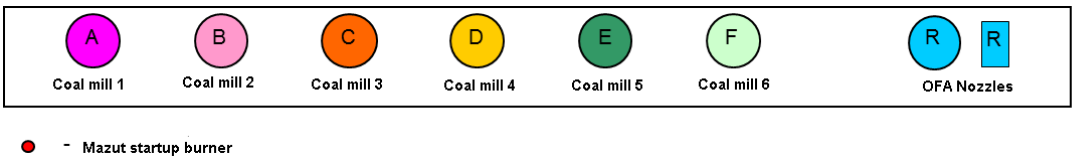


Figure 1.3 Schematics of fuel and air staging burner setup in the K-6 boiler

To achieve the decrease of NO_x concentration in flue gas from the level achievable after installation of low emission burners (around 400 mg/Nm^3) to the levels limited by current law (less than 200 mg/Nm^3) some of the boilers have been retrofitted with the SNCR installation (*Selective Non-Catalytic Reduction*). This method relies on direct injection of a reductant to the incineration chamber of the boiler. The reductant reacts with the nitrogen oxides produced during incineration to produce atomic nitrogen and water. An aqueous urea solution is used as a reducing agent in SNCR. Efficiency of said method and the amount of pollutants after reaction depends mainly on temperature, composition of flue gas before the reaction and the amount of urea solution introduced to the reaction. An optimal temperature window ranges from 1150K to 1350 K (877–1077°C). Such conditions are present in a power plant near the exit from the boiler, therefore SNCR is being installed as a modification to the power boilers. The reduction rate of NO_x in case of correctly operated denitrification installation using SNCR method ranges from 30 to 50%. There are however some major drawbacks to this method. SNCR changes the chemistry of nitrogen transformations within the boiler and causes an increase in the nitrous oxide N_2O concentration in flue gases. Nitrous oxide is a very potent greenhouse gas (with an influence towards global warming during 100 years 298 times more potent than CO_2 for the same volumes of the substances). Other drawbacks include a range of problems with boiler operation caused by spraying the aqueous urea solution inside the incineration chamber – starting with the decrease in overall boiler efficiency caused by the losses due to incomplete combustion that manifest themselves by an increased TOC (total organic carbon) concentration in ashes and a decrease of the combustion temperature due to higher humidity in the combustion chamber, which also causes increased slagging due to wetting of fly ash which in turn damages heated areas of the boiler. Another problem is ammonia slip – not all of the ammonia originated by the aqueous urea solution when it reacts with nitrogen oxides, what may cause increased ammonia concentrations in the fly ash, in the flue gas or in the sewage from the Wet Flue Gas Desulfurisation (*WFGD*). Ammonia slip is also present in SCR method but to a lesser extent.

Selective Catalytic Reduction (*SCR*) is much more effective method to reduce nitrogen oxides. In this particular Power Plant it is used in so called HD variant (*High Dust*). That means it is placed in the so-called high-dust position – the installation is retrofitted just after the boiler before the electrostatic precipitator. Because the catalytic reduction of nitrogen oxides is the most efficient in the temperature range of 320–390°C the existing economiser (reheater of boiler water) has been divided into two parts between which the SCR has been installed. It is capable of decreasing the concentration of NO_x from the level of around 400 mg/Nm^3 to below 100 mg/Nm^3. The reduction process uses ammonia (NH_3), as a reductant over a catalyst. Undisputed advantage of SCR is that it is the most widely available from all secondary denitrification methods with an efficiency of NO_x removal from the flue gas reaching 90%. This method is however the most expensive both in regard to capital and operation costs mostly because of the price of catalyst replacement which usually contain expensive, sometimes noble metals. It is therefore crucial to eliminate or reduce as much as possible the causes of catalyst poisoning. Warranty

parameters for both SNCR and SCR used in an exemplary Power Plant has been juxtaposed in Table 1.3:

Table 1.2 Juxtaposition of warranty parameters for SNCR and SCR used at the exemplary Power Plant

Warranty Parameters	Unit	K-3, K-4, K-6	K-7, K-8
Method		SNCR	SCR
Average concentration of NO_x * (as a sum of nitrogen oxides in conversion to NO_2)	mg/Nm^3	180–200*	< 100
Average use of NH_3 *	mg/Nm^3	< 3,5	< 1,52
Concentration of NH_3 in fly ash (for fuel with ash content equal to 25%)	mg/kg	< 100	< 50
Concentration of NH_3 in fly ash (for fuels with ash content different than 25%)	mg/kg		y = –3·*A*+126 *A* = fly ash content in fuel
Concentration of (residual) NH_3 remaining in gypsum	mg/kg	n/a	< 10
Hourly use of NH_3 (Generator power 220 MW)	dm^3/h	590–690**	< 400***
Hourly use of NH_3 (Generator power 135 MW)	dm^3/h	250–280**	< 238***

** emission parameters for O_2 = 6%, dry flue gas*

*** usage of 40% urea solution depending on NO_x concentration before reduction– 300–340 mg/Nm^3*

**** usage of 24% solution of ammonia water*

1.2.3 Dedust installations

Our exemplary Power Plant similarly to most coal fired power plants uses electrostatic precipitators (ESP) to dedust the flue gases. An electrostatic precipitator uses an electric field to attract particles carrying an electrical load. Flue gas exiting the boiler contains fly ash particles and after leaving the boiler (in case of K-7 and K-8 after leaving the SCR installation) it's brought with flue gas ducts to the electrostatic precipitator. Each unit is equipped with horizontal, dry electrostatic precipitators. Each ESP contains two external and one internal parts together adding up to 15 chambers. Every electrostatic precipitator has three dedusting zones. Removal of fly ash happens through the hoppers located at the bottom of each zone. From the chambers dust is directed to the hoppers and later to the intermediate bunker, from where it goes to the main bunker. From there it is either transported to be sold or to be disposed of. It is crucial for the correct operation and maintenance of high efficiency to maintain the flue gas parameters that the ESP had been designed for. It has to be taken into account that every time boilers run with reduced performance that is during startup or turning off, and every other deviation from rated work conditions will result in a decrease of dedusting efficiency. Every process that happens before the removal of dust, such as denitrification, might influence ESP performance, as well as the composition of incinerated fuel. Important parameters that ought to be monitored for proper work of an electrostatic precipitators include:

- ash content of intake gases,
- chemical composition of the fuel, especially mineral content,

- moisture content of intake gases,
- excess air during combustion (λ).

Aforementioned variables influence the most important fly ash parameter that influences ESP performance – its resistivity. Expressed in Ω·cm should be within the range of $1 \cdot 10^9$-$1 \cdot 10^{11}$ Ω·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, the presence of Fe_2O_3 in the fly ash catalyses the oxidation of SO_2 to SO_3, which causes a synergy in decrease of resistivity. Apart from the resistivity other non-electric factors are important for the correct electrostatic precipitator operation, including 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°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 [1.1].

1.2.4 Desulfurisation installations

Wet flue gas desulfurisation is currently the most popular method worldwide to remove sulfur from flue gases due to incredibly high efficiency of removal (usually higher than 99%), and the fact that a side product of flue gas cleansing is gypsum suitable for usage as a building material. Nowadays the exemplary Power Plant is equipped with two wet FGD installations referred to as IMOS I and IMOS II and desulfurisation is now only done using this method:

- IMOS I in operation since 2008 (absorbers 1 and 2),
- IMOS II, which passed warranty tests in February 2017 (absorbers 3 and 4).

In operating instructions for the WFGD [1.2] design parameters for reference fuels have been specified for IMOS II installation. Inside a WFGD installation SO_2 present in flue gases reacts with a solvent – powdered limestone. This reaction produces gypsum of standard market value. The WFGD is designed so it could work with highest possible efficiency during combustion of any coal appropriate for this Power Plant. Coal parameters most important from the point of view of desulfurisation are:

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

Apart from sulfur dioxide (SO_2) other combustion products are removed during wet desulfurisation:

- sulfur trioxide (SO_3),
- hydrogen chloride (HCl),
- hydrogen fluoride (HF),
- sulfuric acid VI (H_2SO_4),
- remains of fly ash remaining after electrostatic precipitation.

SO_3 content in total emission of sulfur oxides amount to around 1% of SO_2 concentration volume wise. However this is an extremely important compound. Below 200°C it reacts with water vapour (H_2O) through a reversible reaction producing H_2SO_4, which condenses as a mixture of H_2SO_4 and H_2O creating a liquid aerosol. Because of complexity of that process, which is influenced by not only water vapour concentration and temperature of flue gases but also i.e. fly ash concentration it is very difficult to assess how much SO_3 will actually be removed. It is widely accepted that reduction level of SO_3 is around 50%. Reduction levels of HCl and HF are believed to surpass the reduction levels of SO_2, it can be assumed that they are removed from flue gas completely.

Chlorine in form of calcium chloride ($CaCl_2$) remains in the solution almost entirely. Chlorides present in the absorber suspension affect negatively:

- solubility and dissolution rate of limestone,
- SO_2 removal level,
- forming of gypsum.

Therefore from technological point of view, chlorides are undesirable. They also have a strong impact on corrosion induced by chlorides on the surfaces of metallic materials even alloyed metals. As chlorides dissolve rather easily they are removed from the installations as a part of sewage.

In presence of Ca^{2+} ions it is possible that calcium compounds with other components of flue gases can appear in the solution. I.e. fluorine in the form of calcium fluoride CaF_2 precipitates from the solution at the operating pH levels as a solid body and the dissolved part reaches saturation concentration. Solid calcium fluoride is removed from the installation together with gypsum and the dissolved CaF_2 is removed as a part of sewage stream from the WFGD.

1.3 Currently applicable and future Environmental requirements (IED, BREF-BAT)

The IED 2010/75/EU directive (Industrial Emissions Directive) has been prepared in 2010, accepted in the beginning of 2011 and implemented in force on 7th January 2013. Using this document the European Commission has introduced the obligation for the Member States to control and gradually reduce the impact of pollutant emission to the natural environment from industrial sources. So called BAT (*Best Available Technologies*) have been defined and are being constantly updated by the IPCC European Bureau (*Intergovernmental Panel on Climate Change*) based on international experience exchange within the community. Best Available Technologies have been described in BAT Reference Documents (BREF). Both aforementioned documents are result of inter European experience exchange between scientific and industrial institutions and contain descriptions of best available technologies that are working on an industrial scale (BATs) in regard to emissions reduction, usage of primary materials, energy efficiency and so on. According to article 14(3) of the IED directive, for each type of installation

for which BAT documents have been prepared and BREF has been published they must be taken into account while applying for permits and licenses for said installations for usage within the European Union. Applications for integrated permits necessary for industrial activity must include the requirements of Best Available Technologies within published BAT reference documents [1.3].

The 2010/75/EU directive allows some flexibility while imposing less restrictive emission limits. It is possible only in specifically conditioned cases in which the analysis of situation shows that reaching levels of emissions derived from BAT would lead to disproportionately large cost of a small decrease in emissions caused by geographic location, local environmental conditions or technical characteristics of the installation. Such exemptions are called derogations. The government representatives responsible for allowing derogations are obliged to document their reasoning behind such decision every single time. The timeframe for imposing BREF document validity for large combustion plants (LCP) is as follows:

- June 2016 – Final DRAFT of BAT Conclusions,
- 31st july 2017 – implementing decision of the European Commission (UE) 2017/1442,
- 17th august 2017 – public announcement of BAT conclusions for LCP,
- 17th august 2018 – deadline for applications to change permits, including substantiation for possible derogations,
- 17th august 2021 – beginning of validity of BAT conclusions.

A four year adjustment period has been planned between publication of final BAT conclusions until new limits will fully come to force.

The IED directive assumes integrated approach – the permits must take into account full impact of the installation on the environment – including emissions of pollutants to water, air and earth, production of waste, usage of primary resources, energy efficiency noise pollution, and prevention of accidents and reclamation of area after closure of the activity. Except emissions to air, our exemplary Power Plant will have to monitor pollutants removed with waste water from the sewage treatment plant. Values that will be monitored are collected in the Table 1.3 Pollutants removed with waste water to be monitored with regard to the ICP directive along with their appropriate levels derived from BAT-AEL. Based on [1.4]. below:

Table 1.3 Pollutants removed with waste water to be monitored with regard to the ICP directive along with their appropriate levels derived from BAT-AEL. Based on [1.4]

Substance/Parameter	Standard	Frequency	BAT-AEL values (day average)	Comments
Total organic carbon (TOC)	EN 1484	Monthly	20–50 mg/l *	Only one of TOC and COD has to be measured
Chemical oxygen demand (COD)	No standard	Monthly	60–150 mg/l	Monitoring of TOC is preferred, because of toxic reagents usage in COD method.
Total suspended solids (TSS)	EN 872	Monthly	10–30 mg/l	
Fluoride (F^-)	EN ISO 10304-1	Monthly	10–25 mg/l *	
Sulfates (SO_4^{2-})	EN ISO 10304-1	Monthly	1,3–2,0 g/l *	
Sulfides(S^{2-})	No standard	Monthly	0,1–0,2 mg/l *	

Substance/Parameter	Standard	Frequency	BAT-AEL values (day average)	Comments
Sulfites (SO_3^{2-})	EN ISO 10304-3	Monthly	1–20 mg/l *	
Metals and metalloids: As	Different standards available (i.e. EN ISO 11885, EN ISO 17294-2)	Monthly	10–50 µg/l	
Cd			2–5 µg/l	
Cr			10–50 µg/l	
Cu			10–50 µg/l	
Ni			10–50 µg/l	
Pb			10–20 µg/l	
Zn			50–200 µg/l	
Hg	Different standards avaliable (i.e. EN ISO 12846 lub EN ISO 17294-2)		0,2–3 µg/l	
Chlorides (Cl^-)	Different stadards avaliable(i.e. EN ISO 10304-1 lub EN ISO 15682)	Monthly	Not specified	
Total nitrogen	EN 12260	Monthly	Not Specified	

** - Only in case if wet FGD is in use*

Requirements regarding monitoring coal properties resulting from BREF-BAT documents have been included in chapter 2 of this thesis.

