

Abatement of nitrogen oxides in Energy from Waste

Fortum`s Riihimäki units

Jaakko Ylä-Mononen

Bachelor`s thesis January 2020 Technology and transport Bachelor of Engineering, Energy and Environmental Technology

Jyväskylän ammattikorkeakoulu JAMK University of Applied Sciences

jamk.fi

Kuvailulehti

Tekijä(t) Ylä-Mononen Jaakko	Julkaisun laji Opippäytetyö AMK	Päivämäärä tammikuu 2020
	Sivumäärä	Julkaisun kieli
	60	Suomi
		Verkkojulkaisulupa myönnetty: x
Työn nimi Typenoksidien vähentäminen j Fortum Riihimäen laitokset	ätteenpoltossa	
Tutkinto-ohjelma Insinööri (AMK), Energia- ja ym	päristötekniikan tutkinto-ohjelma	1
Työn ohjaaja(t) Kari Hytönen, Jouni Jurvelin		
Toimeksiantaja(t) Fortum Waste Solutions Oy		
Tiivistelmä		
rallisen jätteen korkealämpötila jeja. Opinnäytetyön aiheena oli laitoksissa. Tutkimus kohdistui tövähennys tekniikoihin. Ajanko vertailuasiakirja, sekä Fortumin	irumpu. Laitoksilla käsitellään suu tutkia typenoksidipäästöjen vähe aitoksien polttotapoihin sekä nyk ohtaisen aiheesta teki vuonna 201 halu vähentää päästöjään.	iria määriä erilaisia jätela- entämiskeinoja kyseisissä syisiin typenoksidienpääs- L9 julkaistu ns. BAT-
Opinnäytetyössä on käytetty hy 2010/75/EU teollisuuden pääst päästövähennyksiin ja tekniikal västä teknologiasta on koottu n päätelmien kohdassa 29 on mä tettiin opinnäytetyön tavoitteel	väksi Euroopan parlamentin ja ne öistä. Direktiivissä määritetään pa la saavutettavat päästövähennyks s. BAT-vertailuasiakirjat sekä BAT äritetty tavoiteltavat arvot EU tas ksi.	euvoston direktiiviä aras käytettä tekniikka set. Parhaasta käytettä- ⁻ -päätelmät. BAT- olla. Kohdan 29 arvot ase-
Nykyinen tekniikka on arvioitu o tössä olevan tekniikan soveltav maan käyttämällä laitoksia ilma mahdollisia tapoja vähentää Rii parametrien muutoksissa, joide tokset eivät vaadi suuria muuto muuhun prosessiin. Luotettava lit eri parametreillä ja ajan niuk vattiin parametrien odotettava	opinnäytetyössä. Määrittäminen t uus sekä tehokkuus. Tekniikan toi n päästöjä vähentävää tekniikkaa himäen laitoksien typenoksidipää n tavoitteena on päästä haluttuih ksia kattilan käyttöön, muutoksill n datan saamiseksi olisi tarvittu yl kuuden takia testejä ei kuitenkaa t muutokset kattilan toimintaan.	tapahtui selvittämällä käy- mivuutta pystyttiin arvioi- a. Tuloksena kuvataan istöjä. Painotus on kattilan nin tuloksiin. Nämä muu- la on vähäinen vaikutus li viikon pituiset testausvä- n suoritettu. Tuloksissa ku-

Avainsanat (asiasanat)

Typenoksidit, typenoksidien muodostuminen, jätteenpolttolaitos, polttorumpu, jätteestä energiaa

Muut tiedot (Salassa pidettävät liitteet)

jamk.fi

Description

Author(s)	Type of publication	Date
Ylä-Mononen, Jaakko	Bachelor's thesis	January 2020
		Language of publication:
		English
	Number of pages	Permission for web publi-
	60	cation: x
Title of publication	·	
Abatement of nitrogen oxides in Energy	rgy from Waste	
Fortum`s Riihimäki units		
Degree programme		
Degree programme in Energy and Env	ironmental Technology	
Supervisor(s)		
Hytönen, Kari & Jurvelin, Jouni		
Assigned by		
Fortum Waste Solutions Oy		
Abstract		
Fortum's Riihimäki production facility	is a part of company's City S	olutions division. The di-

Fortum's Rithimaki production facility is a part of company's City Solutions division. The division is responsible for providing the waste management services. The area has two grate combustion units in addition to hazardous waste incineration unit. The facilities handle large quantities of different waste materials. The purpose of the thesis was to examine nitrogen oxide abatement methods in the facilities. The study was focused on the facility incineration methods and the current abatement methods. The topic was made current by so-called BAT-reference document which was released in 2019 as well as by Fortum's desire to reduce emissions.

The European Parliament and Council Directive 2010/75/EU about industrial emissions was utilized in the thesis. The directive specifies best available technology for emission control and the reachable limits for the technology. The best available technology has been compiled into so-called BAT-references and BAT-conclusions. The limit values at the EU level have been introduced in Section 29 in the BAT-conclusions. Hence, the values in Section 29 were used as reference for the thesis.

The Current technology was evaluated in the thesis. The technology was determined, and its suitability was evaluated. The efficiency of the technology could be evaluated by using plants without emission reducing technology. The results are presenting ways to reduce Riihimäki facilities` nitrogen oxide emissions. The emphasis was on changing the boiler parameters with the goal of achieving the desired outcome. These changes do not require major changes in the operation of the boiler. Instead, they have a minor effect on rest of the process. More than a week of testing with different parameters would have necessary to obtain the data, but due to time constraints no tests were performed. The results describe the expected changes in the parameters of the boiler operations.

Keywords/tags (subjects)

Nitrogen oxides, nitrogen oxide formation, waste incinerator, rotary kiln, Energy from Waste

Miscellaneous (Confidential information)

Contents

1	Intro	duction	1	6
2	NOx o	overvie	W	7
	2.1	Forma	ation methods of NO _x	8
		2.1.1	Thermal NOx	8
		2.1.2	Prompt NOx	9
		2.1.3	Fuel NOx	10
	2.2	Stoich	niometry	11
	2.3	DRE		11
	2.4	Nitrog	gen oxide sources	11
	2.5	Nitrog	gen oxides effects on human health and environment	12
		2.5.1	Nutrient enrichment problem	12
		2.5.2	Acid rains	13
		2.5.3	Tropospheric ozone	14
		2.5.4	Effects on human health	14
		2.5.5	Climate policy	15
	2.6	Best A	Available Techniques	16
3	Contr	ol and	reduction methods for NOx	17
	3.1	Reduc	cing peak temperature	18
		3.1.1	Reduced air preheating	18
		3.1.2	Catalytic combustion	18
		3.1.3	Air-staged combustion	19
		3.1.4	Fuel-staged combustion	20
		3.1.5	Steam or water injection	20
		3.1.6	Less excess air	20
		3.1.7	Burners out of service	21
		3.1.8	Flue gas recirculation	21
	3.2	Reduc	cing residence time	21
		3.2.1	Very-low NOx process	22
	3.3	Chem	ical reduction of NOx	23
		3.3.1	Fuel reburning	23

		3.3.2 Low NOx burners	23
		3.3.3 Selective Non-Catalytic Reduction	24
		3.3.4 Selective Catalytic reduction	28
		3.3.5 Baghouse, catalytic filter bags	31
	3.4	Oxidation of NOx/ Non-Thermal Plasma reactor	32
	3.5	Removal of nitrogen	33
	3.6	Sorption, adsorption and absorption	33
	3.7	Helpful tools	34
		3.7.1 Flow model usage	34
		3.7.2 Use of cameras	34
		3.7.3 Optimization of the incineration process	34
4	Refer	rence plants	35
	4.1	Municipal Solid Waste Incinerator, Limoges, France	35
	4.2	Severnside Energy Recovery Centre, UK, DyNOR	36
	4.3	Lausanne, Switzerland, Low oxygen combustion with FGR	37
	4.4	Daesan, South Korea, AGAM	38
	4.5	Covanta Bristol, Connecticut, US, VLN	39
	4.6	SYSAV recycling centre, Malmö, Sweden, SCR	39
5	Riihir	näki production facility	40
	5.1	Production units at Riihimäki	40
		5.1.1 Grate1 (55MW)	40
		5.1.2 Grate 2 (35MW)	41
		5.1.3 Rotary kiln (20MW)	42
	5.2	Fuels	42
	5.3	State and performance of the current SNCR systems	43
		5.3.1 Grate 1	43
		5.3.2 Grate 2	44
		5.3.3 HWTE1	45
6	Appro	oaches for reducing Riihimäki`s NOx emissions	46
	6.1	Grate air flow	46
	6.2	Air preheating	46

	6.3	The possibilities with the SNCR	47
		6.3.1 SNCR in HWTE1	47
	6.4	Implementation of catalytic filter bags	49
	6.5	SNCR/SCR	49
	6.6	Very Low NOx /Flue Gas Recirculation	50
	6.7	Water/steam injection	50
7 Refe	Concle	usions	51 53
Арр	endice	s	57
	Apper	dix 1. NOx values for facilities with and without SNCR	57
	Apper	dix 2. Grate 1 & 2 temperatures	58
	Apper	dix 3. Grate 1 SNCR	59
	Apper	idix 4. Grate 2 SNCR	50

Figures

Figure 1. NO formation rates in different temperatures9
Figure 2. Effect of excessive air on NOx formation9
Figure 3. Fuel Nitrogen conversion path10
Figure 4. NOx pollution contribution of different sectors
Figure 5. Acid sources and their diversion13
Figure 6. Air staged combustion and fuel-staged combustion19
Figure 7. Air ratios with and without the VLN22
Figure 8. VLN system installation23
Figure 9. Temperature effect on reduction efficiency26
Figure 10. Plate-type catalyst28
Figure 11. Honeycomb catalyst29
Figure 12. Corrugated catalyst29
Figure 13. Catalytic filter bag's function31
Figure 14. Non-Thermal Plasma DBD reactor32
Figure 15. FGS cleaning process in Limoges35
Figure 16. DyNOR system
Figure 17. Ammonia slip without and with DyNOR
Figure 18. RFG is diluted directly above the main burning zone
Figure 19. RFG hoses in the grate
Figure 20. Different injection points based on AGAM's temperature profile39
Figure 21. VLN's systems performance with and without SNCR
Figure 22. SYSAV in Malmö, Sweden40
Figure 23. Layout for grate 1 and it's flue gas cleaning41
Figure 24. Weekly NOx values and reagent consumption for HWTE1 facility48
Figure 25. Temperature's effect on reduction efficiency at different residence
times

Tables

Table 1. Nitrogen Oxides and their properties	8
Table 2. Limit values for air pollutants set by EU and WHO guidelines for	
pollutions	.16
Table 3. BAT associated emission levels for channelled NO_x , CO and NH_3	.17
Table 4. Properties of Urea and Ammonia.	.25

1 Introduction

People are raising concerns about the environment, air quality and sustainable development. Awareness of the global warming is increasing. Moreover, nowadays it is trendy to be "green". Based on this thinking, waste management, recycling, reusing products and circular economy have become the main points on many political fronts. Landfills have gained negative reputation and material efficiency has risen to the forefront. However, still in many municipalities waste separation is minimal, and often, wastes are incinerated. These Municipal Waste Incineration (MSWI) units mostly apply grate combustion technology. Their emissions are closely monitored and kept to a minimum. The monitored emissions include carbon dioxide, nitrogen oxides, sulfur, chloride and dust particles. At the end of the stack, there are barely any traces from sulfur, chloride and dust particles. Nitrogen oxides are more prevalent than the rest. Fortum complies with the current emission limits, but the company is willing to take more steps forward and be the leading corporate pollution controller and to secure that future limits will be kept.

