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Full-scale NOx reduction experiments at Norcem Brevik

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Abstract:

The NOx reduction system installed at Norcem Brevik is based on the SNCR technology. It was installed in 2012 and substantial reduction of NOx has been achieved. However, it has never been performed experiments or optimizations of the system. SNCR technology is based on injection of a nitrogen-containing reduction agent, in this case ammonium hydroxide, to reduce the NOx concentration within the required temperature range, 1100-1400K (827-1127^{o}C).

The developed experiments were based on finding an optimal consumption of ammonium hydroxide and effective prescriptions combined with a fuel experiment, divided into two separate tests. During the experiments it was required to maintain a stable process in terms of raw materials, fuels, temperatures and flue gas. Stable conditions were maintained during the first test while at the second test disturbances occurred. The consequences were that the experiments had to be limited by excluding the planned fuel experiment.

The temperature profile at Norcem is very low according to the SNCR technology and at one occasion the temperature dropped down to 820^{o}C. As expected, the NOx concentration raised to a very high level. This confirms that the temperature is a very sensitive factor related to NOx reduction.

NOx is reduced to a greater extent by injecting a larger amount of ammonia. There was found an economical-based optimum amount of ammonia at 150l/h and a reduction efficiency of 46.2%.

The most effective nozzle combination obtained was three activated nozzles at only downstream of the precalciner with a reduction efficiency of approximately 40 %.

The ammonia-slip depends upon two main parameters; amount of ammonia-injected and NOx concentration. Increased flow of ammonia caused increased ammonia-slip. When NOx was reduced to a lower level than 100mg/Nm^3, ammonia-slip was rapidly increased.

Maintaining an average flow of ammonia at 150l/h leads to a NOx concentration in the range of 150-175mg/Nm^3 and a cost of 1.735MNOK/year. This is based on standard clinker production and is expected to be different when producing other types of clinker.

Expenditure of ammonia was compared with corresponding NOx taxes. An optimum of 280l/h where found. At a higher average consumption than 280l/h it will be more profitable to pay taxes. This requires that NOx emissions are at the same level, about 190ton/year. This indicates a maximum expenditure of 3.2MNOK/year.

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Preface

This master thesis is based on collaboration between Telemark University Collage and Norcem AS, Brevik.

As the title states, the aim of the master thesis is to optimize the NOx reduction system installed at Norcem Brevik by executing full scale experiments. The problem definition is further described in the first chapter as well as in the task description that is attached in Appendix A.

It is not required that the reader should be familiar with the cement production and NOx generation but it would be an advantage to have chemical and process background.

Tools used during the experiments: Aspen Process Explorer, MS Excel, MS Visio (drawings), the management system VisionTech (Siemens) and access to Norcem`s database.

I would like to give a special thanks to Ida Husum and Arnstein Jacobsen representing Norcem Brevik. I am so grateful for daily communication and help from Ida. According to the implementation of the experiments, Arnstein has been very helpful. They have been giving me training, access and facilitation of the experiments. I want to thank the shifts for their understanding and cooperation during the plant test. Last but not least, thanks to my supervisor Lars-Andre Tokheim that has consistently made useful contributions during the progress of this master thesis.

I am very grateful that Norcem gave me the opportunity to perform experiments in full-scale and for being so generous to give me free access to an office, computer and help.

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Porsgrunn

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Nomenclature

Abbreviations

NOx	Nitrogen Oxides
TUC	Telemark University Collage
FAB	Processed waste fuel (Norwegian)
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction
FGR	Flue Gas Recirculation
LNB	Low NOx Burners
BOOS	Burners Out Of Service
LEA	Less Excess Air
OFA	Over Fire Air
FR	Fuel Reburning
BZT	Burning Zone Temperature

1 Introduction

Today`s society is based on very well-developed technologies, utilized within the industry. In recent time the focus of the environment has increased since the environmental status nowadays is completely different than it was some decades ago. Industrialization and the development of the society are major reasons of the problems. Climate changes in the world are one of the most serious challenges today and there is great focus on global environmental problems that is often solved internationally. There are many factors that contribute to environmental damages and therefore it is important to develop new technologies for an environmentally future.

1.1 Background

The production of clinker and cement[1] is a well-known process. Briefly summarized this process is based on grinding of raw materials, clinker and cement production. The raw meal is a combination of limestone and other minerals. Raw meal is preheated in a cyclone tower and even more heated in the precalciner[2]. Gradually the meal is calcined and it converts into clinker at a very high temperature during the resident time in the rotating kiln. Hot clinker is rapidly cooled down in a cooler, outlet of the kiln and then storage. By producing the cement, clinker is grinded and some additives are added in various amount determined by the type of cement produced.

Since this is an energy intensive process, it contributes to large amounts of polluted emissions. The polluted components in the flue gas are based on the calcinations in the process and the combustion of fuels. The calcinations process is the reaction that happens to the raw meal when high temperature is achieved; carbon dioxide is released from the limestone. The combustion process is due to extremely high temperatures required in the rotary kiln. Fuel consumption is a mixture of coal, oil and alternative fuels. The consumption of alternative fuels has increased recently. The composition of pollution in the flue gas depends on the fuel combination but mainly the flue gas exists of nitrogen, carbon dioxide, water (vapor) and excess oxygen. Also it contains a small percentage of other pollutants like carbon monoxide, nitrogen oxides and sulfur oxides.

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[1] The production of cement are here referred to as Portland cement which is produced by burning a mixture of specific amounts of lime and clay and then grinding the clinker arising with a certain portion of gypsum to produce cement [1].

[2] Norcem use the most modern cement production technology; preheater with precalciner, described in further detail in 3.1. Other principles are also available.

There are emission limits for most components to restrict current levels. Because of these limitations, measures must be implemented to reduce pollutant emissions.

At Norcem AS, Brevik there has been installed reduction systems for both sulfur oxides and nitrogen oxides. Currently, there is also an ongoing carbon dioxide project to test four different carbon dioxide capture technologies with the intention to find an optimal technology for full-scale CO_2 reduction suited to cement kilns.

The NOx reduction system was installed in 2011/12 and is based on the selective non-catalytic reduction (SNCR) technology. After startup in August 2012 the system has provided a significant reduction. The goal of achieving a reduction of approximately 65 % on an annual basis has been reached. The system has been operated automatically since the installation and it has not been further optimized.

1.2 Problem definition

Optimization of SNCR systems could be based on economy, emission levels, removal-efficiency and minimizing the negative factors like CO or a combination of all these.

By performing experimental tests, it will be possible to find an optimal way to operate the system. The most optimal process would be; Increased removal efficiency, avoid increased emissions of ammonia (NH_3-slip), reduce the ammonia consumption, and avoid increased emissions of other components like TOC and CO. It must be taken into account which type of fuel that is consumed and type of clinker produced.

This chapter provides an introduction to important topics which is described in greater extent in the following chapters. Chapter 2 describes the general NOx formation and the characteristics for NOx formation in the cement production. There are several methods to produce cement, this is explained in chapter 3 as well as a detailed description of Norcem`s process. Chapter 4 contains a description of the design and planning of the experiment. Here is also part of the implementation plan added. Chapter 5 presents the results from the implemented full-scale experiments. The results are mainly shown in charts. Discussion of the experiments and suggestions of further work are given in chapter 6. Finally, in chapter 7 the conclusion of the report is given.

2 Basic NOx theory

NOx is essentially eliminated by combustion processes, especially at high temperatures. NOx reacts to form photochemical smog formation, acid rain and increased concentrations of ground level ozone as well as destruction of the stratosphere. Emissions of NOx can cause damaging effect on the vegetation and also result in adverse health [2].

Global emissions of NOx have increased over the past years and the main reason for this is combustion of biomass and fossil fuels. Because of these increasing trends there have been implemented restrictive NOx emission regulations in most of the industrialized countries. It has also driven the development of NOx to a new level because of stricter regulations. Today this technology is improved significantly and there are several technologies for reduction of NOx [3].

2.1 General NOx formation

Nitrogen oxides are basically formed by the reaction between nitrogen and oxygen present in the air in a combustion process. Nitrogen can form totally seven oxides, listed in Table 2-1.

Only three of the nitrogen oxides are important for combustion processes; NO, NO_2 and N_2O, where only the two first are referred to as NOx. From these nitrogen oxides, around 95 % of the generated NOx is NO and the fraction of NO_2 is less than 5 % [2]. A very small amount of N_2O (laughing gas) can also be generated. The formation of NOx is an endothermic reaction, requiring high temperatures which are obtained from the combustion process.

Table 2-1 Nitrogen oxides [4]

Formula	**Name**	**Properties**	**Health/Damage Effects**
N_2O	Nitrous oxide	Colorless gas Water soluble	Used as anesthetic Destruction of the stratosphere
NO N_2O_2	Nitric oxide Dinitrogen dioxide	Colorless gas Slightly water soluble	Acid rain / Smog formation
N_2O_3	Dinitrogen trioxide	Black solid Water soluble, decomposes in water	May produce nitrite salts
NO_2 N_2O_4	Nitrogen dioxide Dinitrogen tetroxide	Red-brown gas Very water soluble, decomposes in water	Acid rain / Smog formation
N_2O_5	Dinitrogen pentoxide	White solid Very water soluble, decomposes in water	Strong oxidizer, may form explosives from organic components

All these nitrogen oxides can be solved in water and be decomposed. When that happens, the oxide forms nitric acid (HNO_3) or nitrous acid (HNO_2) which can also form salts. The NOx gases, the acid gases and the salts together contribute to pollution of the air, which together with sulphur are important contributor to acid rain. The most commonly nitrogen oxides in the air is NO, NO_2 and N_2O, where most of the NO oxidizes to NO_2 [2].

The main contributor to NO_2 emissions are traffic, both arising from cars and boats. Often the levels of NO_2 are especially high locally like in urban cities, precisely because of the frequent traffic.

In combustion processes nitrogen oxides formed in the flue gas is primarily NO (<90 %), but are here referred to as NOx to include all nitrogen oxides [3]. NO may be formed through 3 mechanisms; thermal NO, prompt NO and fuel NO.

2.1.1 Thermal NOx

The formation of thermal NOx is strongly temperature dependent and this mechanism is also known as the Zeldovich mechanism and comprises three reactions [3]:

$N_2 + O \rightarrow NO + N$ (2.1)

$N + O_2 \rightarrow NO + O$ (2.2)

$N + OH \rightarrow NO + H$ (2.3)

These reactions appear by oxidation of molecular nitrogen present in the combustion air and are referred to as the extended Zeldovich mechanism [2]. In the present of normal temperatures molecular nitrogen and oxygen are not reacting to form NOx. Reaction (2.1) is the limiting reaction because of the strong triple bond in the nitrogen. [5] This reaction requires high energy supply, preferably a temperature above 1400^{o}C. When the temperature increases, especially from 1600^{o}C and above, the NOx formation is strongly accelerated [2]. The required temperatures are obtained in the combustion process. This mechanism is probably in general the most relevant source of NOx formation and is also dependent on the O_2 concentration and the residence time within the given conditions. [1]

2.1.2 Fuel NOx

This mechanism is based on the conversion of fuel-bound organic nitrogen into NOx during combustion. Even though, the mechanism is weakly dependent on temperature. Through the combustion, the nitrogen in the fuel is released as a free radical which further attacks oxygen molecules resulting in the formation of NOx. The total formation of fuel NOx is dependent on the initial concentration of nitrogen in the fuel and the operational combustion characteristics.

Gaseous hydrocarbons usually not contain any nitrogen but liquid and solid hydrocarbons contain small amounts of nitrogen. Studies based on fuel-N have found that different fuels release nitrogen in various forms. The “age” of the fuel determines how the nitrogen is released. One example is that coal releases nitrogen mainly in the form of HCN while “younger” fuels like peat and wood releases nitrogen mostly in the form of NH_3 [2].

Another important factor in the formation of NOx from fuel-N is the condition of the released fuel-N, whether the fuel is released as volatile nitrogen compound or char-nitrogen compounds.

During the pyrolysis of the fuel, the volatiles-N is released as gaseous cyano and cyanide compounds like HCN and NH_3. Figure 2-1 illustrates the formation paths of nitric oxides from fuel-N, respectively released in the form of HCN and NH_3.

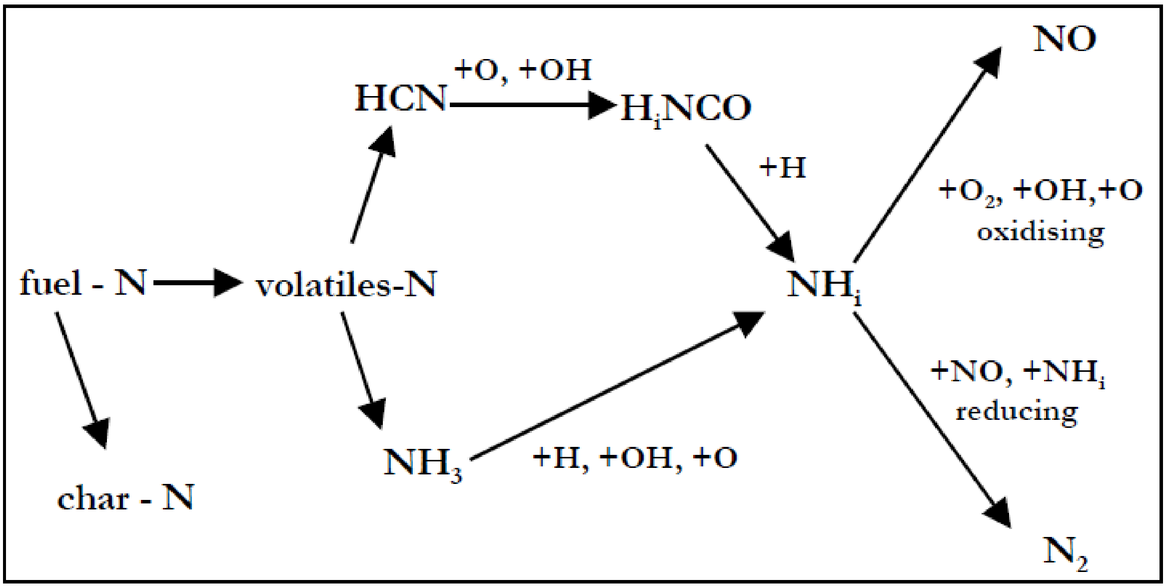


Figure 2-1 Pathways of NOx formation from volatiles-N, fuel nitrogen [2]

There are many intermediate steps in this process and from the form of NH_i the compounds can be either oxidized to NO or reduced to N_2. This is dependent on the presence of oxygen-containing compounds or more correctly the stoichiometric, the relation between fuel and air.

The content of char-N is dependent on the flame temperature and time development. The higher temperature leads to more volatile-N and therefore less char-N [2].

2.1.3 Prompt NOx

This mechanism is based on the reaction between available molecular nitrogen and hydrocarbon radicals like C, CH, and CH_2 (and many others) derived from the fuel. Fenimore investigated in 1970 the formation of NOx in hydrocarbon fuel. He found that the fast formation of NOx in the flame zone could not be described by the thermal mechanism [5]. Also this prompt formation did not occur by other fuels than hydrocarbons. The mechanism can therefore also be referred to as the Fenimore mechanism.

This reaction leads to the formation of NOx and other components by the fast and immediately oxidation around the flame. By having fuel rich conditions, both HCN (hydrogen cyanide), NH_3 (ammonia) and NH (nitrogen monohydride) can be rapidly formed and further oxidized to form NOx. The reactions in the prompt NOx formation is given by the reactions (2.4)-(2.9) [6]:

$C + N_2 \rightarrow CN + N$ (2.4)

$CH + N_2 \rightarrow HCN + N$ (2.5)

$CH_2 + N_2 \rightarrow HCN + NH$ (2.6)

$N + H_2 \rightarrow NH + N$ (2.7)

$NH + H_2 \rightarrow NH_3$ (2.8)

$HCN + O_2 \rightarrow NO + HCO$ (2.9)

The formation of prompt NOx is mainly dependent on the stoichiometric conditions of fuel/air. Also this formation is temperature sensitive but not as much as for thermal NOx. Significant formation of prompt NOx occurs at following conditions; low-temperature, fuel rich conditions and short residence time.

2.1.4 NO_2 formation

Small amounts of NO_2 can also be formed by the generated NO, thereby as a secondary product. This formation occurs at the coldest areas in the flame, often at temperatures below 800°C. At temperatures above 1200°C NO_2 undergoes destruction. NO_2 are formed by the reaction of NO and radicals, given with an example by reaction (2.10):

$NO + HO_2 \rightarrow NO_2 + OH$ (2.10)

The radical HO_2 (hydro peroxide) and other radicals are formed by the prompt mechanism. The NO_2 contribution to the total NOx formation depends upon the fuel. By using coal, the contribution is minor ~5% and the contribution is much more dependent by using fuel gas [7].

2.2 NOx formation in cement kilns

NOx formation in cement kilns are mainly based on the two mechanisms; thermal NOx and fuel NOx. This is because of the high process temperature obtained in the combustion processes. Prompt NOx formation can be neglected for the cement production [8].

Thermal NOx is mainly generated in the primary burning zone where the flame temperature is up to 2000°C. It is also generated some fuel NOx in the primary burner.

Fuel NOx is generated to the greatest extent in the secondary burner, in the precalciner by combustion of nitrogen-containing fuels like coal. The NOx formation in primary and secondary burner is slightly different because of the temperature difference.

In addition to these two mechanisms, also feed NOx formation occurs. This is because the raw material often contains small amounts of nitrogen.

2.2.1 Feed NOx formation

The raw meal in the cement production is directly in contact with the flue gas arising from the combustion processes in both the primary and secondary burner. Flue gas coming from the kiln is carrying the raw meal which is already preheated in the first three cyclones, up and through the precalciner. The raw material may contain small amounts of chemically bound nitrogen, up to 0.01% by weight. The temperature range for formation of feed NOx is 300-800^{o}C and depends on the heating rate. The faster heating rate, the less NOx formation and for slow heating rates, more NOx is formed. For cement production technologies this implies a greater feed NOx formation in wet and log-dry kilns compared to preheater or precalciner systems [8].

For cement processes feed NOx formation arises, but still it is less essential than thermal NOx and fuel NOx in general.

2.2.2 NOx formation in primary burning zone

In the primary burning zone the flame temperature can reach 2000^{o}C, determined by the conditions in the kiln, mainly depending on which type of fuel that is consumed. Also the residence time and the concentration of oxygen (stoichiometric ratio) in the combustion zone are important. Another important factor in the thermal NOx formation is the shape of the flame. If the flame is long and lazy the NOx formation is less than with a short and intense flame. The shape of the flame together with the temperature is dependent on the fuel and air ratio. As an example, gas would give a much more intensive flame compared to coal. Increasing excess combustion air in the burning zone would result in increased NOx formation. Therefore, it is important to measure the concentration of oxygen present in the kiln. Another thing that should be mentioned is the heating value of the fuel. Fuels with high heating values, as oil, diesel and coal, needs less combustion air which results in less NOx formation [6].

2.2.3 NOx formation in secondary burning zone

The cement plants that operate with a precalciner kiln have a secondary burner which is covering more than half of the total amount of fuel consumed. In this secondary burner, the combustion takes place at a lower temperature, often >1200^{o}C which means that the thermal formation of NOx can be neglected [5]. Fuel NOx is the major mechanism in the secondary burning zone. The total formation of NOx is dependent on the content of nitrogen in the fuel and also the oxygen present in the burning zone.

2.3 NOx control technologies

It exist a lot of different technologies to reduce and control the NOx generation. It can be prevented by taking measures to reduce the generation in the combustion process (primary reduction) or it can be implemented a reduction measure after NOx is already generated (secondary reduction). Principles and technologies for both primary and secondary reduction technologies are shown in Table 2-2.

Table 2-2 NOx Control Principle [4]

Control Principle or Method	Technology
Reducing peak temperature	Flue Gas Recirculation (FGR) Natural Gas Reburning Low NOx Burners (LNB) Combustion Optimization Burners Out Of Service (BOOS) Less Excess Air (LEA) Inject Water or Steam Over Fire Air (OFA) Air Staging Reduced Air Preheat Catalytic Combustion
Reducing residence time at peak temperature	Inject Air Inject Fuel Inject Steam
Chemical reduction of NOx	Fuel Reburning (FR) Low NOx Burners (LNB) Selective Catalytic Reduction (SCR) Selective Non-Catalytic Reduction (SNCR)
Oxidation of NOx with subsequent absorption	Non-Thermal Plasma Reactor Inject Oxidant
Removal of nitrogen	Oxygen Instead Of Air Ultra-Low Nitrogen Fuel
Using a sorbent	Sorbent In Combustion Chambers Sorbent In Ducts
Combinations of these Methods	All Commercial Products

The idea of reducing peak temperature is to avoid a stoichiometric ratio in the combustion process, so avoiding the ideal stoichiometric ratio, either rich or lean mixtures depending upon the nitrogen-content in the fuel, leads to a reduction of the highest temperatures, which again means less NOx generation. From Table 2-2 it can be seen that it exist several technologies to reduce the peak temperature depending on the conditions in the combustion process. The temperature may be reduced by a fuel rich/lean mixture, recirculation of cooled flue gas or injecting water. All possible technologies listed as successful technologies for reducing the peak temperature are based on preventing pollution.

Reducing residence time in peak temperature can be implemented by using a timer on the ignition/ injection at the combustor engine. Otherwise the flame can be restricted to a shorter area by then inject fuel, steam, combustion air or circulated flue gas. This technology is also based on preventing pollution.

The third method from Table 2-2 is to implement chemicals to reduce NOx generated. This technology is based on reversing the oxidation by injecting a reduction substance containing nitrogen. Often ammonia and urea are used. All the listed technologies provides chemicals, SCR and SNCR are add-on technology while LNB and FR is preventing pollution.

Oxidation of NOx is based on getting the nitrogen to be available to absorb into water which is done by raising the valence of the nitrogen. This is done by using a catalyst, injecting hydrogen peroxide, creating ozone, or injecting ozone into the air flow. There have to be a scrubber installed to absorb the N_2O_5 generated. Generated nitric acid is a bi-product that has to be neutralized or captured. This is add-on technologies.

Removal of nitrogen from combustion is providing pollution technology. This is performed by preventing nitrogen in the combustion. This can be done by using pure oxygen in the combustion process instead of air or supplying fuel not containing nitrogen (Ultra-Low nitrogen fuel). By using fuels with a low content of nitrogen could lead to a lower temperature and avoiding excess formation of thermal NOx. Using a combination of this may cause elimination of fuel- and prompt -NOx formation.

Using a sorbent, both absorption and adsorption is an add-on technology based on injecting a sorbent that may be ammonia, powdered limestone, aluminum oxide or carbon, which can remove NOx and other pollutions. This technology requires a filtration unit to capture the sorbent.

The last method is a combination of all these technologies. In some cases it may result in higher removal efficiency by applying a combination of the technologies in relation to each individual.

To get a more detailed description of all the technologies from Table 2-2, see the report “Nitrogen oxides (NOx), why and how they are controlled”, written by the U.S. Environmental Protection Agency [4].

2.4 Thermal deNOx systems

"At the present time, the most effective post-combustion methods for reducing NOx emissions from stationary sources, including steam boilers, gas turbines, and diesel engines, are SNCR and SCR, which involve injection of a nitrogen-containing additive into the combustion products"[3].

DeNOx system is a common term of the two secondary reduction technologies; SCR and SNCR technologies, respectively selective catalytic reduction and selective non-catalytic reduction, which can also be referred to as post-combustion methods.

Originally this technology was patented by Exxon who developed the usage of ammonia to control NOx arising from combustion [6].

Additives that can be implemented with this technology are cyanuric acid ($(CNOH)_3$), urea ($CO(NH_2)_2$) and ammonia (NH_3) where cyanuric acid is most used in diesel engines and the two others in boilers and gas turbines. Laboratory tests have proven that the removal efficiency is varying with temperature and the three different additives. The removal efficiency can exceed 90 percent using ammonia, which implies that it is the most effective reduction agent [3].

Ammonia solution is most commonly used in both SCR and SNCR technology. The reason is mainly the fact that urea is a solid that is dissolved in water while ammonia is gas dissolved in water. When the urea solution is injected, it takes some time before the water is completely evaporated and the urea to start the reaction with NOx. Urea decomposes and forms the same intermediate species as ammonia. Opposite, ammonia will be released immediately after passing the nozzles because the pressure is lower and the temperature is higher [9].

The removal efficiency is dependent on the flow of reduction agent. In general, the higher this ratio between flow of reduction agent and NOx becomes, the higher the NOx removal efficiency gets. Additive-to-NO molar ratio in the range of 0.8-1.5 is found to give reduction efficiency above 50 percent and also with an acceptable additive-slip [3].

2.4.1 SNCR technology

SNCR technology is based on reducing the NOx concentration in the flue gas by injecting a reduction agent. NOx reacts with the nitrogen containing reduction agent to form molecular nitrogen and water (vapor).

SNCR technology is cheaper and simpler both in operation and installation compared to the SCR technology. For SNCR technology the temperature range is higher, about 1100-1400K. The chemical reaction requires that high temperatures to achieve a fast reaction without a catalyst. The reduction efficiency is somehow lower compared to the SCR technology. The removal efficiency is very dependent upon the reduction agent used as well as the fuel consumed in the combustion process, so the removal efficiencies can be in the range 30-90% [3].

The process system generally includes a storage module for the reduction agent, a pump and alternative preparation module, piping, injection module and a control system. The process description is given in more details in 3.3.3 Functional description. Figure 2-2 illustrates the principle of SNCR technology where NOx reacts with ammonium hydroxide at optimal temperature range to form nitrogen and water.