Chapter 2

Description of currently used method for fuel selection in the Power Plant. List of parameters supplied with Safety Data Sheets of Fuels

This chapter contains the current methodology for fuel selection and a juxtaposition of parameters that are currently available or will have to be measured since 2021.

2. Description of currently used method for fuel selection in the Power Plant. List of parameters supplied with Safety Data Sheets of Fuels

2.1 Current process of fuel acquisition and juxtaposition of the tested parameters

Currently 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. Unfortunately the salespeople have little consciousness about the quality of the fuel they are buying and today as long as the initial parameters are satisfied, the only criterion for evaluating the fuel is its price. The contract specifies the parameters that procured fuel has to meet along with range of deviation from allowed values. Before contract for fuel is signed, the coal supplier has to provide a safety data sheet for the fuel in which one can find much more parameters than those included in the contract, which can provide additional knowledge about fuel quality. Table 2.1 contains summary of parameters from safety data sheets for 14 different fuels with distinction of how many coal mines is monitoring said parameter.

Table 2.1 Parameters supplied by coal suppliers in safety data sheets of fuel.

Condition	Parameter	Unit	Symbol	Amount of data sheets	%
	Coal size			9	64
	Class			14	100
	Coal type			6	43
Working conditions	Lower heating value	kJ/kg	Q_i^r	***14***	100
Working conditions	Total moisture content	%	W_t^r	***14***	100
Working conditions	Ash content	%	A^r	***14***	100
Working conditions	Total sulfur content	%	S_t^r	***14***	100
Analytical state	Moisture content	%	W^a	***5***	36
Analytical state	Ash content	%	A^a	***5***	36
Analytical state	Volatile compounds content	%	V^a	***5***	36
Analytical state	Total sulfur content	%	S_t^a	***5***	36
Analytical state	Sinterability		***RI***	***8***	57
Analytical state	Free swelling index		***SI***	***6***	43
Analytical state	Higher heating value	kj/kg	Q_s^a	***4***	29
Analytical state	Lover heating value	kJ/kg	Q_i^a	***5***	36
Analytical state	Carbon content	%	C^a	***13***	93
Analytical state	Hydrogen content	%	H^a	***13***	93
Analytical state	Nitrogen content	%	N^a	***13***	93

Analytical state	Phosphorus content	%	P^a	***9***	64
Analytical state	Fluorine content	%	F^a	***14***	100
Analytical state	Mercury content	ppm	Hg^a	***8***	57
Analytical state	Chlorine content	%	Cl^a	***13***	93
Analytical state	Oxygen content (calculated)	%	O^a	***10***	71
Analytical state	Hardgrove grindability index		***HGI***	***13***	93
Analytical state	Real density	g/cm^3	d_r^a	***4***	29
Analytical state	Petrographic analysis (vitrinite, liptinite, inertinite, mineral content)	[…]	R_o, V_t, L, I, M	***4***	29
Dry state	Ash content	%	A^d	***5***	36
Dry state	Total sulfur content	%	S_t^d	***5***	36
Dry state	Higher heating value	kJ/kg	Q_s^d	***4***	29
Dry state	Lower heating value	kJ/kg	Q_i^d	***4***	29
Dry state ash free	Volatile compounds content	%	V^{daf}	***10***	71
Dry state ash free	Higher heating value	kJ/kg	Q_s^{daf}	***4***	29
Characteristic temperatures of ash softening					
Oxidizing atmosphere	Sintering , softening, melting, flow	^oC	t_S, t_A, t_B, t_C	***9***	64
Reducing atmosphere	Sintering , softening, melting, flow	^oC	t_S, t_A/DT, t_B/HT, t_C/FT	***14***	100
Chemical analysis of coal composition					
	Oxides: sodium, magnesium, aluminum silicon, phosphorus, sulfur, potassium, calcium titanium, iron	% wag.	Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, K_2O, CaO, TiO_2, Fe_2O_3	***13***	93
	Manganese oxide	% wag.	Mn_3O_4	***8***	57
Trace elements content					
	Silver, tin, barium, cadmium, cobalt, chromium, copper, strontium, nickel, lead, vanadium, molybdenum, tin, antimony, arsenic	ppm	***Ag, Zn, Ba, Cd, Co, Cr, Cu, Sr, Ni, Pb, V, Mo, Sn, Sb, As***	***8***	57
Remaining					
Sulfur analysis, analytical state	total, ash bound, combustible, pirytic, sulfuric, organic	%	S_t, S_A, S_c, S_p, S_{SO4}, S_o	***4***	29
Ability to spontaneously ignite		$^oC/_{min}$ / kJ/mol/ -	Sz^a $Sz^{a'}$ A spontaneous ignition group.	***8***	57
Transport susceptibility			**Pa**	***7***	50
Spectrometric analysis		Bq/kg	**Potassium, Radiun, Thorium**	***7***	50
		indicator	f_1, f_2	***7***	50

In order to take into account the quality of bought fuel, nowadays the price in PLN per GJ of obtained energy is calculated for each fuel. Another costs associated with fuel incineration such as usage of reagents in flue gas treatment installations, costs of equipment renovation and downtime caused by failures are in no way taken into account. An attempt to evaluate such influence is undertaken by this work. On the stage of procurement process a supplier has to provide a safety data sheet for a fuel and during the delivery has to inform about certain parameters required by the contract. In 2017 final BREF/BAT documents have been made available to public. The documents have been published on 17.08.2017. From that time, Member States of EU have 4 years to implement new solutions in order to fulfil tightened environmental standards. Said documents contain entries obliging the power suppliers to regular fuel quality control in order to check if it is consistent with initial characteristics and specification of construction of the object [2.1]. 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 [2.1]:

1. Lower Heating Value in working conditions (Q_i^r),
2. Moisture content in working conditions (W^r),
3. Volatile matter content in chosen conditions (V),
4. Ash content in working conditions (A^r),
5. Fixed carbon content,
6. Elemental composition: C, H, N, O, S, Br, Cl, F,
7. Metals and metalloids: As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Tl, V, Zn.

These additional requirements mean there will have to be additional research for each fuel conducted by the Power Plants' own laboratory or by the fuel suppliers. Currently some of the parameters mentioned above are not researched. Considering the data from Table 2.1 one might notice that currently:

- volatile compounds content is not researched at four coal mines in any state,
- fixed carbon value is never provided, however it could be calculated based on current analysis by subtracting from one content of moisture, volatile matter and ash in a given sample of coal
- elemental analysis including trace elements is usually researched however incompletely, e.g. bromium and thallium aren't checked by any of the mines.

The necessity to research fuel quality in a more systematic manner opens new opportunities to better understand its influence on the performance of some elements of the technological line and allows optimisation of energy generation process as early as on the stage of fuel procurement.
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.

Fuel is controlled two times – once during the delivery (using a sampler) and during transportation on conveyor belts (settlement with the supplier is based on value of that measurement). For several reasons, including the organization of railway traffic, the long waiting time before gathering the sample and results from laboratory analysis and fuel demand (some deliveries are headed straight to the boiler for incineration), it is extremely rare to send back fuel not fulfilling the requirements back to the supplier. In case there have been deviations from the norm, the power plant files a complaint, even though it happens after the coal has been unloaded, often already burned. Only in cases of coal quality being so poor that it is visible to the naked eye (i.e. train car or coal chutes have been plastered over with coal, or there has been several complaints about a supplier) coal is being unloaded with presence of a laboratory staff member who, after ascertainment of large quality deviations, will send the train back with the fuel to the supplier. Attempts to identify additional indexes for coal quality assessment have been undertaken in chapter 3 of this work. It has to be noted though, that the key to successful optimization of coal quality is the enforcement on suppliers to fulfil parameters already demanded and checked, which alone will help to avoid problems related with incinerating fuel of greatly different parameters than what the boiler and flue gas treatment installations were designed for.

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Chapter 3

Literature review and juxtaposition of coal quality indexes

The following chapter contains results of an extensive literature search regarding coal quality and its impact on each installation that handles coal or its derivatives in a Power Plant with special focus for indicators for different problems related with coal processing due to its chemical composition that may be assessed using available data described in Chapter 2.

3. Literature review and juxtaposition of coal quality indexes

3.1 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 work of a coal mill can be described by: availability to do work, simplicity of replacement of abrasive elements and values such as: pulverizing quality (defined as a % of remain on normalized sieves), unitary energy use for pulverization and rated capacity. The capacity of a coal mill depends on:

- grindability of the fuel and desired fineness,
- heat flux delivered for drying,
- mill ventilation – flux of drying-transporting agent.

The finer the coal dust supplied to combustion chamber, the faster it combusts and the firing losses (related to incomplete combustion), the emission of NO_x and sometimes even the emission of fly ash [3.1] 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 the 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 with a size grade of 0–90 μm and 92% of grains is contained within the grade of 0–200 μm [3.2]. The quality of pulverization usually is defined as a function of fuel type, volatile compounds content V^{daf} I and the type of furnace. In real life however, the 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. As drying of the fuel is also done in the coal mill, high moisture content will extend the amount of time the fuel spends in the mill, and by too long retention time it will change overall dynamics of the work of the coal mill [3.3]. During the milling process coal loses around 2% of moisture compared to the content before pulverization.

Because of its erosive properties and hardness, content of pyrites FeS_2 in coal means faster abrasion of pulverizing elements in coal mills.

A parameter that is often used to characterize the grindability of a coal, defined as the energy consumption of the process of pulverizing energetic blends of coal, is the Hardgrove's Index (HGI). The method for its determination is based on the assumption that the energy expenditure for coal grinding is

proportional to the newly created surface area (accordingly to Rittinger's law). In Hardgrove's method, the change of the surface area of coal sample is compared to the change of standard sample for which the HGI = 100 [3.4]. 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 the total amount of 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 the 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 a direct impact on costs associated with the 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 for shortening the availability of the coal mills as they need to be renovated more often.

In [3.5] *Optimal milling quality* has been defined as minimum sum of costs of preparation and incineration of pulverized coal and emissions of harmful substances related to these processes.

3.2 Combustion (effectiveness as losses on ignition, TOC)

Correct and efficient carrying out of the process of coal combustion is the basis of whole process of electricity production. Any losses related to incomplete combustion result in decreased efficiency of the boiler, as not all chemical energy contained in fuel has been released, that in turns increases the cost of electricity generation. It results in an increase of the concentration of non-combusted carbon in the ash, quantified by the TOC (*Total Organic Carbon*) often measured as LOI (*Loss on Ignition*) which in turn has an impact on quality of combustion side products (UPS) which are mostly ashes whch can be used as admixture to concrete or cement. Increased TOC or LOI makes the ash more difficult to sell.

Loss resulting from incomplete combustion of pulverized coal and accompanying excessive content of unburned combustible solids in slag and fly ash is one of parameters used to characterize power boilers. An increase in values of TOC/LOI in combustion by-products lowers the boiler efficiency and therefore profitability of the whole process, it has an impact on the work on electrostatic precipitators and has a decisive influence on whether side products of combustion are fit for further use (sale) in the construction or cement industry. There are several parameters that are associated with incomplete combustion losses. Some of the parameters are associated with the fuel and its reactivity, however there are several associated with how the combustion process is carried out: appropriate amount of oxygen, residence time of particles in combustion chamber and fineness of coal [3.6]. Reactivity of a fuel can be understood as ability to undergo reaction with a substratum such as steam, oxygen or carbon dioxide. The reactivity defines speed of reaction and decides the efficiency of combustion or gasification processes and impacts the type of side products of said processes [3.7]. 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 [3.8]:

$$S_n = \frac{100W_k}{\dot{m}_b W_r} \sum \dot{m}_{Aj}\, c_{Aj} \tag{3.1}$$

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 due to a decrease 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. A feature that differs between these two incomplete combustion mechanisms is the presence of combustible substances in gas phase, unlike in the case described above when they are only found within solids. Incomplete combustion losses can be described with an equation:

$$S_{CO} = v_s CO \frac{W_{CO}}{W_r} \tag{3.2}$$

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 %

Design of a power boiler has a primary impact on how the combustion process will be conducted. Boilers are devices designed to handle specific types of fuel that are incinerated inside them. Derogations from the design parameters of fuel might result in a series of side effects i.e. an increase of lower heating value may result in aforementioned higher concentration of TOC. However, as mentioned in previous chapters, the parameters of fuel checked at the stage of fuel consumption give approximate information about its properties, they are insufficient to foresee how a certain fuel will behave inside an incineration chamber. Regarding this, two parameters give the biggest insight: volatile compounds content (usually measured in dry, ash free conditions) V^{daf} and sinterability index RI, determined by the Rogi method [3.6]. 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. Remaining parameters that impact efficiency and stability of combustion are: granulation (therefore indirectly grindability), ash melting and softening temperatures, moisture content and carbon content. The higher the amount of moisture in working state W^r the more heat is being used for its evaporation and, to a certain extent, the higher the tendency of particles to glue together and foul the heating surfaces increases. Too much moisture in a fuel supplied to a boiler causes problems with keeping the steam at desired parameters and a decrease in boiler power. The last parameter to be considered combustion wise is hydrogen content in working conditions H^r. H^r indicates

how easy to ignite coal is and can be an indicator of stability of combustion process. It is accepted that hydrogen content in working conditions should be about 2–5% [3.9].