In this paper, nitrogen oxide formation, reduction procedures and technologies are introduced. These can be divided into two main categories: pollution prevention methods, also referred to as primary methods and add-on technologies which are also referred to as secondary methods. Pollution preventive methods aims to reduce the formation of pollutants and the add-on technologies reduce the formed pollutions. These methods are discussed, and the most fitting ones are evaluated for MSWI Nitrogen oxides reduction. The current SNCR systems are also described and evaluated.

Fortum was founded in 1998, and it is a stock market company with high ownership of Finnish state. Fortum mainly focuses on the Nordic and Baltic countries, such as, Poland and Russia. Fortum's core operations are focused on ten different countries and the company has over 8300 employees. Fortum's values are curiosity, responsibility, integrity and respect, and its business structure can be divided into four major segments: Generation, City Solutions, Consumer solutions and Russia. The Generation segment contains Nordic power production from hydro to nuclear power productions. The City Solutions focuses on heating and cooling, waste-to-energy and other circular economy solutions. The main operation areas are the Nordic, and Baltic countries and Poland. The Consumer Solutions cover electricity and gas solutions for consumers. Digital services and solutions are part of the Consumer Solutions segment. The Russia segment includes power and heat generation and sales in Russia. Fortum's vision is "for a cleaner world" and the target is pursued through the mission "to engage costumers and society to drive the change towards a cleaner world". One of the projects, that Fortum works on is a municipal waste incineration facility's carbon capture and storage (CCS) project in Oslo. The goal is to reduce Oslo's carbon footprint by using CCS, which means 400 000 tons of carbon dioxide each year. (A full-scale carbon capture and storage, N.d.)

2 NOx overview

Nitrogen is a chemical element which is mainly found as diatomic molecular nitrogen N_2 . The air in the atmosphere contains 78% of nitrogen. Molecular nitrogen N_2 is inert at normal temperature and pressure, and it is a colorless and odorless gas. In nature, nitrogen occurs in different compounds, such as nitrates and amino acids. The nitrogen cycle is an important part of the naturally living organisms. In industry, nitrogen is used to create a controlled atmosphere for "annealing" steel. Which is a process that secures quality when working with steel. In the NOx group there are seven different compounds (Table 1). NO_2 is the surrogate for this group since when talking about NOx, it is in majority.

Formula	Name	Nitrogen Valence	Properties
N ₂ O	nitrous oxide	1	colorless gas water soluble
NO N ₂ O ₂	nitric oxide dinitrogen dioxide	2	colorless gas slightly water soluble
N ₂ O ₃	dinitrogen trioxide	3	black solid water soluble, decomposes in water
$ \begin{matrix} NO_2 \\ N_2O_4 \end{matrix} $	nitrogen dioxide dinitrogen tetroxide	4	red-brown gas very water soluble, decomposes in water
N ₂ O ₅	dinitrogen pentoxide	5	white solid very water soluble, decomposes in water

Table 1. Nitrogen Oxides (NOx) and their properties (CATC 1999)

Nitrogen oxides are a combination of nitrogen and oxygen. NOx is a common term used to describe nitrogen oxides. In combustion, three main forms of nitrogen oxides are formed, nitric oxide (NO), nitrogen dioxide (NO₂) and nitrous oxide (N₂O). In combustion, mostly NO is produced, but based on the nature of nitric oxide, it is usually oxidized into NO₂ in the presence of oxygen. NOx formation can be divided into three groups: Thermal NOx, Prompt NOx and Fuel NOx. (CATC 1999.)

2.1 Formation methods of NO_x

2.1.1 Thermal NOx

Thermal NOx is formed when molecular nitrogen (N_2) is oxidized in a high temperature (1;2), and the higher the temperature, the higher the rate of NOx formation. Thermal NOx formation before 1600 Kelvins is considered insignificant (see Figure 1). The NOx formation rate also increases with increasing oxygen conditions. However, with excess oxygen ratios, the point is reached after 7% (Figure 2) at which point excess air starts to cool the flame, which limits NOx formation. The NOx formation rate is doubled for every 90K increase in temperature after passing 2200K. Simplified, the Zeldovich reactions are as follows:

$$N_2 + 0 \leftrightarrow NO + N$$
 (1)

$$N + O_2 \leftrightarrow NO + O$$
 (2)



Figure 1. NO formation rates in different temperatures (left) (The Formation of NOx, N.d.)

Figure 2. Effect of excessive air on NOx formation (right) (The Formation of NOx, N.d.)

2.1.2 Prompt NOx

Prompt NOx is formed in the reaction zone in the flame front. It is found in low-temperature (under 750 °C), fuel-rich conditions and with short residue times. It is formed from molecular nitrogen, and the formation starts after the N-N triple bond splits in the presence of hydrocarbon radicals (CH_i). For this reaction the activation energy is much lower than with the Thermal NOx (1). Nitrogen radical forms NOx instead of N₂ most of the times. Prompt NOx formation is usually considered insignificant under normal combustion conditions.

> Radical, also called Free Radical, in chemistry, molecule that contains at least one unpaired electron. Most molecules contain even numbers of electrons, and the covalent chemical bonds holding the atoms together within a molecule normally consist of pairs of electrons jointly shared by the atoms linked by the bond. Most radicals may be considered to have arisen by cleavage of normal electron-pair bonds, every cleavage having produced two separate entities, each of which contains a single, un

paired electron from the broken bond (in addition to all the rest of the normal, paired electrons of the atoms). (Walling N.d.)

2.1.3 Fuel NOx

Fuel NOx is the most dominant factor in Energy from Waste. The conversion rate from fuel-bound nitrogen to NOx is dependent on the process characteristics and the concentration of fuel nitrogen. During combustion, fuel droplets and particles are heated, turning the fuel into a devolatilization stage. At this stage, fuel forms gases at elevated temperatures, while the ash and end products stay in a solid form. From the thermal decomposition of compounds, such as Aniline C₆H₅NH₂, radicals such HCN, NH₃, N, CH and NH can be formed in the reaction zone. These radicals can form NOx under the right conditions. A simplified model for fuel NOx formation is seen below in Figure 3.



Figure 3. Fuel Nitrogen conversion path (Gohlke 2010)

Under oxidizing conditions, the NH_i components formed from the fuel react with oxygen and oxygen containing radicals (OH) (3) forming nitric oxide (NO). Under poor oxygen conditions, the NO formation is inhibited due to the low number of oxidizing

$$NH_i + O_2 \leftrightarrow NO + H_iO$$
 (3)
 $NH_i + NO \leftrightarrow N_2 + H_iO$ (4)

2.2 Stoichiometry

Stoichiometry is the theoretical number of reactants needed to gain desired products. For the combustion of 1.0 mole of chlorobenzene, the stoichiometric ratio of oxygen is 7 to 1. Since air is used in the incineration, the reaction is:

$$C_6H_5Cl + 7O_2 + 26,3N_2 \rightarrow 6CO_2 + 2H_2O + HCl + 26,3N_2$$
 (5)

The reaction above uses (7+26,3) 33,3 moles of air to combust one mole of chlorobenzene. This is with a stoichiometric ratio, so there is 0% excess air (EA). Especially in hazardous waste incineration, the excess air ratio varies between 50-100%. (Santoleri, Reynolds & Theodore 2000.)

2.3 DRE (destruction or removal efficiency)

DRE is a common term when discussing the reduction of pollutants. DRE describes how much of a pollutant or a hazardous compound can be reduced using a specific measure. (Santoleri, Reynolds & Theodore 2000.)

2.4 Nitrogen oxide sources

Mobile sources emit approximately a half of the NOx emissions that are emitted by human activities. Of the stationary sources, most notable ones are electric power plants and the metal industry. Burning is also one of the sources for NOx emissions, as industrial boilers, gas turbines and incinerators involve burning. Natural sources for NOx formation are lightning, forest fires, grass fires, trees and the soils. These are 10% of the total NOx emissions. Of the mobile sources, the most prevalent one is the shipping industry. When any nitrogen oxide (see Table 1.) dissolves in water, it decomposes, and forms nitric acid (HNO₃). When NOx reacts with gases in the atmosphere, they form acid gases. These gases react with the pollutants in the atmosphere, which contributes to acid rain. These oxides can also be spread through air, even across long distances. This is the reason why impacts can spread, and the effects might not remain local. (Santoleri, Reynolds & Theodore 2000.)



Figure 4. NOx pollution contribution of different sectors (Nitrogen oxides emissions 2018)

2.5 Nitrogen oxides effects on human health and environment

2.5.1 Nutrient enrichment problem (eutrophication)

Nitrogen deposition causes problems in the water systems in the form of eutrophication. Eutrophication happens when there is too much plant nutrients available in the ecosystem. This leads to changes in growth, and the increasing growth rate of algal bloom and other plants, causes oxygen deficiency and reduced light below the surface in waters. These circumstances cause death to other plant life in the water. When water systems cannot neutralize the acidic deposition, the result is acidification. The sources of acids are nitrogen oxides, ammonia and sulfur oxides. These compounds are deposited in the ground or water systems through gases and particles as dry deposition or through rain as wet deposition. The most prevalent source for ammonia is animal sludge in agriculture. If acids are too prevalent, the ecosystem might lose its ability to neutralize the acids. This causes serious damage to the ecosystem. (CATC 1999; Acidification N.d.)

2.5.2 Acid rains

Nitrogen oxides that are released into the air contribute to acid rains. Acid rain forms when any of the nitrogen oxides dissolve in water or humidity of the air and decompose. Decomposing with water, they form nitric acid (HNO₃) and nitrous acid (HNO₂). Nitric acid is subject to light or thermal decomposition. Nitric acid is a strong acid, and it is highly soluble in water. Ammonia is also a major contributor to acid rains. When ammonia is dissolved into water it forms ammonium ions (NH₄⁺). These ions can later oxidize into nitrate ions (NO₃⁻). Acids are carried out by air and humidity, and they can transit to the ground as part of deposition. In acid conditions, plants and organs receive dangerous ions, such as heavy metal- and aluminum ions. These ions are dissolved from the ground, while acids are present to a sufficient extent. (Acidification N.d.)



Figure 5. Acid sources and their diversion (Biology N.d.)