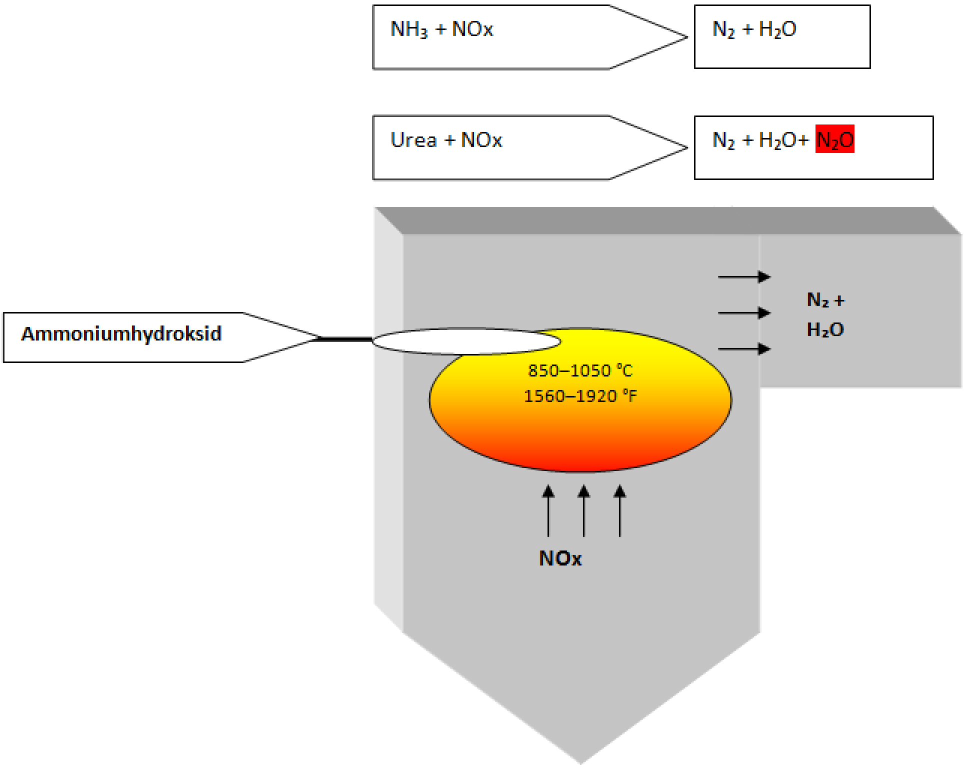


Figure 2-2 SNCR technology [10]

Most likely the reduction agent used is an ammonia solution. The choice of suitable reduction agent is often determined by economy, safety and handling. If the reduction agent is chosen to be urea, this can come from the producer as pellets. In that case, the pellets have to be prepared before injection. The pellets and hot water, at a given specific ratio, is added to a mixing tank. Here the pellets will be dissolved and a perfect mixing is filled on a storage tank. From here the urea solution is pumped into the injection module. This module controls the right amount of urea solution into each injector lances. This regulation is based on the measured NOx emissions emitted [9].

Depending on the sources that describe this technology the temperature range, removal efficiency, catalyst and other specifications are varying slightly, although, the central parameters are summarized in Table 2-3.

Table 2-3 Design parameters for SNCR technology [3]

Design Criteria	**SNCR technology**
NOx reduction efficiency	30-90%
Temperature range	1100-1400K (827-1127^{o}C)
Reduction agent	Ammonia/Urea
Reactor	None
Capital investment costs	Low
Maintenance	Low

2.4.1.1 Chemistry

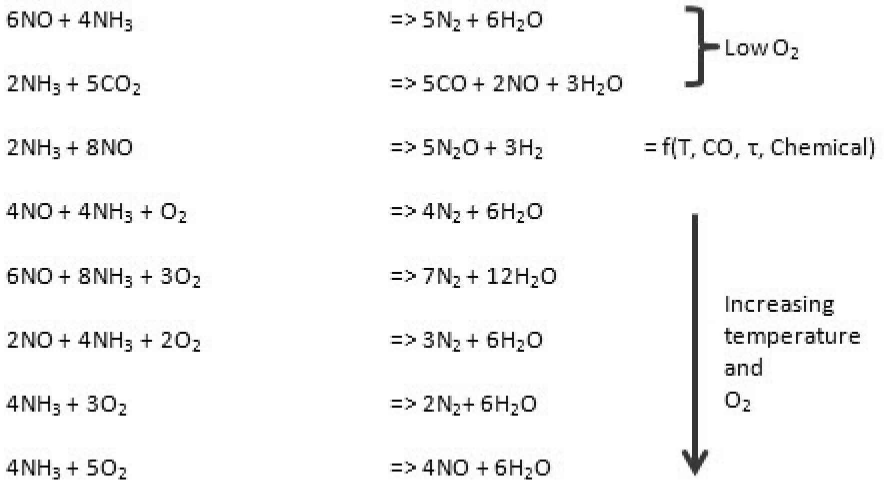
The main reaction for this technology, using ammonia, is given by reaction (2.11) and (2.12) [13].

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O \tag{2.11}$$

$$6\ NO_2 + 8\ NH_3 + \rightarrow 7\ N_2 + 12\ H_2O \tag{2.12}$$

From reaction (2.11) it can be seen that 1 mol of ammonia is needed for each mol of NO present in the flue gas. With respect to the molecular weight it can be stated as 0.57 kg ammonia is needed per 1 kg NO, in other words, the molar ratio NH_3/NO is 0.57 by the stoichiometric reaction. Calculations are given in Appendix B.

Besides the main reactions, it may appear a lot of other intermediate steps in the reactions according to other process conditions. Flow vision has listed reactions that can commence, shown in Figure 2-3. It can be observed that the reactions given are dependent on the concentration of O_2 and temperature.



$$6NO + 4NH_3 \Rightarrow 5N_2 + 6H_2O \tag{2.13}$$

$$2NH_3 + 5CO_2 \Rightarrow 5CO + 2NO + 3H_2O \tag{2.14}$$

$$2NH_3 + 8NO \Rightarrow 5N_2O + 3H_2 \tag{2.15}$$

$$4NO + 4NH_3 + O_2 \Rightarrow 4N_2 + 6H_2O$$

$$6NO + 8NH_3 + 3O_2 \Rightarrow 7N_2 + 12H_2O \tag{2.16}$$

$$2NO + 4NH_3 + 2O_2 \Rightarrow 3N_2 + 6H_2O \tag{2.17}$$

$$4NH_3 + 3O_2 \Rightarrow 2N_2 + 6H_2O \tag{2.18}$$

$$4NH_3 + 5O_2 \Rightarrow 4NO + 6H_2O \tag{2.19}$$

(2.20)

Figure 2-3 Intermediate steps in the SNCR reactions [11]

The two first reactions from Figure 2-2 occur at low oxygen concentrations. Reaction 2.13 is a reduction of NO but reaction 2.14 is an unfortunate and undesirable reaction where NO (and CO) is actually formed instead of reduced. Reaction 2.15 is an example of the creation of N_2O and it can be seen that this reaction is a function of temperature, CO concentration, reaction time and the reduction agent. The next reactions, 2.16-2.20 are determined by the temperature and oxygen profile. By exceeding the maximum temperature for this technology (1400K given in Table 2-3), it can be seen from reaction 2.20 that ammonia is no longer available to reduce NO but instead the reverse reaction happens. Ammonia reacts with oxygen to create NO.

By implementing urea in the process, the chemistry is somehow different, shown by reaction (2.21) [7]:

$$(CO(NH_2)_2) + 2\ NO + ½\ O_2 \rightarrow 2\ N_2 + CO_2 + 2\ H_2O \tag{2.21}$$

Now, only 0.5 mol urea is needed per mol NO given by the stoichiometric reaction. The molar ratio is however higher, $(CO(NH_2)_2)$ /NO is 1.0 (Appendix B). This means that a greater mass of urea is required per mass of NO compared to an ammonia solution.

The chemistry by using cyanuric acid is somehow complex. Even tough, an approximated overall reaction is shown in reaction (2.22) [7]:

$$(HNCO)_3 + 7/2\ NOx \rightarrow 13/4\ N_2 + 2\ CO_2 + 3/2\ H_2O + CO \tag{2.22}$$

Only 0.29 mol cyanuric acid is needed per mol NO given by the stoichiometric reaction. For cyanuric acid the molar ratio is much higher than for both ammonia and urea; $(HNCO)_3/NO$ is 1.23 (Appendix B). This results in an even higher mass flow of cyanuric acid.

The chemical pathways for the three reduction agents are illustrated in Figure 2-4.

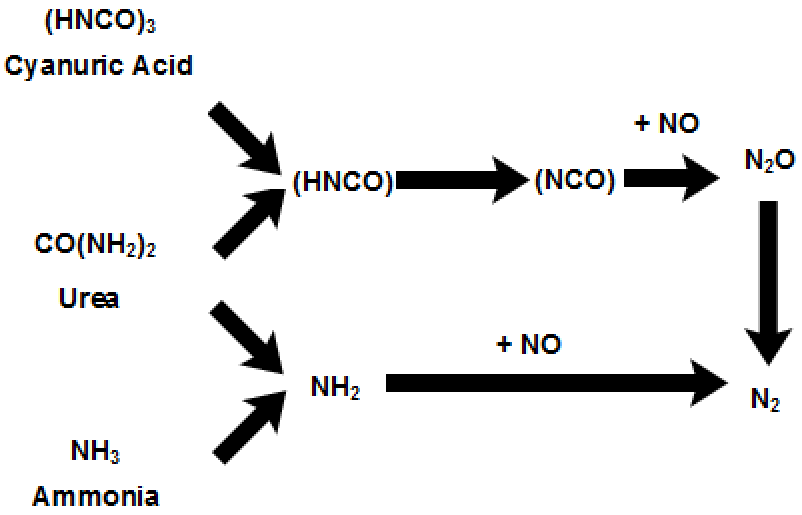


Figure 2-4 NOx reduction chemistry pathways [7]

Urea can behave the same way as both ammonia and cyanuric acid considering the chemical pathways. The simplest reaction takes place for ammonia. More complex reactions and pathways takes place for cyanuric acid where N_2O is formed as an intermediate step before it is reduced to N_2.

2.4.1.2 Ammonia slip

Ammonia slip (NH_3-slip) is a drawback of deNOx technology. Ammonia slip is the un-reacted ammonia from the process which can be measured as pollutant emissions in the flue gas. There are two main reasons for ammonia slip. When the temperature is too low, the reaction will not take place, which leads to ammonia slip. The other reason may be to large amount of ammonia injected, excess ammonia. There is very difficult to regulate the ammonia slip. Even though, a very important factor in achieving low ammonia slip is to install the injection nozzles at the most effective area of the process because of the varying NOx distribution over the cross section [12].

2.4.2 SCR technology

This technology is a NOx reduction method that uses a catalyst and a nitrogen based reduction agent to convert NOx into nitrogen, N_2 and water vapor, H_2O. The reduction agent is added to and mixed with the flue gas stream before it passes through the catalyst chamber which initiates the reaction.

The most common additive used in this technology is also ammonia. The catalyst material is typically a mixture of metal oxides and other components. All types of catalyst have advantages and disadvantages. Some of them are expensive and some are missing high thermal durability.

The advantage of SCR technology compared to SNCR technology is somehow higher reduction efficiency and lower operating temperature. The high reduction efficiency is about 80-90 percent [3]. Temperature ranges for SCR is 500-700K where the highest temperatures are most ideal. Lowest temperature limits are determined by the reaction rate and the possibility of ammonia not to react with the NOx and deposition of sulfur salts. The upper temperature limits are determined by the catalysts physics, the possibility of destroying the catalyst and also by oxidation of the injected ammonia to generate furthermore NOx [3].

The chemical reaction using ammonia in SCR is the same as for SNCR technology and repeated in reaction (2.23) and (2.24) [13]:

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O \tag{2.23}$$

$$6\ NO_2 + 8\ NH_3 + \rightarrow 7\ N_2 + 12\ H_2O \tag{2.24}$$

The same applies here, that the process variables are varying slightly according to the sources used, although the central parameters are summarized in Table 2-4.

Table 2-4 Design parameters for SCR technology [3]

Design Criteria	**SCR technology**
NOx reduction efficiency	80-90%
Temperature range	500-700 K (227-427^{o}C)
Reduction agent	Ammonia/Urea
Reactor	Catalyst
Capital investment costs	High
Maintenance	3 to 5 years (depends on the catalysts lifetime)

By-products; N_2O and SO_3 (if SO_2 is present) generally neglected but depends upon the catalyst [3].

2.5 NOx reduction in cement kiln

In chapter 2.3 NOx control technologies, all general approaches for controlling and reducing the NOx emissions where defined. The best suited and most applied technologies for controlling NOx in precalciner cement kilns are listed below.

Low-NOx burners

The principle of low NOx burners is to reduce the formation of NOx in the burning zone by installing special-designed burners. The aim with these special-designed adjustable burners is to reduce NOx formation in terms of lowering the flame temperature, adjust the flame turbulence and imply recirculation zones in the flame. Reducing the temperature causes less thermal NOx formation and by recirculation of cooled flue gas, the present NOx could be re-burned, further reducing the NOx emissions [8]. This can be implemented in both primary and secondary burning zone.

Fuel staging

The idea of this technology is to add fuel in two or more stages to obtain a zone where NOx can be chemically reduced to N_2. This technology is based on primary measures, preventing or avoiding the formation of NOx [8]. In general, the technology can only be implemented for cement kilns equipped with a precalciner.

Flame cooling

Reducing the peak temperature in the primary burning zone is another approach for preventing NOx formation. This can be done by either injecting water or recirculation of cooled flue gas. The burning zone temperature (BZT) is the main factor which contributes to NOx formation. By reducing BZT from 1500^{o}C to 1300^{o}C, the NOx formation can be reduced by 200-400 ppm [8]. Limitations for flame cooling can be product quality and impacts on the systems stability.

2.5.1 SNCR experiments

In 2006-2007 Petro Miljø[3] performed series of tests run at cement plants that operate with precalcination cyclone towers and involving SNCR system for NOx reduction. Seven different cement plants where investigated, located in Italy and Spain. Petro Miljø did use a mobile system to perform the tests over a three day period at each plant. The tests performed were run with 15-36 trials per plant with a reference of 15-30 minutes before and after the

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[3] Petro Miljø is the supplier of the installed SNCR system at Norcem Brevik, further described in 3.3 NOx reduction system at Norcem. In October 2011, Yara acquired Petro Miljø and are today known as “Yara Miljø”. Yara Miljø is a world leader of the SNCR technology with a team of experts which is specialized on the cement- and waste-incinerators [14].

trials. The temperature range was 850-900°C. The main parameter considered was reduction agent, reduction efficiency, NH_3-slip and CO.

The two most commonly used reduction agents, urea and ammonium hydroxide, where analyzed and considered during the test. As a result, Petro Miljø found that urea is separating into ammonia (NH_3) and isocyanic acid (HNCO), which contributes to NOx reduction and also to form NCO which turns into laughing gas (N_2O). More direct is the reaction by the usage of ammonium hydroxide which does not form unwanted substances from the nitrogen.

Defined by these tests the reduction efficiency with ammonium hydroxide was found to be much higher than with urea. The average reaction efficiency by injecting ammonium hydroxide was 78 % compared to an average reduction efficiency of urea at 28 %. Ammonium hydroxide is then on the average 2.85 times more efficient than urea solution.

By considering the reduction efficiency of NOx the average value of the highest reduction was 87 % with ammonium hydroxide as reduction agent and a maximum NH_3-slip of 18 mg/Nm^3. Without a limitation of the NH_3-slip it was expected to obtain even higher reduction efficiency. By comparison to urea the average value of the highest reduction was 41 %.

According to the NH_3-slip the trend was showing an increase of NH_3-slip while the NOx reduction increases but still the NH_3-slip was less than 20 mg/Nm^3. It was also shown that the NH_3-slip was higher at the plant with the lowest temperature. This means that NH_3-slip is temperature dependent; the higher temperature, the less NH_3-slip.

Urea (NH_2CONH_2) contains a CO molecule, so by using urea as a reduction agent it contributes to a CO increase. The formation of CO depends on the process conditions as well as the oxygen in the flue gas. In 3 of 7 plants there was noticed a CO increase with a significant correlation between the amount of CO formed and NOx reduction. This means that there may be a dependency of CO according to the NOx reduction; the less NOx in the flue gas (high reduction efficiency), the higher CO concentration in the flue gas.

After performing these tests, Petro Miljø found how an SNCR system could operate optimally for cement plants. By installation of a SNCR system with ammonium hydroxide as reduction agent it is possible to reduce NOx emissions below the EU directives for waste incineration in cement plants. It is also expected that it is possible to reach future stricter demands [15].

3 Norcem Brevik

The cement manufacture Norcem, located at Brevik, is a part of the Heidelberg Cement Group that has employees in over 40 countries. In Norway there are only two places to produce cement, Kjøpsvik and Brevik. The production capacity at Norcem Brevik is respectively 1.050.000 tons of clinker and 1.300.000 tons of cement. The production at Norcem consist 3 types of clinker and 7 types of cement [16]. Norcem is relatively new upgraded and is based on the most modern method; precalciner system.

In the previous chapter, NOx formation and reduction methods where described both generally and specially adopted to cement kilns. There are several ways to produce cement. This chapter starts with a general description of various methods for producing cement and then further provides a detailed process description of the process at Norcem.

3.1 Cement kiln processes generally

It exist several types of cement processes and rotary kilns. New installations of cement systems are currently often equipped with precalciner or preheater with the intention of increasing the overall energy efficiency.

What often determines whether the process should be dry or wet is the moisture in the raw materials. If the moisture is above 15-20 %, it is preferred to install a wet process.

Wet Process Kilns

This process is most likely the oldest technology with the smallest capacity. The raw materials are first mixed and grounded containing 30-40 % water, forming a fine and homogeneous slurry. The slurry being fed into the long rotary kiln is first undergoing heating and drying. The kilns are specially designed with metal chains inside at the cold part. The intention with the chains is to absorb the heat from the gases and then transfer the heat to the material which comes in direct contact. This is due to the large amount of moisture that has to be evaporated. The calcination reaction is carried out through the kiln. At the outlet and when the cooling commences, clinker minerals crystallize from the melt and the solid clinkers are formed. The energy efficiency is very poor because of all the moisture that has to be evaporated. When the fuel prices escalated in the 1970s the profitability dropped drastically and only a very few wet kilns have been installed since [8].

Dry Process Kilns

This process, long dry kilns, utilizes approximately the same capacity as the wet kiln process. The feed in this kilns are dry raw materials which constitute the advantage over wet kilns. Dry long kilns are very much alike the wet long kilns, equipped with metal chains which increases the effect of heat exchanging. The overall energy efficiency is better than for the wet kiln because there is almost no moisture to be evaporated. The heat transfer in the dry long kilns was also improved by adding metallic crosses and ceramic heat exchangers which somehow split the kiln into three or four parts.

Cyclone Preheater Kilns

This process is a newer technology than wet and dry long kilns and utilizes a higher capacity. Dry pulverized raw meal is put into series of 2-6 cyclones placed vertical. The intension with the cyclones is to promote heat exchanging. Raw meal flows downwardly by gravity and is preheated so the calcination reactions can start. The temperature obtained in the cyclone tower is about 800-900^{o}C. Preheated raw meal entering the kiln is partly calcined, approximately 20-30%. This process is very energy effective compared to the other technologies because of the good heat exchanging obtained as a result of the directly contact between gas and raw meal [8].

Precalciner Systems

This is the most modern technology and provides the largest capacity. Almost all new installations of cement manufactures nowadays are based on this technology. In addition to the preheater there is also installed a second burner as a riser duct attached to the preheater to carry out calcination. This secondary burner uses hot air from the clinker cooler and consumes about 60% of the total fuel. By utilizing the precalciner system, the raw meal can be calcined up to 90% before the kiln. This leads to a requirement that gives smaller dimensioning of the kiln. This type of technology can be provided with a lot of different configurations, different numbers of preheater towers and calciner towers [8].

3.2 Process description

Cement is produced by grinding limestone and other additives into meal for then gradually heat it to a temperature about 1450^{o}C. During this thermal process, partial fusion occurs and during the resident time in the rotary kiln, so called clinker is formed [5]. Clinker produced is rapidly cooled down and storage before it is added some gypsum, and other additives depending on the type of cement that is produced. This mixture is grinded into fine cement meal. The overall cement process is illustrated in a block diagram in Figure 3-1. The process can be divided into 3 sections; Quarrying and pretreatment of raw materials, clinker production and cement production.

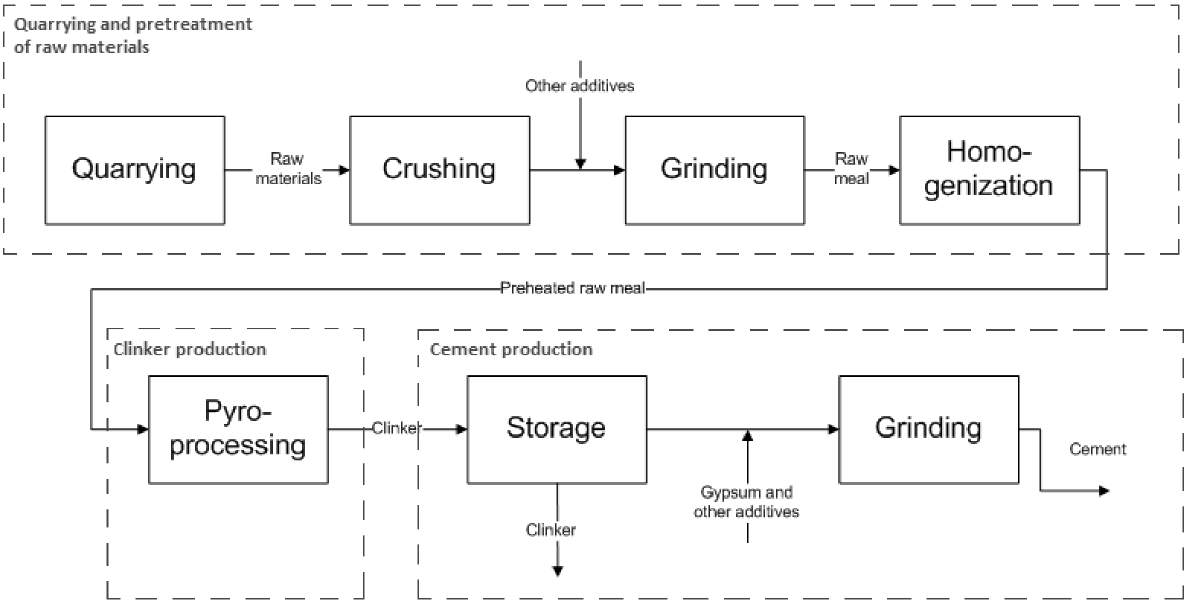


Figure 3-1 Overview of the total cement production

3.2.1 Quarrying and pretreatment of raw materials

The cement production starts with extraction of the main raw material, limestone ($CaCO_3$). It is taken out from the quarry and mine. Lime (CaO) is the basic component in the raw meal composition but three other important components in the mixture are silica (SiO_2), alumina (Al) and iron oxide (Fe_2O_3). These oxides are all found in different mineral components like limestone, marl and clay. To obtain the correct mixture of the raw meal it is often added some other additives like sand, bauxite and iron ore. Also fly ash is added in some content. This is a suitable substance that can replace clay because it provides mainly silica and alumina. The purpose of these additives is to replace the proportion of the components lacking. The mixture of the raw materials is crushed and grinded in several mills into fine raw meal.

3.2.2 Pyroprocessing

There are two parallel strings, each consisting of four cyclones, shown in Figure 3-2. These cyclones are also known as the preheater section. The intention with this kind of heat exchanging is to dry the meal and start the reactions. Raw meal is added into the gas stream between the two upper cyclones and flows downwardly by gravity. The cold raw meal achieves good contact with the hot gas flowing upwards so the raw meal is dried and partly calcined. At a temperature up to 100^{o}C, uncombined water is driven out and eventually evaporates. From 100-430^{o}C, dehydration occurs, so oxidation of silicon, aluminum and iron takes place.

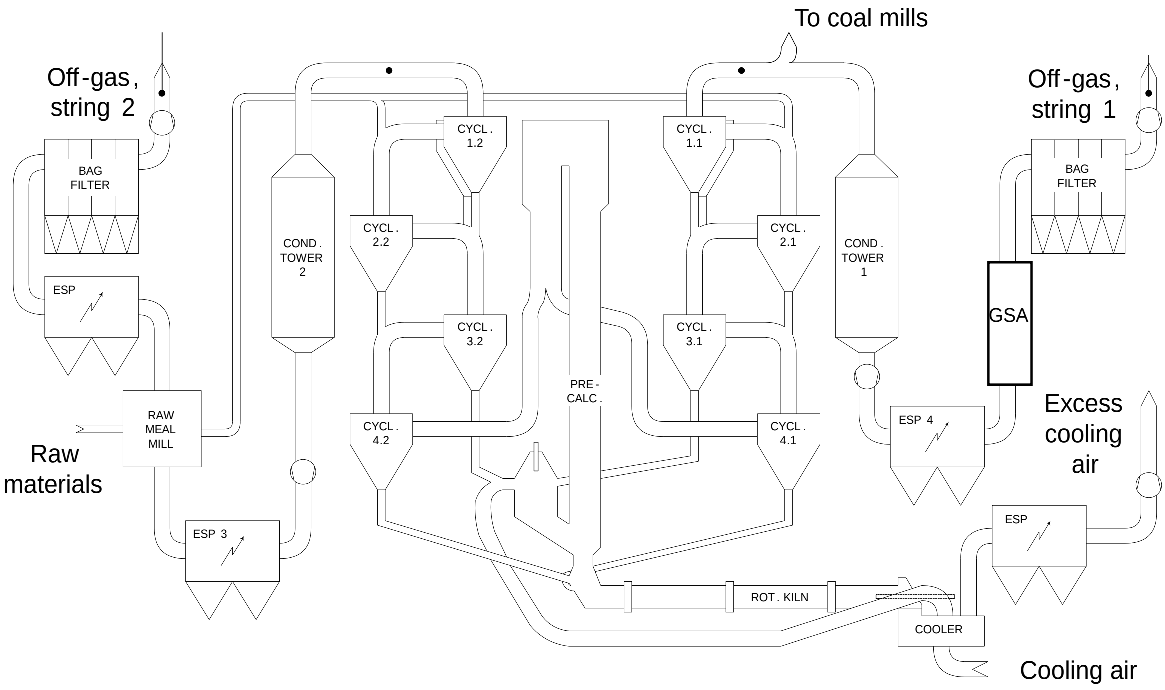


Figure 3-2 Pyroprocessing [18]

After passing the three first cyclones, the meal is entering the precalciner. This is a riser duct placed between the preheater and the rotary kiln. This is a separate furnace which consumes more fuel than the primary burner in the kiln. The meal is partly calcined, calcium carbonite ($CaCO3$) decomposes to calcium oxide (CaO) and carbon dioxide (CO_2) in the temperature range 600-900^{o}C [5].

More than 90 % of the meal is already calcined by entering the kiln. By achieving this high effect of the precalciner, it requires a less length of the rotary kiln. In the start of the kiln the rest of the meal is calcined where after the sintering (clinker formation) takes place in the presence of liquid phase. The kiln has a slightly inclination while it rotates at low speed. Typically the residence time in the kiln is 30 min. The primary burner is placed at the outlet of the kiln so it works like a countercurrent heating device. The temperature reaches 1450^{o}C from the primary burner so the clinker produced has a high temperature.