3.3 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 [3.1]:

- 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 CO_2 emissions in relation to each unit of useful heat produced.

Fouling causes problems mainly in the middle section of a boiler – in the region of III and V primary steam superheaters and II secondary steam superheater. Same regions will be characterized by an increased risk of deposit sintering. In extreme cases the deposits grow so much that it is necessary to turn the boiler off in order to clean up the heated surfaces. To minimize the risk of downtime soot blowers are being used to clean up the surfaces when the boiler is running however they only can deal with loose powders or lightly sintered deposits. Generally, the deposits can be divided between

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

The process of sintering is caused by high temperatures, although not high enough to reach ash melting temperature.

Another distinction of deposits can be derived from the temperatures they are created in. Based on that one can divide the deposits into [3.1]:

- high temperature (slags) – formed above the ash melting temperature on waterwalls and first parts of superheaters. Their chemical composition is significantly different from that of a fly ash. This kind of deposit is highly metamorphosed and are characterized by high mechanical resistivity.
- mid temperature (slags, ashes) – formed within the range of softening temperature of ash to the temperature of acid dew point in flue gases t_r. They cover the superheaters inside the convection row and water heaters. They are not metamorphosed as compared with ash covering them and they are characterized by very low mechanical resistivity.
- low temperature – formed below the temperature of acid dew point t_r. Because of additional binding agent – acid condensates they may grow into significant sizes.

Ash fusion temperatures are characteristic temperatures which define the ability of ash to form deposits and are determined for both reducing conditions (such as are present near the burners inside a boiler) and oxidizing conditions (such are present above OFA nozzles up until around furnace arch). 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*).

Temperature of flue gases leaving the combustion chamber should always be at least 50 K lower [3.1] than ash softening temperature, at which the ash softening process begins. In case when the temperature of flue gas is equal to or higher than ash softening temperature, the soft fly ash will stick to the heat exchange surfaces causing their fouling. In the first phase of combustion, characterized by the presence of reducing conditions and very high temperatures there is a risk of slagging. This phenomenon worsens the heat exchange between the combustion chamber and the heated agent which in turn causes larger heat load at other parts of boiler, not being subject to slagging in order to keep the steam parameters high enough, which in consequence may lead to overheating and rupture of pipes. In case of such damage boiler operation needs to be stopped and the pipes fixed which is not only very costly *per se* but also disables the ability to produce electricity.

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. Coal composition may be described not only but its chemical composition but also by its petrographic properties, namely content of macerals: vitrinite, inertinite and liptinite. In a laboratory analysis their content and reflexivity are usually determined. These properties of coal may have an impact on the slagging tendency. According to [3.10] a large share of inertinite in coal causes rise of elongated flames, which increases the probability of hot particles of blazing coal, coke or fly ash to reach the wall of combustion chamber. This phenomenon is especially visible in substochiometric conditions, so basically in every boiler that uses low emission burners.

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 [3.1]:

$$\boldsymbol{AFI} = \frac{\mathbf{4 \cdot DT + HT}}{\mathbf{5}} \tag{3.3}$$

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.

Characteristic temperatures are not the only factor that impacts slagging. Most of the indicators of susceptibility slagging are based on oxide analysis of fly ash. The chemical composition of ash gives a lot of information about it behaviour during combustion, however, the mass analysis of oxide composition 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.
According to [3.11] 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 [3.1]:

$$\boldsymbol{C_m} = \frac{\boldsymbol{Fe_2O_3 + CaO + MgO + Na_2O + K_2O + P_2O_5}}{\boldsymbol{SiO_2 + Al_2O_3 + TiO_2}} \tag{3.4}$$

In literature [3.12] one can often find its simplified version:

$$\boldsymbol{C'_m} = \frac{\boldsymbol{Fe_2O_3 + CaO + MgO}}{\boldsymbol{SiO_2 + Al_2O_3}} \tag{3.5}$$

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. Lowest temperatures of softening and melting are observed around C_m = 0,75. An increase of C_m parameter above 1 means that the ash contaminating the boiler furnace will have a strong tendency towards binding properties or in other words to the appearance of sintering phenomenon and an increase in its thermal conductivity λ_z. It can be defined as the ability of fly ash to sinter. Above C_m = 2 the influence of acid to basic oxides ratio in fly ash is not clearly visible anymore.

Sediment density directly affects its own thermal conductivity – and following that – its sinterability [3.1]. 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 [3.1]:

$$\boldsymbol{\lambda_z = 0,773 lg C_m + 0,673} \; [\frac{W}{mK}] \tag{3.6}$$

C_m is closely linked to another parameter:

R_s – the Babcock factor, defining the ability of coals to form slag within the first draft of the boiler, which takes into account the sulfur content in dry state S^d and defined by the equation [3.1]:

$$\boldsymbol{R_s = c_m S^d} \tag{3.7}$$

If:

- R_s < 0,6 – coal poses a low risk of slagging,
- R_s = 0,6–2,0– coal poses a mediocre risk of slagging,
- R_s = 2,0–2,6– coal poses a high risk of slagging,
- R_s > 2,6 – coal poses a very high risk of intense slagging.

A parameter that defines viscosity of formed slag is S_R.

S_R – % silica concentration – an indicator that defines tendency of coal towards slagging defined in a following equation [3.1]:

$$\boldsymbol{S_R = \frac{SiO_2}{SiO_2 + Fe_2O_3 + \mathrm{CaO} + MgO} \cdot 100} \tag{3.8}$$

If:

- S_R > 72 –coals shows little tendency towards slagging,
- 72 ≥ S_R > 65 – coal shows mediocre tendency towards slagging,
- S_R ≤ 65 – coal shows high tendency towards slagging.

Ability of coal ash to form ash deposits is defined by following F_u – defined by an equation [3.1]:

$$\boldsymbol{F_u = R_s \frac{Na_2O + K_2O}{S^d} = c_m(Na_2O + K_2O)} \tag{3.9}$$

If:

- F_u ≤ 0,6 – No tendency towards formation of deposits,
- 0,6 < F_u ≤ 40 – high tendency towards formation of deposits,
- F_u > 40 – very high tendency towards formation of deposits and risk of its sintering.

F_u can also be understood as an indicator of tendency towards formation of deposits that initiate slagging, even though it relates mainly towards fouling of the surface of superheaters, where a dominant mechanism of heat exchange is convection. Fouling of pipes in which steam of high temperatures is flowing (steam superheaters and regenerative superheaters) occurs under the influence of formation of liquid forms of silicates.

In case of low temperature fouling in the water economiser region, the deposits are formed under the influence of sulfur compounds in flue gases, which react with alkali components (Ca, Na, K) forming sulfates which act as adhesives, joining new fly ash particles upon impact. Except from sulfate formation, the alkali compounds may also form fusible, viscous eutectics with other elements i.e. with iron. An indicator of deposit formation that takes the influence of alkali compounds to create eutectics may therefore be sodium oxide content in ash.

(Na_2O) taking into account the ratio of calcium and magnesium oxides to iron oxides. For CaO + MgO < Fe_2O_3 [3.13]:

Na_2O < 0,5 – coal with a low tendency to form deposits,
Na_2O = 0,5–1,0 – coal with a mediocre tendency to form deposits,
Na_2O = 1,0–2,5 – coal with a high tendency to form deposits,
Na_2O > 2,5 – coal with a very high tendency to form deposits

Sodium content in fly as as Na_2O if CaO + MgO > Fe_2O_3 [3.13], gives following values:

Na_2O < 2,0 – coal with a low tendency to form deposits,
Na_2O = 2,0–6,0 – coal with a mediocre tendency to form deposits,
Na_2O = 6,0–8,0 – coal with a high tendency to form deposits,
Na_2O > 8,0 – coal with a very high tendency to form deposits

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 OP-650 boilers results of calculation of this parameter correlate particularly well with factual conditions within a boiler

$$\boldsymbol{A_K = (Na_2O + 0,9659K_2O)\frac{A^d}{100}} \tag{3.10}$$

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

The ratio of Fe_2O_3/CaO should also be noted – it has been found that fly ashes characterized by values of said parameter within the range of 0,3–3,0 contain eutectics that enhance slagging.

Presence of chlorides that can be simplified to chlorine content in coal Cl^r is also indicator of slagging tendency. [3.14]. If:

- Cl^r < 0,2 – coal with a low slagging tendency,
- Cl^r = 0,2–0,3 – coal with a mediocre slagging tendency
- Cl^r = 0,3–0,5 – coal with a very high slagging tendency
- Cl^r > 0,5 – coal with a very high risk of intense slagging.

The amount of fly ash turned into slag is very strongly associated with ash temperature [3.1]. Slagging will not happen below a certain initiating temperature t_{is} below which the boiler walls may be attacked only by loose impurities. In [3.13] the relation between the initiation temperature t_{is} [°C] and ash composition is presented based on statistical analysis:

$$\boldsymbol{t_{is} = 1218 + 8.22\frac{\sum K}{\sum A} - 273\ for\ \frac{\sum K}{\sum A} > 1.8} \tag{3.11}$$

$$\boldsymbol{t_{is} = 1188 + 60.15\frac{\sum A}{\sum K} - 273\ for\ \frac{\sum K}{\sum A} < 1.8} \tag{3.12}$$

where: $\Sigma K = SiO_2 + TiO_2 + Al_2O_3$, $\Sigma A = CaO + MgO + K_2O + Na_2O$

3.3.1 CCSEM Index(Computer Controlled Scanning Electron Microscopy)

CCSEM Index presents an alternative approach. It defines fouling tendency based on popular in american and british literature analysis using Computer Controlled Scanning Electron Microscopy. It can be used to foresee the tendency towards fouling for coals and fuel mixtures based on advanced fuel characteristics. Proposed by Gibbs index looks as follows [3.15]:

$$\boldsymbol{I_{ccsem} = \sum_{mineral\ substances}\left\{w_A\left[Ca + Fe_2O_3\left(1 - 0.5\frac{Fe_2O_3}{Fe_2O_3 + Al_2O_3 + SiO_2}\right)\right]\right\}} \tag{3.13}$$

If:

- I_{ccsem}> 30,6 fuels shows a very high tendency towards fouling,
- 15.3 ≥ I_{ccsem}> 30,6 fuel shows a mediocre tendency towards fouling,
- I_{ccsem}≤ 15,3 fuel shows a low tendency towards slagging

Laboratory tests conducted in a flow reactor for 27 coals from all over the world conducted within [3.16] show that CCSEM index is not a universal tool and in some cases could not appropriately foresee the tendency towards slagging. Statistically though it is better suited to classify coals than an indicator based on basic to acidic oxides ratio. The usage of CCSEM index is problematic to classify polish coals as it requires data about ratio of mineral to vitreous substances in fly ash. In order to achieve such data it is necessary to perform XRD (*X-Ray Diffraction*) analysis, which is currently not used during coal analysis in Poland. Another problem, which has been brought to attention by the author of the index himself, is that the perfect indicator describes fuel impact on a certain boiler. Even though the author suggests that even though coals with CCSEM index in range of 12–16 should not cause any problems with boiler exploitation, this range might and will change in accordance to the boiler the coal is combusted in.