2.5.3 Tropospheric ozone (troposphere; lowest layer of atmosphere)

Ozone in the troposphere is formed from nitrogen oxides, carbon monoxide and hydrocarbons. In the presence of air, NO₂ reacts with ultraviolet light forming ozone and nitric oxide (O₃: NO). NO further reacts with the radicals in the air, forming NO₂ again. This is caused by the radicals acting with the volatile organic compounds (VOC) in the presence of UV light. The formed ozone can oxidize nitrous oxide (N₂O), forming molecular oxygen (O₂) with nitric oxide (NO) or dinitrogen dioxide (N₂O₂). These products are oxidized quickly (under two hours) into nitrogen dioxide (NO₂). This can form ozone again and the NO can form N₂O again, if it is hit by a photon of ionizing radiation from the sunlight. Nitrous oxide (N₂O) is a greenhouse gas, and like carbon dioxide, it absorbs long wavelength infrared radiation, thus holding the heat radiation which would otherwise leave the planet. This contributes to the global warming, which can be seen in increasing in temperature. (Weather Institute N.d.; CATC 1999.)

2.5.4 Effects on human health

During the last few decades, air impurities have seen a significant decline. This can be seen in the decline of the content of these harmful impurities. The main contributors to air impurities are fine particles (PM_{2.5}) with a share of 64%. These particles contain heavy metals and compounds that contribute to cancer. Nitrogen dioxide and PM₁₀ particles both contribute for 13%. Ozone contributes for 2% and the final 8% percent is covered by Sulphur and other pollutants.

Particles are carried out through air to every part of human respiration. They can cause direct allergic reactions, as well as immunological and toxic effects. These can later transfer into the rest of the body and cause harm in the hearth muscle and brain. These contribute to increasing death rates.

NOx causes the same effects, but the concentration of the pollutant needs to be bigger. Exposure to nitrogen oxides in high concentration can cause a burning feeling in the lungs, cough, dizziness, illness and difficulty of breathing. Skin and eye damage are also possible in high concentrations. The damage is caused by the nitric acid. Prolonged exposure can hinder the lung's ability to uptake oxygen. This can lead to increase in other respiratory illnesses. This is more prevalent with young children and people with asthma. (National climate protection program N.d.)

Tropospheric ozone's harmful effects are based on ozone's ability to react with different substances. In the human body, ozone can oxide enzymes, proteins and fats. It has also been proven that ozone will increase the effectiveness of carcinogens which contribute to cancer. (Weather Institute N.d.)

2.5.5 Climate policy

Finland has a good air quality and the quality is monitored all the time while constantly reducing emissions. This is especially the case in the cities which are densely populated and where the pollution contents can rise. Air pollution control is constantly monitored and planned according to urban development and population. Air pollution control aims to improve people's wellbeing and ensure good air quality and good quality of the environment. Preserving biodiversity is also a part of the goal. Regulations, such as using BAT and emission limit value regulations, are used to limit emissions. (Ministry of Environment 2019.)

The Environmental Protection Act controls and guides the environmental protection in Finland. Air quality control is a part of this (chapter 15, 141§). Overall, the law requires the operators to be aware of their impacts of the activities, which includes to being familiar with the environmental impacts, environmental risks, how to control these and how to reduce the effects of these operations (awareness obligation 6§). Section 7§ requires the operator to set activities so that the pollution of the environment can be prevented. If it is not possible to prevent contamination, it shall be kept to a minimum. Air Quality Act 141 § requires operators to pursue air quality so that there are no dangerous or harmful substances or compounds. Exceptions can be regulated by government decrees, if it is necessary for the implementation of the European Union Law. These laws are monitored by the Climate Change Act as set in sections 167-169 §. (Environmental Protection Act: 27.6.2014/527) Limit values for air quality control are given by μ g/m³, mg/Nm³ or ppm. Hourly emissions cannot exceed the hourly limit (see Table 2). Municipalities and the state have to keep track of the annual limits. The limits have been set to protect human health and the environment. (European Environmental Agency N.d.)

		WHO Guidelines			
Pollutant	Averaging Period	Objective and legal nature and concentration	Comments	Concentration	Comments
PM2.5	Hourly			25 μg/m³	99th percentile (3 days/year)
PM2.5	Annual	Limit value, 25 µg/m³		10 μg/m³	
PM10	Hourly	Limit value, 50 µg/m³	Not to be exceeded on more than 35 days per year	50 µg/m³	99th percentile (3 days/year)
PM10	Annual	Limit value, 40 µg/m³		20 µg/m³	
O3	Maximum daily 8-hour mean	Target value, 120 μg/m³	Not to be exceeded on more than 25 days per year, averaged over three years	100 µg/m³	
NO2	Hourly	Limit value, 200 µg/m³	Not to be exceeded on more than 18 times a calendar year	200 µg/m³	
NO ₂	Annual	Limit value, 40 µg/m³		40 μg/m ³	

Table 2. Limit values for air pollutants set by EU and WHO guidelines for pollutions (European Environmental Agency N.d.)

2.6 Best Available Techniques (BAT)

Best Available Techniques are determined by the Environmental Protection Act 527/2014 (YSL 5 §). According to the European Union Directive 96/61 EC:

Best Available Techniques (BAT) means the most efficient and sophisti cated production and purification methods that are technically and eco nomically feasible, and the methods of planning, construction, maintenance, operation and decommissioning that prevent or reduce most effectively the environmental pollution caused by the operation. (Council Directive 96/61/EC 1996) BAT is the technology approved by legislators or regulators for meeting output standards for a particular process such as pollution abatement. BREF (BAT reference document) is a document which is result from the exchange of information organized pursuant to article 13 of the Indus trial Emissions Directive (IED). The European IPPC Bureau (EIPPCB) or ganizes and co-ordinates the exchange of information between Member States and the industries concerned on Best Available Techniques (BAT), as required by Article 13 of the IED. The EIPPCB produces BAT reference documents (BREF) and BAT conclusions. (BAT, N.d.)

Table 3. BAT associated emission levels (BAT-AELS) for channelled NO_x, CO and NH₃. (WI BAT conclusions)

Parameter	BAT-AEL (mg/Nm ³)		Averaging period
1 al ameter	New plant	Existing plant	
NOX	50–120 (¹)	50–150 (¹) (²)	
СО	10-50	10-50	Daily average
NH ₃	2–10 (1)	2–10 (¹) (³)	

(¹) The lower end of the BAT-AEL range can be achieved when using SCR. The lower end of the BAT-AEL range may not be achievable when incinerating waste with a high nitrogen content (e.g. residues from the production of organic nitrogen compounds).

 $(^2)$ The higher end of the BAT-AEL range is 180 mg/Nm³ where SCR is not applicable.

 $^{(3)}$ For existing plants fitted with SNCR without wet abatement techniques, the higher end of the BAT-AEL range is 15 mg/Nm³.

3 Control and reduction methods for NOx

NOx control methods can be divided into two main categories: pollution prevention methods (primary measures) and add-on technologies (secondary measures). The pollution preventive methods aim to reduce the formation of the nitrogen oxides before any is formed or limiting some of the factors that contribute to NOx formation. The add-on technologies reduce NOx emission after their formation, converting the NOx into harmless substances. These methods can be further divided into six more sections: 1. Reducing the peak temperature, 2. Reducing the residence time at the peak temperature, 3. Chemical reduction of NOx, 4. Oxidation of NOx with subsequent absorption, 5. Removal of nitrogen, 6. Use of sorbent. Each of the methods has many ways to reduce nitrogen oxide formation and the methods can be used side by side to gain the desired outcome. (CATC 1999; Santoleri et al. 2000.)

3.1 Reducing peak temperature

When limiting the temperature in burning, it is usually done by diluting calories. This is usually done by injecting steam/water, or flue gas into the furnace. It can also be done with fuel rich mixtures which limit the excess oxygen, or using fuel lean mix-tures, or by injecting cooled flue gas with added fuel. (CATC 1999.)

3.1.1 Reduced air preheating

When talking about power plants and processes, the main concern usually is a high efficiency, and this is the reason why air is usually preheated with the energy from the flue gases. This can cause problems with NOx, since excessive air preheating increases the temperature of the air, and an increase in temperature will rapidly increase NOx formation. Changes in the combustion air temperature directly affect the amount of combustion air supplied to the boiler and may increase or decrease the excess air. Reducing air preheating will lower the temperature, and, thus hinder NOx formation. Reducing the flame temperature can cause problems in the boiler while burning non-convectional fuels, such as municipal or hazardous waste (reduced drying in the grate). The method can be very effective when reducing NOx formation. (CATC 1999.)

3.1.2 Catalytic combustion

Catalytic combustion is a flameless process, where a heterogenous catalyst is used to control the oxidation. The catalyst uses platinum group metals as catalysts. This allows a wide range of fuels and air ratios. The temperatures for the process are lower than in noncatalytic combustion, which is the main reason why it is an effective way of reducing NOx emissions. The cons for catalytic combustions are specific conditions, such as limited fuel use on gases and liquids. Moreover, the method is also very expensive. This method is usually used in catalytic gas combustion engines. (CATC 1999; A Review of Catalytic Combustion 1984.)

3.1.3 Air-staged combustion (air staging and over fire air (OFA))

Air-staged combustion is a widely used method for reducing NOx formation. Air staging is implemented by dividing the air flow into the primary and secondary air stream. Primary air stream has air deficiency which limits the burning temperature with the stoichiometric range of 0,8-0,9 (fuel rich condition; see Figure 6). A secondary combustion zone has excess air, which makes the net air ratio slightly higher than the stoichiometric ratio (oxygen rich condition). This completes the combustion. Secondary air is directed against the flue gas flow. Secondary air nozzles need to be placed correctly in order to reach the right flame volume. This requires good boiler design. The goal of the system is also to create a longer residence time with low temperature. High temperatures will increase NOx reduction under fuel rich conditions and high temperatures will increase NOx formation in oxygen rich conditions. (Gohlke, Weber, Seguin & Laborel 2010; Clean Coal Technologies N.d.)



Figure 6. Air staged combustion (left) and fuel-staged combustion (right) (Gohlke et al. 2010.)

3.1.4 Fuel-staged combustion

In fuel-staged combustion an extra burning zone is used, which is located above the main burning zone. The fuel is injected into a fuel reburning zone. This is usually gas, such as natural gas. The primary combustion zone contains NOx rich conditions. Hy-drocarbon radicals react with the NOx (formed from the fuel reburn), reducing NOx to molecular nitrogen (see Figure 3). A burnout zone completes the burning of any remaining fuel in oxygen rich conditions (see Figure 6). Fuel-staged combustion is not optimal for MSWI, since many of the gases, which are used in the FSC are not "CO₂ free". (Gohlke et al. 2010.)

3.1.5 Steam or water injection

Water or steam can be injected into the flame. This dilutes the calories and weakens the flame by decreasing the temperature of the flame. The injection causes stoichiometry of the mixture to change. It has been reported that water or steam usage will increase fuel NOx formation. In addition, using water causes erosion and wear in the system. Using this method will cause efficiency loss, and it can cause problems with the flame stability (increase in CO and other pollutants). Overall, the method has moderate costs and it can be effective, but if implemented wrongly it can hinder the boiler performance. (Water or steam injection N.d.)