To maintain the structure of the formed clinker it is necessary to rapidly cool it down. That is done in a clinker cooler right after the outlet of the kiln. The cooling air that recovers the heat from the clinker is used with several purposes. The first part, secondary air is used as air supply to the primary burning zone in the kiln. The next part, tertiary air, is used as air supply to the burner in the precalciner. The last part of the cooling air is excess air and is released to the surroundings at a temperature of 200-300^{o}C.

3.2.3 Cement production

The cooled clinker is transported to storage tanks. From here, the clinker and gypsum and some other components like iron sulphate and fly ash is mixed in different quantities according to which type of cement that is produced. This mixture is grinded in mills to produce cement.

The produced cement are either stored on cement silos or packed in bags. The distribution of the cement is done by boats and truck-transport.

3.2.4 Energy and fuel consumption

The cement production at Norcem Brevik had a total energy consumption of 3.65 GJ/ton clinker in 2013 where the ratio of alternative fuels were 57.1%. The optimal energy consumption would be to consume as large amounts as possible of alternative fuels. The goal for Brevik is to replace at least 75% of the fossil fuel energy with alternative fuels within 2016 [19].

The energy required in this process is supplied in the main burner in the rotary kiln (primary burner) and in the precalciner (secondary burner). Even though the kiln burner is called primary burner, it is the secondary burner in the precalciner that consumes the largest amount of fuel, approximately 60 %.

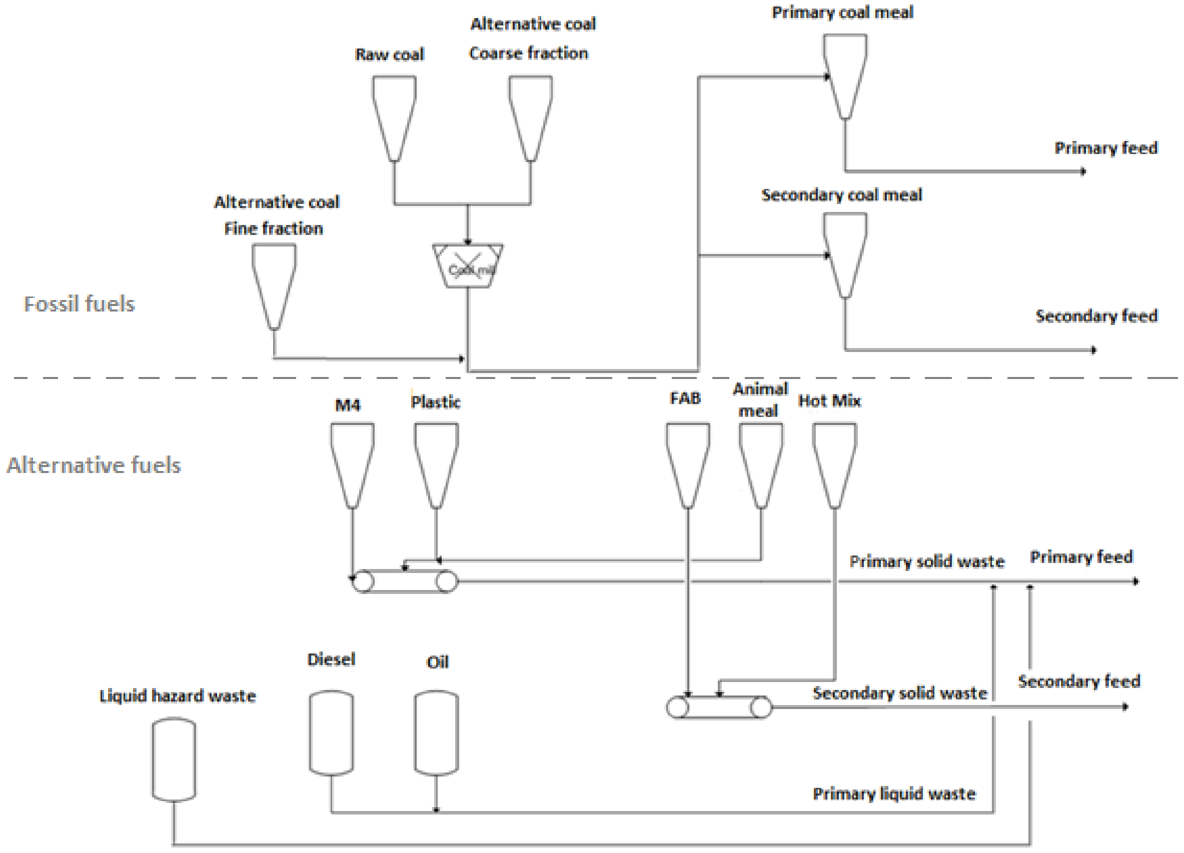


Figure 3-3 Fuel consumption at Norcem Brevik

In the main burner there are consumed both solid and liquid fuels. Most commonly used is coal meal but also as much alternative fuels as possible. The fuel consumption to the main burner is called primary feed as illustrated in Figure 3-3. It can be seen that the alternative fuels supplied to the main burner is M4, plastic and animal meal, also referred to as primary solid waste. During startups, liquid waste, respectively oil and diesel, can be fed in addition to the solid waste.

In the secondary burner, the precalciner, it is also a mixture of different fuels supplied but only solid fuels. From Figure 3-3 it can be seen that Hot Mix and FAB are referred to as secondary solid waste.

FAB stands for processed waste fuels (in Norwegian) and consists of waste from households and industry, a mixture of paper, cardboard, wood and loose cloth. Food waste, metals, glass and most of the plastic are sorted out. This mixture of waste is grounded to pieces of less than 50 mm. The animal meal (bone meal) consists of waste from slaughterhouse industry and is also grounded into small pieces. The Hot mix is a mixture of solid, hazardous waste and woodchips. M4 is a finer mixture of Hot mix [16].

FAB is very unpredictable because of the varying moisture. FAB has the greatest impact on the CO development in the flue gas. The heating value is somehow low compared to other fuels. The total fuel consumption at Norcem Brevik in 2013 is summarized in Table 3-1. The consumption is illustrated in percentage [%] and flow [ton/year] as well as the specific heating values for all the fuels. The table is based on the total energy consumption in 2013 which can also be found graphical presented in Appendix C.

According to the specific heating values of the fuels, most of them are calculated as average values throughout the year because of the variety. For alternative anode coal, waste oil and diesel, the heating values are fixed.

Table 3-1 Fuel consumption Norcem Brevik 2013 [20]

Fuel	Heating value [kcal/kg]	Consumption [%]	Consumption	Unit
Animal meal	4281	4.4	9414	ton/year
Plastic	6881	1.5	2044	ton/year
M4	3436	1.1	2880	ton/year
Coal	6226	42.8	62 724	ton/year
Alternative coal (anode)	7500	8.9	10 810	ton/year
Waste oil	9500	1.9	2045	m^3/year
Diesel	10105	0.1	142	m^3/year
Liquid hazard waste	3336	4.2	11 533	ton/year
FAB	2725	20.2	67 477	ton/year
Hot Mix	3416	14.8	39 536	ton/year

3.2.5 Emission characteristics

The main gaseous pollutants of concern from cement plants are carbon dioxide (CO_2), nitrogen oxides (NOx), sulphur oxides (SOx) and organic emissions; total organic carbon (TOC). These gaseous emissions are products of the combustion process. The volumetric order of all emissions in the stack is respectively nitrogen (N_2), carbon dioxide (CO_2), water (H_2O), oxygen (O_2), NOx, SOx, CO, and organic carbons (TOC) [21]. In addition to the specified gaseous pollutants it can also be found small parts of NH_3, HCl, HF and minor components like metals in the flue gas.

The largest sources of pollutants from the flue gas are continuously measured and reported. All the components are put into tables and reported daily and also summarized in a monthly report. There is taken some manually measurements, 2 times pr. year, of several types of metals, dioxins and furans.

In addition there are measurements of dust, noise, smell, vibrations (from blasting in mine) and temperatures.

Dust is mainly a local problem but since the electrostatic- and bag filters installed operates very well, dust is not considered as a problem [22].

Carbon dioxide (CO_2)

CO_2 emissions originate from two sources; the calcinations of carbonates (from the raw materials) and from the combustion of carbonaceous fuel, where the former is the most important. In general the emission of CO_2 is about 1 ton of CO_2 emitted per ton of clinker produced. This is influenced by the overall thermal efficiency at the plant. The greater thermal efficiency the less CO_2 is emitted per clinker produced [21]. There is also an ongoing project of different CO_2 capture technologies at Norcem as a measurement to reduce CO_2 emissions.

Nitrogen oxides (NOx)

There are totally four mechanism of NOx formation in the cement production. NOx emissions originate mainly from the oxidation of nitrogen in the combustion air, thermal NOx, and also from fuel-bound nitrogen. In addition there are feed NOx- and prompt NOx - formation which is minor contributors to the total NOx formation in cement kilns.

Sulfur dioxide (SO_2)

SO_2 emissions originate mainly from oxidation of sulfide from the fuels and organically bounded sulphur in the raw materials. Optimal conditions for the oxidation of sulfide/sulfur are in the temperature range 300-600^{o}C and where excess oxygen is present [21].

Total organic carbon (TOC)

Total organic carbon is the total amount of carbon found in all organic compounds. TOC emissions mainly originate from the raw materials in the cement production. Small parts of petroleum and kerogens can be found in the raw meal, depending upon the type of raw materials. TOC is generated during evaporation/cracking of these components. Another possibility of the formation of TOC can be incomplete combustion [21].

Ammonia (NH_3)

Very small quantities of ammonia can be observed in the flue gas from cement kilns. The ammonia originates from the pyrolysis of nitrogenous fuels and raw materials. In addition there may be emissions of excess ammonia when the cement kilns has SNCR/SCR systems with ammonia as reduction agent installed.

Emission limitation which applies for the cement kiln flue gas during normal operation is given in Table 3-2. The actual emissions at Norcem Brevik are average weighted amounts of emissions from string 1 and string 2.

Table 3-2 Emission limitations and reported measurements [23]

Pollutant	**Daily average [mg/Nm^3]**		**Yearly total [tons]**	
	Permit Limit	Actual Emission	Permit Limit	Actual Emission
Dust 1)	30	2.6	**50**	**15.2**
HCl 1)	10	2.2	**25**	**5.8**
HF 2)	1	0.02	**0.25**	**0.053**
NOx 1)	800	133	**2200**	**429**
SO$_2$ 1)	500	92	**300**	**298**
NH$_3$ 1)		9		**29.1**
TOC 1)	30	15.6	**-**	**50.8**
Cd + TI 2)	0.05	0.00007	**-**	**0.19 kg**
Hg 2)	0.05	0.010	**30 kg**	**25 kg**
Metals (Sb+As+Pb+Cr+Co+Cu+Mn+Ni+V) 2)	0.5	0.033	**-**	**89 kg**
Dioxins and furans a)3)	0.1	0.13	**-**	**0.39 kg**

1) Continuously measurement
2) At least 1 measurement per six months
3) At least 1 measurement per six months. Unit TE (toxin equivalents)
a) Unit ng/Nm^3

Emission of CO_2 is reported according to the MR-regulation for greenhouse gases [24]. The emissions are calculated based on the production volume and amount of fuel used in the process. Only the fossil fuels and the raw materials are required to be within the European Union Emission Trading Scheme, not the alternative bio-fuel. For Norcem Brevik it was 759 kg CO_2/ ton clinker in 2013 [25].

3.3 NOx reduction system at Norcem

In 2007, new obligation was introduced with the requirement to pay taxes of NOx emissions coming from energy production from machinery with higher efficiency than 750kW, motors, boilers and turbines with higher efficiency than 10MW and also flares. Incineration of waste was also included to this agreement in 2010 [26].

3.3.1 NOx-fund

In 2010 it was introduced a NOx-environmental agreement 2011-2017, actually an extension of the NOx-environmental agreements from 2008-2010, that ensured reduction of NOx and also included a NOx-fund that was signed by 15 business organizations. All organizations that endorse this agreement are exempted from taxes. The funds primary mission is to finance specific NOx reduction measures. In this environmental agreement, all industry organizations commits to reduce NOx emissions by a total of 16 000 tons. This agreement is important contributions to meet Norway's obligations under the Gothenburg protocol. It is expected that these commitments will be even stricter in 2020 [26].

In 2009 Norcem AS, Brevik applied for founding from the NOx fund, with the intention to invest in a SNCR system, a measure to reduce the NOx emissions. The estimated investment costs was 6.2 MNOK and estimated operational costs was 5 MNOK/year. The application was based on obtaining a reduction efficiency of 65 % [27].

The requirements of NOx emissions were given by Norwegian Environment Agency in an emission permit and from 18.04.2012 the requirements are:

Concentration of NOx:	$< 800 mg/Nm^3$
Amount of NOx per year:	< 2200 t/y

It is expected that the requirements will be stricter in 2014 when the new regulations (IED-directive) is introduced. The new requirements for NOx are expected to be $< 500 mg/Nm^3$.

The SNCR system comprises injection of ammonium hydroxide in the calciner through 6 operative nozzles. The system involves a storage tank for reduction agent, piping, injection nozzles, management system and analyzer of NH_3 in the flue gas. The system was provided by Petro Miljø3.

3.3.2 Installation

In 2011/2012 Norcem installed the NOx reduction system. It was first started in April 2012 but it was observed that there remained traces of ammonia in the pipes from the filling of the storage tank. The location of the filling station was thereby moved to avoid the unpleasant smell of ammonia. The SNCR system was fully operational from August 2012.

Emissions of NOx are continuously measured in both string 1(main pipe) and string 2 (AF-pipe), but the NOx reduction system are only based on string 1, i.e. the control signals to the system obtains the setpoint from string 1.

The concentration of NOx is reduced from 524mg/Nm^3 (average for 2006-2008), to 140mg/Nm^3 (average 2013). The yearly average is reduced from approximately 1600 t/y to 450t/y, which gives a total reduction efficiency of approximately 72 %.

Table 3-3 Norcem NOx emissions [27]

Year	NOx (mg/Nm^3)	NOx emissions yearly (t/year)	Concentration of NOx mean value (mg/Nm^3)
2006	431	1 270	431
2007	573	1 813	573
2008	567	1 700	567
2009	506	1 498	506
2010	606	1 760	606
2011	554	1 533	554
2012	332	951	332
2013	140	450 *	140 **

*Quantity for 2013: Quantity in ton per year is estimated based on quantities to and including October 2013 + estimated quantity for November and December.

**Concentration for 2013: Average quantity for the period to and including October 2013.

3.3.3 Functional description

PETRO SNCR System is based on the existing Selective Non-Catalytic Reduction (SNCR) technology for reduction of NOx from combustion processes. This technology is a chemical process where nitrogen oxides convert to nitrogen and water. The reaction is obtained by injecting a reduction agent like ammonia or urea directly into the flue gas after the combustion process. The reaction is strongly dependent on the given temperature range.

PETRO SNCR System operates with 4 different modules [10].

- System for storage and distribution of reduction agent
  - Storage tank for reduction agent
  - Pump module for reduction module (PMR)
  - Pump module for water (PMW)
- System for blending and distribution of reduction agent
  - Process unit (PU) including a blend module (BM) and injection module (IM)
- Injection system
  - Nozzles
- System for controlling and management of the process
  - Control and management module (CMM)

Usually PETRO SNCR System operates with a pump module for reduction agent (PMR) and a pump module for water (PMW). The pump module for reduction agent distributes the reduction agent from the storage tank to the process unit (PU). This module is provided with a gas indication system in case of leakage. In addition there is also installed a safety shower near the storage tank.

The pump module for water can be installed in order to flush the system and dilute the ammonia. At Norcem it was decided not to include the water system, mostly because of the special treatment needed, thinking of frost risk.

As mentioned above the system for blending and distribution of reduction agent comprises a blend module (BM) and an injection module (IM). Basically this module is a process unit cabinet that can supply 12 injectors, but at Norcem there are only 6 injectors.

The blend module (BM) usually has three incoming lines; one for the reduction agent, one for the water and one for compressed air. In this case there is no water included, so it exist only two incoming lines. This module is provided with valves, strainers, flow meters and other accessories. Every injector module (IM) is supplying a nozzle with a given amount of reduction agent, determined by a prescription from the control- and management module (CMM). The activated nozzle combinations are determined by these prescriptions. Also this process unit module is provided with a gas indication system in case of leakage.

There are 6 nozzles installed in the precalciner, 3 at the upward stream and 3 on the downward stream, illustrated in Figure 3-4. These cover the entire cross-section of the precalciner. The nozzles are supplied with compressed air as well as the air is cooling when the nozzles are in standby. The nozzles have flexible hoses for both air and reduction agent and is provided with a quick coupling to the precalciner. This provides the ability to perform a quick and secure inspection of the nozzles without disconnecting the pipe connections.

The control- and management module (CMM) controls and monitors all the process functions.

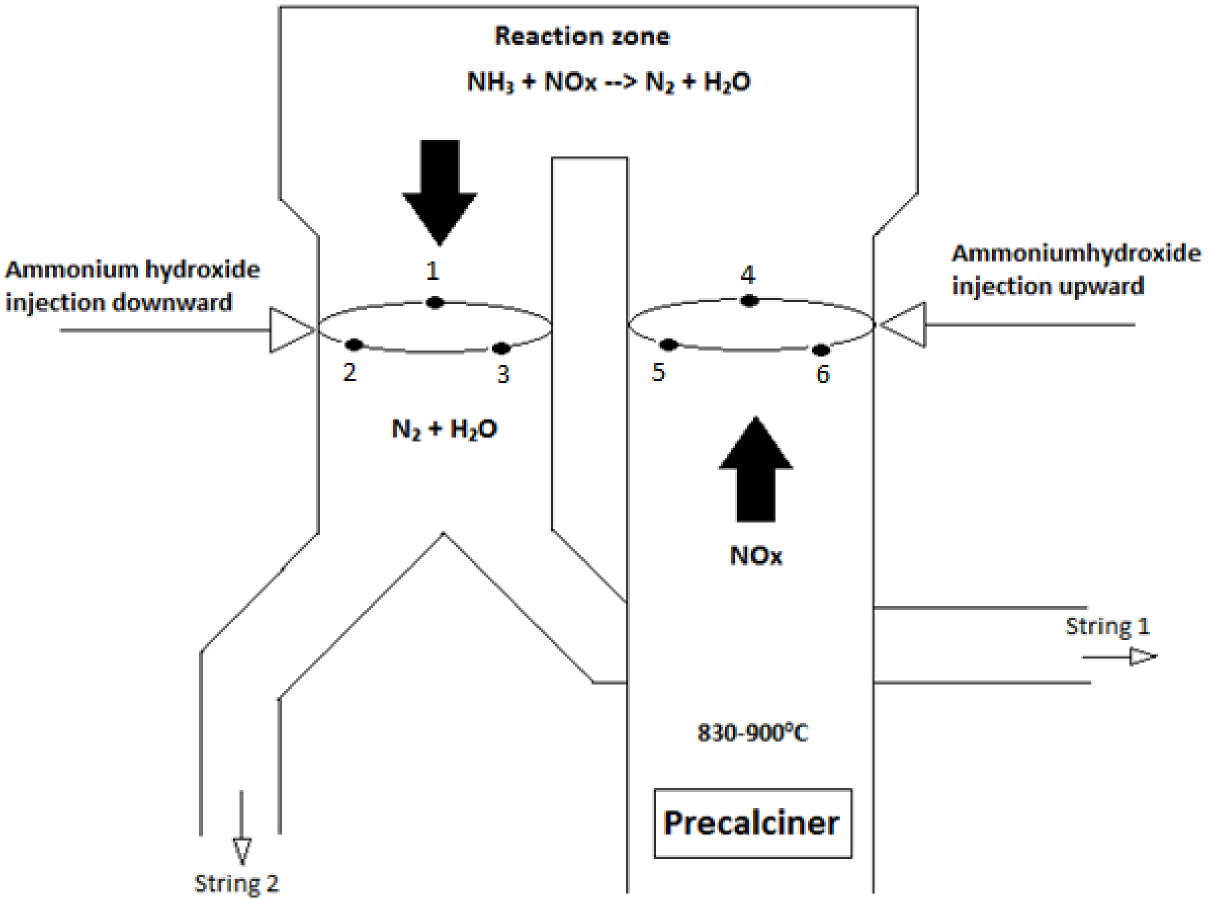


Figure 3-4 injection nozzles in the precalciner

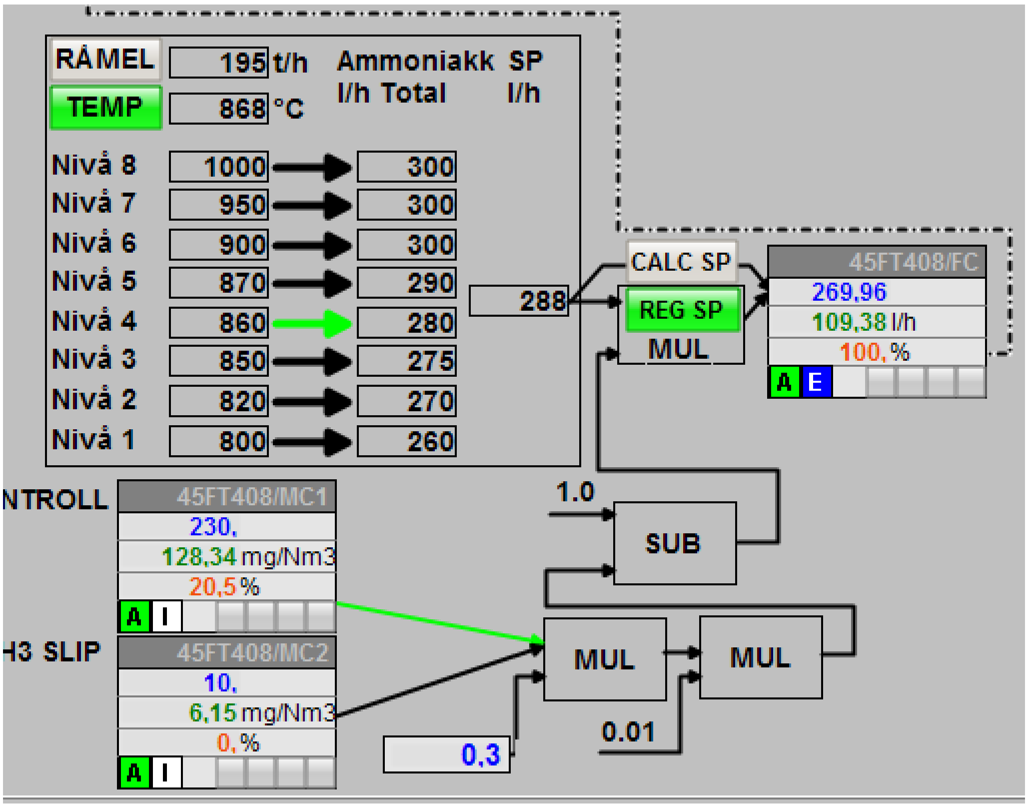
3.3.4 NOx regulation

A print screen of the NOx reduction control system is attached in appendix D but all the important operational factors and how the system is operated is described in further details below.

Tank 9 is the storage tank of the reduction agent. This tank is provided with a level measurement and a pressure indicator which can also be found in the P&ID given in Appendix E. In addition, there are also a leakage sensor which is within the red stippled lines and two overfilling protection guards [28]. There is a separate pumping system for filling the storage tank.

The reduction agent is a liquid ammonia solution, 24.5% ammonium hydroxide (NH_4OH) delivered by Yara. The storage tank has a volume of 50 m^3 and the ammonia is filled from trucks.

The regulator in the system controls the total amount of ammonia to be injected in the precalciner. The first choice is whether to get the incoming signals for the blending module based on the amount of raw-meal or the temperature in the top of the calciner. From this choice there is fixed prescriptions. Figure 3-5 show the regulator as it is operated. There is a flow/temperature range divided into 8 different levels and what determines which level one should be at is the load of the flow/temperature. Level 1 indicates the lowest acceptable load for the system to be activated. From the prescriptions setup the different levels provide a specific amount of ammonia. This amount will be the set point into the regulator.



		Ammoniakk l/h Total
Nivå 8	1000	300
Nivå 7	950	300
Nivå 6	900	300
Nivå 5	870	290
Nivå 4	860	280
Nivå 3	850	275
Nivå 2	820	270
Nivå 1	800	260

Figure 3-5 NOx reduction regulator

As an example from Figure 3-5; the choice of temperature-driven prescription with a load of 868°C corresponds to an amount between level 4 and 5. Level 4 indicate that a temperature of 860°C provides a quantity of ammonia at 280l/h. Since the temperature is a bit higher this is taken into account by an integrated interpolation-function in the prescription which leads to a setpoint at 288l/h to the controller.

Also, from Figure 3-5 it can be seen that the regulator, 45FT408/FC, have two options of how to obtain the set value. Actually there are three options if the manual set value that is not shown here are included. The first option is CALC SP; using this operation the calculated amount of ammonia from the prescription is used directly as the given set point to the regulator. The second option is REG SP; the calculated amount of ammonia is multiplied with a factor (0-1) which is influenced by NOx and NH_3-slip regulator monitors. This regulation is based on the emission levels of NOx and NH_3-slip. The purpose of this function is to reduce the amount of ammonia while at the same time maintaining the emission levels. The emission limits are customized for Norcem Brevik and set to respectively 200mg/Nm^3 NOx and 10mg/Nm^3 NH_3-slip.

The NH_3 regulator-part function is to control the NH_3-slip. If the NH_3-slip exceeds the setpoint, the regulator will reduce the amount of reduction agent.

The NOx regulator-part function is to control the NOx level. When the operating level is below the setpoint, the regulator will compensate by reducing the amount of reduction agent.

The master in this regulation is the NH_3-slip, in order to limit an excessive consumption of ammonia. Normally the NOx-control is the one in operation with an aim of keeping the NOx emissions as close as possible to the setpoint. As soon as NH_3-slip exceeds the limitations, this will take over management.

There is a possibility to determine how much NOx and NH_3-slip regulators are allowed to affect the regulator, called efficiency factor. The factor is 0-1 corresponding to 0-100% where 1 means 100%; with other words, no impact on the regulator. It can be set manually by the operator and can be seen in Figure 3-5 as the blue value. This function helps to keep the system stable.