3.3.2 Alternative approach

Numerous literature comparisons [3.17], [3.18] and experience with boiler operation show low (not higher than 50%) reliability of indicator evaluation towards actual foulness of heated surfaces. The indicators evaluate only the influence of fuel composition, it is however inseparable from other influences such as the specificity of combustion process within certain boiler. As suggested by Gibbs [3.15] the tendency to ash deposition is a function of its flux, its path through the combustion chamber and efficiency of adhesion which can be understood as adhesiveness of the substrate. Every aforementioned indicator, excluding A_K are influenced only by the chemical composition of the ash, not taking into account most aspects of ash deposition mechanism other than adhesiveness of fly ash. In order to be able to compare experimental results, such indicators should be enhanced by introduction of parameters relating to the amount of fly ash and the trajectory of flue gas flux within the boiler. One can safely assume that the main mechanism of mass deposition is inertial free-fall [3.19]. The deposition depends on the chance of a particle to hit the pipe instead of missing it. It is assumed that it is a function of Stokes number, which is defined as the ration between inertial forces to friction forces acting on a grain of fly ash moving within flue gases [3.19]. Another substantial parameter for inertial deposition is aforementioned adhesiveness of the substrate. The Stokes number depends on the second power of aerodynamical diameter of ash particle, it can be therefore associated with fouling. The diameter can be assessed by CCSEM analysis or by sieve analysis. As suggested in [3.15], consideration of the fly ash particles diameter alone is not enough to improve correlation of fouling indicators with reality. This results among others from the fact that this value is never constant. It depends on the configuration and work of coal mills, it can i.e. increase while the generator load is close to maximum, when the boiler and because of that coal mills have to work with throughput close to maximum. Multiplication of I_{CCSEM} index by the aerodynamic diameter alone causes visible improvement of fouling prognosis as compared to the index that does not take into account the diameter as checked in laboratory tests in [3.16], however there are no know conducted studies on regular scale power boilers. In order to achieve index usable in day-to-day power engineering it has to take into account factual amount of fly ash in the boiler, that can be expressed as ratio of ash content in coal to its lower heating value (the lower the LHV the more coal will be burned in order to sustain steam parameters resulting in more fly ash). An example of index taking those parameters into account looks as follows [3.16]:

$$\boldsymbol{I_{ccsem_dA}} = \left(\frac{\boldsymbol{A_p}}{\boldsymbol{100 * LHV}}\right) \cdot \boldsymbol{I_{ccsem}} \cdot \boldsymbol{d_{pa}} \tag{3.14}$$

where: A_p – Ash content in coal, LHV – Lower heating value, d_{pa} – aerodynamic diameter of grain

A similar approach has been undertaken towards other indicators in [3.15] and each time introduction $\left(\frac{A_p}{100 \cdot LHV}\right) \cdot d_{pa}$ factor drastically improved the correlation of the results with factual state of fouling. Calculation of corrected indexes for historically documented examples of boiler fouling (however often with omission of d_{pa}, as realistic measures of this parameter has not been available) suggests that indicators calculated this way would help to assess the fouling tendency in a more correct and reliable way and possibly prevent some failures and downtimes. Aforementioned multiplier still does not take into account the specifics of the boiler, resistance of pipe materials from corrosion and erosion, the mechanism of particle deposition, temperature and dynamics of combustion process.

Recommendation: Parameters that up to this date have been quite reliable for foreseeing the tendency towards fouling and slagging in case of this particular Power Plants' boilers are C_m and A_K. It should be assessed for already examined cases of fouling and slagging (i.e. as a part of currently ongoing coal tests) how the introduction of $\left(\frac{A_p}{100 \cdot LHV}\right) \cdot d_{pa}$ or $\left(\frac{A_p}{100 \cdot LHV}\right)$ factor will influence the correlation of indicators with factual deposit formations within the boiler.

3.4 Corrosion of pipes

Two main, most common mechanisms of corrosion occur in power boilers [3.20]:

- 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 [3.1],
- incineration of fuels with high content of chlorine and alkali elements – biomass, waste, coals with chlorine content Cl > 0,2% [3.21],
- raising of steam temperatures in order to increase the efficiency of power unit.

Corrosion rate and type generally depend on [3.1]:

- 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.

The mechanism of sulfate-sulphite corrosion has been more precisely described in [3.20]. Usually it begins with emergence of alkali metal sulfates on the surface of the pipe (K_2SO_4, Na_2SO_4). They can be sourced to volatile compounds emerging in the flame and molten slag. As a result of growth of sulfate layer, that acts as an insulator for the heated surface, the temperature raises to the value at which adhesion of ash particles takes place, which in turn undergo sintering finally turning into in molten slag. Said reactions take place with the participation of SO_3. Both the formation of iron sulfates as well as pyrosulfates is conditioned by the presence of sufficient amount of SO_3. With low partial pressure of oxygen and high temperatures, the concentration of SO_3 in flue gases is usually low (below 35 ppm) [3.1]. However the concentration of SO_3 in direct proximity to the deposits is associated with presence

of iron oxides, which have catalytic impact on oxidation of sulfur dioxide to the form of trioxide. Enrichment of SO_3 is also a result of melting of outside layer of ash deposit on the surface of pipe. This type of corrosion can also occur without the slagging phenomenon, because of presence of iron sulfides, in contrast to the case described before. Except from sulfur, other elements can also cause emergence of deposits that increase corrosion rate. It has been observed that, corrosion occurs faster near the deposits containing around 0,5–1% of lithium [3.1], which decreases the ash melting temperature. All the pollutants decreasing the ash melting temperature and stabilizing the liquid phase can lead to increased corrosion rate [3.1]. Aforementioned considerations attribute large corrosion rates to the presence of liquid phase on the surface of pipes, however it is not always the mechanism that leads to this type of corrosion. As has been noted in [3.20] aggressive gas environment may destroy the integrity of protective layer of the pipe and accelerate metal degradation. Probably it is the layer of FeS that increases the concentration of defects and stronger diffusion of cations present in the sulfide. This phenomenon occurs in reducing conditions and depends on concentration of H_2S without the need for presence of deposits in liquid phase. Reactions in gas phase are probably influenced by ash deposits leading to emergence of sulfides below the deposit. Unoxidised pyrite on the pipe causes sulphidisation, and the unburnt carbon is a buffer for oxidation, maintaining low oxygen concentration [3.1].

A different type of fireside corrosion of power boilers is high temperature chlorine corrosion manifesting itself be a dark layer of metal oxides, arranged in multiple layers and loosely attached to the pipe. Usually thickness of this layer is only around 0,1–0,3 mm [3.1]. If the layer would be removed, a thin layer of a brown, russet substance emerges in immediate contact with pipe material. Usually a layer of ash is thicker if this type of corrosion occurs on the superheater pipes, and thinner if it occurs on the evaporator. Chlorine corrosion is caused by the presence of gaseous chlorine in the combustion chamber. This mechanism is most prevalent in waste to energy plants and in boilers fired by fuels of high chlorine content such as straw biomass, however it is occurs at concentrations as low as Cl^r > 0,15% [3.1]. According to [3.22] the relation between Cl^r, and relative corrosion rate is as described in Table3.1:

Table 3.1. Relative corrosion rate as a function of Cl^r [3.22]

Cl^r, %	0	0,2	0,3	0,4	0,5	0,6
Relative corrosion rate, %	100	150	210	310	430	590

In reducing conditions it is possible that HCl and CO will in a way cooperate while attacking the protective layer [3.20]. 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) [3.22], [3.23] 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.

3.5 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 angle of attack between the flue gas stream and the surface washed by the stream $\phi_{e\ max}$ for which the risk of erosion is the highest ranges from around 40° for soft structural steels up to about 75° for hardened alloy steels [3.1]. The difference in erosion rate as a function of the angle of attack increases with increase of ash particles [3.24]. 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 [3.25] that the simplified form of c_m indicator mentioned before in chapter 3.3 has the biggest influence on erosive properties of fly ash e_e and can be described by an equation:

$$\boldsymbol{c_m}'' = \frac{\boldsymbol{Fe_2O_3}}{\boldsymbol{SiO_2+Al_2O_3}} \tag{3.15}$$

The results of research described in [3.25] have been developed by the method of regression as a following function:

$$\boldsymbol{e_e = 4,78(c_m'')^{-0,421}} \tag{3.16}$$

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

A conclusion can be drawn that the increase of silica and aluminum in fly ash leads to the increase of erodibility indicator. Of course it is not an only attempt to describe the intensity of erosion described in literature. In [3.26] a relation between the increase of erosion accordingly with increase of indicator also based on silica and aluminium oxides(SiO_2-$2Al_2O_3$). It takes into account the effect of highly erosive minerals based on silicon oxide (quartz, chalcedony) and much less erosive aluminosilicates (i.e. mullite or anorthite).

Another, indicator, that can be found in literature and perhaps in more quantitative form [3.27] is the erodibility index *EI* that can be defined with a following equation:

$$EI = \overline{(c_q H_q + c_p H_p) A^r v^n} \quad (3.17)$$

where: EI – Erodibility index c_q, c_p – mass fractions of respectively: quartz and pyrite within the size range of 5 to 50 µm, H_q, H_p – Vickers' hardness respectively for quartz (1350 kg/mm^2) and pyrite (1200 kg/mm^2), A^r – Ash content in working conditions, v – velocity of a particle m/s, n – exponent usually equal to 2.3 [3.27]

The problem with application of the *EI* index comes from the fact that the velocity of a particle is variable dependant on where in the boiler it is at the moment. Local constrictions (throats) and slag build up will interfere with the boilers aerodynamic properties, flue gas stream velocity and potential of erodibility at the same time. In order to be able to use this indicator it is necessary to know the quartz content (not only silicon oxides that are usually identified) and pyrite in fly ash, and most importantly the velocity of the particle both in longitudinal and transverse cross section of the boiler. The last, however not the least important problem is the inability to unambiguously determine the operating range of the boiler within which there might be problems with its exploitation. This indicator would probably work better as a basis for CFD model with consideration given to different mineral fractions within fly ash, which are however practically never analysed in Poland. It would be very problematic to use *EI* as the parameter for fuel selection.

Selection of coal with low ash content and high LHV 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. Modification of combustion process in order to decrease the emission of nitrogen oxides also covers air staging and decrease of maximum temperature within the boiler which also decreases the frequency of reaching ash softening and melting temperatures, therefore problems with fouling and slagging are far less frequent than before.

3.6 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 [3.28]:

- 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 [3.29]. 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* [3.19]. 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 [3.28]. With higher nitrogen content in volatile mater comes lower NO_x emissions which can be accounted to [3.28]:

- 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

In Figure 3.1 one can witness the dependence of NOx emerging in a test 70 kW boiler from the fuel ratio calculated for several fuels and oxygen concentration in the furnace. Based on works of Mereb [3.30].

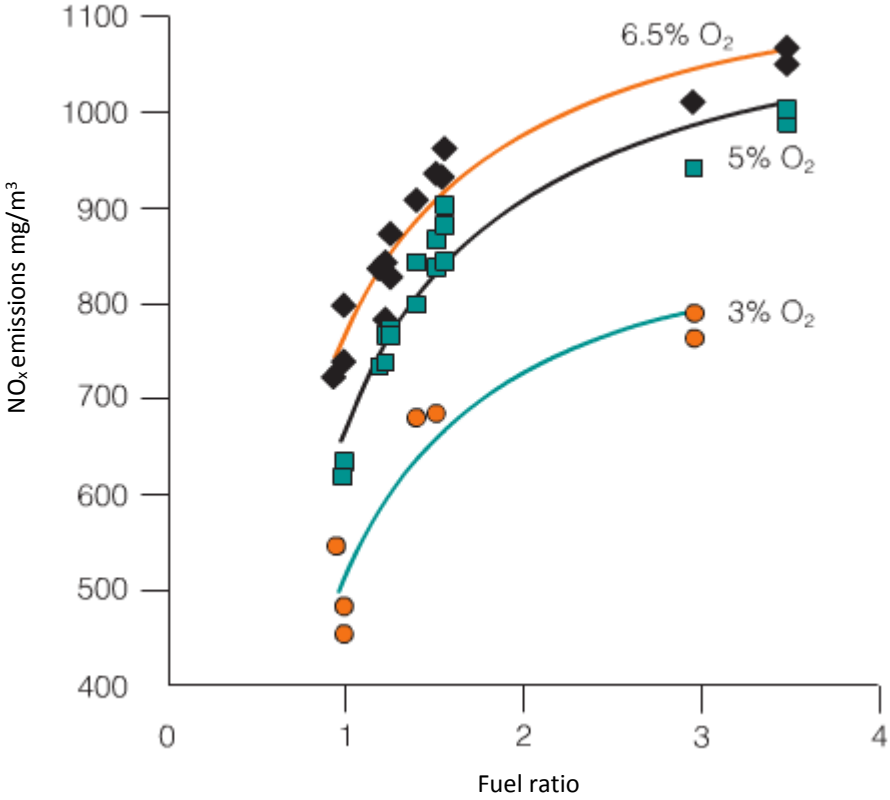

Figure 3.1 Relation between NOx emissions from fuel ratio. [3.30]

This relation is clearly visible in laboratory tests. However high temperature conditions and excessive and intensive heat transfer that prevail in boilers may and usually will change the amount of nitrogen that would react together with volatile matter from those in laboratory conditions. It is connected to actual speed of release of nitrogen during the combustion process [3.28] in industrial conditions. Fuel ratio will therefore provide information regarding the tendency to formation of certain amounts of nitrogen oxides, however in order to be able to connect solid numerical values with the amount of nitrogen oxides created, there should be research conducted with a particular type of industrial boiler. Similar tests have been

conducted by Nakata [3.31] in contrast to [3.30] fuel ratio has been divided by nitrogen content in the fuel. Results of his work are displayed on Figure 3.2. 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.