3.1.6 Less excess air (LEA)

Limiting excess air reduces the available oxygen in the stoichiometric ratio and only provides oxygen for the burning (see Figure 2), thus limiting the oxidation of nitrogen from the fuel and air. The method does not require any additional inputs, but efficient pollution monitoring is required. LEA can cause CO levels to increase if the burning is incomplete. Other pollutants may increase as well. LEA is a good method for reducing nitrogen oxides. It is cheap to implement but it has limited reduction possibilities and the risk of increasing CO emissions and reducing flame stability. (CATC 1999; Summary of NOx control methods 1992.)

3.1.7 Burners out of service (BOOS)

Burners out of service are common in utility boilers. A furnace with multiple burners can utilize this method. In this application some burners are used as BOOS, these burners are only supplying air. The goal is to stage the combustion by using the burners in fuel-rich conditions and supplying the excess air via BOOS. When there are fewer burners active lower temperatures are obtained than with every burner active. Effectiveness of the method is dependent on the burner locations and it can widely change from boiler to boiler but usually, the highest burners act as BOOS. This creates a zone of air at the top where the fuel-rich components need to pass, before exiting the furnace. This method is cheap to use and requires no additional costs, but the method is only suitable for furnaces that have a large capacity of burners such as utility boiler. The method can reduce the power output from the boiler. The utility boilers are large capacity boilers that are mainly used for electrical power production. (Burners out of service N.d.)

3.1.8 Flue gas recirculation (FGR)

With FGR some of the cooled flue gases are recirculated back to the boiler/burner. This lowers the temperature of air by cooling and sharing the heat with a greater volume of air. This also dilutes the oxygen with a greater volume, thus reducing the overall oxygen level (see Section 3.1.5 LEA). In addition, FGR reduces the overall fresh nitrogen supply. The method is usually implemented by directly taking flue gases from the stack. This will require more fan capacity. FGR works best with low nitrogen fuels and usually <30% of the flue gases are recirculated. Drawbacks are the same as with the LEA method, but with FGR furnace pressure can become an issue. FGR is not suitable for HWI since hazardous wastes need to be burned in high excess air ratios. (CATC 1999; Energy from waste 2012)

3.2 Reducing residence time

The goal with short residence time is to prevent the nitrogen from becoming ionized and the method is not impacting the total residence time of the flue gases. In boilers, it is done by restricting the flame. This can be done by increasing mass flow rates. Or with injections, such as air and steam. (CATC 1999)

3.2.1 Very-low NOx process (VLN)

VLN system fits grates that employ a moving grate with two sources of combustion air (see Figure 8). With VLN the secondary air is reduced and VLN gas nozzles are applied to the higher levels of the furnace, around the level where temperature is 1000°C, usually below the ammonia injections. VLN gas is taken from the roof of the lower furnace at end of the grate. Changes in overall air ratios can be seen in Figure 7.



Figure 7. Air ratios with and without the VLN (MARTIN GmbH N.d.)

This "VLN gas" is relatively cool and non-corrosive. The gas has two major effects: Firstly, it promotes the conditions which reduces NOx to molecular nitrogen. Secondly, the VLN gas mixes the flue gases. Thus, helping the SNCR system to reach more optimal mixing and lower temperature ranges. Intense mixing of the flue gases also creates a turbulence barrier. The barrier blocks the passage for the flame and unburned material. As the unburned material cannot reach the second pass of the boiler some of the corrosion threat is hindered. VLN process combined, with the SNCR has been reported to achieve NOx levels down to 60mg/Nm³. (Process for achieving Very Low NOx (VLN) 2009; Gohlke el at. 2010.)



Figure 8. VLN system installation (Gohlke 2010)

3.3 Chemical reduction of NOx

These methods are aiming to remove the oxygen from the NOx, with chemical substances by reducing the valence level of nitrogen. The methods are quite expensive to apply since they are additive methods. (Richardson, Lee 1999)

3.3.1 Fuel reburning (FR)

With fuel reburning, a new level of burning is added. The fuels are added to the level with the combination of cooled flue gases, to create the dilution of calories. This will lower the peak temperature and causes the NOx to react back to the molecular form (N_2) . After the FR stage, an air zone is required to ensure the proper combustion of the added fuels. (CATC 1999.)

3.3.2 Low NOx burners (LNB)

LNB is an advanced design from a regular burner. The burner air and fuel are distributed in a manner that makes the flame much wider and shorter. This reduces the temperature and oxygen levels in the hottest parts of the flame. Thereby the NOx formation zone has fuel-rich, and oxygen-deficient circumstances. LNB is in general introduced with FR, to gain the best DRE. (Maxwell, Richardson, Mentzer, Lee 1999)

3.3.3 Selective Non-Catalytic Reduction (SNCR)

SNCR reduces NOx into molecular nitrogen (N₂) and water (H₂O). The reagent is injected into the flue gas after the combustion. The target temperature for the reagents is 850-1300 °C. The reaction is selective, since it needs a specific temperature and oxygen to work. The reagent is injected thought nozzles, which are located usually into two zones, each zone covers one layer. Two reagents are used: ammonia (NH₃) and urea [CO(NH₂)₂], both are ammonia-based. "**Reactants** are substances initially present in a chemical reaction that are consumed during the reaction to make products." Both reagents first vaporize in the boiler and then decomposes, into free radicals (NH₃; NH₂). With proper mixing, these radicals are in contact with the nitrogen oxides, reducing the NOx into N₂. The reductions reaction for ammonia is as follows:

$$2NO + 2NH_3 + \frac{1}{2}O_2 \to 2N_2 + 3H_2O$$
(6)

Reaction for urea is as follows:

$$2NO + CO(NH_2)_2 + \frac{1}{2}O_2 \to 2N_2 + CO_2 + H_2O(7)$$

Both reactions (6,7) can form nitrous oxide (N_2O), as a by-product. However, with the urea the formation is more prevalent, which can be up to 30% of the products. Ni-trous oxide is a greenhouse gas.

Main costs from the SNCR-system comes from the reagents, which are used. Urea is more expensive than ammonia. The reagents have different properties; thus, the reagents need different storing conditions. Typical properties of the reagent are shown in the Table 4.

Property	Urea Solution	Aqueous Ammonia
Chemical formula	CO(NH ₂) ₂	NH₃
Molecular Weight of reagent	60,06	17,03
Liquid or gas at normal air temperature	Liquid	Liquid
Concentration of reagent normally supplied	50% by weight	29,4% by weight
Ratio of NH₃ to solution	28,3% by weight of NH₃	29,4% by weight NH₃
Density of solution @16°C	1,14 g/cm³	0,9 g/cm³
Vapour pressure @27°C	<7 KPa	102 KPa
Crystallization temperature	18°C	–78°C
Flammability limits in air	Non-flammable	Lower explosion limit = 16% NH₃ by volume Upper explosion limit = 25% NH₃ by volume
Threshold limit value (health effects)	Not specified	25ppm
Odor	Slight (ammonia-like)	Pungent odor @ 5ppm or more
Acceptable materials for stor- age	Plastic, steel, or stainless steel (no copper or copper- based alloys or zinc/alumi- num fitting)	Steel tank, capable of handling at least 172 Kpa pressure (no copper or copper-based alloys, etc)

Table 4. Properties of Urea and Ammonia. (Sorrels, John L. 2015, adapted)

Ammonia can be used in anhydrous or aqueous form, and it requires permits when stored greater than 28% concentrations by weight. The aqueous form (NH₄OH) is usually preferred since the easier storing conditions. However, this requires more space and causes increase in the transportation costs. The anhydrous ammonia requires a pressurized container as it a gas in normal pressure. The Urea has a low freezing point of 18 °C compared to the -78 °C of anhydrous ammonia (more properties in Table 4). This causes problems with the storing and injection, since a heating system is usually required. The urea is stored in 50% aqueous form. In addition, the urea solution is usually more economical, since the transport costs are lower. The main benefit for urea over ammonia, is nontoxicity of the urea. Furthermore, the liquid form of urea is less volatile and storing the reagent is safer. Lastly the droplets can have better mixing since they push further into the flue gas stream.

3.3.3.1 SNRC design variables

Reaction temperature

Reaction temperature needs to be considered, when placing the injection nozzles to the boiler. If the temperature is too low, reaction will be too slow and ammonia slip is possible. When the temperature is too high, reagents forms NOx via oxidization. For the ammonia ideal temperature range is 870-1050 °C and for the urea 900-1150 °C. At excessive high temperatures ammonia decomposes into nitric oxide as follows:

 $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ (8)



Figure 9. Temperature effect on reduction efficiency (Sorrels, John L. 2015, adapted)

Residence time

Residence time represents how long the reactants are present in the reaction. With longer residence times, comes better efficiency for conversion. Low residence time, in high temperatures, or high residence time, in a controlled temperature (980 °C) provides the highest reduction efficiency. Residence time depends on the boiler design and overall residence time is not the most significant factor in NOx reduction. The reagents have a different reaction paths when injected. When urea is injected the water from the mixture starts to evaporate, while it is mixing with the flue gases.

After water evaporation urea is decomposed into NH₃. Up next ammonia decomposes into free radicals and NH₂. Lastly free radicals react, and NOx reduction takes place in the flue gas. This causes longer residence times and allows urea to work in higher injection temperatures. Ammonia evaporates and decomposes while being heated by the flue gases. Furthermore, causing ammonia to react faster and in lower temperature range.

Degree of mixing and coverage

Degree of mixing and coverage needs to be sufficient. This is done by atomizer nozzles, which are divided around the boiler. Usually for more than one level, depending on the boiler temperature ranges. The diameter of the droplet specifies the evaporation time and trajectory for the droplets. Large droplets survive further into the stream and the large droplets have a longer volatilization time, increasing the required residence time. The modifications that will have an impact on the NOx reduction are as follows: pressure (energy of the droplets), boiler level coverage (number of injectors), increase in injection levels, different nozzle designs (particle size, spray, angle, direction). Ammonia needs to be distributed sufficiently, due to its volatile nature.

Uncontrolled NOx

NOx concentration affects to the reaction rate of the reduction process. The lower the concentration, lower the efficiency of the reduction. Lower concentrations of NOx also need a lower temperature to convert. Thermodynamic factors are limiting the conversion in low NOx concentrations.

Normalized Stoichiometric Ratio

Normalized Stoichiometric Ratio (NSR) shows how much reagent is needed for each mole of NOx. Usually the NSR is 0,5 to 3moles of ammonia for each mole of NOx. The ratio is determined by boiler characteristics. In addition, the ratio can be decreased if degree of mixing, residence time and temperature ranges are optimal.

Ammonia slip

Ammonia slip is excess reagent in the flue gas stream. Desired NOx reduction always has ammonia slip, due to flue gases cannot be mixed well enough, to gain the perfect NSR. The unreacted ammonia is carried out into the atmosphere and where it causes several, health related issues through the air. Ammonia creates ammonium-bisulfate (NH₄)HSO₄ and ammonium sulfate (NH₄)₂HSO₄. This can cause corrosion in the boiler, ducts and fans. (Richardson, Lee 1999; CATC 1999; Sorrels, John L. 2015)

3.3.4 Selective Catalytic reduction (SCR)

SCR is a chemical process which reduces the nitrogen oxides into molecular nitrogen (N_2) and water (H_2O) . Ammonia based reagent is used alongside a catalyst. Main reagents which are used, are anhydrous ammonia, aqueous ammonia and urea. Properties for the reagents can be seen in Table 4 (see 3.3.3). In SCR three main types of catalyst are used: plate-type-, honeycomb-, corrugated catalyst.