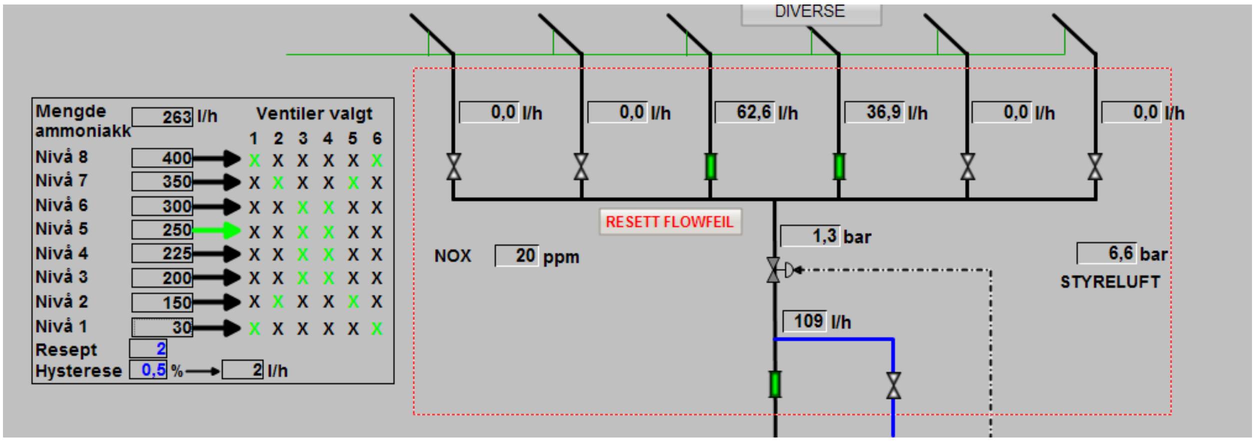


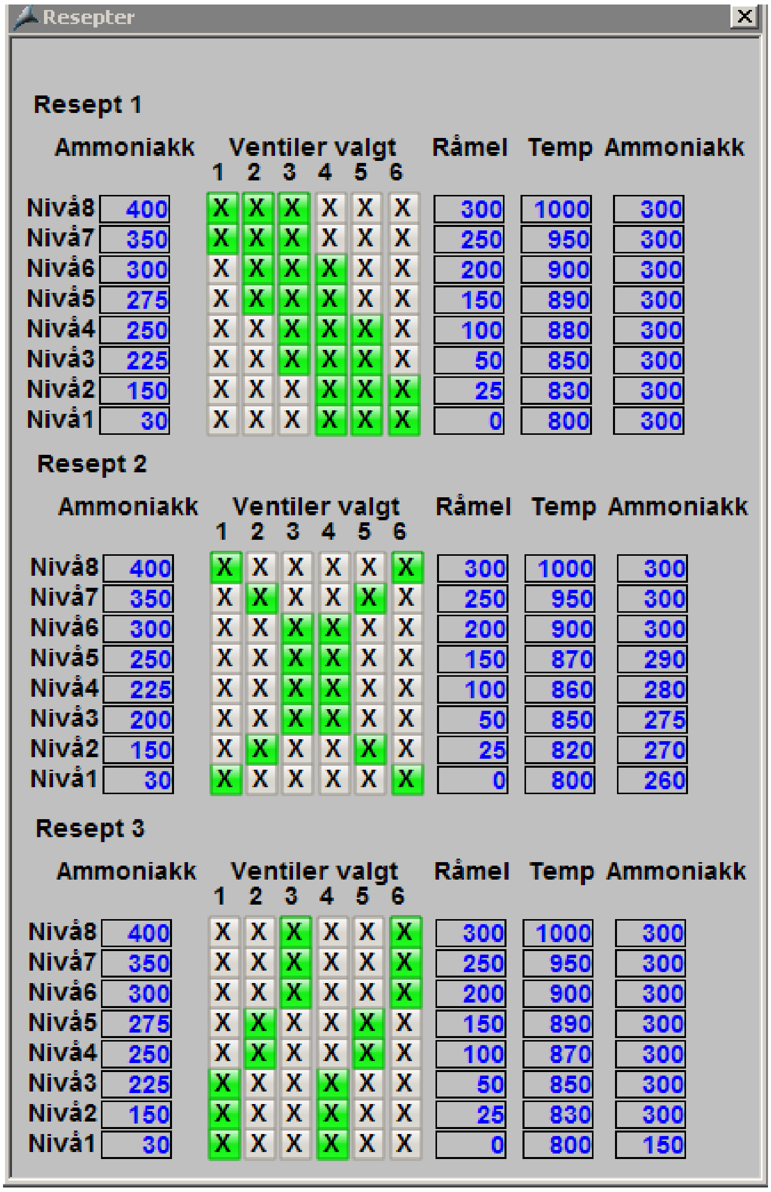
Figure 3-6 Prescription and injecting nozzles

From Figure 3-6 it can be seen that in the box to the left, the calculated amount of ammonia coming from the regulator is shown at the top. This amount decides the actual level in the prescription. In this example there is level 5 that is in operation with a total amount of ammonia at 263l/h. The green arrow on this level indicates that there is nozzle 3 and 4 which are activated. That is also shown to the right in this figure; nozzle 3 and 4 are operational.

If the temperature load increase so that the new calculated reduction agent amount will reach over 300 l/h it would lead to a change in the actual level; going from level 5 to level 6.

Totally, it exist 3 different prescriptions. These prescriptions can be customized to the different process conditions of the different clinker production. It is mainly the type of clinker, considering the operational conditions, that determines which prescription to be run. Change of prescription is performed in this box.

In order to go from a higher to a lower level, the value must be below the lower level, or opposite from a lower to a higher level, as well as the hysteresis. The purpose of the hysteresis is to prevent wear of the nozzles and to keep the process stable. With a hysteresis of 0.5 %, or 2l/h, this will be the same as a safety margin. In practice this will mean that a change of the operation on a nozzle have to be 2l/h over/under the limitation. This ensures that the valve will not get a wiggle around the level adjustment.



Resept 1

	Ammoniakk	Ventiler valgt						Råmel	Temp	Ammoniakk
		1	2	3	4	5	6			
Nivå8	400	🟩 X	🟩 X	🟩 X	X	X	X	300	1000	300
Nivå7	350	🟩 X	🟩 X	🟩 X	X	X	X	250	950	300
Nivå6	300	X	🟩 X	🟩 X	🟩 X	X	X	200	900	300
Nivå5	275	X	🟩 X	🟩 X	🟩 X	X	X	150	890	300
Nivå4	250	X	X	🟩 X	🟩 X	🟩 X	X	100	880	300
Nivå3	225	X	X	🟩 X	🟩 X	🟩 X	X	50	850	300
Nivå2	150	X	X	X	🟩 X	🟩 X	🟩 X	25	830	300
Nivå1	30	X	X	X	🟩 X	🟩 X	🟩 X	0	800	300

Resept 2

	Ammoniakk	Ventiler valgt						Råmel	Temp	Ammoniakk
		1	2	3	4	5	6			
Nivå8	400	🟩 X	X	X	X	X	🟩 X	300	1000	300
Nivå7	350	X	🟩 X	X	X	🟩 X	X	250	950	300
Nivå6	300	X	X	🟩 X	🟩 X	X	X	200	900	300
Nivå5	250	X	X	🟩 X	🟩 X	X	X	150	870	290
Nivå4	225	X	X	🟩 X	🟩 X	X	X	100	860	280
Nivå3	200	X	X	🟩 X	🟩 X	X	X	50	850	275
Nivå2	150	X	🟩 X	X	X	🟩 X	X	25	820	270
Nivå1	30	🟩 X	X	X	X	X	🟩 X	0	800	260

Resept 3

	Ammoniakk	Ventiler valgt						Råmel	Temp	Ammoniakk
		1	2	3	4	5	6			
Nivå8	400	X	X	🟩 X	X	X	🟩 X	300	1000	300
Nivå7	350	X	X	🟩 X	X	X	🟩 X	250	950	300
Nivå6	300	X	X	🟩 X	X	X	🟩 X	200	900	300
Nivå5	275	X	🟩 X	X	X	🟩 X	X	150	890	300
Nivå4	250	X	🟩 X	X	X	🟩 X	X	100	870	300
Nivå3	225	🟩 X	X	X	🟩 X	X	X	50	850	300
Nivå2	150	🟩 X	X	X	🟩 X	X	X	25	830	300
Nivå1	30	🟩 X	X	X	🟩 X	X	X	0	800	150

Figure 3-7 Prescriptions

Figure 3-7 illustrates the prescriptions in detail. As mentioned above it exist three prescriptions, each consisting of 8 levels.

Looking at the right side of the prescriptions there is three columns, respectively raw-meal, temperature and ammonia. The actual temperature/amount of raw-meal decides the given amount of ammonia into the regulator. The calculated amount of ammonia with respect to the NOx-control is put as a column to the left of the prescriptions in this figure. This column is the actual amount of ammonia and this level determines which nozzles to be operational.

4 Experimental development

As mentioned above there are several ways to optimize the system, depending on the aim of the experiment. The intention with this experiment was to find some optimal operating setpoints for the SNCR system in order to achieve a significant reduction of NOx, or maintaining current NOx limits (200mg/Nm^3). All this while at the same time minimizing the consumption of reduction agent and avoiding increased emissions of other pollutants.

By performing these experiments it is important to remember that there are many factors that may contribute and act disturbing to the experiment. It is difficult to relate to all possible factors. Essential operating parameters and the operational philosophy to the cement manufacturer are described below to provide a better understanding of the major connections.

4.1 Previous experiments

It has never been executed any optimization of the SNCR system at Norcem Brevik. However, it has been performed other types of experiments on cement plants which also have an SNCR system installed. One example is the Swedish cement plant, Slite.

Normally the SNCR system is installed with a reduction agent module and a water module. By including the water module there is a possibility to adjust the mixture of ammonia and water. There are examples of other manufactures that has the same principle as Norcem, thus with only the reduction agent module installed.

In 1998 a Swedish group of students did develop a paper for Cementa Slite, a cement manufacture in Sweden [29]. The aim was to reduce the consumption of ammonia at their SNCR system. The group of students performed several experiments and analyzed the results with the help of various improvement tools. To decrease costs of ammonia solution it was provided experiments of the total mixture. By increasing the amount of water it could be concluded with an optimum of 18-19% of ammonia dissolved in water.

This type of experiments cannot be performed at Norcem due to the omitted water module in the system that is not possible. Anyway, it would be irrelevant as a diluted ammonia solution would require a larger volume and more energy to evaporate the water content.

It was never an option for Norcem to install the water module with the aim of dilute the ammonia hydroxide. If it should be included, then it would be just in use to flush the system. Taken into account the difficulties of handling the water module, it was decided to exclude it. At Norcem the reduction agent is ammonium hydroxide 24.5%. This is because of classifications of the chemicals. By choosing ammonium hydroxide above 25% it would have resulted in a higher classification, which means stricter requirements of handling and storage.

4.2 Operational philosophy

The overall energy consumption is an important factor, measured as energy consumed per unit clinker produced. By achieving a high thermal efficiency, the consumption of fuel/energy would decrease as well as decreasing the generation of NOx per unit clinker [6].

To obtain the best possible quality of clinker and cement production it requires a lot of training and expertise from the operators. There are several parameters that must be controlled and some of the most important parameters for the operators are “free lime”, “kiln ampere” and the degree of calcination.

There is a limitation of the “free lime” varying depending on the type of clinker produced. This is a measure of the lime in the raw meal that is not converted. The greater this fraction is the poorer quality the clinker gets. The operators’ job is to maintain this fraction as low as possible to obtain good quality of the product.

The calcinations degree inlet of the kiln should be as high as possible, optimal around 95%, which means that most of the meal is already calcined throughout the precalciner. If the calcination degree starts to decrease, the operators have to increase the temperature in order to reverse that tendency. A high percentage of conversion results in a viscous fluid.

The ampere of the kiln can be an indication of the quality of the clinker. If the ampere is high this indicates that the calcination process is working optimally in terms of consistency of the fluid. The higher ampere in the kiln, the more viscous fluid there is which indicates optimum conditions in the kiln. Opposite, if the calcination process is not optimal the fluid will be thin which leads to a lower ampere of the kiln.

In terms of adjustment of the raw meal, this will impact the rest of the process. If the consumption of raw meal is reduced, consumption of fuels will be reduced which leads to a lower temperature profile and less thermal NOx formation.

Optimal operation of the fuel consumption is to obtain lowest possible cost which means to provide most possible alternative fuel. Limitations of alternative fuel consumptions might be CO development, flame temperature and free lime.

4.3 Design of experimental plan

The planned experiments are based on series of different combinations of the consumption of reduction agent and nozzles activated and also include a variation of the fuel as a part of it. Each experiment are planned to be run for 30 minutes. As a reference there will be 30 minutes on both sides of all the single trials, with the SNCR system turned off. By implementing the reference the results will be easier to read. The reduction efficiencies are based on the references. The operators where informed before the implementation since they had to be included in the fuel experiments, see Appendix F. The designed experimental plan is described below, but for more detailed implementation plan, see Appendix G.

The experiments were planned to be executed on days with standard clinker production. Another requirement was stable process conditions. This provides a stable reference throughout the experiments, leading to minor uncertainty.

FAB, one part of the secondary solid waste is expected to have the greatest impact of the CO development. The planned tests are therefore based on varying the consumption of FAB while the rest is planned to be as stable as possible. (Secondary coal supplements for reduction of FAB.)

During the planning of the experiments, it was selected process parameters which are important to the operation of the SNCR system. The most important ones are the temperature in the precalciner, the flow of reduction agent and the emissions from the stack. In addition it was important to monitor the fuel consumption, the raw-meal feeding and concentrations of central parameters like oxygen and carbon monoxide. Collected, a total of 60 parameters were included in the monitoring. All of these parameters can be found in the implementation plan, Appendix G, with all tag numbers included.

Aspen Process Explorer is a product installed at the desktops at Norcem which provides visually real-time and historical process data. This is an effectively way to monitor the process and trends in the process.

MS Excel was used to import all the process parameters from Aspen Process Explorer. By defining a period of time with a given time interval, it was made a dynamic spreadsheet in Excel. All the imported process parameters where put into charts.

4.3.1 Test 1; Reduce the consumption of reduction agent

The first experiment was carried out by manually operate the total flow of reduction agent into the system. That was done by manually adjustment of the setpoint of the regulator 45FT408/FC while the rest of the system was operated automatically.

Before the execution of the experiments, a set of hypotheses where made. This is hypotheses which in theory should be correct and what was planned to be proved. The hypotheses is compared against each other and given in Table 4-1.

Table 4-1 Hypotheses for test 1

Parameters in the flue gas	***Maximum reduction agent***	***Minimum reduction agent***
NOx	Lower	Higher
CO	Higher	Lower
NH_3-slip	Higher	Lower
O_2	Lower	Higher
TOC	Higher	Lower
Other emissions	Higher	Lower

The hypotheses are expectations with the overall reaction in mind, reaction (2.11) and (2.12) from 2.4.1.1 Chemistry. With a very high consumption of the reduction agent it is expected that NOx emissions will be very low because there is “more than enough” reduction agent available. The reduction agent that is left over will cause high level of NH_3-slip. O_2 are also consumed in a greater extent and CO is expected to have an opposite effect than NOx. TOC and other emissions are expected to increase parallel to the consumption of reduction agent.

The amounts of reduction agent will cover the typical operating range. Normal amount is approximately 180 l/h and the maximum amount is somewhere around 300 l/h.

Test 1 takes place over two days and is specified in Table 4-2. At day 1 there will be one test where the reduction agent is increased from 100 l/h to 300 l/h with initial steps of 100 l/h. This is done at a constant level of FAB, or more correct the amount of secondary solid waste. This test is repeated to reinforce the result. At the end of these parallel tests the flow of FAB is reduced while injecting a constant amount of reduction agent, 200 l/h, mainly to see if CO depends on the fuel to the greatest extent.

At day 2 the test is done by increasing the reduction agent from50 l/h to 300 l/h, now with a wider range, initially with steps of 50 l/h. This will also give a parallel to the two first parallels from day 1. At the end of this test the flow of FAB is reduced and then gradually increases until it reach the start value, all with a constant level of reduction agent at 200l/h.

Table 4-2 Experimental plan, test 1

Day 1		
Time	**Reduction agent (l/h)**	**Flow of FAB (t/h)**
08:00	0	12
08:30	100	12
09:00	0	12
09:30	200	12
10:00	0	12
10:30	300	12
11:00	0	12
11:30	100	12
12:00	0	12
12:30	200	12
13:00	0	12
13:30	300	12
14:00	0	12
14:30	0	8
15:00	200	8
15:30	0	8
16:00	200	8
16:30	0	8

Day 2		
Time	**Reduction agent (l/h)**	**Flow of FAB (t/h)**
08:00	0	12
08:30	50	12
09:00	0	12
09:30	100	12
10:00	0	12
10:30	150	12
11:00	0	12
11:30	200	12
12:00	0	12
12:30	250	12
13:00	0	12
13:30	300	12
14:00	0	12
14:30	200	8
15:00	200	9
15:30	200	10
16:00	200	11
16:30	200	12
17:00	200	8

4.3.2 Test 2; Create new prescriptions of the SNCR system

The second experiment was planned to be carried out by creating new prescriptions that may be more effective in terms of increasing the reduction rate of NOx. The tests will be performed by operating with a constant amount of reduction agent while adjusting the prescriptions. Since the temperature is practically equal upstream and downstream the precalciner, the injection nozzles that is activated should not be temperature dependent. Considering the reaction time it is expected that it should be advisable to inject the reduction agent as early as possible, i.e. at the upstream. It is also interesting to see if there is a difference by using 2 or 3 nozzles with constant injection of reduction agent. Also at this test it was created a set of hypotheses, shown in Table 4-3.

Table 4-3 Hypotheses for test 2

Parameters in the flue gas	***Only upstream nozzles***	***Only downstream nozzles***
NOx	Lower	Higher
CO	Higher	Lower
NH_3-slip	Lower	Higher
O_2	Lower	Higher
TOC	-	-
Other emissions	-	-

The hypotheses are expectations with the reduction time in mind; longer residence time should result in better reduction efficiency. The parameters are compared against each other. By injecting all reduction agent at only upstream nozzles the NOx emissions should be lower due to a longer reaction time. CO is expected to have an opposite effect than NOx and ammonia slip should be approximately equal, maybe a bit lower using only upstream nozzles because more ammonia helps reducing NOx.

At this test the amount of reduction agent will be kept at a constant level, 200 l/h. This is done because only the different nozzle combinations should be evaluated. Test 2 is also distributed over two days, respectively referred to as day 3 and 4, is shown in Table 4-4. On day 3 the test will be performed in the following manner; as mentioned above, the amount of reduction agent are kept constant at 200l/h, while the system runs 2 times on only upstream and 2 times on only downstream, respectively 3 and 2 nozzles at the time. At day 4 the amount of reduction agent is still constant and the nozzle combinations are chosen to still be on either upstream or downstream. The difference this time is that the prescriptions exist of combinations of only 2 nozzles at the time, the combinations that have still not been tested.

Table 4-4 Experimental plan, test 2

Day 3			
Time	**Reduction agent (l/h)**	**Flow of FAB/ Hot Mix (t/h)**	**Prescription**
08:00	0	12	Off
08:30	200	12	Nozzle 1, 2, 3
09:00	0	12	Off
09:30	200	12	Nozzle 1, 2
10:00	0	12	Off
10:30	200	12	Nozzle 4, 5, 6
11:00	0	12	Off
11:30	200	12	Nozzle 4, 5
12:00	0	12	Off
12:30	200	12	Nozzle 1, 2, 3
13:00	0	12	Off
13:30	200	12	Nozzle 1, 2
14:00	0	12	Off
14:30	200	12	Nozzle 4, 5, 6
15:00	0	12	Off
15:30	200	12	Nozzle 4, 5
16:00	0	12	Off
16:30	200	8	Nozzle 1, 2, 3
17:00	0	8	Off
17:30	200	8	Nozzle 4, 5, 6
18:00	0	8	Off

Day 4			
Time	**Reduction agent (l/h)**	**Flow of FAB/ Hot Mix (t/h)**	**Prescription**
08:00	0	12	Off
08:30	200	12	Nozzle 2, 3
09:00	0	12	Off
09:30	200	12	Nozzle 1, 3
10:00	0	12	Off
10:30	200	12	Nozzle 5, 6
11:00	0	12	Off
11:30	200	12	Nozzle 4, 6
12:00	0	12	Off
12:30	200	12	Nozzle 2, 3
13:00	0	12	Off
13:30	200	12	Nozzle 1, 3
14:00	0	12	Off
14:30	200	12	Nozzle 5, 6
15:00	0	12	Off
15:30	200	12	Nozzle 4, 6
16:00	0	12	Off
16:30	200	8	Nozzle 2, 3
17:00	0	8	Off
17:30	200	8	Nozzle 1, 3
18:00	0	8	Off

5 Full scale experiments

To present the results it was in advance created a number of spreadsheets that included all the main parameters affecting the system, in total four excel files. Two of the files was monitoring and displaying each individual parameter. The third file was created with the intention to combine important parameters to find correlations, where some of the figures are included in this chapter. During the experiments, the response of the system was measured and monitored dynamically in these files.

In the last file, all the resulting mean values of each trial were collected, as well as presented the results in combinations. Reduction efficiencies and cost optimizations was also created here. This was the only file that was not dynamically dependent on Aspen Process Explorer.

5.1 Implementation of the experiments

A screen print of the NOx reduction system can be found in appendix D and was described in details in 3.3.3 Functional description and 3.3.4 NOx regulation.

Both test 1 and 2 were carried out over 2 days each. The process conditions were kept as stable as possible by the operators those days but some disturbances occurred. Special things that were affecting the tests are explained in the next subchapters.

During the experiments there was observed some general things which was repeated:

- By stopping the system, the valve (45FT408/FC) stops by once and the air-flushing valve opens. The time of flushing the system was 1 minute.
- By starting the system with a specified amount of reduction agent, the response time of the valve (45FT408/FC) was approximately 30 seconds and it took about 1 minute before the valve was reaching full opening.
- By starting the system it took between 2-4 minutes before it could be noticed any response of the concentration of NOx and NH_3-slip.
- Every 30 minute the total flow through the nozzles showed a peak in the charts. The reason why is the flushing of the system. Pressurized air is flushing through the pipeline and nozzles. This is only shown in Figure 5-2.

All the figures presenting the results are showing the concentrations/emissions that are measured on string 1, the main stack. The same applies for the graphs presented in the appendices. String 2 was included in the created files with the intention to ensure that the tendency was the same on both strings.

Automatic + external

SP 120. l/h

PV 119.79 l/h

MAN 14.7 %

OUT 14.7 %

Completely running

Figure 5-1 NOx reduction system regulators

All experiments were carried out by starting and stopping the system every 30 minute. In addition, the flow of ammonia was manually regulated. Figure 5-1 illustrates how this was done. The image to the left is representing the controller and how it was operated. Since the flow should be often regulated, the controller was put in auto + internal. By doing that it was blocking out all other inputs than the given set point. The operational level from the prescription was still operating automatic. SP means the inserted set point and PV is the real process value. The image to the right shows how the system was turned on and off.

5.2 Results of experiment

The results are presented in charts created in excel. The process data was extracted as dynamically values to produce the results clear and transparent. To answer the deployed hypotheses, these parameters were set up against each other in diagrams.

Figure 5-2 illustrates an example of how the process variables were monitored. In this figure it can be seen that two streams of reduction agent are presented, respectively total flow nozzles (light blue) and total reduction agent (pink). These two streams represents the same stream, the only difference is that the total reduction agent (pink) is the measured flow through the regulator and the total flow nozzles (light blue) is the sum of all the individual flow-meters measured. Figure 5-2 was included to prove that there was always a deviation between the two measured streams and that the deviation was rising with increased amount of reduction agent injected. Average deviation was observed to be 10% with respectively minimum of 5% and maximum of 11.8%.

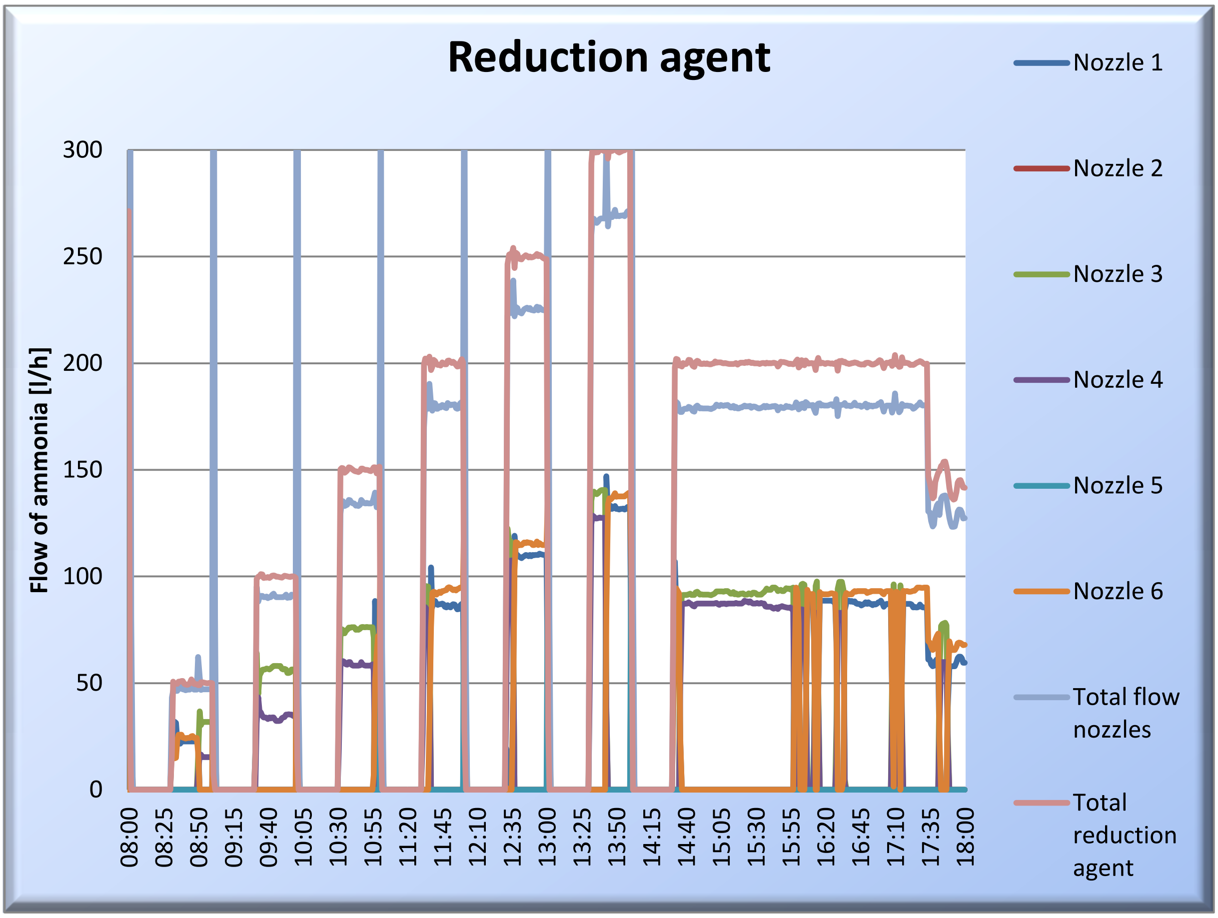


Figure 5-2 Example of the dynamic graphs of reduction agent

The figure also shows that all the individual flow-meters of all the nozzles are included. The aim was to show the different nozzle combinations but in order to simplify the graphs it was decided to only include the total reduction agent stream in the rest of the presented results. The reason why the total reduction agent (pink line) was chosen as the most reliable measurement is due to the greater uncertainty of the individual flow meters on each valve. The uncertainty is caused by the individual air-pressure at each nozzle. The pressure can be adjusted due to wear. The pressure is increased if the nozzle is worn or clogged. Increased air pressure leads to increased backpressure, which in turn leads to a smaller flow rate through the nozzle. This is also illustrated in the figure where it can be seen that the flow through nozzle 3 (green line) and nozzle 4 (purple line) is quite different. This indicates that nozzle 4 is more worn than nozzle 3. Nozzle combination 1 (blue line) and 6 (orange line) is more evenly distributed.