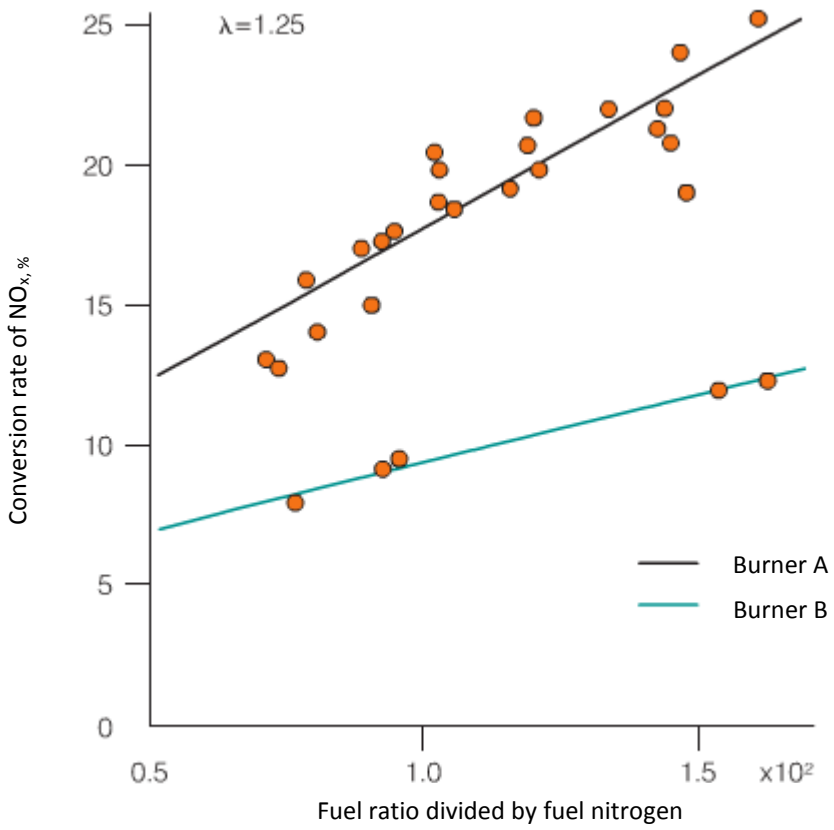

Figure 3.2 Relation between fuel quality and nitrogen conversion to NOx [3.31]

According to van der Kooij [3.29] 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 OP-650k in this particular Power Plant.

Recommendation: As a part of a large scale experiment during which only one type of fuel is used *fuel ratio* should be measured along with the amount of nitrogen oxides produced in boiler are measured (before SCR installation or in a boiler not equipped with secondary denitrification methods) along with several other parameters: nitrogen, carbon, hydrogen, oxygen and sulfur content, solid content, volatile matter in coal in dry state along with its humidity, temperatures and oxygen concentrations throughout the boiler (in the same places where NO_x concentrations are measured if possible).

3.6.1 Efficiency of SNCR

The technology of selective non-catalytic reduction of nitrogen oxides (SNCR) depends on introduction of a reagent to the combustion chamber which is usually ammonia or urea, which in appropriate

conditions reacts with nitrogen oxides present in flue gases. Power Plant discussed in this thesis uses urea as a solvent so the denitrification follows the following equation:

$$\boldsymbol{NH_2CONH_2 + 2\,NO + ½\,O_2 -> 2\,N_2 + CO_2 + 2\,H_2O} \tag{3.18}$$

Using SNCR it is possible to decrease the emission of NO_x by around 20–55%, although most commercially used installation achieve real reduction levels around 20–30% [3.28]. The most important factor conditioning the correct performance of SNCR installation is the temperature within the boiler as SNCR is a highly temperature sensitive process – the urea solution has to be injected at the right height and place to ensure the temperature with tolerance of more or less 50 K. Usual temperature ranges depend on the solution used and of installation specification, things like size of droplets can change the reaction speed. Usually right temperature for SNCR is within the window of 900–1100°C. If the temperature is too low it may result in so called “ammonia slip” when not all solvent reacts with nitrogen oxides and leaks further to the atmosphere. This is also dangerous as in case of high sulfur content in fuel, when unreacted urea may form ammonium sulfate in presence of sulfur trioxide with can settle on further flue gas ducts, impede gas flow and contribute to corrosion. In case the temperature is too high urea will undergo thermal oxidation contributing to even higher NOx emissions (mainly nitrous oxide that is extremely potent greenhouse gas). In order to prevent it AGAM systems (Acoustic Gas Temperature Measurement) are used to find a grid of temperature within the boiler, so the operator or an automated system knows which lance to inject urea with to ensure the most suitable temperature for denitrification. A correct operation of SNCR, and hence eventual ammonia slips depend on:

- combustion conditions (temperature, air excess, amount of combusted fuel)
- appropriate system of urea injection, its monitoring, variability of thermal load etc.

Fuel composition is therefore not a crucial factor.

Most available data and experience of boiler operators that use the SNCR installation along with Life Cycle Analysis (LCA) [3.33] lead to a single conclusion – the one and only benefit of SNCR is ability to meet the environmental requirements at low cost (only temporarily in light of enforcement of BAT conclusions). Other than that the SNCR usage does more harm than good. Additional humidity in the combustion chamber caused by using water as a carrier for the reagent decreases the efficiency of combustion process and causes problem with degradation of heated surfaces (i.e. increased ash deposition on economizer, corrosion of pipes induced by ammonium sulfate). Ammonia slip causes trouble during sewage treatment and dedusting in electrostatic precipitators and decreases quality and therefore market value of fly ashes, contributes to emission of nitrous oxide, so with SNCR in operation means higher emission of greenhouse gases as can be seen on Figure 3.3. [3.50]:

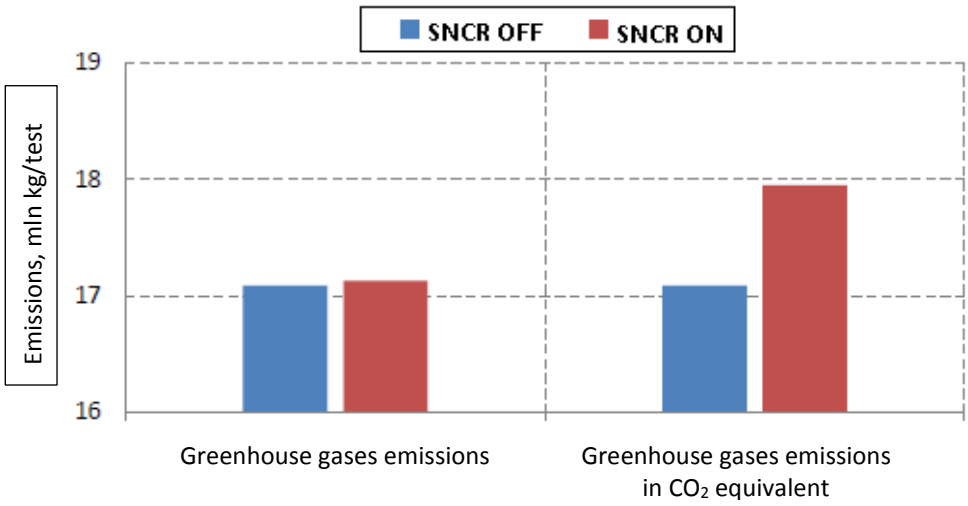

Figure 3.3 Emission of greenhouse gases during a chosen test period, direct and in calculated CO2 equivalent

Optimisation of SNCR by fuel selection is inexpedient – maintenance of conditions within the combustion chamber is much more crucial. Optimisation of SNCR operation is done by i.e. maintaining stability of flame so it is easier to determine height of desired temperature range. It is easier if one type of coal is combusted at the time – unlike currently, when fuels are almost always constantly blended.

3.6.2 Efficiency of SCR

Selective catalytic reduction of nitrogen oxides (SCR) depends on the injection of the reagent to the flue gas duct right before an installed catalyst aimed to reduce the nitrogen oxides. The usage of the catalyst allows to decrease the temperature required to initiate the reaction between flue gas components and the reducing agent. The efficiency of the process achieves efficiencies as high as 90%, though usually most installations reach about 65–80% of reduction. Compared to SNCR, SCR offers a range of advantages:

- higher level of NO_x reduction,
- no limits regarding installation size (usually the higher the power of a power plant, the lower the cost of using SCR),
- lower ammonia slip,
- no influence on quality parameters of fly ash.

On the downside, SCR is definitely more expensive regarding both capital and operational costs, as it requires periodical replacement or regeneration of catalysts. Usage of SCR technology also requires careful monitoring of sulfur content within the fuel as well as the composition of mineral substance within the fuel. Due to required optimal temperature for catalytic reduction of nitrogen oxides (300–400°C) the catalysts usually are placed past the boiler, before the flue gases enter to electrostatic precipitators – because of that flue gas, even though sufficiently hot, contain a lot of fly ash which may cause problems with deactivation of catalyst. Such a placement, used in this particular case is called a High Dust (HD) position. 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 [3.34]:
    - 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 – contribute to ammonias 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 dedicated chapter.

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 [3.34]. 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 [3.34]. The components which catalyse the conversion of SO_2 to SO_3 are i.e. vanadium oxide (V) 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 [3.35] 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. It is likely that the aluminum content in fly ash has little to no influence for this process. In [3.35] aluminum content in fresh and deactivated catalyst have been compared and a subtle difference has been noted, which suggests that the sulfur trioxide reacted with aluminum from the surface of the catalyst itself.

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. Aforementioned compounds react with sulfur oxides, chlorine or carbon dioxide producing sulfates, carbonates and chlorides that have a tendency to form depositions and plugging of catalysts [3.36]. 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 [3.36] it has been noted that activity of catalyst is disrupted by the same factors that cause fly ash deposition. Cichanowicz and Muzio in their work [3.37] based on the German and Japanese experiences noted the influence of Na and K on the decrease of catalyst activity, visible in range of 8–15% of total alkali content (K + Na + Ca + Mg) in fly ash. In the work of Licat [3.38] the connection of alkaline-earth elements has been indicated, such as calcium, which contribute to formation of sulfates plugging the catalyst pores and prevent contact of NH_3 with the active centres. Plugging of catalyst has been observed with calcium content in ash around 3-5% [3.38].

3.7 Efficiency of ESP (operation of electrostatic precipitators)

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.

Calcium, potassium and sodium salts dissociate under the influence of moisture strongly decreasing resistivity of fly ash [3.40]. Ashes characterised by high content of silicon and aluminium (> 90%), low content of sodium oxides (< 5%) may result in lower dedusting efficiency [3.41]. 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 [3.42] that size distribution of ash particles is directly connected with size distribution of pulverized coal, therefore dependant on the operation of coal mills. In the attachment to this work one can find the calculation

sheet for determination of resistivity of fly ash based on the fuel oxide composition, moisture and SO_3 concentration in flue gas. The model used should find use for coals of quality suitable for incineration in an exemplary Power Plant and has been developed based on [3.43].

3.8 Wet Flue Gas 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. Proposal of implementation of new parameters seems inexpedient; sufficient control over operation of other installation and processes within the power plant is much more crucial than choice of new parameters to aim for desulfurisation optimisation.

3.9 Quality of combustion side products – fly ash and gypsum

Most important side products of combustion (referred to as UPS short from polish *Uboczny Produkt Spalania*) produced in a power plant are gypsum, slag, furnace ashes, fly ashes and waste from water and sewage treatment such as slime and sediments. According to Research and Development experts surveyed during an internship 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. Fly ash is a mineral substance with puzzolanic properties, which is formed as a result of combustion of pulverized coal and leaves the furnace with flue gases. It has a form of fine, mineral dust with colour raging from light to dark grey or light brown and is composed mostly of silica, aluminum and iron oxides. Ashes from coal fired power plants may be used for [3.44]:

- 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.

The requirements for fly ash quality used for production of mixtures have been juxtaposed in Table 3.2. [3.45]:

Table 3.1 Quality requirements for fly ash from coal to produce concrete mixtures according to the norm PN-EN 206:2014 [3.45]

Property	Desired value
Losses on Ignition (LOI)	≤5% (cat. A) ≤7%(cat. B) ≤9% (cat. C)
Chlorides Cl^-	max. 0.1%
Sulfur oxides (VI) SO_3	max. 3.0%
Calcium oxide CaO – free	≤ 1,5% (if this value is exceeded, the ash might be accepted under condition of constant volume preservation)
Calcium oxide CaO – active	≤ 10%
Fineness	Category N ≤ 40%
	Category S ≤ 12%
Puzzolanic activity indicator after 28 days	≥ 75%
Puzzolanic activity indicator after 90 days	≥ 85%
Bulk density	Maximum difference of ± 200 kg/m^3 as compared to values declared by the producer
Beginning of settling time of grout containing 25% of fly ash and 75% of portland cement CEM I	Should not be twice longer than the beginning of settling time of grout made of 100% comparative cement (CEM I)
Volumetric constancy due to Le Chatelier (researched only if free CaO ≥ 1,5%)	max. 10 mm
Water demand (only for cat. S)	≤ 95% of water demand for comparative cement (CEM I)

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). Fineness of fly ash is measured as the remaining faction on the sieve with side mesh 0,045 mm. Losses of ignition of fly ash is mostly unburned carbon in the form of coke.