Plate-type catalysts

These catalysts are made from stainless steel base, alongside with the ceramic coating. Titanium oxide (TiO_2) is most used catalytic material. Plate-type catalyst has good resistance against erosion, poisoning and the catalyst has a minimal pressure drop.



Figure 10. Plate-type catalyst (Hailing, N.d.)

Honeycomb catalyst

The catalyst has square-opening structure and it usually uses titanium oxide as a catalytic material. Furthermore, it has a better height than plate-type catalyst, thus the catalyst has a better reduction rate and a higher pressure drop.



Figure 11. Honeycomb catalyst (Matthey, Johnson 2018.)

Corrugated catalyst

The catalyst has a steel carrier with its corrugated coating. In addition, it uses Titanium oxide alongside fibres to create pores. The catalyst has the lowest SO_2 oxidation, out of the three catalysts.



Figure 12. Corrugated catalyst (Air pollution control 2013.)

The catalysts are loaded into steel frames to create modules. A catalyst can deactivate through masking, plugging and poisoning. In masking substances such as fly ash blocks the catalyst surface. In plugging particles go into catalyst pores, blocking the reacting surface. Catalyst poisoning occurs, when unwanted reaction happens within the catalyst pores, e.g. alkaline metals can react undesirably in the catalysts.

SCR is the ultimate NOx reduction method and it works best with low NOx concentrations, to ensure best performance. Reduction rates can be up to 95% with minimal ammonia slip. SCR system consists of the regent injection zone, dilution system, possible mixing plates (if needed to create better reagent distribution) and from a catalyst bed. Temperature range is more forgiving that in SNCR. SCR works within 250-430 °C. However, the system has very high to capital costs, and operating costs are also significant.

Ammonia based reagent is injected into the flue gas, mixing the reagent with the flue gases. When nitrogen oxides and the reagent reach the catalyst bed, the catalyst converts the substances into molecular nitrogen and water. Reactions 9 and 10 are desired reactions from the catalyst. (9) Conversion of nitric oxide. (10) Conversion of nitrogen dioxide.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O (9)$$
$$2NO + 2NO_2 + 4HN_3 \rightarrow 4N_2 + 6H_2O (10)$$

Some of the reactions are undesired within the catalyst. These are usually caused by pollutants in the flue gas stream, such as sulfur. (11) Conversion of sulfur dioxide into sulfur trioxide (12) Sulfur trioxide conversion into ammonium bisulfate, ammonium bisulfate is harmful to the catalyst. (13) Ammonia can convert into nitrogen and water. However, the reaction undesired since it hinders the catalyst efficiency.

$$SO_2 + \frac{1}{2}O_2 \to SO_3 (11)$$

$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4$$
 (12)

$$4NH_3 + 3O_2 \to 2N_2 + 6H_2O \ (13)$$

(Air pollution control technology fact sheet N.d.; Matthey, Johnson 2018)

3.3.5 Baghouse, catalytic filter bags

Catalytic filter bags are made from catalytic materials. These materials are usually noble metals (gold silver palladium), also non-noble catalyst materials can be used. One option is to use iron-chromium oxide mixtures with the catalyst. Basic principle is to inject ammonia before a baghouse, which contains the catalytic filter bags. Ammonia reacts on the bag surface with catalytic material and reduces the nitrogen oxides into harmless substances: water and molecular nitrogen. Filter bags has a vide temperature range, which allows wide range of use. System requires a proper ammonia injection and distribution system. Furthermore, ammonia measurement is added after the baghouse for system control and analysis. The catalytic filter bags can reach nitrogen oxide values under 100mg/Nm³. Catalytic filtering bags are feasible since they are easily implemented into existing systems, with low modifications costs. However, the bags are more expensive to use than traditional filtering bags since the bags are made from various materials. Relatively low-pressure drops occur then flue gases flow through the filter bags. (United states patent 1984.)



Figure 13. Catalytic filter bag's function (GORE filtration products N.d.)

3.4 Oxidation of NOx/ Non-Thermal Plasma reactor

Oxidation of the nitrogen oxides raises the valence level of nitrogen by design. Higher valence level of the nitrogen ion can easily be absorbed by water. Raising the valence level is done by a reagent or a catalyst. Non-thermal plasma reactor is built from two electrodes. One of these is a metal pipe and the another, electrode is metal wire that runs down the middle of the pipe. Between these is an empty space, which is supplemented with glass beads. The reactor is called Dielectric-Barrier Discharge (DBD).



Figure 14. Non-Thermal Plasma DBD reactor (Non-Thermal Plasma N.d.)

Flue gases flow through the pipe, while an alternating current is applied to the reactor. When the beads cannot insulate the electrical current anymore, multiple mini discharges occur. This breaks the inlet compounds into radicals and the radicals quickly form steady compounds. Then oxygen (O₂) enter the reactor, it splits into O⁺ and O⁺, forming ozone with molecular oxygen. Oxygen radicals also react with other compounds such as NOx, CO, SO₂, thus forming N₂O₅, NHO₃, CO₂, SO₃. There are many ways to implement NPT-reactors, most commonly the system contains an DBD reactor and scrubbers to absorb the acids, which are formed from the radicals and the flue gages. Another implementation is to use ozone to convert the pollutants into higher-oxidized state. In addition, removing the hydrolysed compound via caustic scrubber. Reagents, such as ammonia can be used to gain better DRE. (Non-Thermal Plasma N.d.; NOx removal with NTP 2012)

3.5 Removal of nitrogen

Removal of the nitrogen can be achieved in two ways: using oxygen in combustion instead of air or using low nitrogen fuels. Consequently, fuel- and prompt NOx can be eliminated almost entirely. Thermal NOx is formed in minimal quantities because of air quenching (rapid cooling with substance such as water or air). When just oxygen is used in combustion, flame becomes very intense. The flame needs to be diluted suitably, when adding the excess oxygen. Intermediate for this system is to use enriched oxygen. This mean that air with the oxygen levels of 25-30% are used. Normally air contains 21% of oxygen. Method is commonly implemented with FGR (see 3.1.7) to reduce the amount of nitrogen in combustion. This can be ineffective, since the temperature rises with the introduction of excess oxygen. The nitrogen concentration is reduced to an extent. DRE of 20% can be achieved with oxygen combustion and air quenching. With low nitrogen fuels DRE of 70% can be achieved. (NOx formation N.d.)

3.6 Sorption, adsorption and absorption

Sorption is common name used for adsorption and absorption. In adsorption gas phase material is adhered into a solid material. In absorption a substance is absorbed into another phase. Sorbent material can be dry or slurry. Most common method is to use dry limestone. The limestone is crushed into dust and injected into flue gas stream. In the flue gas stream limestone will react with sulfur and nitric acids. Limestone can be injected: into the boiler, before baghouse or before electrostatic precipitator. Wet methods such as spray dryers can be applied. Sorbents are collected with a baghouse, ESP or via a wet scrubber. NaOH has been proven to be useful, because when injected via spray dryer it has been shown to improve sorption rates and reducing the need for the sorbent. Many NOx-sorbing catalysts can be found and those can be divided into five types. 1. The NOx is ionized and the NO⁻,NO⁺ desorb as NOx, in sufficient temperature. After that NOx is decomposed into nitrogen and oxygen. The adsorption capacity is proportional to the surface area of the adsorbent. 2. Formation of nitrate or nitrite salts at elevated temperatures on basic oxides. At higher temperatures these salts are decomposed forming molecular Oxygen and Nitrogen. 3. Intercalation with catalyst structure, without changing the catalyst. 4. Carbonate materials, not functional in moderate temperatures. 5. Bulk absorption of molecules by forming solvates. (M.A. Gomez-Garcia, V. Pitchon, A. Kiennemann, 2005.)

3.7 Helpful tools

3.7.1 Flow model usage (Computational Fluid Dynamics, CFD)

The use of computerized flow models can help to determine the proper boiler design, which includes no hot spots, proper placement of air nozzles etc. Use of CFM can help existing plans to gain better understanding of the burning process (hot spots, flow turbulence). Furthermore, it can help when valuating existing SNCR or SCR. Optimization helps to reduce harmful particles and substances, via proper burning. (BAT REF 2018.)

3.7.2 Use of cameras

Infrared cameras can be used to maintain a proper combustion. For the grate combustion infrared cameras can be used to determine the proper air ratio for the waste bed. With the camera can be determined if some stages of the grate are too cold to maintain proper combustion. This can be used to improve logic control of the grate by implementing computer-controlled image processing, which provides parameters for the grate operation. Main benefits are better combustion, which can be monitored as: less unburned fuel, less unburned particles and a process which reacts faster for unstable fuels. (BAT REF 2018.)

3.7.3 Optimization of the incineration process

Each of the combustion stages should have own air fan, to allow better and more precise control of the air injections. The stages should be in individual boxes, thus

there would be no interference between the stages. This would allow better control for the burning: warmer air for better volatilization and drying. Together with the optimization of the waste feed, temperature and air injections, can majorly increase the oxidation rate, while reducing NOx emissions. (BAT REF 2018.)

4 Reference plants

This chapter discusses certain existing plants and methods as reference points. NOx pollution levels and methods are discussed in this section. The methods are described above with more details. Some of these methods are utilizing a reduction method to the full extend.

4.1 Municipal Solid Waste Incinerator, Limoges, France

The Limoges waste facility has three incinerator lines in use. The incinerators needed to comply better with pollution standards. Therefore, all units were equipped with catalytic filter bags. After their installation, values constantly under 80mg/Nm³ have been reported. The system uses ammonia slip in the catalyst thus, eliminating any ammonia pollutions. The technology is provided by GORE. GORE is a 60-years-old company which focuses on material development and applications, and whose most notable material is polytetrafluoroethylene (PTFE). (GORE filtration products N.d.)



Figure 15. FGS cleaning process in Limoges *CEMS continuous emission monitoring system (GORE filtration products N.d.)

4.2 Severnside Energy Recovery Centre, UK, DyNOR

The Severnside Energy Recovery Centre has two incinerator lines both of which are equipped with the Dynamic NOx Reduction system. The incinerators have a capacity to burn 22 tons of waste per hour. NOx levels under 150mg/Nm³ have been reported in the incinerators. Pithiviers, France and Trondheim, Norway use a similar system and reach the same levels of nitrogen oxides emissions. (Severnside N.d.; DyNOR 2010)

DyNOR is an advanced SNCR system (see Figure 16). DyNOR uses infrared thermometers to determine the furnace temperature. In this way, the system can react to the temperature variation which is caused by fuel composition. These are the controlling factors driving the nozzles and ammonia injection. The furnace is divided into four or more segments, and each individual segment has its own thermometer. The nozzles are usually located on three different planes. This depends on the boiler size. The system automatically controls the segments separately in order to always have the right amount of ammonia going into the furnace. DyNOR minimizes the ammonia slip to a minimum (see Figure 17). Values of 100mg/Nm³ can be reached with DyNOR. (DyNOR 2010.)