5.2.1 Test 1; Reduce the consumption of reduction agent

The resulting NOx concentration related to the flow of ammonia from day 1 is presented in Figure 5-3. This figure shows all the trials performed with different flows of ammonia. When the system was turned off, the NOx level can be found in the range of 300-400mg/Nm^3. It appears that NOx (dark line) was reduced to a greater extent when the amount of ammonia (light line) was increased. The reduction efficiency is calculated and presented in 5.2.1.4 Reduction efficiency.

After the two parallels, each consistent of three trials, it can be seen that there was two trials at 200l/h. The intention was to was to perform trials with a reduction of the FAB (secondary waste fuel), illustrated in Appendix H1.1.

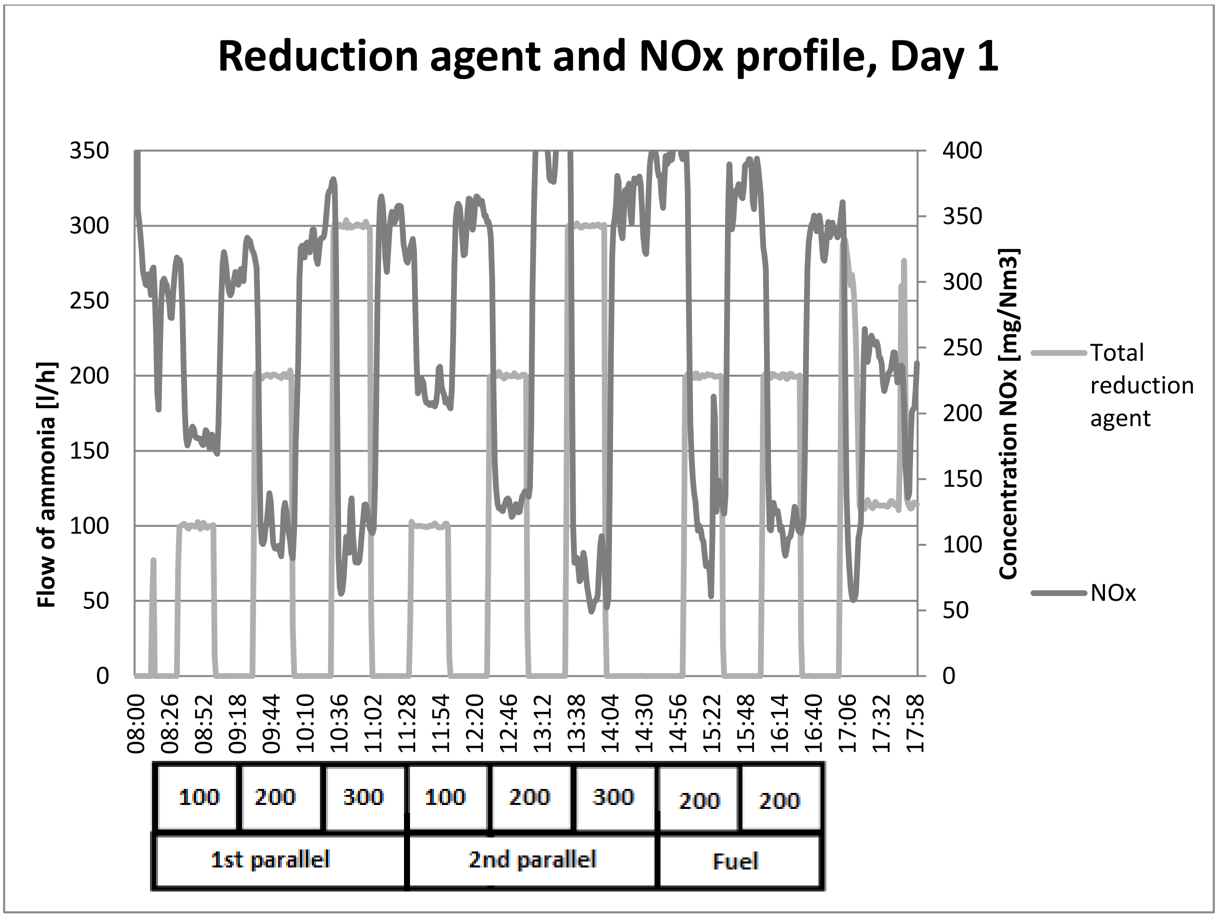


Figure 5-3 NOx concentration as a function of reduction agent, day 1

Figure 5-4 represents the NOx concentration related to the amount of ammonia during day 2. It can be seen that there was six trials with smaller steps compared to day 1, resulting in a 3rd parallel to be compared with the two parallels from day 1. At the end of the 3rd parallel it was injected a constant flow of 200l/h while at the same time the fuel was varied, see Appendix H2.1. When the system was turned off, the NOx level was in the range of 250-400mg/Nm^3. It comes out clear that NOx (dark line) was reduced to a greater extent when the amount of ammonia (light line) was increased.

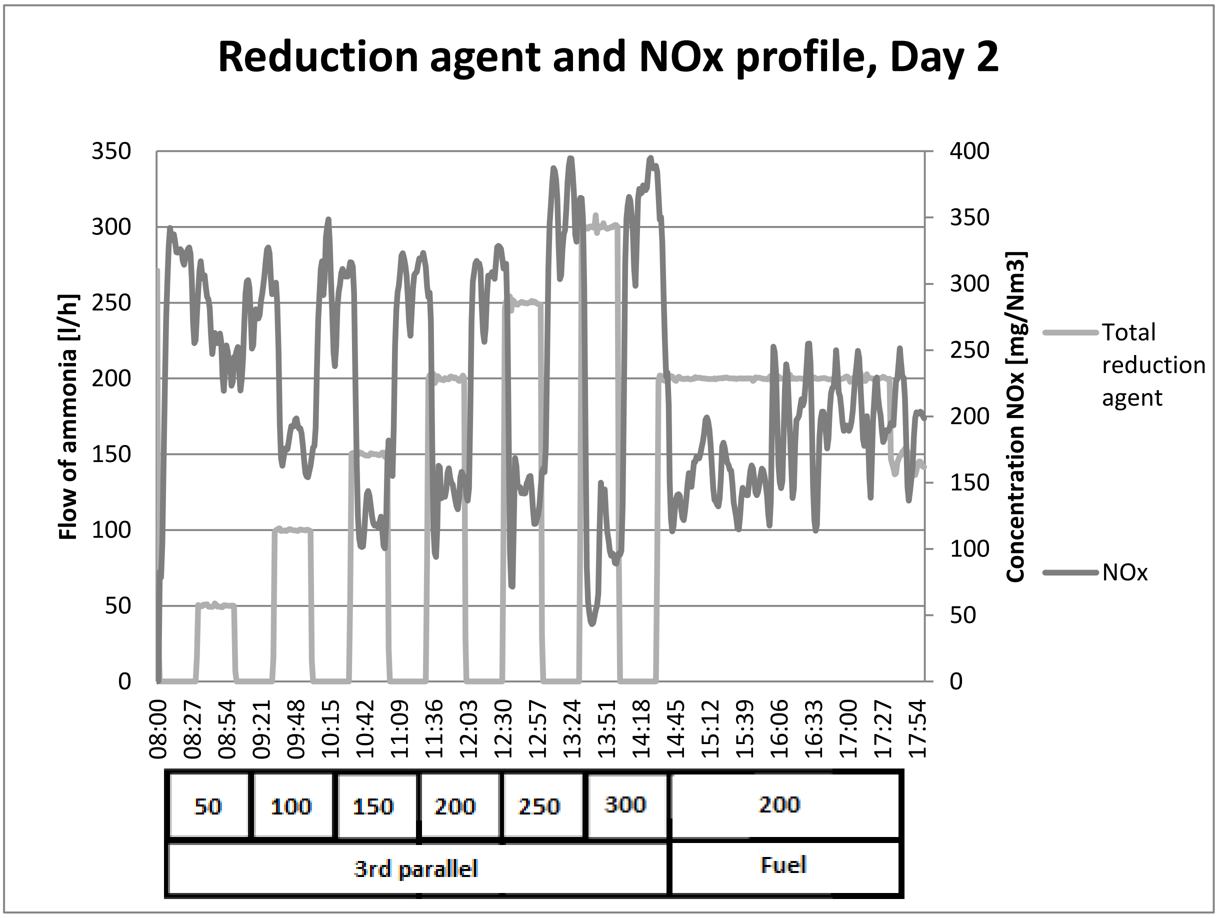


Figure 5-4 NOx concentration as a function of reduction agent, day 2

5.2.1.1 Process condition

The planned experiments given in Table 4-2 was implemented without any changes due to relatively stable process conditions. The basis of stable process conditions is mainly due to fuel consumption, raw material consumption, flue gas stream and the temperature profile. All these fundamental factors are very important to obtain a realistic result of the implemented experiments. All the graphs described can be found in Appendix H1/H2.

Day 1

According to the systems stability during day 1 this can be found in Appendix H1. The fuel consumption (H1.1) was kept quite stable, only a planned reduction of FAB consumption at the two last trails and additionally an unplanned stop of the kiln during these two trials, approximately at 15:05. The stop lasted a few minutes and can be observed in all the graphs.

The total consumption of raw materials (H1.2) was kept stable at a level of 230t/h except the period when the kiln was stopped. Also the flue gas stream (H1.3) was stable at a level of 185-200 km^3/h. The temperature profile (H1.4) was varying from 840-865^{o}C but anyway, not any drastically changes.

Day 2

According to the systems stability during day 2 this can be found in Appendix H2. The fuel consumption (H2.1) was kept stable and the planned fuel experiment from 14:30 was working very well.

When the level of FAB was reduced from 12t/h to 8t/h the consumption of secondary coal increased to maintain the same required energy consumption. The total consumption of raw materials (H2.2) was kept stable at a level of about 220t/h. Also the flue gas stream (H2.3) was stable at a level of about 190km^3/h. The temperature profile (H2.4) was varying from 840-883^{o}C where it can be found steeper variations compared to the first day. The maximum temperature is obtained as a result of the reduction of FAB and at the same time increased consumption of coal. When the consumption of FAB increases every 30 minutes and the consumption of coal stabilizes, the temperature also stabilizes around a level of 850^{o}C.

5.2.1.2 Reference time

In Figure 5-5 all the reference periods from test 1 is collected. All the bars represent 30 minutes without the system operating. The mean value of all the reference periods is 313.46mg/Nm^3. This mean value is used further on to calculate the reduction efficiencies during the test. Maximum NOx concentration at reference time was 386.3mg/Nm^3 and minimum was 264.6mg/Nm^3.

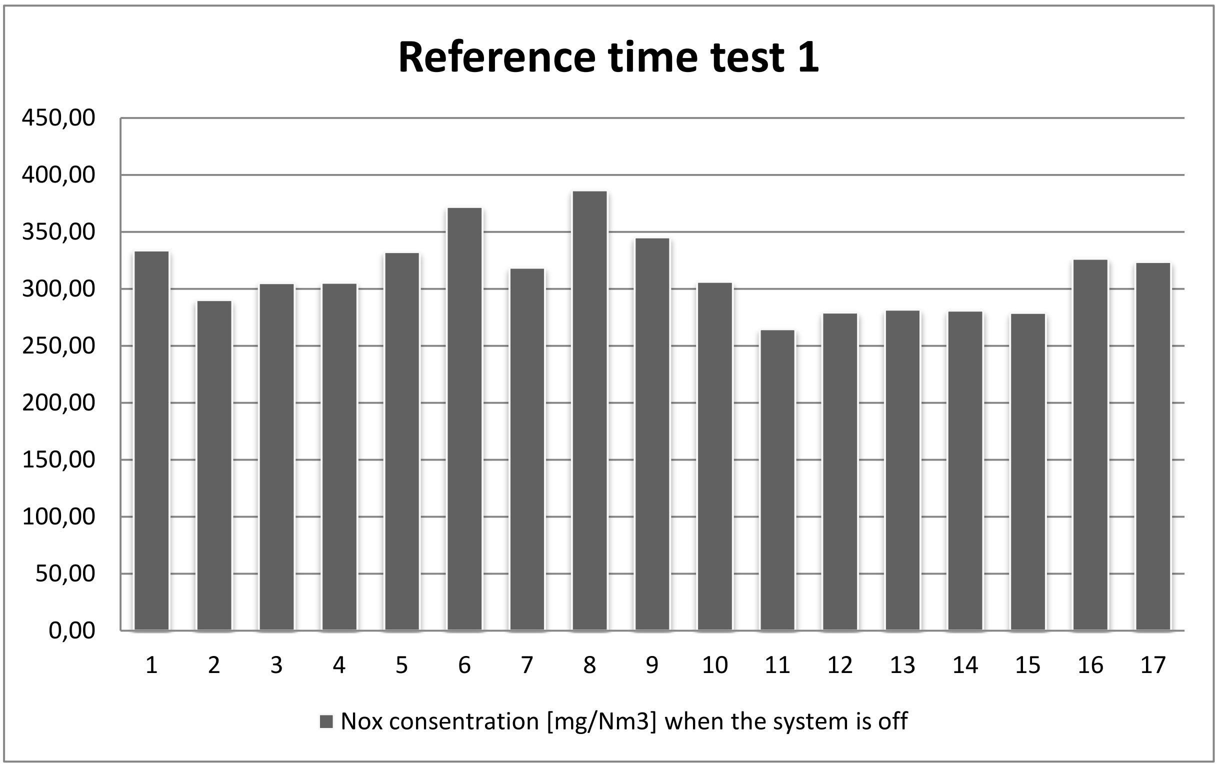


Figure 5-5 Reference periods from test 1

Bars 1-10 represents day 1 and bars 11-17 represents day 2. Reference number 8 characterize the period when the kiln was stopped. The reason of increased NOx level at bars 7, 8 and 9 is the increased consumption of coal. Number 16 and 17 is a bit higher than the rest of day 2 because of a small reduction of the secondary fuel.

5.2.1.3 Hypotheses

The aim of the experiments was in addition to find the optimum flow of reduction agent to answer the stated hypotheses in Table 4-1.

NOx

According to the hypotheses, NOx concentration should be reduced by increased amount of ammonia. From Figure 5-6 it can be seen that this in some extent is consistent to theory.

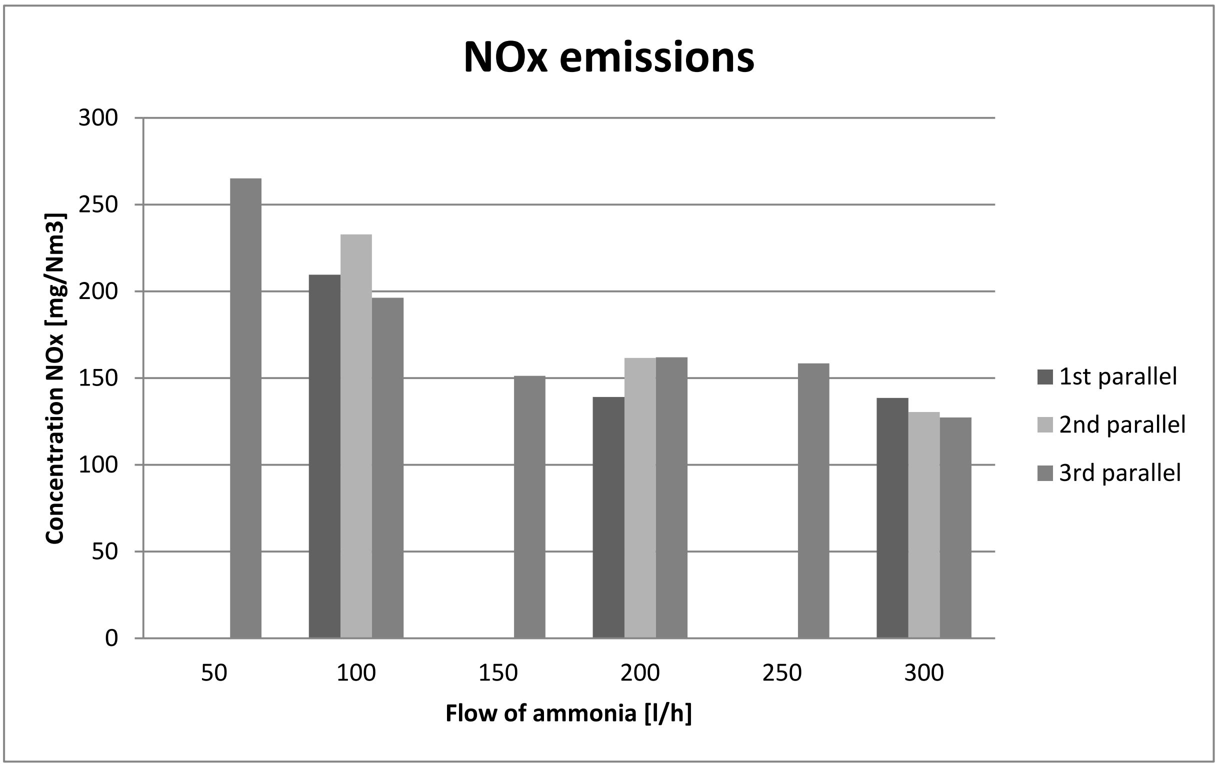


Figure 5-6 NOx emission levels test 1

It can also be observed that the reduction of NOx concentration is not greatly improved from 150l/h to 300l/h. For the 1st parallel (darkest), there is not any improvement using 300l/h compared to 200l/h. For the 2nd parallel (lightest) the reduction is improved in a small extent from 200l/h to 300l/h but not so much that it will be profitable to run with such large amounts. The 3rd parallel (middle) is performed with smaller intervals and provides a more accurate reflection of the process. The reduction efficiency is increased in great extent from 50l/h to 150l/h but the two next steps are not resulting in further increased efficiency. The last step at 300l/h gives a small improvement but not very essential.

By further processing of the NOx concentration there was used an average of the 3 resulting concentrations at 100l/h, 200l/h and 300l/h.

NH_3-slip

According to the hypotheses, the ammonia slip was expected to increase with increased consumption of ammonia, expected as excess ammonia. From Figure 5-7 it can be seen that the 1st parallel (squares) and the 3rd parallel (crosses) somehow confirms this theory, while the 2nd parallel (triangles) deviates.

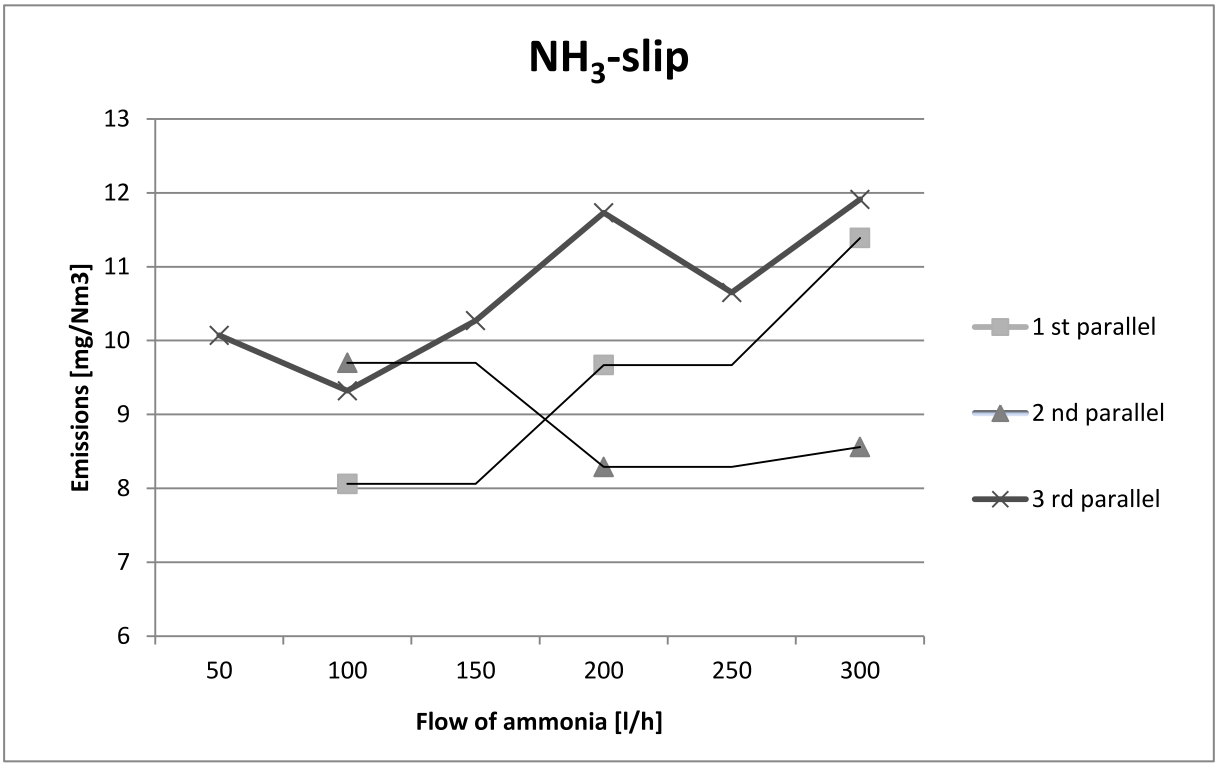


Figure 5-7 Ammonia slip test 1

Because of the deviation on the 2nd parallel, other parameters had to be checked to see if the hypotheses could be confirmed or if the NH_3-slip was independent due to the ammonia consumption. NOx concentration was investigated with the intention to see if it exist stronger correlations between NOx and NH_3-slip. Figure 5-8 illustrates the NOx and NH_3-slip profile for day 1. The figure shows that NH_3-slip starts increasing when the NOx concentration is reduced to 100mg/Nm^{3}or lower.

The explanation to the deviation occurring for the 2nd parallel is that the NH_3-slip is falling from the highest value at the 1st parallel. Since the NH_3-slip does not have any increasing tendency at 100l/h it continues to fall to stabilize at a lower level. This could be avoided by introducing longer reference time between the two parallels.

It is evident from the figure that this declining trend is reversed by adding 300l/h. The NH_3-slip is then almost stabilized and in addition the NOx concentration is reduced in a great extent, below 100mg/Nm^3.

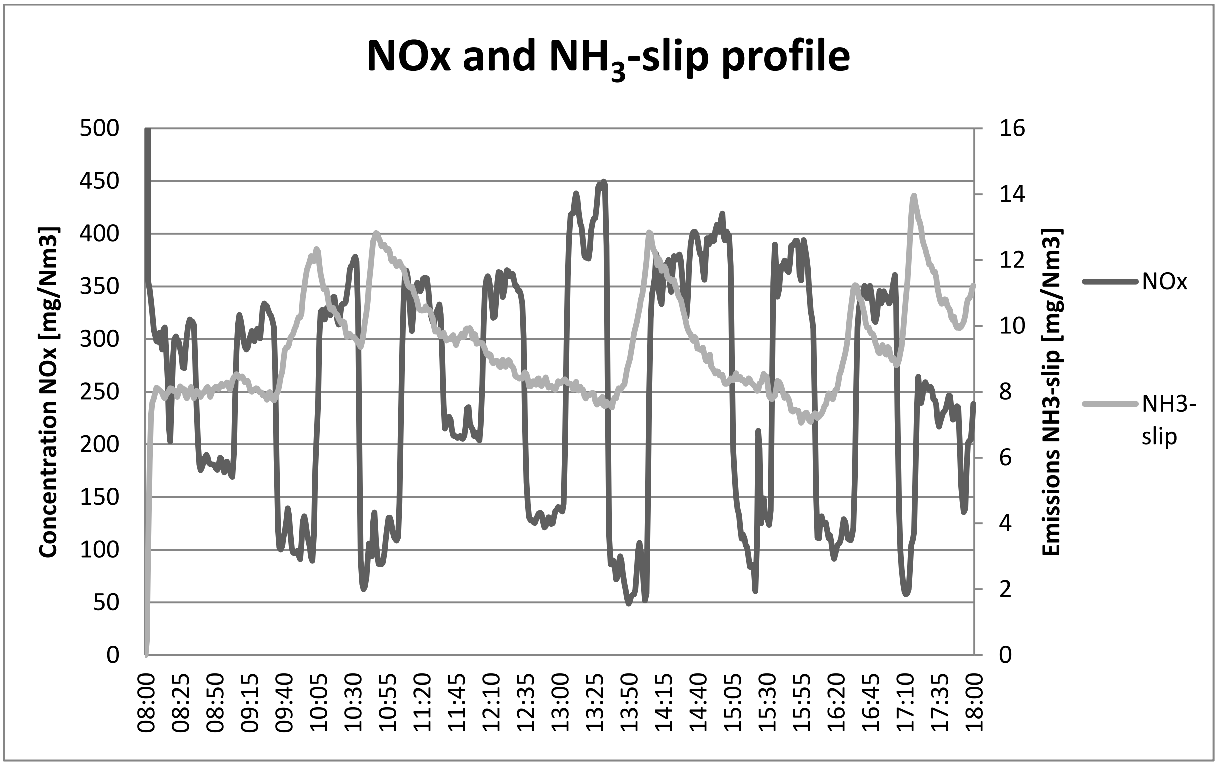


Figure 5-8 NOx and NH_3 profile at day 1

The NOx and NH_3-slip profile figure for the 3rd parallel indicates the same result and can be found in Appendix H2.5. This figure shows even more apparent that the sensitivity is very strong around 100mg/Nm^3.