The main factor influencing quality of fly ash and amount of unburnt carbon is the composition and quality of fuel [3.46]. It is however not the only factor, in report [3.47] 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.

Even though range of parameters change starting from shape and size of particles to increase in porosity and fragility, by far the most impactful is the increase in degree of coalification measured in LOI. It is

that parameter that directly impacts puzzolanic properties of fly ash and therefore its most important property for any business – if it can be sold with profit. To some extent the increase in fineness can be associated with lower combustion temperature; and associated with that lower amount of melt quartz and its higher concentration in ash. This impact can be however mitigated by skilful adjustment of coal mills and boiler operation (by adjusting coal stream flow and air staging). In case if SNCR or SCR is used, parameter worth monitoring is ammonia concentration in ash. Its impact on production of concrete has been researched by van der Kooij and described in more detail in [3.29] and [3.48]. There is a risk that ammonium compounds in the form of ammonium salts or ammonia particles physically adsorbed on the surface of TOC in contact with water will be released into air which poses a threat to health of people nearby the process of concrete production.

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. The most important parameters from the point of view of sales of gypsum produced in a power plant are presented in Table 3.3 [3.49]:

Table 3.2 Quality requirements for gypsum produced in wet FGD installations according to the Eurogypsum norm [3.49]

Parameter	Expressed as:	Required range:	Unit
Moisture content [1)]	H_2O	< 10	% weight
Calcium sulfate (VI) dihydrate	CaSO4 ·2H2O	> 95	% weight
Magnesium salts (soluble)	MgO	< 0,10 < 0,02*	% weight
Sodium salts (soluble)	Na_2O	< 0,06 < 0,02**	% weight
Potassium salts (soluble)	K_2O	< 0,02**	% weight
Chlorides	Cl	< 0,01	% weight
Calcium sulfate (IV) hemihydrate	CaSO3 ·1/2H2O	< 0,25	% weight
$CaCO_3$ + $MgCO_3$ content	$CaCO_3$ + $MgCO_3$	< 1,2***	% weight
pH	–	5–9	–
Colour[(2)]	Ry	> 50	%
Smell		neutral	

[1]) moisture content expressed as a weight percentage of raw gypsum.

All other parameters values are expressed for calcium sulfate dihydrate after drying in 450°C.

[2)] Colour measurement by differential colorimeter calibrated with $BaSO_4$ as ideal whiteness.

** additional requirement applicable for gypsum usage to manufacture products especially susceptible to „blooming" and to produce plasterboards according to EN 12859*

*** additional requirement applicable for gypsum usage to manufacture products especially susceptible to „blooming" and discoloration*

**** additional requirement applicable for gypsum used to produce binders*

3.10 Summary of literature research

In Table 3.3 below coal parameters new or unused before at the stage of fuel selection have been juxtaposed. If the range applicable for boilers in this exemplary Power Plant exists and is known it has been noted in an appropriate column, if not, it is necessary to compare experimental results from boiler operation using fuel of known properties with calculated values in order to find border values.

Table 3.3 Summary of coal quality indices

Parameter	Influences	What it says	Range (if applicable)	Comments
R_s	Slagging	Tendency towards slagging in the combustion chamber	R_s < 0,6 – low tendency R_s = 0,6 ÷ 2,0 – mediocre tendency R_s = 2,0 ÷ 2,6 – high tendency R_s > 2,6 – very high tendency	
S_r	Slagging	Slag viscosity/sticking	S_R > 72 – low tendency 72 ≥ S_R > 65 – mediocre tendency S_R ≤ 65 – high tendency	
F_u	Fouling	Tendency towards deposit formation	F_u ≤ 0,6 – no tendency 0,6 < F_u ≤ 40 – high tendency F_u > 40 – very high tendency	
AFI	Slagging	Tendency towards slagging	1232 < AFI < 1342°C – low tendency 1052 < AFI < 1232°C – high tendency AFI < 1052°C – very high tendency	
T_{is}	Slagging	Initiating temperature	Has to be referenced to temperatures inside the boiler	
S+Fe	Slagging	Tendency towards slagging	S < 1,5% + Fe < 7%	
Fe_2O_3/CaO	Slagging	Tendency to form eutectics that enhance slagging	< 0,3 or > 3,0	
C_m	Fouling	Tendency towards fouling	< 0,4 or > 0,7	Base to acid oxide ratio
λ_z	Sintering	Tendency towards sintering	> 1 – tendency towards sintering < 1 – tendency towards loose deposits formation	Heat condictivity of the sediment
Na_2O	Fouling	Tendency to form deposits	For CaO + MgO < Fe_2O_3: Na_2O < 0,5 – low tendency Na_2O = 0,5–1,0 – mediocre tendency Na_2O = 1,0–2,5 – high tendency Na_2O > 2,5 – very strong tendency Dla CaO + MgO > Fe_2O_3: Na_2O < 2,0 – low tendency Na_2O = 2,0–6,0 – mediocre tendency Na_2O = 6,0–8,0 – high tendency Na_2O > 8,0 – very high tendency	
A_k	Fouling	Tendency to form ash formations	A_K < 0,3 – low tendency 0,3 < A_K < 0,45 – mediocre tendency 0,45 < A_K < 0,6 – high tendency A_K > 0,6 – very high tendency	
I_{ccsem}	Fouling	Tendency towards fouling	I_{ccsem}> 30,6 – high tendency 15,3 ≥ I_{ccsem}> 30,6 – mediocre tendency I_{ccsem}≤ 15,3 – low tendency	

Parameter	Influences	What it says	Range (if applicable)	Comments
Cl	Corrosion, Slagging	Risk of chlorine induced corrosion	Cl^r < 0,2 – low tendency towards slagging Cl^r = 0,2–0,3 – mediocre tendency towards slagging Cl^r = 0,3–0,5 – high tendency towards slagging Cl^r > 0,5 – very intesive slagging	No range for corrosion, but similar may be assumed
S/Cl	Corrosion	Tendency to induce corrosion	< 2	
e_e	Erosion	Erosive properties of fly ash	-----	
EI	Erosion	Intensityof erosion	------	
Ca	SCR poisoning	Threat of poisoning	< 3% mass	
CaO + MgO + Na_2O + K_2O	SCR poisoning	Threat of poisoning	< 8% mass	
Ash resistivity	Dust removal	Correct ESP operation	10^9–10^{11} Ω·cm	Check the excel sheet
Fuel Ratio Nakata's Indicator	NO_x formation	Nitrogen conversion ratio	Has to be assessed for a particular boiler	

Chapter 4

Evaluation of NO_X formation indicator

This experimental chapter evaluates NO_x formation indicator described in Chapter 3.6 using real life data from a boiler installed at a Power Plant described in Chapter 1. During six days of an experiment that boiler was fuelled by coal from a known source and known composition so it was possible to assess whether the indicator derived in laboratory conditions could be used to predict emissions from a real, large scale boiler .This chapter also includes an attempt at adjusting the equation constants.

4. Evaluation of NO_x formation indicator

During six days of an experiment a boiler has been fed with only one type of coal with known parameters both from safety data sheet and some checked every day on samples from the boiler feed.

Parameters of researched coal are as follows for following dates:

Table 4.1 Properties of fuel supplied to the boiler during the period of the experiment

Data	Q^r_i [kJ/kg]	W^r_t [%mas]	A^r [%mas]	V^{daf} [%mas]	S^r [%mas]	FC [%mas]	FR [-]
14.03	19 996	8,6	27,4	38,08	0,55	25,92	0,68067
15.03	19 278	8,7	29,3	39,21	0,57	22,79	0,58123
16.03	18 638	8,7	30,7	39,77	0,53	20,83	0,52376
21.03	20 294	8,2	26,8	39,64	0,56	25,36	0,63976
22.03	18 596	8,5	31,3	39,91	0,55	20,29	0,50839
23.03	18 373	9,8	30,3	39,63	0,54	20,27	0,51148

N^a – Nitrogen Content (air-dried basis) = 1,06%

$$\boldsymbol{CR = a_1 x + a_2} \tag{5.1}$$

CR: NO_x conversion ratio (%)

a_1, a_2 : Constants equal to a_1=10,94 and a_2=6,77 [3.31] for wall-mounted burners.

Please note that aforementioned coefficients are a result of a laboratory scale experiment, and are supposed to work for laboratory scale boiler. This chapter aims for discovery of new constant coefficient values fitted for OP-650k boilers.

$$\boldsymbol{x = \frac{FR}{N^a}} \tag{5.2}$$

FR: fuel ratio (= fixed carbon/volatile matter wt%/wt%)

Relationship between the NO_x conversion rate and concentration is pictured in following formula:

$$NO_x = CR \cdot \left(\frac{2.24141 \cdot 10^{-2} \cdot \frac{N^{a} \cdot 10^{-2}}{14.0067 \cdot 10^{-3}}}{V_{dry}} * 10^{6} \right) \cdot 10^{-2} \quad (5.3)$$

NO_x: NOx concentration (PPM)

V_{dry}: Volume of flue gas (Nm^3/kg)

$2.24141 \cdot 10^{-2}$: Perfect gas volume (Nm^3/mol)

14.00674: Nitrogen atomic weight (g/mol)

By combination of above equations concentration of NO_x is obtained in the form of following equation:

$$NO_x = \frac{160.0}{V_{dry}} \cdot (a_1 \cdot FR + a_2 \cdot FN) \quad (5.4)$$

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 NOx measurements. Following periods have been selected for evaluation:

On 14.03.17 from 02:00 to 03:00 the boiler has been working with constant power and coal feed for around 5 hours and with no urea injection for more than 10 hours.

Table 4.2 Average process parameters important for NOx formation during stable period 1

Parameter	Value	Unit
Total coal fed to the boiler	62.428	t/h
Generator active power	135.254	MW
Air excess coefficient λ at final stage of combustion	1.430	—
Primary air feed	176.366	kNm^3/h
Total air feed	579.303	kNm^3/h
Average NO_x concentration	310.230	mg/Nm^3
Average oxygen content	6.903	%
Wet flue gas stream	536359	m^3/h

On 14.03.17 from 18:15 to 19:00 the boiler has been working with constant power and coal feed only for this period and has remained without urea injection for over 2 hours.

Table 4.3 Average process parameters important for NOx formation during stable period 2

Parameter	Value	Unit
Total coal fed to the boiler	84.337	t/h
Generator active power	175.328	MW
Air excess coefficient λ at final stage of combustion	1.385	—

Primary air feed	205.025	kNm^3/h
Total air feed	715.028	kNm^3/h
Average NO_x concentration	264.022	mg/Nm^3
Average oxygen content	6.396	%
Wet flue gas stream	674590	m^3/h

On 15.03.17 from 04:00 to 05:00 the boiler has been working with constant power and coal feed for over 6 hours and with no urea injection for over 12 hours

Table 4.4 Average process parameters important for NOx formation during stable period 3

Parameter	Value	Unit
Total coal fed to the boiler	63.075	t/h
Generator active power	135.235	MW
Air excess coefficient λ at final stage of combustion	1.420	—
Primary air feed	162.123	kNm^3/h
Total air feed	571.842	kNm^3/h
Average NO_x concentration	278.306	mg/Nm^3
Average oxygen content	6.790	%
Wet flue gas stream	531387	m^3/h

On 16.03.17 from 08:00 to 09:00 the boiler has been working with constant power and coal feed for 13 hours and without urea injection for around 17 hours

Table 4.5 Average process parameters important for NOx formation during stable period 4

Parameter	Value	Unit
Total coal fed to the boiler	60.093	t/h
Generator active power	135.428	MW
Air excess coefficient λ at final stage of combustion	1.463	—
Primary air feed	157.763	kNm^3/h
Total air feed	582.389	kNm^3/h
Average NO_x concentration	269.000	mg/Nm^3
Average oxygen content	7.187	%
Wet flue gas stream	547143	km^3/h

On 21.03.17 from 17:50 to 18:50 the boiler has been working with constant power and coal feed for around 30 minutes and without urea injection for around 2 hours and 30 minutes

Table 4.6 Average process parameters important for NOx formation during stable period 5

Parameter	Value	Unit
Total coal fed to the boiler	102.661	t/h
Generator active power	215.569	MW
Air excess coefficient λ at final stage of combustion	1.279	—
Primary air feed	235.891	kNm^3/h
Total air feed	835.828	kNm^3/h
Average NO_x concentration	273.863	mg/Nm^3
Average oxygen content	5.097	%
Wet flue gas stream	774452	m^3/h

On 22.03.17 from 04:00 to 05:00 the boiler has been working with content power and coal feed for around 4 hours and without urea injection for around 13 hours

Table 4.7 Average process parameters important for NOx formation during stable period 6

Parameter	Value	Unit
Total coal fed to the boiler	69.094	t/h
Generator active power	135.310	MW
Air excess coefficient λ at final stage of combustion	1.347	—
Primary air feed	148.442	kNm^3/h
Total air feed	548.900	kNm^3/h
Average NO_x concentration	244.796	mg/Nm^3
Average oxygen content	5.880	%
Wet flue gas stream	518611	m^3/h