Figure 16. DyNOR system, columns are representing the boiler segments (DyNOR 2010)



Figure 17. Ammonia slip without and with DyNOR (DyNOR 2010)

4.3 Lausanne, Switzerland, Low oxygen combustion with FGR

An experiment was done in Lausanne, Switzerland. In the experiment, oxygen concentration was examined in the grate combustion. The study found that oxygen concentration was very low in the stoker side of the boiler (with 2.0 oxygen). This was further examined with low oxygen ratios (1.3). The problems increased in low oxygen concentrations. A Flue Gas Recirculation (FGR) system was added to the incinerator (see Figure 18). The FGR stream was set to face the stoker side of the grate. This caused intense mixing of the fire above the grate and caused the oxygen concentration to steady out. These modifications reduced the NOx levels to under 200mg/Nm³ from 340mg/Nm³, without any additional NOx reduction methods. The process achieved reduced FG rates because of lower primary and secondary air injection due to the Flue Gas Recirculation. (Energy from waste 2012)



Figure 18. RFG is diluted directly above the main burning zone (Energy from waste 2012)

Figure 19. RFG hoses in the grate (Energy from waste 2012)

4.4 Daesan, South Korea, AGAM

AGAM stands for Acoustic Gas Temperature Measurement. AGAM is an advanced SNCR, and its accuracy is based on gas temperature measurement by using sound. The system determines the furnaces` current temperature profile by continuous sound measurements because the speed of a sound in a gas depends on the gas temperature. SNCR is operated with this information to direct the reagent into the correct level and place (see Figure 20). The system is almost maintenance free because the transmitters are not in the boiler. The method is widely applied in Germany, Sweden and The Netherlands to meet emission limits of 100mg/Nm³. (Bonnenberg & Drescher N.d.: SNCR Process 2008.)



Figure 20. Different injection points based on AGAM's temperature profile (Bonnenberg & Drescher N.d.)

4.5 Covanta Bristol, Connecticut, US, VLN

In 2006 Martin and Covanta retrofitted Covanta's recovery facility's boiler with a technology called VLN, which was developed by the two companies. The recovery facility was the first where the VLN was demonstrated in full scale. 100mg/Nm³ were reported (see Figure 21). Since then VLN has been implemented in 13plants by MARTIN GmbH. (MARTIN GmbH N.d.; Process for achieving Very Low NOx (VLN) 2009.)



Figure 21. VLN's systems performance with and without SNCR (Gohlke 2012)

4.6 SYSAV recycling centre, Malmö, Sweden, SCR

The SYSAV Recycling Centre receives municipal waste from 14 municipalities. These wastes are handled in the Malmö WTE plants. The SCR system is in use to tackle NOx emissions at the Malmö WTE plants. It is used together with the primary reduction methods in order to gain better DRE. 50mg/Nm3 has been reported, and the same numbers come from the Salmisaari plant in Finland. SYSAV uses addition of RFG in the secondary air. (SYSAV`s waste to energy plant, N.d.)



Figure 22. SYSAV in Malmö, Sweden (SYSAV's waste to energy plan, N.d.)

5 Riihimäki production facility

The Riihimäki's production facility delivers district heating and electricity to the people and the properties in Riihimäki and Hyvinkää area. Production in Riihimäki is CO₂ neutral. (Fortum Riihimäki, N.d.)

5.1 Production units at Riihimäki

5.1.1 Grate1 (55MW)

Grate 1 burns mainly municipal waste, which is sorted at the source. In addition, industrial wastes are burned on the grate. Wastes are delivered to the waste bunker, where the waste are mixed via a crane. The crane feeds the waste to the chute, which is then dispensed to the furnace via stokers. Waste burns in the grate, and at end of the grate, bottom ash and unburned materials such as metals drop to the extinguishing. In addition, the metals are collected and separated from the bottom ash. The boilers fist pass contains the SNCR equipment which distribute aqueous ammonia to the boiler.

After the fourth pass flue gases leave the boiler to the spray dryer (see Figure 23). After the dryer particles are separated at the electrostatic precipitator. Next the flue gases, go through a heat exchanger to a specific temperature that the wet scrubbers require. The wet scrubber is two staged. In the first stage HCL and HF are absorbed by water, HCL and HF becomes ionized. Calcium hydroxide (aka slaked lime) is added to the washing liquid, the calcium hydroxide dissolves and captures the ions from the "washing liquid", slurry is removed or recycled from bottom of the washer, based on the PH-measurements.

At stage two, the sulfur is absorbed from the flue gases. The slaked lime is also added to the second stage. In addition, it reacts with the sulfur, forming calcium bisulfate Ca(HSO3)2. Lastly calcium bisulfate is oxidized into calcium sulfate CaSO₄·2H₂O this is also known as gypsum. The gypsum slurry is removed from bottom of the washer. After second stage the flue gases are reheated and directed to the bag house. Before the bag house lime and activated carbon are added to the flue gas duct. The slaked lime together, with the activated carbon gets stuck on the fabric filter bags where it adsorbs dioxins, furans and mercury. Lastly the clean flue gases are directed to the stack.



Figure 23. Layout for grate 1 and it's flue gas cleaning (Fortum N.d.)

5.1.2 Grate 2 (35MW)

Grate 2 handles the wastes in a similar way as grate1, but the flue gases are treated with the NID reactor (Novel Integrated Deacidification). Method does not produce any waste waters. The reactor is located as part of a flue gas duct and it has two parts: extinguisher and mixer. Calcium hydroxide is formed in the extinguisher and calcium hydroxide is reacting with the acids from the flue gas. Particles are separated and gathered from the baghouse. Stack wet scrubber washes any leftover particles from the flue gas.

5.1.3 Rotary kiln (20MW)

Main components are a rotary kiln and a secondary combustion chamber. The kiln has high temperature of 1300°C, where wastes are volatilized and oxidized. These compounds exit the kiln to the secondary combustion chamber (SCC), where additional oxygen completes the combustion. After the SCC, flue gas is directed to the boiler where heat is recovered. Flue gas treatment is similar to grate 1 FGT system. In addition, of three staged reactor and filter press for slurry handling from the scrubbers.

5.2 Fuels

Fuel NOx plays the most comprehensive part then talking about nitrogen oxides. According to EAA (Nitrogen oxides emissions, 2018) up to 80% of the nitrogen oxides are formed from the fuel bound nitrogen. At the Riihimäki`s grates fuel mixing is done for the waste to ensure proper mixing. The main fuels for the grates are municipal wastes, which are delivered daily to the waste bunkers. Construction waste is also incinerated at the grates. Furthermore, hazardous wastes are incinerated at the grates. In the fuel department NOx reduction cannot occur since the fuel type is municipal. The municipal waste contains 0,5%-5% fuel bound nitrogen. However, with the right burning conditions thermal NOx formation can be controlled.

In the hazardous waste incineration (hazardous waste to energy, HWTE), fuel bound nitrogen is still a significant problem. The hazardous wastes contain overall less fuel bound nitrogen, but the variations in the amounts are more significant compared to municipal wastes. The fuel bound nitrogen can change a lot in HWTE, when burning fuels with impurities such as waste oil, crude oil and when supporting the incineration with a heavy fuel oil. The thermal NOx has insignificant impact even at 13001400°C. In HWTE fuel mixing is also important, to ensure proper mixing of the fuels, thus avoiding high concentrations of sulfur and chlorine. Lowering the temperature is not an option in HWTE, since the temperatures high enough need to be maintained to fully decompose the wastes.

5.3 State and performance of the current SNCR systems

Before the SNCR systems can be evaluated burning conditions need to be set. Burning conditions can be roughly divined into summer and winter times, due to varying fuel properties. As burning low calorific value fuels temperature of the furnace stays at the lower end. Causing the boiler temperatures to be lower. In the summer times calorific value of the fuel is higher. The average values in the summer are between 11kJ/kg and 15kJ/kg. However, these values are from 8kJ/kg to 11kJ/kg in the winter times.

Each of the SNCR-systems are evaluated below. The values to calculate the efficiencies comes from the process history data. Tests were performed to get the Nitrogen Oxides values without the SNCR-system. The half hour limit values intervened with the test. Thus, reducing the test time to a very brief time window. This gives an indication of the NOx levels without any secondary abatement methods.

5.3.1 Grate 1

Grate 1 SNCR system keeps the NOx levels down at 160-200mg/Nm³. In a boiler there are two planes for the ammonia distribution (see Appendix 3) and each level have five injection points. Two of the injection points are on each side of the boiler, the left and the right side of the boiler. The stoker side (aka. front wall) has one injection point. Injection lances are directed downwards in an angle, this causes the droplets to go down stream. Furthermore, amplifying the temperature, since the droplets are not cooled going upstream. Top of the boiler in first pass has two more points for injection, these are only active when the level one is in use. Only one injection point is in use at each boiler wall, due to lack of pressure when using all seven lances at once (level 1 and top of the boiler lances). Thus, limiting the possible coverage that could be provided via the SNCR system. The levels are controlled by the temperature. Level two is rarely in use, due to inadequate boiler temperature. The level one is mainly used when the boiler is at full load. Any ammonia slip is absorbed in the wet scrubber when ammonia is in contact with water. The emission monitoring in the stack is controlling the ammonia injection to the boiler. The composition is slow to react for any kind of chances in the process due to the time between the stack measurements and the injection point. Injection lances are cleaned regularly to keep the nozzles clean. Reduction values for the system can be calculated from formula 14:

$$\eta_{SNCR} = \frac{S_1 - S_2}{S_1}, \%$$
(14)

where, S1- concentration of NOx in flue gas, without the SNCR system, % and S2concentration of NOx in flue gas, with the SNCR. See Appendix 1 for s1, s2 values.

$$\eta_{SNCR} = \frac{(310 - 176)}{310} \frac{(\frac{mg}{Nm^3})}{(\frac{mg}{Nm^3})} = 0,432 = 43\%$$

For grate 1 DRE value of 43% can be calculated from the estimated values from appendix 1 with current lance setup and a setpoint of 180mg/Nm³ for the SNCR. While burning low calorific value fuels in larger quantities temperature between the first pass and the furnace is lower than with the high calorific value fuels. With the higher calorific value fuels the temperatures closer to 1000°C can be seen at the end of first pass. Consequently, the temperatures at SNCR levels 1 are around 1050°C. In the winter temperatures are slightly lower. Due to the low calorific value fuels, the temperatures are closer to 950°C at the end of first pass, and 1000°C at the SNCR level 1. For further description see appendix 3 for lance positioning.