CO, TOC and O_2

During the experiments and the preliminary work of process analysis it was evident that CO and TOC respond equally. According to the hypotheses, CO and TOC should be increasing with increased amount of ammonia injected. This theory cannot be proven at the executed experiments, where it can be observed that CO and TOC vary regardless of the amount of ammonia. See Appendix H1.6 and H2.6 for the resulting CO and TOC concentrations during test 1. Most likely, the CO and TOC are mainly dependent upon the fuel consumption, especially the consumption of FAB. From appendix H1.7 it can be seen that the concentration of oxygen operates as expected, opposite of CO/TOC.

High CO (and TOC) concentrations means that complete combustion is not achieved. The fact that oxygen behaves the opposite of CO has a natural explanation; it means that there is not enough excess air available to oxidize the CO.

The drop of CO/TOC concentration during the fuel experiment, as seen in H1.7, is caused by the short stop, i.e. a reduction of the fuels.

5.2.1.4 Reduction efficiency

The calculated reduction efficiency is shown in Figure 5-9. The darkest line represents the reduction efficiency relative to the calculated mean value of all the reference periods during test 1, 312.46mg/Nm^3. The lightest line is representing the reduction efficiency relative to the reference period before and after each individual trial so it makes the result more precise and therefore more trustworthy.

The calculated reduction efficiencies can also be found as calculated values in Appendix H3.

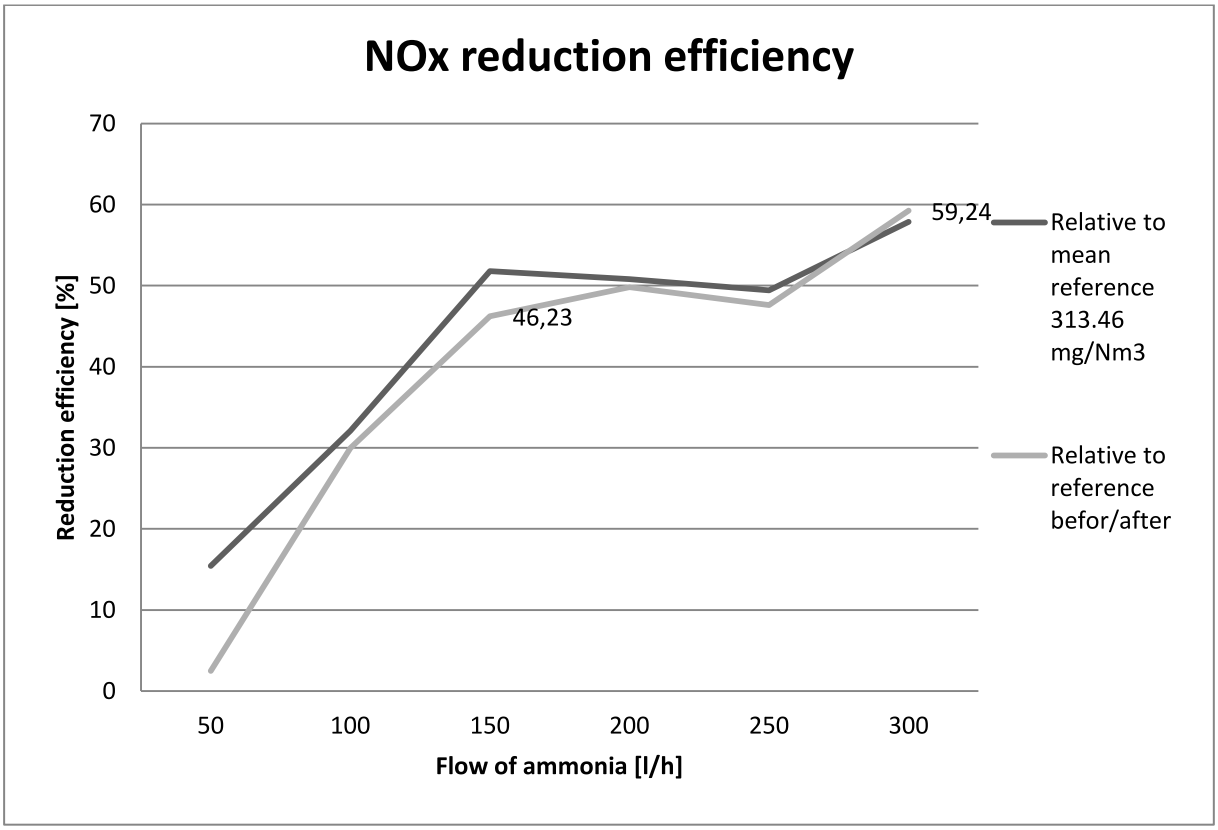


Figure 5-9 Reduction efficiency test 1

The lightest line indicates that by injecting 150l/h ammonia the resulting reduction efficiency becomes 46.2%. By increasing the amount of injected ammonia, it could further indicate that the reduction efficiency stagnates. The reduction efficiency achieves an increasing tendency by injecting as much as 300l/h of ammonia. Still, this implies that from a level of 150l/h to 300l/h the amount of ammonia is increased by 100%, resulting to only achieve an increase of the reduction efficiency of about 22%.

It is important not to mix the calculated reduction efficiency from the experiments with the overall reduction efficiency of the NOx reduction system stated to be approximately 65 %. This stated reduction efficiency was based on the total NOx reduced given in tons/year which represents a much wider range.

5.2.1.5 Cost optimization

The emission limits of NOx are set to be 800mg/Nm^3 by the government, see Table 3-2. NOx emissions from Norcem have always been within the range with good margin, which can be seen in Table 3-3. After installation of the SNCR technology, the emissions have been further reduced and therefore Norcem have set their own guidance limits to be 200mg/Nm^3.

Figure 5-10 shows the operational cost level of ammonium hydroxide relatively to the reduction efficiency. The ammonia price and calculations is shown in Appendix H4. The price of ammonia is an average of all the expenses of the “fillings” documented, 1.54NOK/l. The operational hours are copied from 2013; 7513h/year.

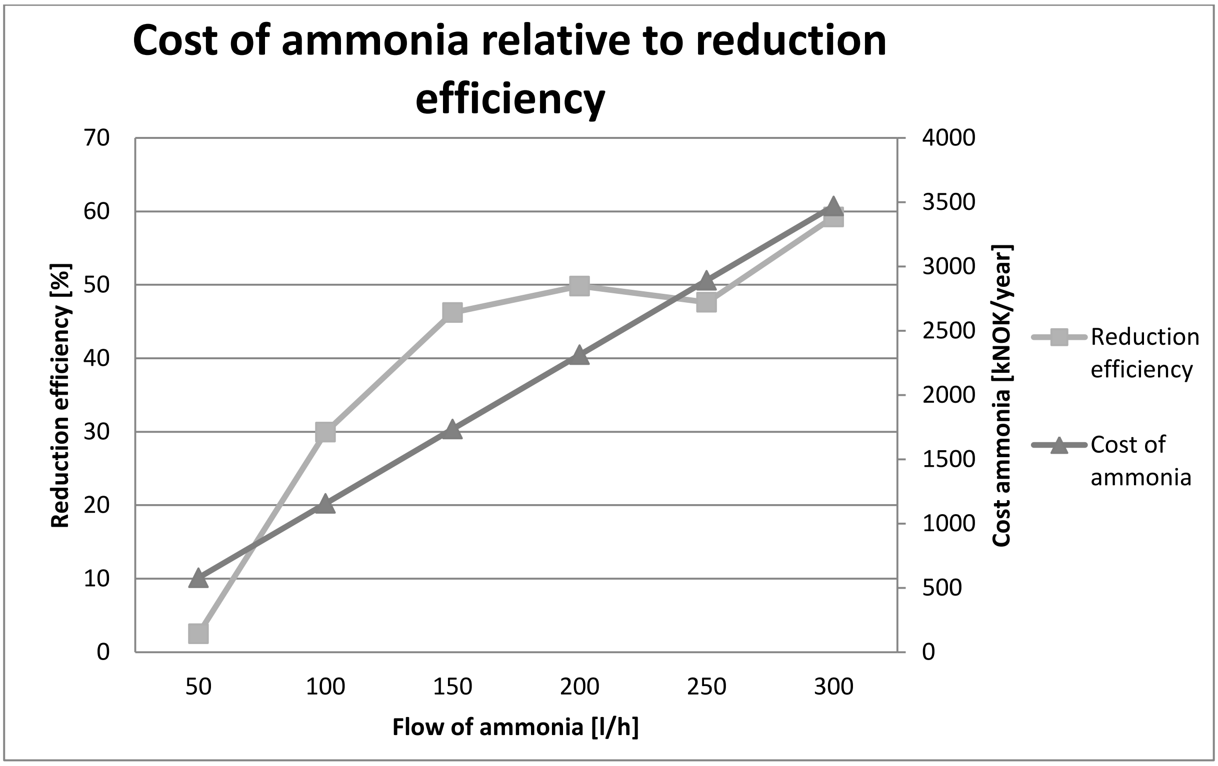


Figure 5-10 Operational cost ammonium hydroxide

The average level of NOx at a consumption rate of 100l/h of ammonia is 212.8mg/Nm^3 and can be found in Appendix H5. This is very close to the limit of 200mg/Nm^3. By interpolating, the specific amount of ammonia should be 110l/h-116l/, see Appendix H3, to fulfill the guidance limit of 200mg/Nm^3

Economically, 150l/h is the optimal amount of ammonia. This can be proven by the figure and a simple calculation. By increasing the consumption of ammonia from 150l/h to a level of 200l/h, it will result in a cost increase of additional 25% while the reduction efficiency is further increased by only 8% which in terms is very little profitable.

The yearly cost of ammonia would be 1,735MNOK by obtaining an average consumption of 150l/h which leads to a NOx reduction of about 46%. This corresponds to a mean NOx concentration of 150-175mg/Nm^3. As mentioned earlier, all organizations that endorse the NOx-environmental agreement which includes the NOx-fund are exempted from taxes.

Norcem is a part of this agreement, have utilized the NOx-fund and is therefore exempt from paying taxes of NOx emitted. If this had not been the case, it might be appropriate to pay tax on NOx which currently is 17.33NOK/kg NOx emitted [30].

The estimated cost of ammonia was therefore compared with the potential expenses of NOx taxes, illustrated in Figure 5-11.

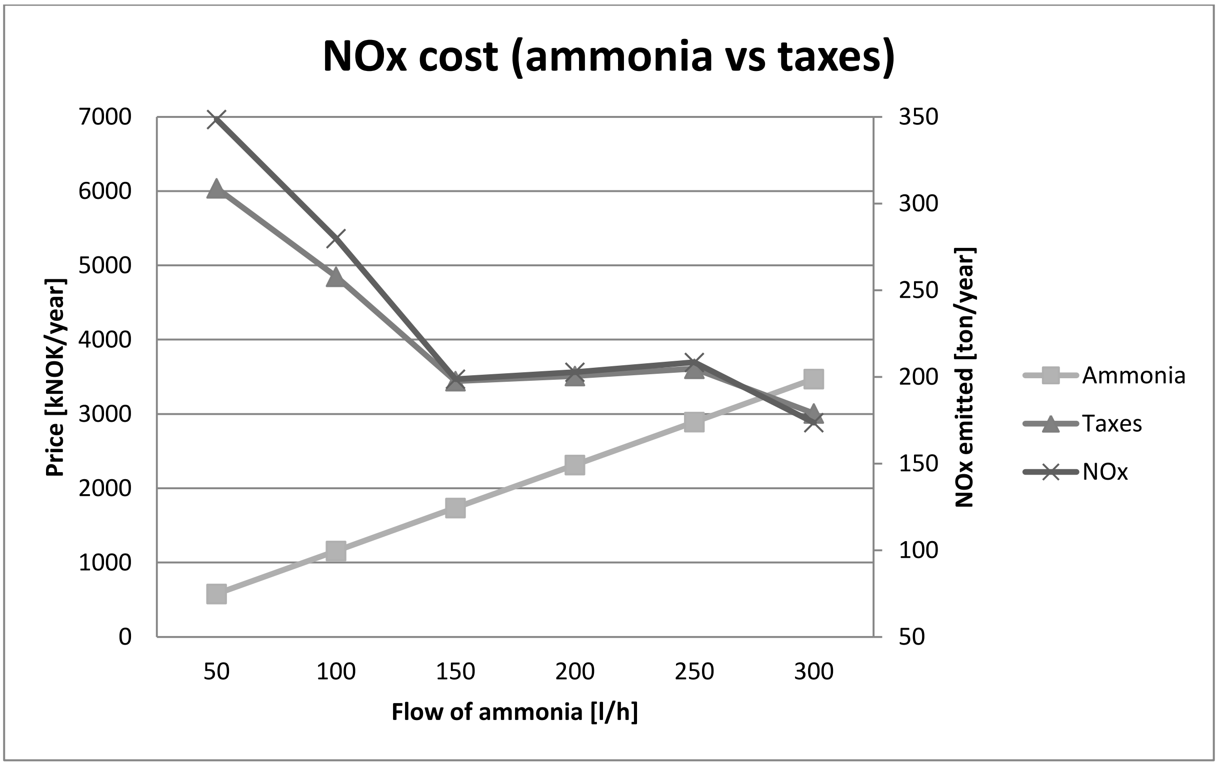


Figure 5-11 NOx cost (ammonia versus taxes)

The presented amount of NOx emitted (crossed line) are average values from the three parallels that was run in test 1, converted into NOx emitted in tons/year, as a function of the flow of ammonia. The price of NOx taxes (triangle line) has the same tendency as NOx because the price is a factor times NOx emitted. The price of ammonia (squared line) is the same as presented in Figure 5-10, a linear function of the flow of ammonia.

Also this figure confirms that the optimal flow of ammonia is 150l/h. At this flow of ammonia the NOx emission would be approximately 200tons/year. At this point, the cost of ammonia is 1.735MNOK. Without the NOx reduction system and an obligation to pay NOx taxes the price would have been 3.44MNOK for the same level of NOx emissions, 200tons/year.

The figure shows a clear optimum between the two alternative costs where the lines are crossed. This optimum can be found at an ammonia flow of approximately 280l/h. Based on test 1 this implies that the maximum amount of ammonia injected to the system should be 280l/h as an average during the year. With this amount the NOx emitted is approximately 190 tons/year and a price of 3.2MNOK/year.

5.2.1.6 Fuel experiment

As mentioned earlier, the short stop that occurred during the fuel experiment at day 1 led to instability of the production. As a result of the disturbances it was too difficult to process the results. It was therefore decided to focus only on the fuel experiment executed on day 2. It can be seen from Figure 5-12 how the secondary solid waste (FAB and Hot Mix) was varied. The secondary coal responded to replace the energy loss occurring by the reduction of solid waste. The primary fuel consumption is not shown here but it was very stable and can be found in Appendix H2.1. Secondary solid waste was reduced from 12t/h to 8t/h and every 30 min it was increased with 1t/h until it reached 12t/h. At the end of this increase there were conducted another big drop to see how CO responded. The intention with this kind of experiment was to observe the CO development relative to the secondary solid waste.

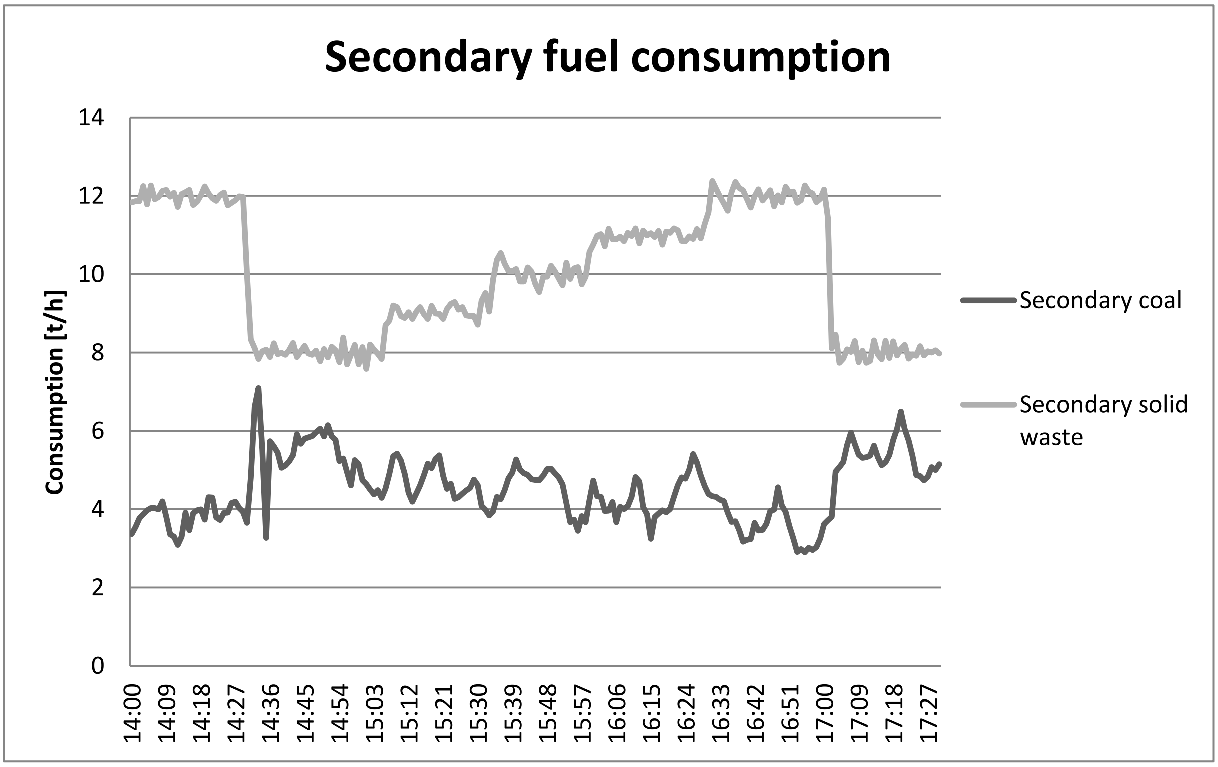


Figure 5-12 Secondary fuel consumption during fuel experiments

The result of the CO development according to the fuel experiments are illustrated in Figure 5-13. The development of CO was as expected, increasing with increased consumption of FAB. The first trial at 8t/h was a bit higher compared to 9t/h but it can most likely be explained by the short response time after the great reduction from 12t/h to 8t/h just before the experiment.

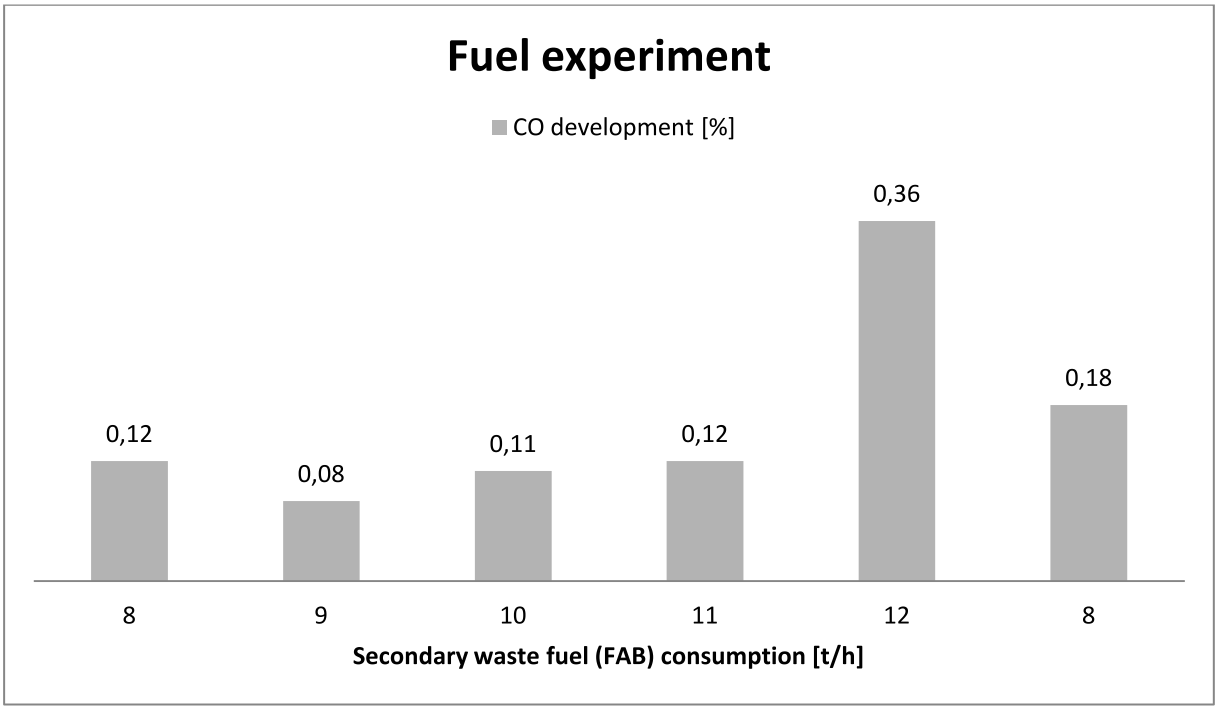


Figure 5-13 Fuel experiment

5.2.2 Test 2; Create new prescriptions of the SNCR system

According to some problems with the coal-weights at Norcem, tests and calibrations of the weights were executed at the same time as the implemented NOx experiments, test 2. Following from this it means that the fuel consumption was varying a lot, which means unstable conditions during the NOx experiment.

Because of these disturbances, the planned test was changed. Table 5-1 shows the updated experimental plan of test 2. The planned part with fuel reduction (on both days) where deleted because of the unstable fuel consumption. Instead of implementing the planned test on day 4 it was decided to repeat the same test as day 3 on day 4. In other words; there were executed in total 4 parallel tests, all with unpredictable fuel consumption.

Table 5-1 Updated and actual executed test 2

Day 3				**Day 4**			
Time	**Reduction agent (l/h)**	**Flow of FAB (t/h)**	**Prescription**	**Time**	**Reduction agent (l/h)**	**Flow of FAB (t/h)**	**Prescription**
08:00	200	12-13	Off	08:00	200	11	Off
08:30	200	13	Nozzle 1, 2, 3	08:30	200	11	Nozzle 1, 2, 3
09:00	200	13	Off	09:00	200	11	Off
09:30	200	13	Nozzle 1, 2	09:30	200	11	Nozzle 1, 2
10:00	200	13	Off	10:00	200	12	Off
10:30	200	14	Nozzle 4, 5, 6	10:30	200	12	Nozzle 4, 5, 6
11:00	200	14	Off	11:00	200	12	Off
11:30	200	14	Nozzle 4, 5	11:30	200	12	Nozzle 4, 5
12:00	200	14	Off	12:00	200	12	Off
12:30	200	14	Nozzle 1, 2, 3	12:30	200	12	Nozzle 1, 2, 3
13:00	200	14	Off	13:00	200	12	Off
13:30	200	14/15	Nozzle 1, 2	13:30	200	12	Nozzle 1, 2
14:00	200	14	Off	14:00	200	12	Off
14:30	200	14	Nozzle 4, 5, 6	14:30	200	12	Nozzle 4, 5, 6
15:00	200	14	Off	15:00	200	10	Off
15:30	200	14	Nozzle 4, 5	15:30	200	10	Nozzle 4, 5
16:00	200	14	Off	16:00	200	10	Off

Figure 5-14 presents the resulting NOx concentrations obtained from day 3, 1st and 2nd parallel. The NOx concentration (darkest line) was quite stable through the 1st parallel but during the 2nd parallel it was very unstable.

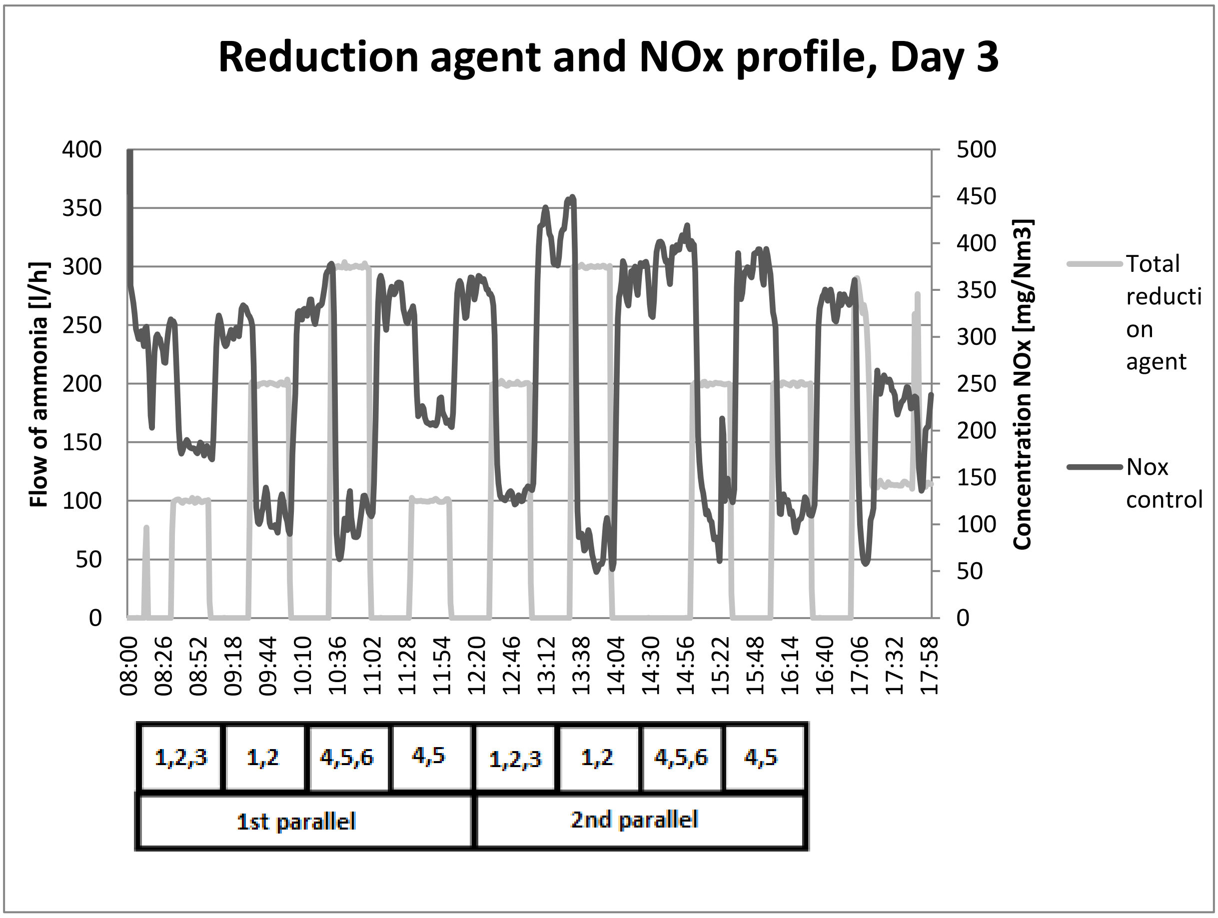


Figure 5-14 NOx concentration as a function of reduction agent, 1st and 2nd parallel

Figure 5-15 presents the resulting NOx concentrations obtained from day 4, 3rd and 4th parallel. It can be seen that the NOx concentration (darkest line) was very high and unpredictable during the 3rd parallel. At the last trial of 3rd parallel and throughout the 4th parallel, NOx concentrations was more stable and seemed to respond quite smoothly.