On 22.03.17 from 12:15 to 13:15 the boiler has been working with constant power and coal feed for around 2 hours and no urea injections for around 2 hours and 30 minutes

Table 4.8 Average process parameters important for NOx formation during stable period 7

Parameter	Value	Unit
Total coal fed to the boiler	99.021	t/h
Generator active power	215.608	MW
Air excess coefficient λ at final stage of combustion	1.270	—
Primary air feed	231.548	kNm^3/h
Total air feed	810.818	kNm^3/h
Average NO_x concentration	265.415	mg/Nm^3
Average oxygen content	4.885	%
Wet flue gas stream	744371	m^3/h

On 22.03.17 from 14:45 to 15:45 the boiler has been working with constant power and coal feed factor only for the following period and without urea injection for 4 hours

Table 4.9 Average process parameters important for NOx formation during stable period 8

Parameter	Value	Unit
Total coal fed to the boiler	81.608	t/h
Generator active power	175.236	MW
Air excess coefficient λ at final stage of combustion	1.321	—
Primary air feed	206.708	kNm^3/h
Total air feed	688.252	kNm^3/h
Average NO_x concentration	268.721	mg/Nm^3
Average oxygen content	5.619	%
Wet flue gas stream	652233	m^3/h

On 23.03.17 from 06:00 to 07:00 the boiler has been working with constant power and coal feed for around 8 hours 30 minutes and with no urea injection for around 20 hours

Table 4.10 Average process parameters important for NOx formation during stable period 9

Parameter	Value	Unit
Total coal fed to the boiler	61.222	t/h
Generator active power	135.408	MW
Air excess coefficient λ at final stage of combustion	1.399	—
Primary air feed	154.878	kNm^3/h
Total air feed	564.482	kNm^3/h
Average NO_x concentration	266.772	mg/Nm^3
Average oxygen content	6.533	%
Wet flue gas stream	533393	m^3/h

On 23.03.17 from 19:45 to 20:45 the boiler has been working with constant power and coal feed for an hour and without urea injection for 5 hours

Table 4.11 Average process parameters important for NOx formation during stable period 10

Parameter	Value	Unit
Total coal fed to the boiler	102.295	t/h
Generator active power	215.587	MW
Air excess coefficient λ at final stage of combustion	1.272	—
Primary air feed	233.442	kNm^3/h

Total air feed	819.895	kNm^3/h
Average NO_x concentration	280.503	mg/Nm^3
Average oxygen content	4.923	%
Wet flue gas stream	760705	m^3/h

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 [3.31]. 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 weather archive for the town in southern Poland where this Power Plant is located [5.1][5.2]. 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} 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}. The results of aforementioned calculations are available in table 5.12 below. For each case they are also represented on graphs – for cases 1, 2, 3 and 4 respectively on pictures 5.1, 5.2, 5.3 and 5.4. 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.

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 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 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.

Table 4.12 Juxtaposition of NOx concentration levels measured on site and calculated in 4 different cases

Period	NOx measured by a sensor [mg/Nm^3]	NOx calculated in case 1 [mg/m^3]	Error in case 1 [%]	NOx calculated in case 2 [mg/m^3]	Error in case 2 [%]	NOx calculated in case 3 [mg/m^3]	Error in case 3	NOx calculated in case 4[mg/m^3]	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%

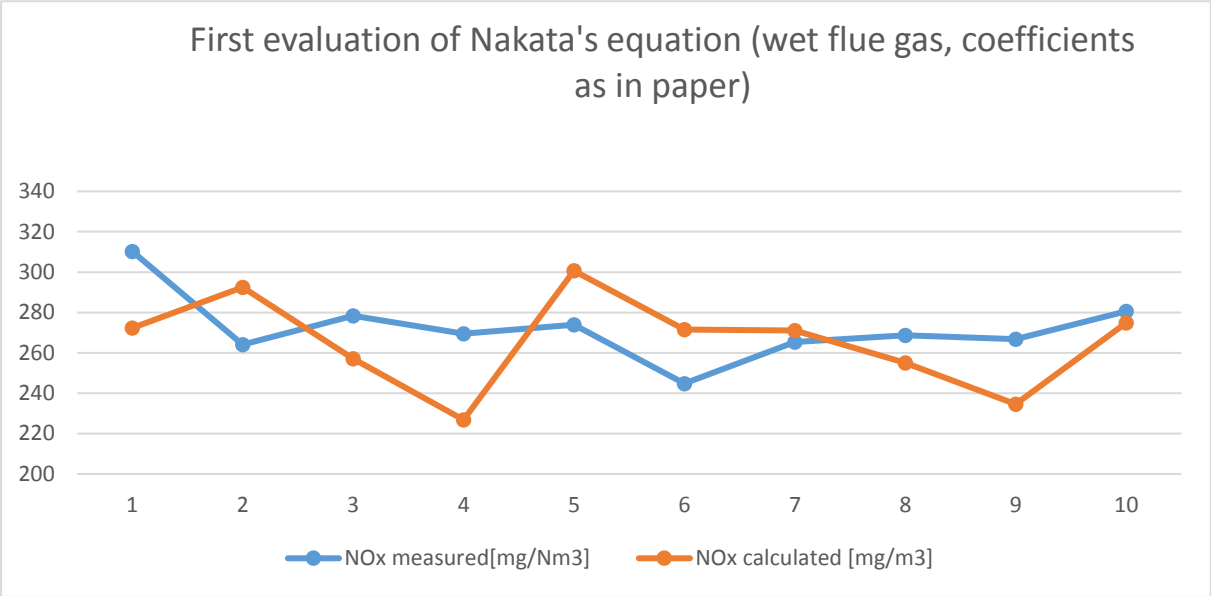

Figure 4.1 NOx calculated in comparison to measured in case 1

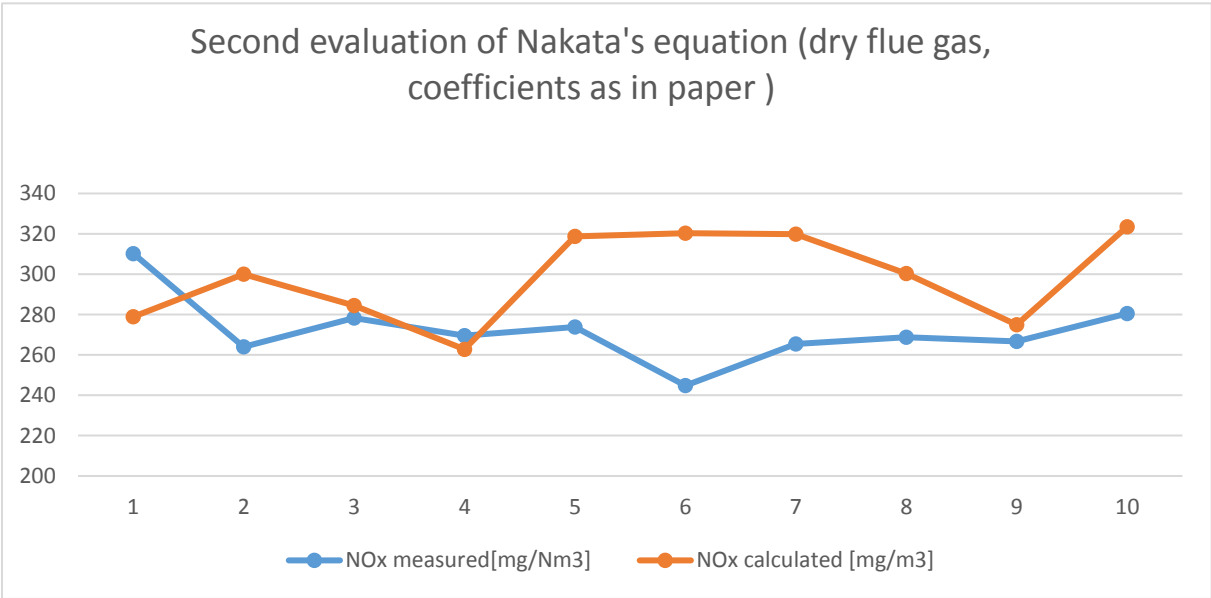

Figure 4.2 NOx calculated in comparison to measured in case 2

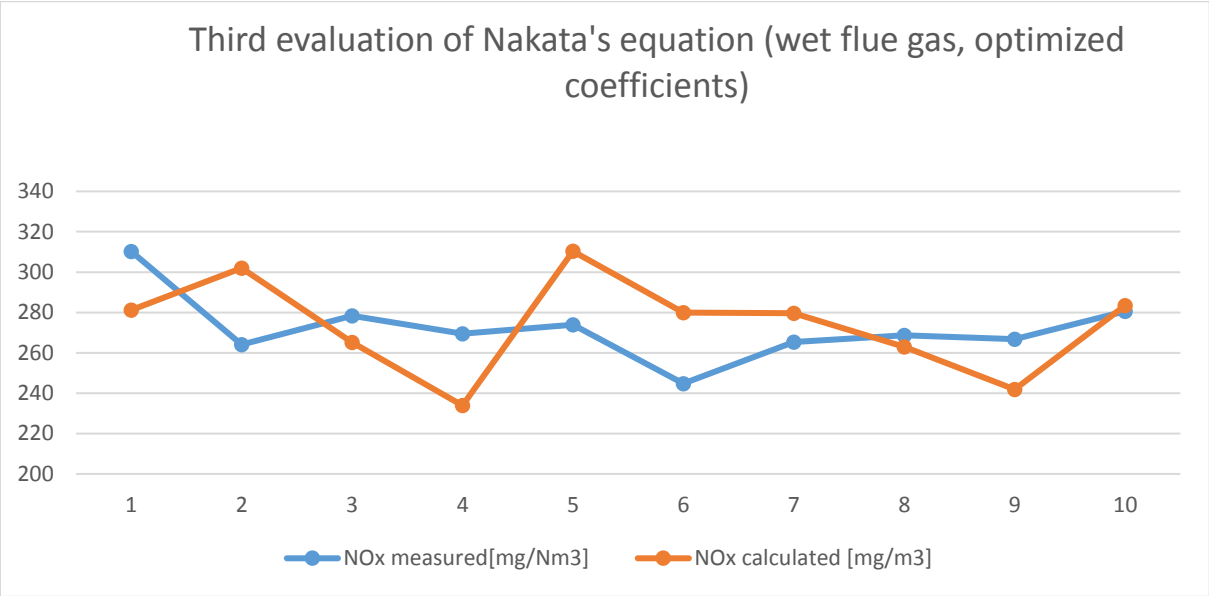

Figure 4.3 NOx calculated in comparison to measured in case 3

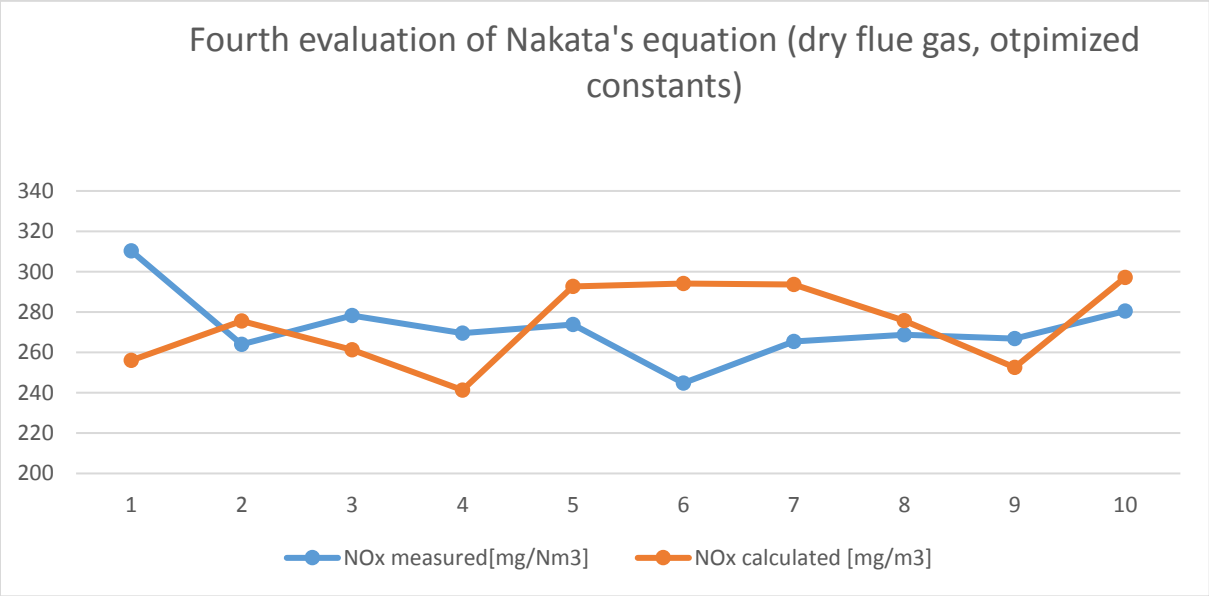

Figure 4.4 NOx calculated in comparison to measured in case 4

5. 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.