5.3.2 Grate 2

Grate 2 has the SNCR system with the same function as grate 1. Injection points are in better positions than in Boiler 1. Lowest injection points are not in use since they are too close to the primary combustion zone. Thus, being always in non-preferable temperature ranges. Grate 2 has a different lance design. Lances are perpendicular to the boiler walls and the nozzle is pointing away from this surface within 30° angle. (see appendix 4) Direction for the nozzles can be set manually, when placing the lances to the boiler. Locations of the lances are in better positions and there are more injection points compared to the grate 1. There are two main levels for the system and each level has 8 injection points, four at front wall and two on each side. Wear from the heat and ammonia can block the lances. Grate 2 has OFA (see Section 3.1.3 for more details) and air staging. These tools help to cool the boiler for better SNCR ranges. In addition, providing lover raw NOx values. Reduction efficiency of the SNCR system can be determined with the same formula (14) than previously:

$$\eta_{SNCR} = \frac{S_1 - S_2}{S_1}, \%$$
(14)

where, S1- concentration of NOx in flue gas, without the SNCR system, % and S2concentration of NOx in flue gas, with the SNCR. See Appendix 1 for s1 and s2 value determination. For the grate 2 DRE value of 29% can be determined with negligible ammonia slip of 0-0,5 mg/Nm³, with the setpoint of 180mg/Nm³.

$$\eta_{SNCR} = \frac{(242 - 172) \left(\frac{mg}{Nm^3}\right)}{242 \left(\frac{mg}{Nm^3}\right)} = 0,289 = 29\%$$

For grate 2 temperatures in the first pass are lower than in grate 1. This allows the SNCR to work in more favourable ranges. The first pass temperature at the higher SNCR levels is around 900°C, which is to the lower end of the efficient temperature range, when considering the cooling in the boiler while injecting the reagent.

5.3.3 HWTE1

The rotary kiln's SNCR system is in minor use, due to the low NOx concentrations in the stack. In addition, depending on the current temperature and fuels, values around 80-200mg/Nm³ are seen, while accumulation for the NOx is 107mg/Nm³. The current systems injection lances are poor. Lances are direct pipe which points at the centre of the flue gas duct. There are two injection points on each side of the flue gas duct and on each side only one of them is in use. Long lances help to avoid the

colder walls of the secondary combustion chamber (SCC). The temperature points for these lances can be measure with a thermocouple. This can help to understand is it even efficient to renew the system due to the ammonia decomposition in excessive temperatures. However, based on the closest temperature measurement (T-1533) the flue gas temperatures can be expected to be around 1050°C.

6 Approaches for reducing Riihimäki's NOx emissions

The easiest and the most cost-efficient way to reduce NOx at Riihimäki is to utilize the possible methods that will not require any additional technology. These are the primary methods (see Chapter 3). Another choice is to improve the current SNCR for better performance (see Chapter 3.3.3). The goal is to create more favourable burning conditions at the grate, which promotes NOx deformation and creates better conditions for SNCR.

6.1 Grate air flow

- 1. Reducing the total excess air reduces the available oxygen. Thus, it hinders the NOx formation (see Figure 2).
- 2. Increasing secondary air flow for better mixing and increasing the residence time. The secondary air cools the flue gases. Increase in temperature in **oxygen rich** (λ >1) conditions increases NOx formation.

An insufficient amount of air increases the risk for unburned materials, which increases boiler soot. Increase in CO is a risk if the air is diluted poorly. Fuel drying can be hindered if the primary air is reduced from the early stages of the grate. This can become a major issue with low calorific fuels. The expected outcome is reduced NOx formation with small increase in CO, and with increased secondary air better mixing is acquired. In addition, gaining better temperature profile.

6.2 Air preheating

Reducing or not preheating the air causes the incineration temperature to drop. Thus, reduces the overall temperature in the whole boiler. The main problem in MWI is the variable fuel composition. This can cause serious problems with fuel drying. A reduced thermal load can help the SNCR-system to work on more efficient levels. This can be helpful with grate 1 since the temperatures for SNCR are around 1050°C. At this point efficiency starts to decrease rapidly and ammonia starts to oxidize.

6.3 The possibilities with the SNCR

One of the options with the SNCR system is to introduce more reagent. In addition, to monitoring the ammonia slip, it increases the Normalized Stoichiometric Ratio (NSR). By lowering the set point for NOx reduction, the SNCR starts to distribute the reagent more rapidly. When monitoring the ammonia slip and reagent injection, it can be determined if the system is able to reduce nitrogen oxides formation. However, the ammonia slip needs to be monitored in order to avoid boiler contamination and the formation of harmful salts. Risks for increased NSR are increased ammonia concentrations, which can increase oxidation to ammonium bisulphate (NH₄)HSO₄ and other unwanted compounds. The ammonia slip needs to be monitored in order to be monitored in order to find a good value for NOx reduction with an acceptable ammonia slip. The expected changes are increased aqueous ammonia consumption, reduced NOx levels and increase in the ammonia slip (see Table 3). This option viable method for the grate 2 due to the good temperature ranges and sufficient coverage.

6.3.1 SNCR in HWTE1

As seen in the Figure 24, the HWTE1 SNCR system does not serve its purpose in NOx reduction. Lack of injection points causes insufficient reagent dilution and coverage. This can be seen from the massive spikes in the reagent flow with relatively small increase in NOx (see Figure 24). In addition, to massive reagent flow increases (purple) in higher NOx increases. With the implementation of new lances which are directed along the flue gas flow can help to cover a larger area from the flue gases.



Figure 24. Weekly NOx values and reagent consumption for HWTE1 facility

By directing the flow downstream, the reagent has time to react. Furthermore, this causes cooling before reacting in the flue gases. Effects of time on the residence time can be seen in Figure 26. Directing the injection directly towards the flue gases can reduce the residence time, which can help to improve the SNCR efficiency by forcing the reagent to contact with the flue gases. However, the best results are gained with long residence time and lower flue gas temperatures.



Figure 25. Temperature's effect on reduction efficiency at different residence times (Sorrels 2015, adapted)

6.4 Implementation of catalytic filter bags

Catalytic filter bags are an affordable option for NOx control. The main cost comes from implementing ammonia injection before the baghouse. The system is easy to retrofit into the existing baghouses. Catalytic layers have a longer lifespan than the typical filter bags which are used to remove the particles. A regular filter bag protects the catalytic filter bag, since dust and corrosive materials are absorbed by the regular filter bags. In some cases, ammonia injection is not needed, because in the absence of wet scrubbers', the ammonia slip from the SNCR can be used as a reagent for the catalytic filter bags. In addition, the bags can serve an important role for removing ammonia slip.

Catalytic filter bags are thin, which makes the pressure drop from minimal to negligible. This is another reason why the catalytic filter bags are an available option for use. The low pressure drop means that the filter bags do not intervene with the draught fan power requirements. Operating costs for the catalytic filter bags are low, because most of the cost comes from the reagent and replacement of filter bags in case of a bag rupture.

6.5 SNCR/SCR

Selective Non-Catalytic Reduction might not be considered the Best Available Technology in its current state. However, the system with additional measures can be easily considered BAT, such as AGAM. These systems bring SNCR-systems up to date, which can be an alternative option for retrofitting into Riihimäki. The main concerns with retrofitting will be extensive boiler modification. These can be time-consuming and expensive due to the need for stoppage while making the modifications. Overhaul would not affect the rest of the process, and it would not require additional space.

Selective Catalytic Reduction can be considered BAT. The main concerns with SCR are the need for space and massive pressure drop within the catalyst. Retrofitting the catalyst would mean that it needs modifications in the ducts and enough space for the catalyst. The SCR system has high capital costs and high operational costs which makes the option undesirable. SCR would fit better if a massive reduction in NOx was necessary.

6.6 Very Low NOx /Flue Gas Recirculation

Very Low NOx is a viable option for the NOx reduction method. It requires a moderate number of changes to the boiler and requires minimal space for implementation. The VLN system would support the existing SNCR-system by reducing the temperature differences around the boiler, thus reducing the hot and cold spots in the boiler and allowing the SNCR-system to operate more reliably and with less fluctuation in temperature. The overall air values are not affected since the secondary air is partially replaced by VLN gas.

Flue Gas Recirculation would benefit low excess air burning, since it can help to dilute the oxygen above the grate by reducing the temperature and mixing the flue gases for a more even stream. Moreover, it reduces overall oxygen levels and carbon dioxide formation. Unburned particles together with carbon dioxide can cause issues in the boiler if proper oxygen levels are not preserved. FGR has moderate costs and decent NOx reduction potential, but it requires comprehensive changes to the boiler.

6.7 Water/steam injection

Via water or steam injection calories can be diluted more effectively. This helps to reduce temperature in the areas where it is not convenient. The injection helps air to dilute properly in the primary combustion zone, especially when excess air is kept at a minimum. The temperature decreases, creating more favourable conditions for NOx reduction in the secondary combustion zone and it helps the SNCR-system to stay in the preferable ranges when using the boiler at the maximum load. The injection hinders the boiler efficiency to an extent. The DRE values are similar to FGR.

7 Conclusions

The Goal of the study was to get an understanding of nitrogen oxides abatement methods in energy from waste. In addition to better understand the problems with nitrogen oxides, formation methods, effects on human health and to the environment were introduced. The goal was to find the best options for reducing Nitrogen oxides emissions in Municipal Waste Incineration. Hazardous Waste Incineration unit was also looked at, but the focus was to find out the best possible methods for NOx abatement in MWI. Existing SNCR systems are evaluated briefly by calculating their efficiency based on the data from tests. Result from these tests cannot be very accurate, due to the compliance to the NOx limit values. Tests were very short, so the process state mattered a lot (e.g. low calorific fuel). Test were done three times in different weeks to get representative results.

The result from the tests without SNCR-system showed the effectives of the OFA and lower temperature in the end of first pass. This can be seen as 30% lower NOx output from the grate 2 without any additive abatement systems. To get more accurate results the system would have been of for a few times for a fixed amount of time. Best result for abatement system is difficult to conclude, since there is no information about desired NOx levels. However, the 150mg/Nm³ (see the Table 3.) can be used as a desired level. In this thesis minimal modifications and impact on the process were considered as a best option.

For grate 1 additive methods should be considered, which would assist the SNCRsystem to gain a better efficiency range and mixing. The method should be effective at reducing temperature and diluting oxygen more efficiently. Very Low NOx or water/steam injection would fit this purpose. Since they would have minimal effects on the overall process. With water or steam injection the reduced overall excess air needs to offset the load which the water/steam add to the draught fan. Due to the draught fan power limitation. However, focus should be to retrofit the SNCR pumps to gain desired coverage with the 7lances. This would mean that ammonia will be distributed more evenly, and the overall flow in water would off sett the higher end temperature of the first pass. Levels one lance positions can be also changed to face upwards instead of downwards. This would allow the ammonia to go upstream and the temperatures effects would be reduced when going along with the flue gas.

Grate 2 should be able to meet NOx values of 150mg/Nm3 with the current SNCR system. However, this need to be confirmed with prolonged boiler tests. Preferably in summertime then the boiler is dirtier, and the temperature is in the higher end with high calorific value fuels. This would require the boiler ammonia measurement to be fixed. Since determining the ammonia value before NID will be hard, without the proper measurement. In case of higher reduction is desired the catalytic filter bags would be the optimal solution for the grate 2, since the semi dry flue gas treatment and the ammonia slip from the SNCR can be used without needing any additional injections. Values under 100mg/Nm³ can be expected.

Reformation of the HWTE1's SNCR system should be sufficient to limit the NOx level fluctuation and reduce overall NOx values. Slurry of powdered limestone can be introduced to the boiler to reduce NOx. This would mean an increase in dust before the electrostatic precipitator.