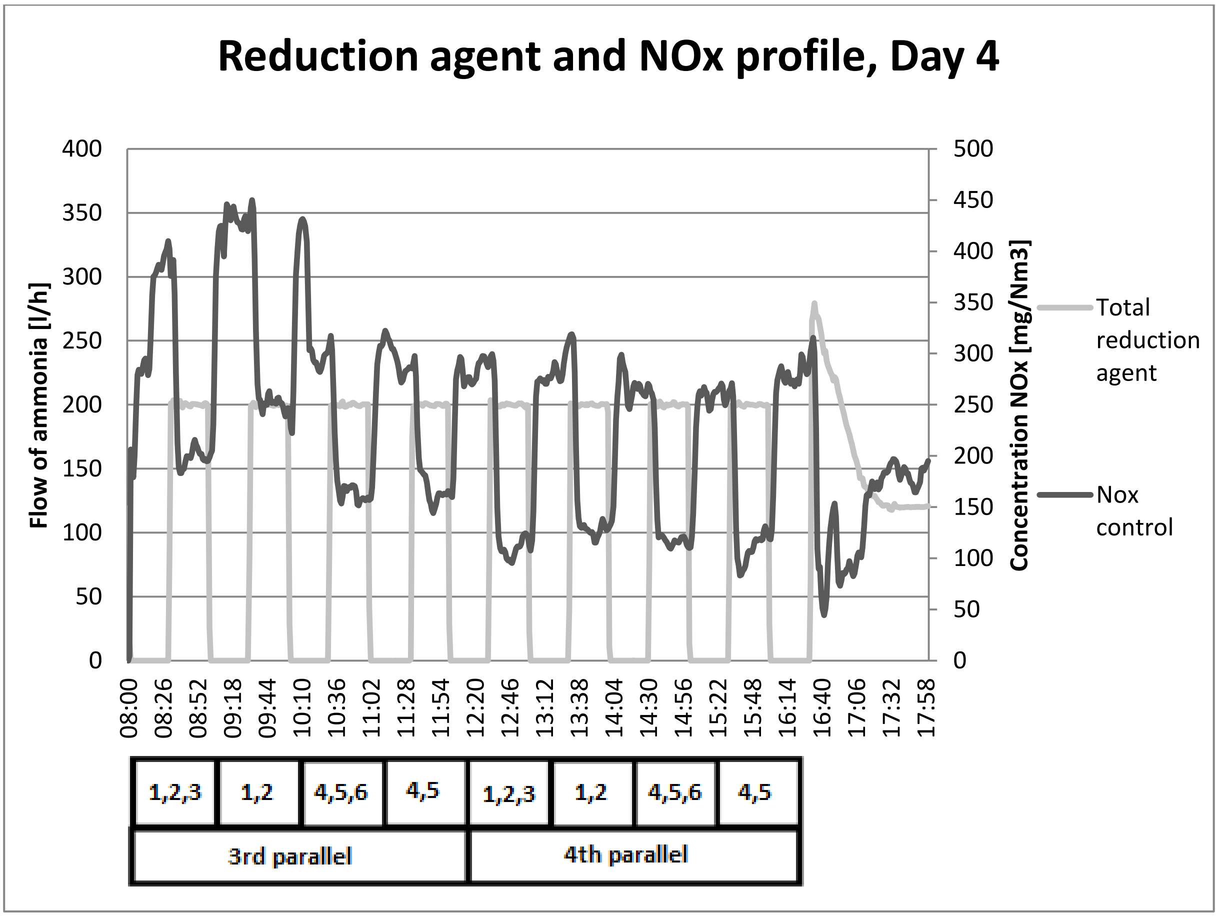


Figure 5-15 NOx concentration as a function of reduction agent, 3rd and 4th parallel

5.2.2.1Process condition

The planned experiments from table 4-3 were changed due to unstable process conditions. The basis of stable process conditions is mainly due to fuel consumption, raw material consumption, flue gas stream and the temperature profile. All these fundamental factors are very important to obtain a realistic result of the implemented experiments. All these graphs can be found in Appendix I1/I2.

Day 3

The fuel consumption during the 1st parallel was a bit varying, at the first trial (nozzle combination 1,2,3) FAB was increased from 12t/h to 13t/h and at the third trial, (nozzle combination 4,5,6) FAB was increased from 13t/h to 14t/h, which can be seen in Appendix I1.1. These disturbances did not affect the NOx concentration in a great extent. The raw material consumption (Appendix I1.2), flue gas stream (Appendix I1.3) and temperature profile (Appendix I1.4) was very stable.

The fuel consumption during the 2nd parallel was very unstable which is also clearly evident in Figure 5-14. From Appendix I1.1 it may look like there was added primary oil from 13:20 but it was proved later on that the flow-meter was irregular.

The secondary coal was greatly increased according to the low temperatures. From 12:43 to 13:31 the temperature did drop from 865°C to 823°C, a total reduction of 42°C on approximately 1 hour which may cause bad conditions in the kiln. As a measure to optimize the process, the consumption of raw materials was reduced from 220t/h to 190t/h. The flue gas stream was varying with a flow of 175-200 km^3/h in this period.

From day 3, only the 1st parallel was stable enough to be produced as result.

Day 4

The fuel consumption during the 3rd parallel was a bit varying. At 10:00, large fluctuations of the secondary coal consumptions started because of the calibrations on the coal weights. The FAB consumption was increased from 13t/h to 14t/h at the same time, see Appendix I2.1.

It can be observed that the concentration of NOx is within a higher range for the 3 first reference periods at the 3rd parallel in Figure 5-15. This can be explained by the temperature profile (Appendix I2.4). The mean temperature for the 3 first reference periods was 845°C while for the next 3 reference periods it was about 855°C. This observation provides a very interesting result; it confirms that the NOx reduction is strongly dependent upon the temperature profile.

Approximately at 15:00 the total raw material consumption (AppendixI2.2) was reduced from 210t/h to 200t/h. As a measure to keep the process stable, a reduction of the FAB consumption was also implemented, from 12t/h to 10t/h. These adjustments are barely remarkable according to the NOx concentration. The flue gas stream (Appendix I2.3) was very stable.

From day 4, only the 4th parallel was stable enough to be produced as result.

5.2.2.2 Reference time

In Figure 5-16 all the reference periods from test 2 was collected. All the bars represent 30 minutes with the system un-activated. Bar 1-9 represents day 3 and bar 10-18 represents day 4.

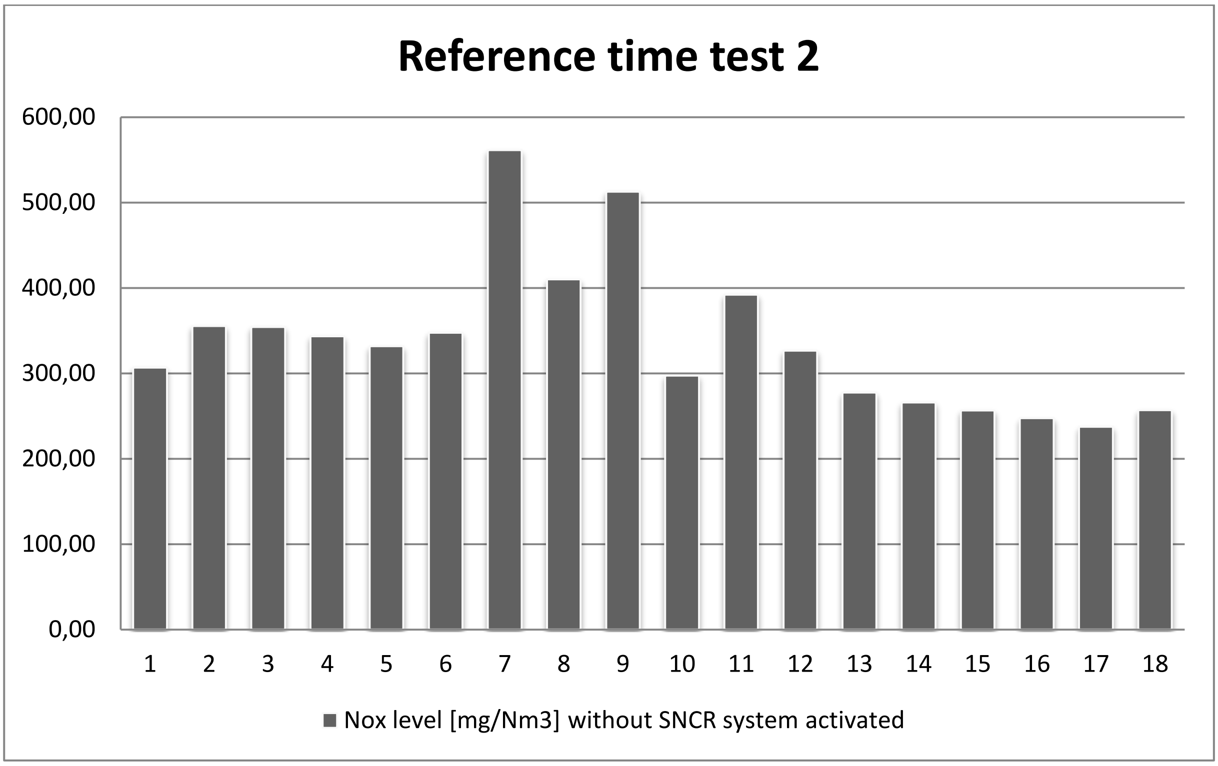


Figure 5-16 Result of reference times for test 2

The mean value of all the reference periods is 337.72mg/Nm^3 with respectively a maximum reference of 561.17mg/Nm^3 (bar 7) and minimum reference of 237.33mg/Nm^3 (bar 17). It is worth noticing that this maximum value is due to a very low temperature profile (see Appendix I1.4) and the highest reference time therefore affects the mean value to increase.

Because of the large deviations of the 2nd and 3rd parallel it was decided to only use the 1st and 4th parallel in further results. The mean value of reference times from 1st and 4th parallel (1-5 and 14-18) is 295.5mg/Nm^3.

5.2.2.3 Hypotheses

The aim of the experiments was in addition to find the optimal nozzle combinations to answer the stated hypotheses in Table 4-3. As stated above; due to the instabilities, only the 1st and 4th parallels are further processed.

NOx

It was expected to find different NOx reduction levels by using only upstream nozzles (4,5,6) and only downstream nozzles (1,2,3). As stated in the hypotheses; According to a longer reaction time it was expected to obtain greater NOx reduction (lower NOx concentrations) using only upstream nozzles. In addition it was expected to obtain a greater reduction using 3 nozzles compared to 2 nozzles, in terms of exploiting the full cross-section in the calciner.

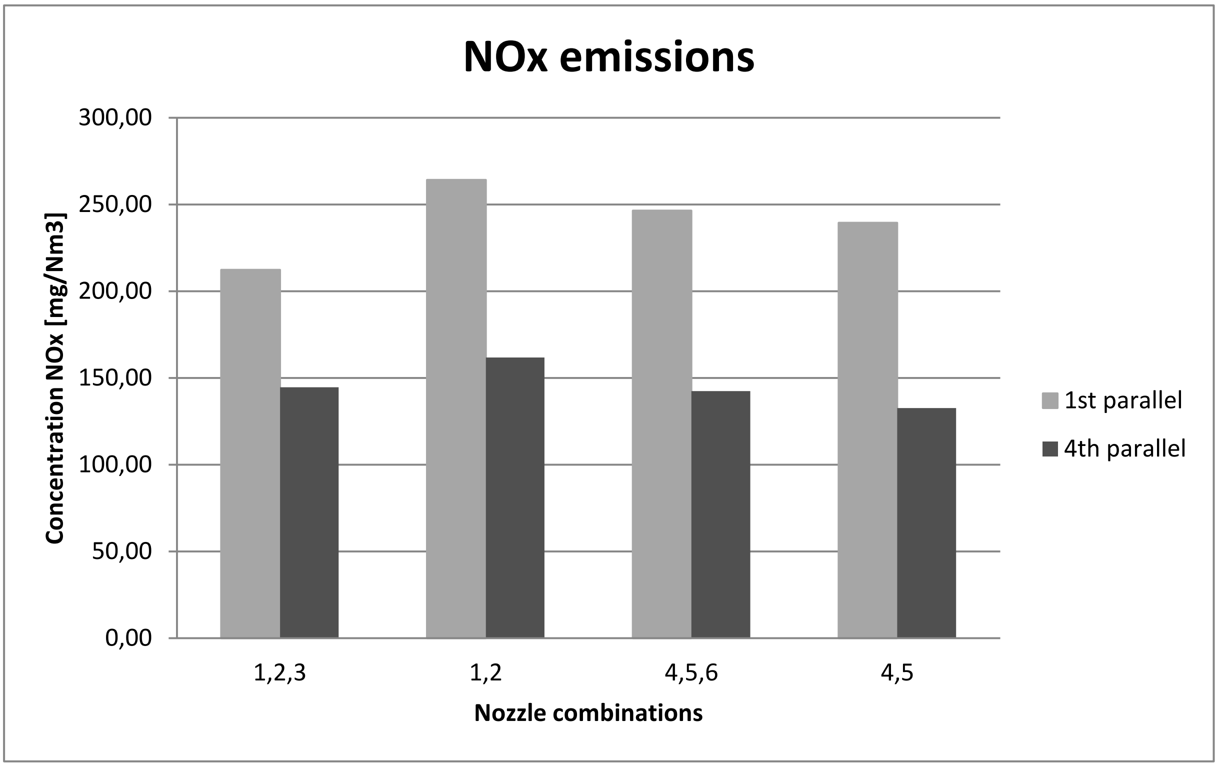


Figure 5-17 NOx emission levels test 2

From Figure 5-17 it can be seen that it is very small differences in the NOx concentration for the various trials. Anyway, there is a tendency which is repeated for both the 1st and 4th parallel, actually also for the two other parallels which are deleted, see Appendix I4. At upstream nozzles (4,5,6), 2 nozzles activated gives a bit better NOx reduction than 3 nozzles activated. At downstream the results are opposite. 3 nozzles give better NOx reduction than 2 nozzles.

NH_3-slip

According to the hypotheses it was expected that the NH_3-slip should be somehow lower for only upstream (4,5,6) nozzles. The idea of this expectation was according to the reduction time. Greater NOx reduction was expected at only upstream which applies more consumed ammonia which again leads to less NH_3-slip.

All the parallels were performed with a constant flow of ammonia at 200l/h. With an overall stable production it would have implied that the ammonia-slip should not vary so much.

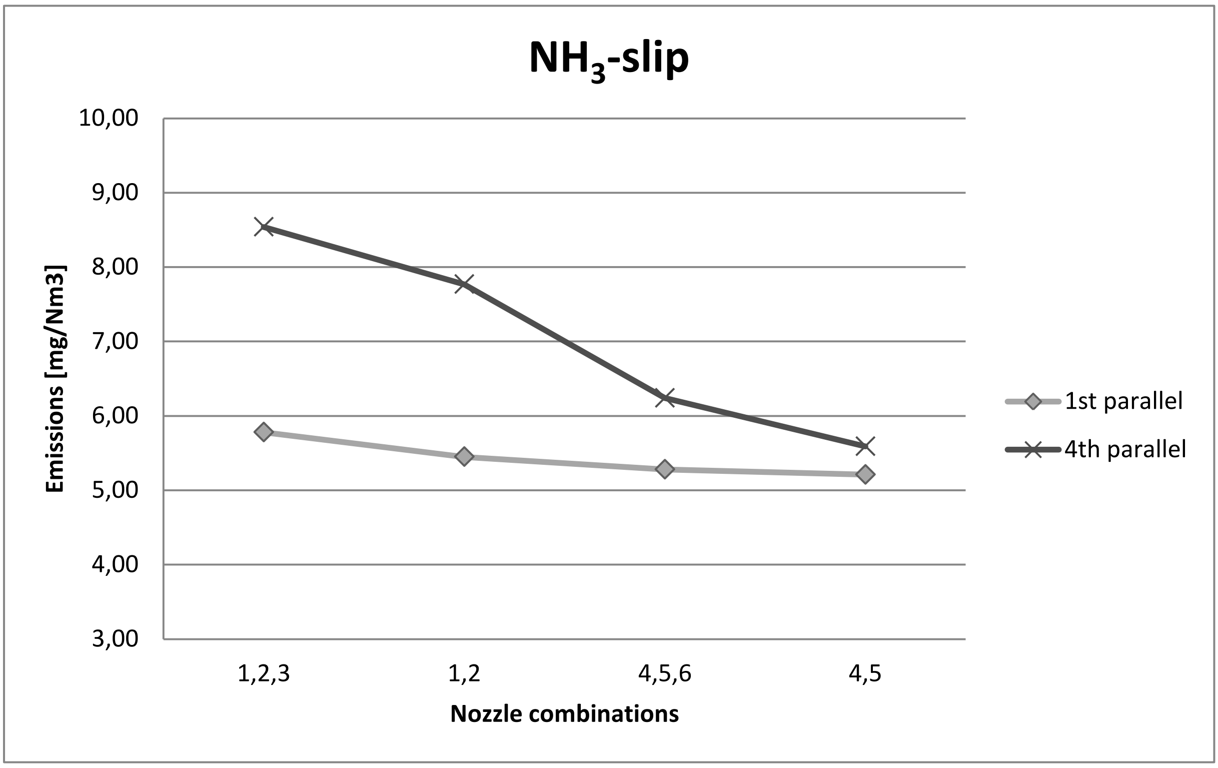


Figure 5-18 Ammonia slip test 2

From Figure 5-18 it can be seen that the 1st parallel is quite stable. In Appendix I1.5, NOx and NH_3-slip profile day 3, it can be seen that the reason why the first trial at 1st parallel (1,2,3) is slightly higher than the rest is because the NOx concentration is a little lower than the rest. This implies the great impact of the NOx concentration sensitivity on the NH_3-slip.

The 4th parallel has a decreasing trend. Figure 5-19 shows the NH_3-slip relative to the NOx concentration at day 4. From the 3rd parallel the production was unstable, which resulted in a high NH_3-slip at the start of the 4th parallel. The decreasing trend is due to the overall process stabilization which leads to lower NOx concentration and thereby also reduced NH_3-slip. At one point during the 4th parallel the NH_3-slip obtains a small peak due to the NOx concentration which at that time is reduced below 100mg/Nm^3.

The resulting ammonia slip shown in Figure 5-18 does not show any apparent difference between upstream and downstream after finding the explanation of the decreasing tendency at the 4th parallel.

NH_3-slip is most likely more dependent upon the NOx concentration and temperature than the nozzle combinations.

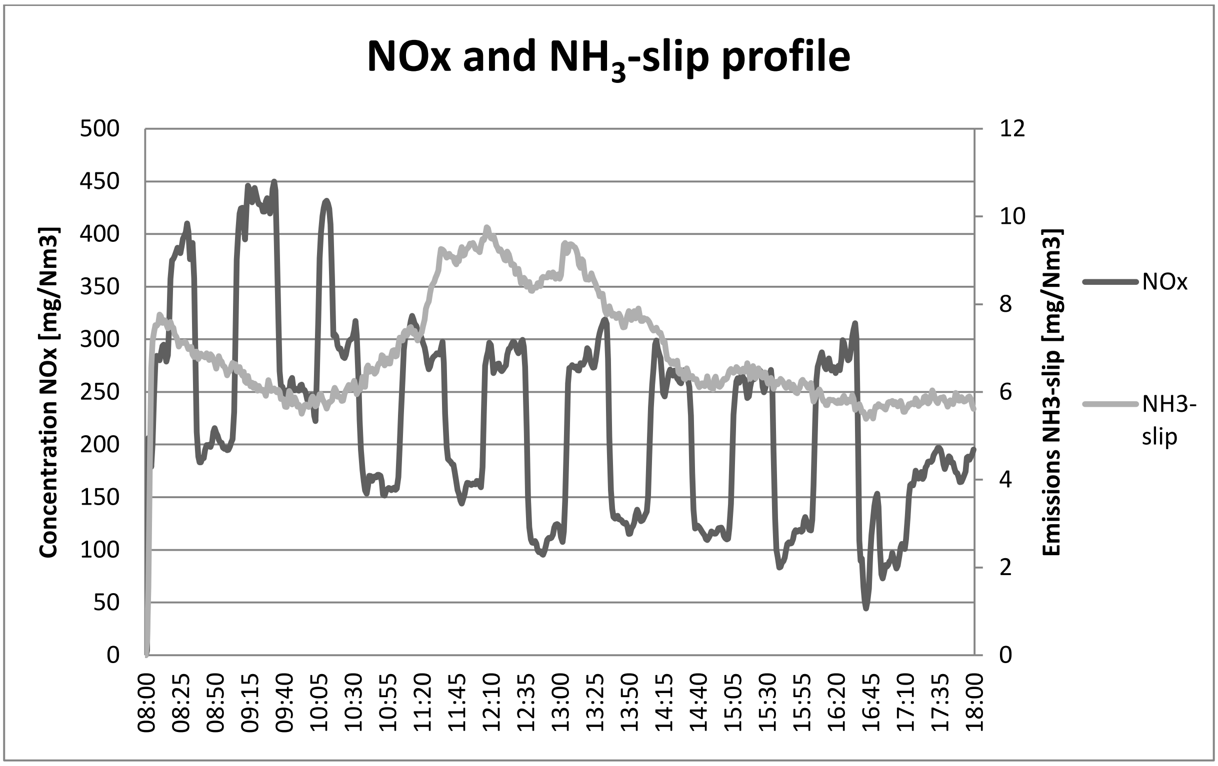


Figure 5-19 NOx and NH_3-slip profile at day 4

CO, TOC and O_2

According to the deleted part of fuel experiments, CO/TOC and O_2 was less emphasized. The intention with the fuel experiments was to investigate the correlations between CO and the fuel. Anyway, because of the varying fuel consumption during the 2nd and 3rd parallel, this can be observed at the resulting CO/TOC concentrations, attached in Appendix I1.6 and I2.6.

During the second parallel the NOx concentration increases to a higher level caused the decreasing temperature. To prevent the bad conditions in the kiln, the production capacity was reduced, as well as the fuel consumption. The CO/TOC concentration responds by a significant reduction, which confirms the hypotheses and theory. When the CO concentrations are low, the O_2 concentrations are high. The oxygen profile can be found in Appendix I1.7 and I2.7.

5.2.2.4 Reduction efficiency

The calculated reduction efficiency is shown in Figure 5-20. The darkest line represents the reduction efficiency relative to the mean reference of the 1st and 4th parallel. The lightest line represents the reduction efficiency relative to the reference before/after each trial, which in term leads to the most reliable result. Anyway, the results are quite similar.

The calculated reduction efficiencies can also be found as calculated values in Appendix I3.

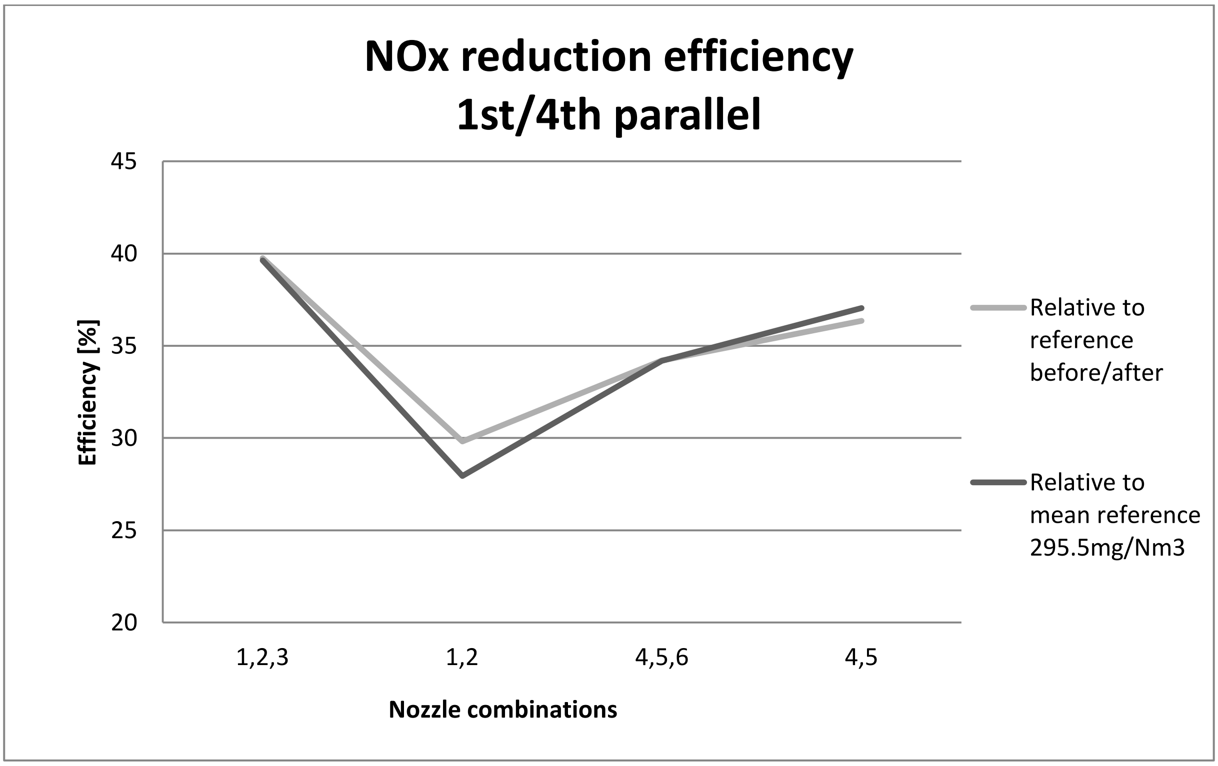


Figure 5-20 Reduction efficiency test 2

The figure illustrates; 3 nozzles give higher reduction efficiency compared to 2 nozzles for downstream while the reduction efficiency at upstream is slightly better with 2 nozzles than 3. The results does not confirm the hypotheses in a great extent and it should have been executed a lot more experiments before making any conclusion.

Even though the two other parallels (3rd and 4th) were not included in the production of the results, it is attached in appendix I4. The purpose of this is to prove that the great difference in removal efficiencies of 2 and 3 nozzles at downstream (1,2,3) is not a coincidence but repeats regardless the process conditions. According to the upstream nozzle combinations the results does not show any apparent trend.