As time passes it can be expected that emission standards will be even tighter and soon every thermal power plant will have to use SCR as the most efficient denitrification method. Focus will turn to other previously not researched pollutants such as HF and HCl which in certain cases might not be removed by WFGD in a sufficient amount. Composition of flue gas is a crucial parameter that influences every process of flue gas treatment, side products production and might cause corrosion damage to boiler and flue gas ducts. Besides fuel composition, it strikingly often can be seen as correct performance of one system influences all the others within a power plant. A topic that would require more research is the behaviour or sulfur trioxides within the power plant. In recent years it has been noted that concentration of SO_3 is not related to sulfur content in coal, as low sulfur coals still may have caused sulfur induced corrosion. It is known that certain metal oxides such as iron or vanadium catalyse oxidation of SO_2 to SO_3 but there has been no successful examples of prediction or modelling of SO_3 concentration within the boiler. With SCR installations that also catalyse SO_2 oxidation becoming a staple in most thermal power plants, finding new ways to mitigate this process would be beneficial.

[1.1] Internal documents *Instrukcja Eksploatacji Elektrofiltrów,* 2014r.

[1.2] Internal documents *Specyfikacja Techniczna dla IMOS*, 2013r.

[1.3] https://www.mos.gov.pl/srodowisko/pozwolenia-zintegrowane/

[1.4] BREF Document for Large Combustion Plants 06.2016, Final Draft.

[2.1] Commission Implementing Decision (EU) 2017/1442 of 31 July 2017 establishing best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council, for large combustion plants (notified under document C(2017) 5225) (Text with EEA relevance.) C/2017/5225 page 20.

[3.1] Pronobis M.: *Modernizacja Kotłów Energetycznych*, Wydawnictwo Naukowo-Techniczne, 2002.

[3.2] Szponder D.K.: *Badania wybranych właściwości popiołów lotnych z zastosowaniem analizy obrazu*, Rozprawa doktorska AGH WGiG, 2012.

[3.3] Odgaard P. F., Mataji B. *Estimation of moisture content in coal in coal mills.* http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.214.2388&rep=rep1&type=pdf

[3.4] Tora B., Fecko P., Nowak A., Tajchman Z.: *Badanie zależności podatności na mielenie od wybranych parametrów węgla kamiennego.* Górnictwo i Geoinżynieria, Zeszyt 4/1, 2010.

[3.5] Krupa M.; *Optymalna jakość przemiału węgla dla kotłów pyłowych.* II Konferencja Naukowo-Techniczna „Budowa i eksploatacja młynów do przemiału węgla" Centrum Postępu Technicznego SIMP, Rydzyna 1988.

[3.6] Róg L.: *Wpływ czynników wynikających z jakości paliwa na proces spalania w kotłach energetycznych*, Główny Instytut Górnictwa, 2011.

[3.7] Smoliński A., Howaniec N., Stańczyk K.: *Metody badania reaktywności węgla w procesach spalania i zgazowania*, Prace Naukowe GIG Górnictwo i Środowisko, 4/2006.

[3.8] Pawlik M., Strzelczyk F.: *Elektrownie*, WNT – Warszawa, wyd. piąte zmienione, 2009.

[3.9] Internal documents. *Program szkoleń technicznych – Kocioł OP-650,* 2015r.

[3.10] Aumüller A., Bobik M., Cox W.: *On-Line Korrosionsmessung an Verdampferrohren während luftsteiger Primärmaßnahmenfahrweise zur NO_x-Reduktion bei einer steinkohlengefeuerten Großanlage unter Berücksich tigung des Einsatzes Von Importkohlen. 9. VGB-Konferenz "Forschung in der Kraftwerkstechnik 1995"*. D 4, 6-7.09.1995, Essen.

[3.11] Żelkowski J.: *Kohleverbrennung. Brenstoff, Physik und Theorie, Technik*. VGB-B008. Essen, VGB Kraftwerkstechnik, 1986.

[3.12] Ots A., Żelkowski J. *Abschätzung der Kohleneigung zur Verschlackung und Verschmutzung auf Grund von Kohledaten und erweiterter Laboruntersuchungen*. Dresden: XXXII Kraftwerkstechnisches Kolloquium; 2000.

[3.13] Alehnovich A.: *Forecasting of slagging basing on chemical composition of fly ash particles* (Prognozirovanie schlakovania po chemiceskomu sostavu casticek letucej zoly). Teploenergetika 1995/8 [in russian].

[3.14] Bryers W. R.: *Fireside slagging impurities in steam-rising fuels*. Progress in Energy and Combustion Science 1996, Vol. 22.

[3.15] Gibb W.H.: *The UK collaborative research programme on slagging pulverized coal-fired boilers: summary of findings*, in: L. Baxter, R. DeSollar (Eds.), *Applications of Advanced Technology to Ash-Related Problems in Boiler*. Proceedings of the Engineering Foundation Conference. Waterville Valley, New Hampshire., July, 1621, 1995, pp. 41–65.

[3.16] Barroso J., Ballester J., Pina A.: *Study of coal ash deposition in an entrained flow reactor: Assessment of traditional and alternative slagging indices,* Fluid Mechanics Group/LITEC, University of Zaragoza, María de Luna 3, Zaragoza-50018, Spain Fuel Processing Technology 88 (2007), pp. 865–876.

[3.17] Barrett R.E.: *Designing boilers to avoid slagging and fouling.* Power 1990, No2.

[3.18] Bryers R.W.: *Fireside slagging, fouling, and high-temperature corrosion of heat-transfer surface due to impurities in steam-rising fuels*. Progress in Energy and Combustion Science 1996, Vol. 22.

[3.19] Wacławiak K.: *Obliczenia numeryczne procesu tworzenia osadów na rurach przegrzewaczy kotłowych*, Wydawnictwo Politechniki Śląskiej, Gliwice 2012

[3.20] Harb J. N., Smith E.E.: *Fireside corrosion in PC-fired boilers*. Progress in Energy and Combustion Science 1990, Vol.16, pp. 169-188.

[3.21] *Korozja wysokotemperaturowa w kotłach pyłowych.* Zakład Spalania i Detonacji, Politechnika Wrocławska, http://www.spalanie.pwr.edu.pl/badania/korozja/korozja.htm.

[3.22] Nielsen H.P., Frandsen F.J., Dam-Johansen K., Baxter L.L.: *The implications of chlorine-associated corrosion on the operation of biomass-fired boilers*. Progress in Energy and Combustion Science 2000, Vol. 26.

[3.23] Frandsen F.J. et al..: *Deposition and corrosion in straw- and coal-straw co-fired utility boilers. Impact of Mineral Impurities in solid Fuel Combustion*, ed. By Gupta, New York, Kluwer Academic/Plenum Publishers 1999.

[3.24] Heiermann G.: *Erosionen an Heizflächen in hochstaubbeladenen Rauchgasströmungen*. Seminar: Aktuelle Probleme der Verbrennungstechnologie in der Kraftwerkstechnik, Most (CSSR) 1988.

[3.25] Świrski J.: *Badania erozji popiołowej i ocena zużycia rur kotłowych wskutek jej działania*. Prace Instytutu Energetyki, z.1, Warszawa, 1975.

[3.26] Schreier W., Schuster H.: *Feuerungssysteme für schwierige Kohlen.* XXXII Krafterkstechnisches Kolloquium, Dresden, 2000.

[3.27] Nayajm R.V., Bauer F.W., Tonden T.P.: *Mineral Matter in Coal – Origin, Identification, High-Temperature Transformation and Boiler Erosion.* [in:] *J. of Coal Quality* 1987, 37–43.

[3.28] Carpenter A.M., Davidson R.M., Fukasawa K., Garner L., Mitchell S.C., Moreea-Taha R., Scott D.H., Sloss L.L., Smith I.M., Soud H.N., Takeshita M., Wu Z.: *No_x – emissions and control*. IEA Clean Coal Centre, 2006.

[3.29] van der Kooij et. al.: *The effect of coal quality on NO_x emissions.* Ref: 02003Ren9769, Paris, France, UNIPEDE Thermal Generation Study Committee Group of Experts: Chemistry of Power Stations, 42 pp (1997)

[3.30] Mereb J.B.: *Assessing the effects of coal properties on NOx emissions in combustion systems.* In: *EPRI-DOE-EPA combined air pollution control symposium: the MEGA symposium, Vol.2: NOx and multi-pollutant controls,* Atlanta, GA, USA, 16-20 Aug 1999. EPRI-TR-113187-V2, Palo Alto, CA, USA, 1999, pp 14.1-14.14.

[3.31] Nakata T., Sato M., Makino H., Ninomiya T.: *Methods for predicting NO_x emissions in coal combustion and unburned carbon in fly ash – effects of coal properties*. CRIEPI EW87003, Tokyo, Japan, Central Research Institute of the Electric Power Industry, 30 pp, Feb 1988.

[3.32] O'Connor M.: *The effects of coal quality on NO_x emissions and carbon burn out in pulverized coal-fired utility boilers.* COAL R-153, Harwell, UK, Energy Technology Support Unit, 47, pp. 1999.

[3.33] Møller J., Munk B., Crillesen K., Christensen T. H.: *Life cycle assessment of selective non-catalytic reduction (SNCR) of nitrous oxides in a full-scale municipal solid waste incinerator,* Waste Management 31 (2011) pp. 1184–1193

[3.34] Baxter L.: *Biomass Impact on SCR catalyst performance*, IEA Bioenergy Task 32, Technical Report, 2005.

[3.35] Yu Yan-ke et al.: *Deactivation mechanism of de-NO_x catalyst (V_2O_5-WO_3/TiO_2) used in coal fired power plant.* Journal of Fuel Chemistry and Technology, 2012, 40(11): 1359−1365.

[3.36] Deng L., et al.: *A study on deactivation of V_2O_5/WO_3/TiO_2 SCR catalyst by alkali metals during entrained-flow combustion*, Journal of the Energy Institute (2016).

[3.37] Cichanowicz J.E., Muzio J.: *Twenty-five years of SCR evolution: implications for US applications and operation*, EPRI-DOE-EPA Combined Utility Air Pollution Control Symposium: The MEGA Symposium, AWMA, Chicago, IL, Aug 20–23, 2001.

[3.38] Licata A., Hartenstein H.U., Gutberlet H.: *Utility experience with SCR in Germany*, 16th Annual International Pittsburgh Coal Conference, Pittsburgh, PA, Oct 11–15, 1999.

[3.39] Carpenter A.M., Davidson R.M., Mitchell, S.C., Scott D.H., Sloss L.L., Smith I.M., Soud H.N., Wu Z., Zhu Q.: *Particulates – emissions and control,* IEA Clean Coal Centre, 2006.

[3.40] Jaworek A. et. al.: *Properties of biomass vs. coal fly ashes deposited in electrostatic precipitator,* Journal of Electrostatics, Volume 71, Issue 2, 2013, Pages 165-175.

[3.41] Bibbo P.P.: *The impact of coal blending and switching on the performance of air pollution control equipment.* In: *Coal-blending and switching of low-sulfur western coals,* Snowbird, UT, USA, 26 Sep-1 Oct 1993. New York, NY, USA, American Society of Mechanical Engineers, 1994, pp 301-321.

[3.42] Sing B.: *Pulverised fuel size distribution influence in a power generating utility boiler.* In: *Practical workshop on impact of coal quality on power plant performance,* Brisbane, Qld, Australa 15-18 May 1994. Boovalm Qld, Australia, Australian Combustion Technology Centre, ACIRL Ltd, 11 pp, 1994.

[3.43] *Guidelines for Estimating ESP Performance When Switching to Alternate Fuels:* Interim Report, EPRI, Palo Alto, CA: 2002. 1004075.

[3.44] Kasprzyk K, Pietrakowski P.:, *Wykorzystanie popiołów lotnych w gospodarce,* Politechnika Wrocławska. http://www.spalanie.pwr.wroc.pl/badania/witryfikacja/popioly.htm

[3.45] Giergiczny Z.(pod redakcją): *Vademecum Technologii Betonu,* Górażdże 2016.

[3.46] Jones A.R, Gibb W.H., Irons R.M.A., Price H.J., Stallings J.W., Mehta A.K.: *An integrated full, pilot and laboratory scale study of the effect of coal quality on NO_x and unburnt carbon formation.* Paper presented at: *EPA/EPRI Joint Symposium on Stationary NO_x Control,* Kansas City, USA, May 1995.

[3.47] Scott D.H.: *Improving existing power stations to comply with emerging emissions standards.* IEACR/92. London, UK, IEA Coal Research, 76 pp, March 1997.

[3.48] Adams D.M.B., Clarke L.B., Nilsson C., Sloss L.L., Smith I.M.: *Utilisation of ashes, slags and residues*, IEA Clean Coal Centre 2005.

[3.49] Internal documents *Raport końcowy z testów wpływu współspalania biomasy na eksploatację IMOS i jakość gipsu poreakcyjnego,* 2016.

[3.50] Internal documents *Badanie efektywności instalacji SNCR oraz jej wpływu na pracę kotła w porównaniu do technologii SCR*, 2012r.

[5.1] https://pogoda.interia.pl/archiwum-pogody-15-03-2017,cId,30092

[5.2] http://www.ekologia.pl/pogoda/polska/slaskie/