References

27.6.2014/527. Ympäristönsuojelulaki [Environmental Protection Act], N.d., Referred 14.10.2019

https://www.finlex.fi/fi/laki/ajantasa/2014/20140527#L

A full-scale carbon capture and storage, N.d., Project in Norway, Oslo, Referred 19.11.2019 https://www.fortum.com/media/2018/11/full-scale-carbon-capture-and-storage-ccs-project-initiated-norway

A review of Catalytic Combustion, 1984, journal archive, Referred 15.10.2019 https://www.technology.matthey.com/article/28/1/12-12/

Air pollution control technology fact sheet, N.d., Referred 22.10.2019 https://www3.epa.gov/ttncatc1/dir1/fscr.pdf

Air pollution control, 2013, technology, Referred 5.11.2019 http://www.mcilvainecompany.com/Universal_Power/Subscriber/PowerDescriptionLinks/Craig%20Sharp,%20Haldor%20Topsoe%20-%209-19-13.pdf

BAT, N.d., BREF's and BAT conclusions, EPA, Referred 2.12.2019 https://www.epa.ie/licensing/info/bat/

BAT REF, 2018, Waste Incineration, referred 4.11.2019 https://eippcb.jrc.ec.europa.eu/reference/BREF/WI/WI_BREF_FD_Black_Watermark.pdf

Biology, N.d., Pollutions and pollutants, Referred 18.11.2018 https://biologyeducare.com/pollution-and-pollutants/

Bonnenberg & Drescher, N.d., SNCR, Referred 20.11.2019 https://www.budi.de/en/denitrification.html

Burners out of service, N.d., Referred 18.10.2019 https://www.etecinc.net/BOOS-Background/#.Xagb-X9S-UI 15

CATC, 1999, Bulleting from nitrogen oxides, PDF, Referred 7.10.2019 https://www3.epa.gov/ttncatc1/dir1/fnoxdoc.pdf

Clean coal technologies, N.d., Air staging, referred 15.10.2019 https://www.iea-coal.org/air-staging-for-nox-control-overfire-air-and-two-stagecombustion/

Council Directive 96/61/EC, 1996, concerning integrated pollution prevention and control, referred 3.12 https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31996L0061:en:HTML DyNOR, 2010, Performance confirmed in further plants, Referred https://pdfs.semanticscholar.org/b56a/6c37dd6eb233eab8ff8e9308a25c3556975e.pdf?_ga=2.1165065 66.1157704417.1573195733-1932193446.1572333046

Energy and fuels, 2016, Simplified method for calculating SNCR system efficiency, Referred 12.11.2019 https://www.e3s-conferences.org/articles/e3sconf/pdf/2017/02/e3sconf_ef2017_02003.pdf

Energy from waste, 2012, Transitions in combustion efficiency and NOx control, Referred 7.11.2019 http://www.hz-inova.com/cms/images/stories/pictures/Waste_Management_Energy from Waste Clean efficient renewablex.pdf

European Environmental Agency, N.d., Air quality standards, Referred 14.10.2019 https://www.eea.europa.eu/themes/air/air-quality-standards

Fortum Riihimäki, N.d., Riihimäen tuotantolaitos [Riihimäki`s production facilities], referred 12.12.2019 https://www.fortum.fi/tietoa-meista/yhtiomme/energiantuotantomme/voimalaitoksemme/riihimaen-tuotantolaitos

Fortum, N.d., services, Referred 19.11.2019 https://www.fortum.com/

Gohlke, Oliver, Weber, Toralf, Seguin, Philippe, Laborel, Yann, 2010, NOx reduction methods and fundamentals, 1348-1354, PDF, Referred 8.10.2019 https://www.sciencedirect.com/science/article/pii/S0956053X10001108

GORE filtration products, N.d., MSWI France, Referred 6.11.2019 https://www.gore.com/sites/g/files/ypyipe116/files/2017-10/GORE-DeNOx-FilterBags-CaseHistory-Limoges.pdf

Hailing, N.d., products, Referred 10.11.2019 http://hlcoppertube.com/6-2-plate-type-catalyst/

Happamoituminen [Acidification], N.d., Referred 9.10.2019 http://www.edu.helsinki.fi/malu/kirjasto/mbl/kemia/happamoituminen.htm 4

Ilmatieteenlaitos [Weather Institute], N.d., Otsoni [Ozone], Referred 11.10.2019 https://ilmatieteenlaitos.fi/otsoni-ilmansaasteena

Influence of temperature on NOx formation, 2015, PDF, Referred 2.12 http://www.ees.uni.opole.pl/content/04_15/ees_15_4_fulltext_08.pdf

Joseph, J., Santoleri, Joseph, Reynolds, Louis, Theodore, 2nd ed. 2000. Introduction to Hazardous Waste Incineration, Wiley Interscience: publications

Kansallinen ilmansuojeluohjelma 2030 [National climate protection program] N.d., Referred 15.10.2019 https://julkaisut.valtioneuvosto.fi/bitstream/handle/10024/161467/Kansallinen%20ilmansuojeluohjelma%202030.pdf?sequence=4

MARTIN GmbH, N.d., references, Referred 8.11.2019 https://www.martingmbh.de/en/references.html

Matthey, Johnson, 2018, SCR Catalyst technology, Referred 23.10.2019 http://unia-ups.pl/wp-content/uploads/2018/11/SCR-catalysttechnology_15102018.pdf

Maxwell, Richardson, Mentzer, Lee, 1999, Solid sorbent control of NOx, Referred 21.10.2019 https://apps.dtic.mil/dtic/tr/fulltext/u2/a364151.pdf

M.A. Gomez-Garcia, V. Pitchon, A. Kiennemann, 2005, NOx abatement by sorbing catalytic materials. Referred 30.10.2019 https://www.sciencedirect.com/science/article/pii/S0160412004001503?via%3Dihub

Nitrogen oxides emissions, 2018, Referred 18.11.2018 https://www.eea.europa.eu/data-and-maps/indicators/eea-32-nitrogen-oxides-noxemissions-1/assessment.2010-08-19.0140149032-3

Non-Thermal Plasma, N.d., Referred 24.10.2019 https://www3.epa.gov/ttncatc1/dir1/fnonthrm.pdf

NOx removal with NTP, 2012, Referred 25.10.2019 http://www.iesj.org/content/files/pdf/IJPEST_Vol6_No1_13_pp074-080.pdf 23

NOx formation, N.d., Overview and Limitations, Referred 8.10.2019 http://jullio.pe.kr/fluent6.1/help/html/ug/node621.htm

Otto, Hänninen, Antti, Korhonen, Heli, Lehtomäki, Arja, Asikainen, Isabell, Rumrich, 2016, Ilmansaasteiden terveysvaikutukset [Health effects of air pollutions], Ympäristöministeriö [Ministry of environment], PDF, Referred 10.10.2019 https://julkaisut.valtioneuvosto.fi/bitstream/han-dle/10024/74861/YMra_16_2016.pdf

Process for achieving Very Low NOx (VLN), 2009, Referred 28.10 http://www.seas.columbia.edu/earth/wtert/sofos/nawtec/abstract/nawtec17/nawtec17-2372.pdf

Severnside, N.d., Energy recover centre, Referred 7.11.2019 http://www.hz-inova.com/cms/wp-content/uploads/2016/10/Severnside_Online_E.pdf SNCR Process, 2008, Best available technology for WTE NOx reduction, Referred 7.11.2019 https://www.ms-umwelt.de/wp-content/uploads/downloads/denox/en/SNCR-Best Available Technology for NOx Reduction in Waste To Energy Plants.pdf

Sorrels, John L., 2015, Selective Noncatalytic Reduction, Referred 22.10.2019 https://www3.epa.gov/ttnecas1/models/SNCRCostManualchapter_Draftforpubliccomment-6-5-2015.pdf

Summary of NOx control methods, 1992, Referred 17.10.2019 https://nepis.epa.gov/Exe/ZyPDF.cgi/00002HPV.PDF?Dockey=00002HPV.PDF

SYSAV's waste to energy plant, N.d., Operations overview, Referred 11.11.2019 https://www.sysav.se/globalassets/media/filer-och-dokument/informationsmaterialbroschyrer-arsredovisningar-faktablad-rapporter-etc/broschyrer-och-arsredovisningar-pa-andra-sprak/heat-and-electricity-from-waste.pdf

The Formation of NOx, N.d., Effect of temperature, Referred 9.10.2019 https://www.alentecinc.com/papers/NOx/The%20formation%20of%20NOx_files/The%20formation%20of%20NOx.htm

United states patent, 1984, catalytic filter house bags, referred 5.11.2019 https://patentimages.storage.googleapis.com/dc/31/4f/9678f64bebe8f4/US4309386.pdf

Walling, Cheves T., N.d., Radicals, Referred 19.10.2019 https://www.britannica.com/science/radical-chemistry

Water or steam injection, N.d., Referred 16.10.2019 https://www3.epa.gov/ttnchie1/mkb/documents/B_17a.pdf

WI BAT conclusions, N.d., PDF, Annex, Referred 1.12.2019 https://eippcb.jrc.ec.europa.eu/reference/

Ympäristöministeriö [Ministry of Environment], 2019, National Air Pollution Control Programme 2030, Referred 15.10.2019 http://julkaisut.valtioneuvosto.fi/bitstream/handle/10024/161701/National%20Air%20Pollution%20Control%20Programme%202030.pdf?sequence=1&is-Allowed=y

Appendices

Appendix 1. NOx values for facilities with and without SNCR

Average NOx values with SN	CR and setpoint of 180mg/Nm ³ (s2)
----------------------------	---

	November 18	December 18	January 19	May 19	June 19	July 19	AVG	
Grate 1	182	170	180	170	179	179	176	mg/Nm3
Grate 2	166	170	163	203	166	167	172	mg/Nm3
HWTE 1	104	99	110	Maintenance	116	113	107	mg/Nm3

Average NOx values without SNCR (s1)

NOx without					
SNCR	13.11.2019	25.11.2019	16.12.2019	Total avg	
Grate 1	335	274	322	310	mg/Nm3
Grate 2	253	251	221	242	mg/Nm3

Appendix 2. Grate 1 & 2 temperatures

	Furnace 1	Pass 1 end, 1	SNCR 1 lvl1	Furnace 2	Pass 1 end, 2	SNCR 2
May 2019	1091	954	1036	1157	973	980
June 2019	1060	924	1006	1140	940	940
July 2019	1070	940	1018	1131	950	950
avg	1074	939	1020	1143	954	957
November 2018	1138	990	1079	1110	940	940
December 2018	1100	970	1048	1099	933	940
January 2019	1072	940	1019	1096	935	940
avg	1103	967	1049	1102	936	940
May 2018	1117	991	1067	1063	890	890
June 2018	1100	960	1044	1022	844	850
July 2018	1118	972	1059	1080	900	900
avg	1111	974	1057	1055	878	880
November 2017	1056	921	1002	1086	912	920
December 2017	1048	913	994	1064	891	900
January 2018	1093	954	1038	1013	851	860
avg	1066	929	1011	1054	884	893
avg total	1089	952	1034	1088	913	918