6 Discussion

The cement production at Norcem Brevik is a complex process with many process parameters that are very interdependent. It becomes particularly complicated considering the usage of alternative fuels in the combustion process. It is difficult to know exactly the quality of the fuel at all time.

There is always a risk that there may be errors from human sources in such experimental development. Regardless, the known negative factors which may affect the presented results are discussed below.

6.1 Experiment development

A part of the preparation for the thesis consisted of raising important parameters that affects the NOx reduction system. All the parameters extracted from Aspen Process Explorer was updated dynamically. While creating the spreadsheets, there was found various things that are worth mentioning.

The production of clinker is not a real measurement but an estimated value. The value is estimated by the consumption of raw meal times a factor of 1.57.

As shown in Figure 5-2 there is a deviation between the total flow of reduction agent through the nozzles and the total reduction agent, the sum of all individual flow-meters. This deviation was calculated in excel by adding a simple calculation.

Animal meal is a calculated value, Primary solid waste minus M4 and Plastic.

The Hot-mix weight is false so the measured weight must be corrected or it must be implemented a correction factor during the calculation. Total consumption of Secondary solid waste is correct, but the ratio between FAB and Hot-mix is incorrect. Even if the flow of secondary solid waste is constant at a level of 12t/h, the ratio between FAB and Hot mix could be varying.

The measures of CO have a maximum value of 3000mg/Nm^3. It is observed that this value often exceeds that limit, which means that it cannot be seen how great the peaks are. The same applies for the measurements of TOC with a maximum value of 40mg/Nm^3.

At string 1, CO_2 is measured as a flow [mg/Nm^3] while at string 2 CO_2 is measured as a fraction [%]. This is not a concern since string 1 is the only measure that is used in the results.

Flue gas 2 string 2 is defect. If the flow had to be presented in Nm^3/h, it had to be calculated via the temperature in the stack. Anyway, flue gas at string 1 is the only included in the appendix.

6.2 Experiment analysis

By analyzing the process before the execution it was observed that continually peaks and valleys happened, something that is considered to be process disturbances. This may be due to inaccuracies in the measuring instruments and are hard to prevent. The same peaks and valleys were observed during the execution of the tests. One example can be seen at 08.00 in Appendix I1.5, NOx and NH_3-slip profile. Both NOx and NH_3-slip parameters are disturbed at this time, resulting in a peak of NOx and a valley of NH_3. In the analysis this may cause higher/lower average values which leads to increased uncertainty.

It is expected that by running all the trials over a longer period it would result in higher reduction efficiency. This is presumed on the basis of observations during the experiments, which indicated that NOx would have been purified to a greater degree by running the trials over a longer period. The same applies for the reference periods.

The results were obtained and presented with average values for each and every single trial of the experiments, i.e. an average of the 30 minutes of all trials/reference periods. As observed from the execution, the response time of the system was 2-4 minutes. It means that 2-4 minutes of each trial have the same values as the previous trial. As an example; when the system was turned off, the concentration of NOx where high. By starting the system with ammonia injection it took about 2-4 minutes before the concentration started to decrease. This was not taken into account when the results were produced. If it was taken into account, the result would have been even better, giving higher reduction efficiencies. This is considered to be a source of error in terms of the presented results. It is expected that by conducting the same test with 1 hour instead of 30 minutes at each trial/reference, the results would have been even more correct. Another method that could be implemented by the production of the results to achieve a more precise result was to take an average of only the values measured after the trial had stabilized, i.e. about 15 minutes.

The obtained reduction efficiency at the different nozzle combination did not confirm the hypotheses. It was expected to be a greater difference, a higher NOx reduction at only upstream because of the longer reaction time. Since that is not true, the reaction time between the two injecting points is not that great. One reason for not obtaining a greater reduction upstream could be the fact that the combustion process is not completely fulfilled at the upstream injection point, so more NOx is possibly generated after the upstream nozzles. If that is so, this NOx is not reduced.

Because of the very unstable fuel consumption during the experiments, the focus on CO development was less. There was no time to conduct new fuel experiments as the implemented experiments had already been postponed twice earlier of process related reasons. It was only on day 2 it was possible to perform the planned fuel experiment.

7 Conclusion

NOx reduction is calculated as the difference between NOx emitted during the trials and NOx emitted during the reference period. This implies that the NOx generation (or NOx in) is not calculated and taken into account.

According to Figure 5-2 there was found a deviation between the two measured streams representing the same flow of reduction agent. Average deviation was 10% and the most reliable stream was “total reduction agent” because of greater uncertainty on the individual flow-meters at each nozzle.

NOx is reduced to a greater extent by injecting a larger amount of ammonia. There was found an optimum amount of ammonia at 150l/h at a reduction efficiency of 46.2%. The optimal amount was determined by the reduction efficiency which seemed to stagnate while the amount of ammonia was still increasing. This can be seen from Figure 5-9. The highest obtained reduction efficiency was 59.2% but this is not profitable according to the consumption of ammonia. By maintaining 150l/h as average consumption throughout the year it will correspond to an expenditure of 1.735MNOK/year.

Using ammonia at 50l/h (265mg/Nm^3) the current guidance limits of 200mg/Nm^3 is not maintained. Using 100l/h (212.8mg/Nm^3) one is barely within the limits while using 150l/h (151.1mg/Nm^3) the limitations are kept by wide margin, see Appendix H5.

If it would be necessary to pay NOx taxes, Figure 5-11 indicates an economical optimum compared to the expenses of ammonia. Maintaining an average flow of 280l/h of ammonia throughout the year, it would lead to expenses at 3.2MNOK/year. The figure confirms that with a higher consumption of ammonia it would be more profitable to pay NOx taxes, subject to keeping the NOx emissions remain at the same level, about 190 tons/year.

According to the investigation of the nozzle combinations the conclusion might be that all three nozzles at the downstream (1,2,3) should be activated according to the highest obtained reduction efficiency, about 40%. The stated hypotheses which implied that the reduction efficiency should be somehow greater by implementing ammonia at only upstream nozzles cannot be confirmed.

The optimal temperature was stated to be in the range of 827-1127^{o}C (1100-1400K), slightly dependent on the source. Some sources even claims that the lowest temperature is around 900^{o}C. The NOx concentration is very dependent upon the temperature profile.

During the experiments at Norcem, the temperature was in the range of 820-890^{o}C, average of 850^{o}C, which is very low regarding the SNCR technology. When the temperature dropped as low as 820^{o}C, it was observed that the NOx concentration came to an abrupt rise, see Appendix I1.4. Also it can be seen that bar 7 in Figure 5-16 has a very high NOx concentration caused by the very low temperature.

Experiments indicated that the NH_3-slip depends upon two main parameters, the amount of injected ammonia and NOx concentration emitted. NH_3-slip increases with increased amount of ammonia, at least at an amount over 150l/h. When the NOx concentration is reduced to a level of 100mg/Nm^3 the NH_3-slip is rapidly increased.

Both tests confirm the relation and dependence of the three parameters; flow of ammonia, NH_3-slip and NOx concentration.

Based on the implemented fuel experiment on day 2 it can be confirmed that CO is very dependent upon the fuel consumption, especially FAB. Figure 5-13 illustrates the resulting CO concentration that is increasing with increased consumption of fuel. Comparing the CO development with the NOx concentration and flow of ammonia does not give any direct connections but it seems like CO and NOx behaves opposite. This confirms the theory that low O_2 leads to increased CO (which is not oxidized) and minimized NOx (nitrogen is not oxidized).

Other parameters were mentioned in the hypotheses. These parameters are; HCl, HF, SO_2 and CO_2. All these minor components where continuously measured and analyzed. One example of the graphs is attached in Appendix J. These parameters were not included in the report because the analysis along the way indicated no major changes.

7.1 Further work

There is not likely a risk that the regulations of NOx will be reduced below 200mg/Nm^3 in the near future. Anyway, if the reduction efficiency at the NOx reduction system at Norcem Brevik is going to be further improved, it could be interesting to focus on a combination of reduction methods instead of using more/stronger ammonium hydroxide.

A solution could be to combine this already installed SNCR system with other NOx reduction technologies like stage combustion, LNB (Low NOx-Burners), or OFA (over fire air) [2].

The experiments are performed at standard clinker production. It could be interesting to investigate the same experiments performed at other clinkers to see if the results of NOx concentration, NH_3-slip and other factors are in the same range or if there exist large deviations.

Ammonia slip is an interesting parameter that could be further investigated. At the experiment development, ammonia-slip was expected to fall downwards to zero when the system was turned off. According to the results obtained, that did not happen. During the experiments the lowest noticed level of NH_3 was respectively 7mg/Nm^3 (test 1) and 4.5mg/Nm^3 (test 2). This implies that NH_3 is generated in small amounts somewhere else in the process.

In chapter 2.1.2 Fuel NOx, the pathways of NOx formation is described. It can be seen that NH_3 is an intermediate product in the formation of NOx from fuel-N. If the NH_3-slip is not only dependent on the excess ammonium hydroxide from the NOx reduction system, another reason could be the fuel-N formation mechanism. The intermediate state of NH_3 in the mechanism requires oxygen containing compounds to be further oxidized to NO, i.e. stoichiometric conditions. If those conditions are not obtained, the NH_3 should be reduced to form N_2 or it could remain as NH_3.

Another reason can be the additives to the raw meal. Instead of using bauxite as an additive in the production of clinker it can be used oxiton or serox. This is cheaper additives but it might contain small parts of pollutants. There can be found small parts of NH_3 in these additives which may be flushed off the raw meal in the cyclone towers and thereby released as polluted emissions measured in the stack.

It could be interesting to get into more details about the NH_3-slip and the possible generation of ammonia coming from the fuel or raw meal. Because of the relatively large differences in the consumption of serox/oxiton depending on the type of clinker produced, this context could be investigated.

First, it should be identified what is the “normal” NH_3-slip without injecting ammonia in the NOx reduction system for all types of clinker. A simple experiment is then to turn of the system over a longer period.

References

1. Bye, G.C. Portland cement, second edition. [Internet]. London, Thomas Telford Publishing; 1999 [cited 2014 April 23] Available from: http://books.google.cm/books?id=W8oYW15gH18C&printsec=frontcover&dq=portland+cement+bye+g+c&hl=no&sa=X&ei=XAWCU6umCKX9yAOzsYCIBA&ved=0CD8Q6AEwAA#v=onepage&q=portland%20cement%20bye%20g%20c&f=false

2. Zevenhoven, R. & Kilpinen, P. Control of pollutants in flue gases and fuel gases, third edition, Ch. 4.1-4.60. Helsinki: Helsinki University of Technology Espoo; 2004

3. Bowman, C.T. Control of combustion generated nitrogen oxide emissions: Technology driven by regulations, pg. 859-978. Pittsburgh: The Combustion Institute; 1993.

4. Clean Air Technology Center, U.S. Environmental Protection Agency, Nitrogen Oxides (NOx), Why and How They Are Controlled. North Carolina: Research Triangle Park; 1999

5. Tokheim, L.A. The impact of staged combustion on the operation of a precalciner cement kiln, PhD, chapter 2-4. Porsgrunn: Telemark University Collage; 1999

6. Baukal, C.E. Industrial Burners Handbook [Internet]. Boca Raton, Florida. CRC Press; 2004. [cited 2014 May 25] Available from: http://books.google.no/books?id=cCJ_YyAEqnQC&printsec=frontcover&dq=industrial+burners+handbook&hl=no&sa=X&ei=duZ9U5uuLcql0QW224Bg&ved=0CDUQ6AEwAA#v=onepage&q=industrial%20burners%20handbook&f=false

7. Lewandowski, D.A. Design of thermal oxidation systems for Volatile Organic Compounds, pg. 262-272. Boca Raton, Florida. CRC Press; 2000. [cited 2014 May 19] Available from: http://books.google.no/books?id=L-lKUWd-QOwC&printsec=frontcover&hl=no&source=gbs_ge_summary_r&cad=0#v=onepage&q&f=false (ISBN 1-56670-410-3)

8. Bhatty, J.I., Miller, F.M. and Kosmatka, S.H. Innovations in Portland Cement Manufacturing, chapter 3.1. Portland Cement Association, Skokie,Illinos, U.S.A.; 2004. (ISBN: 0-89312-234-3)

9. Flow vision. Urea Versus Ammonia Water. [Internet] 2008-2010 [cited 2014 May 26] Available from: http://www.flowvision-energy.com/urea-nh3

10. Petro SNCR System, Anleggsbeskrivelse. 2011.06.29 rev 00. Norcem database.

11. Flow vision. SNCR DeNOx Technology. [Internet] 2008-2010 [cited 2014 May 26] Available from: http://www.flowvision-energy.com/sncr-denox-technology

12. IEA, Clean Coal Centre. Selective non-catalytic reduction (SNCR) for NOx control. [Internet] London [cited 2014 May 29] Available from: http://www.iea-coal.org.uk/site/ieacoal/databases/ccts/selective-non-catalytic-reduction-sncr-for-nox-control

13. Flow vision. SCR DeNOx Technology. [Internet] 2008-2010 [cited 2014 May 26] Available from: http://www.flowvision-energy.com/scr-denox-tech

14. Noxcare. SNCR, the cost effective system for reducing NOx. [Internet] Oslo; headquarter. [cited 2014 May 07] Available from: http://noxcare.com/en-us/sncr-scr-systems/sncr/

15. Rungger, W. Selective Non-Catalytic Reduction of NOx. Petro Miljø, Sweden, reprinted from World Cement; 2008.

16. Norcem plakat. [2008 September 24, updated 2014 February 03] Norcem database.

17. Battye,R. Walsh,S. Lee-Greco,J. U.S. Environmental Protection Agency. NOx control Technologies for the Cement Industry, chapter 4.1.3. North Carolina: Research Triangle Park; 2000

18. Husum, I. HeidelbergCement Northern Europe – Kort presentasjon av Norcem Brevik-HiT studenter April 2013. Brevik; [2007 November 08, updated 2014 February 03] Norcem database.

19. Norcem Brevik, HCNE- External environment 2014-2016 Norcem Brevik Actual and budget figures. Norcem database.

20. Gautestad,T. PRL4, Utslippsrapportering, excel. [1999 September 10, updated 2014 January 02] Norcem database.

21. Bhatty, J.I., Miller, F.M. and Kosmatka, S.H. Innovations in Portland Cement Manufacturing, chapter 6.1. Portland Cement Association, Skokie,Illinos, U.S.A.; 2004. (ISBN: 0-89312-234-3)

22. Verdu, D. Norcem utslippskontroll, PowerPoint [2011 March 22, updated 2014 February 02] Norcem database.

23. Utslippstabell fra Ida Utslipstillatelse sft [2007 February 05, updated 2012 September 20] Norcem database.

24. EUR-Lex. Commission Regulation (EU) No 601/2012 of 21 June 2012 on the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC of the European Parliament and of the Council Text with EEA relevance. [Internet] 2012 [cited 2014 May 27] Available from**:** http://eur-lex.europa.eu/legal-content/EN/ALL/;jsessionid=3lFWTGbb2LL1vzdXrgx2j5JF2WvtYwRTvH8tRqbQ9CphXrywKfJL!-451414052?uri=CELEX:32012R0601

25. Tokheim, L.A. CO_2 reporting 2013 Brevik [2004 December 20, updated 2014 February 27] Norcem database.

26. NHO-Næringslivets Hovedorganisasjon. Miljøavtalen om NOx [Internet] 2013[updated 2013 September 27; cited 2014 April 23] Available from: https://www.nho.no/Prosjekter-og-programmer/NOx-fondet/Dette-er-NOx-fondet/Miljoavtalen-om-NOx/

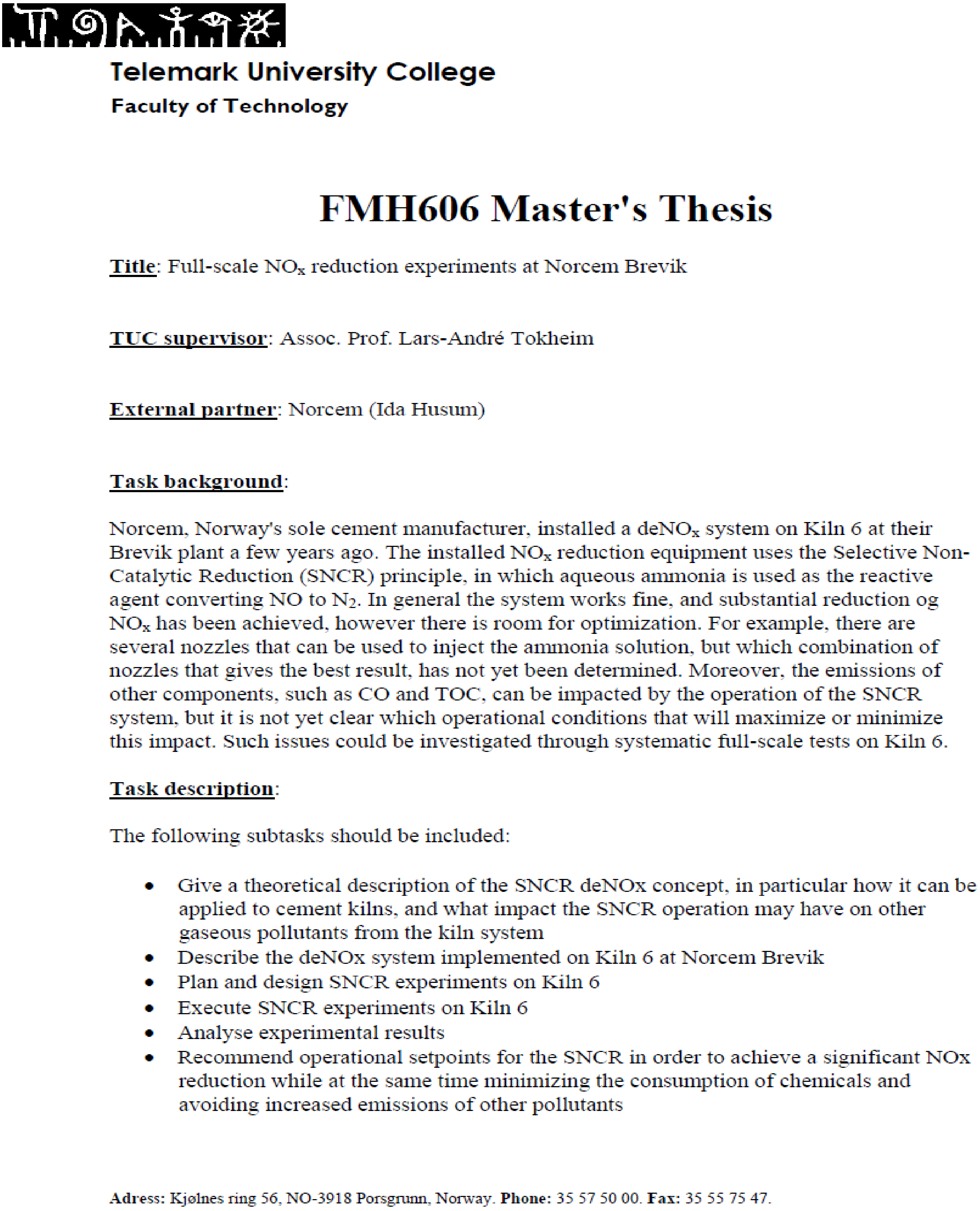
27. Husum, I. Redusert utslipp av NOx etter installasjon av SNCR-renseanlegg i ovn 6 ved Norcem Brevik. Brevik: Norcem Brevik; 2013
28. Petro Miljø. Technical description_AltA_rev1 Petro l. [2011 September 09] Reference NO: NA8776/ AltA. Norcem database.

29. Andresson, A., Andersson, O. Dahlin, G. and Åhgren, J. Processforbattring av anlaggning for reduction av kvaveoxider. Visby, Sweden; Ingeniørskolan Visby; 1998.

30. Johnsen,T. NOx fondet: Status, endringer og fremtid. 2013/2014 [cited 2014 May 24] Available from: https://www.nho.no/siteassets/nhos-filer-og-bilder/filer-og-dokumenter/nox-fondet/nox-fondet-info-runde-vinter-2013-skrivebeskyttet.pdf

Appendices

Appendix A: Task description



Telemark University College
Faculty of Technology

FMH606 Master's Thesis

Title: Full-scale NO_x reduction experiments at Norcem Brevik

TUC supervisor: Assoc. Prof. Lars-André Tokheim

External partner: Norcem (Ida Husum)

Task background:

Norcem, Norway's sole cement manufacturer, installed a deNO_x system on Kiln 6 at their Brevik plant a few years ago. The installed NO_x reduction equipment uses the Selective Non-Catalytic Reduction (SNCR) principle, in which aqueous ammonia is used as the reactive agent converting NO to N_2. In general the system works fine, and substantial reduction og NO_x has been achieved, however there is room for optimization. For example, there are several nozzles that can be used to inject the ammonia solution, but which combination of nozzles that gives the best result, has not yet been determined. Moreover, the emissions of other components, such as CO and TOC, can be impacted by the operation of the SNCR system, but it is not yet clear which operational conditions that will maximize or minimize this impact. Such issues could be investigated through systematic full-scale tests on Kiln 6.

Task description:

The following subtasks should be included:

- Give a theoretical description of the SNCR deNOx concept, in particular how it can be applied to cement kilns, and what impact the SNCR operation may have on other gaseous pollutants from the kiln system
- Describe the deNOx system implemented on Kiln 6 at Norcem Brevik
- Plan and design SNCR experiments on Kiln 6
- Execute SNCR experiments on Kiln 6
- Analyse experimental results
- Recommend operational setpoints for the SNCR in order to achieve a significant NOx reduction while at the same time minimizing the consumption of chemicals and avoiding increased emissions of other pollutants

Adress: Kjølnes ring 56, NO-3918 Porsgrunn, Norway. **Phone:** 35 57 50 00. **Fax:** 35 55 75 47.

Student category:

PT or EET students

Practical arrangements: The student will carry out full-scale experiments at Norcem Brevik.

Signatures:

Student (date and signature): 3/2-14 Christine Bregge

Supervisor Lars-André Tokheim (date and signature): Lars André Tokheim 3/2-14

Appendix B: Ratio calculations

Molar ratio of the total reduction reaction for SNCR/SCR technologies:

Ammonia:

$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N2 + 6\ H_2O$

NO = 30g/mol

NH_3 = 17g/mol

Molar ratio: $NH_3/NO = 17/30 = \underline{0.57}$

Urea:

$(CO(NH_2)_2) + 2\ NO + ½\ O_2 \rightarrow 2\ N_2 + CO_2 + 2\ H_2O$

NO = 30g/mol

$(CO(NH_2)_2)$ = 60g/mol

Molar ratio: $(CO(NH_2)_2)/2NO = 60/60 = \underline{1.0}$

Cyanuric acid:

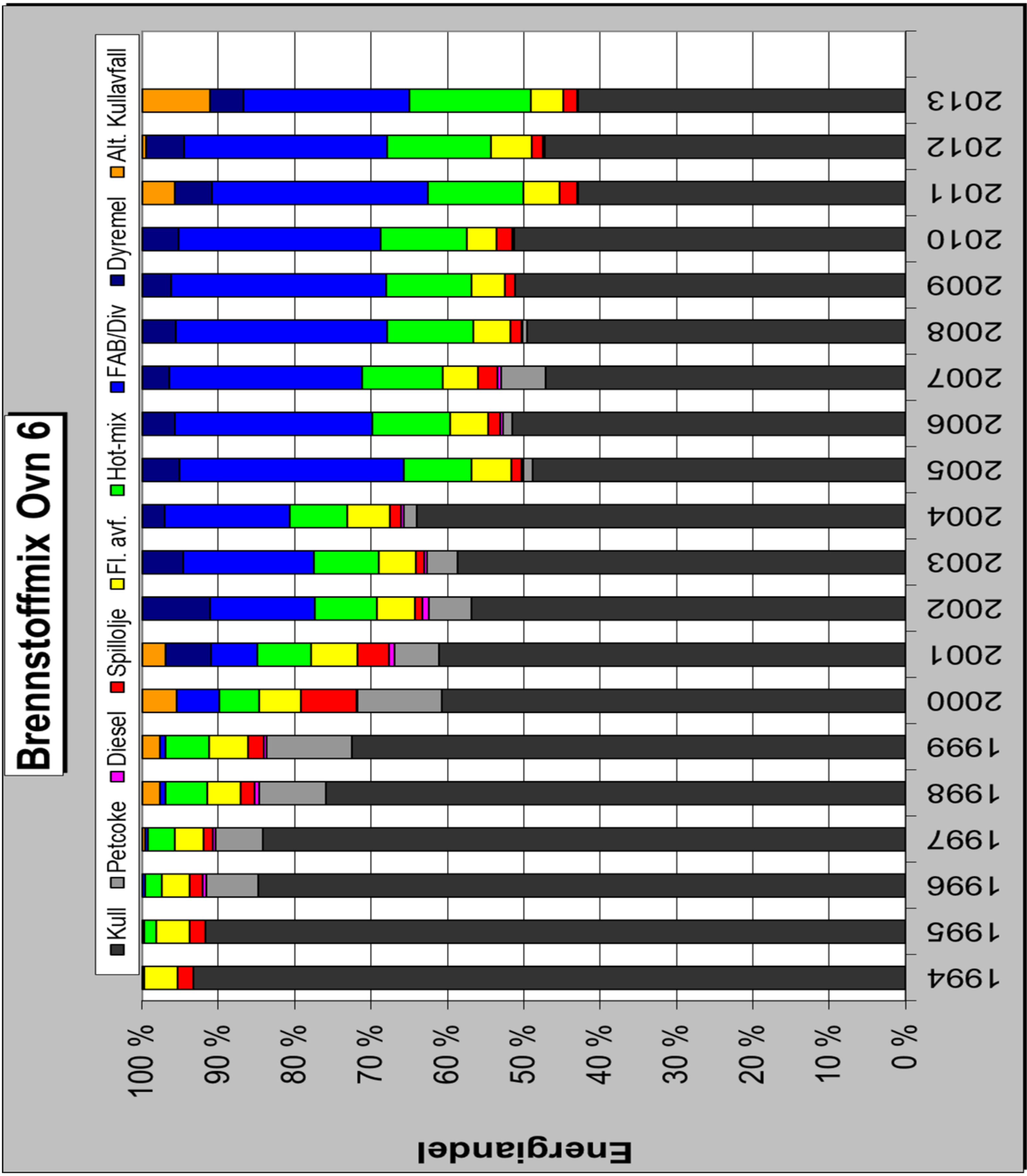
$(HNCO)_3 + 7/2\ NOx \rightarrow 13/4\ N_2 + 2\ CO_2 + 3/2\ H_2O + CO$

NO = 30g/mol

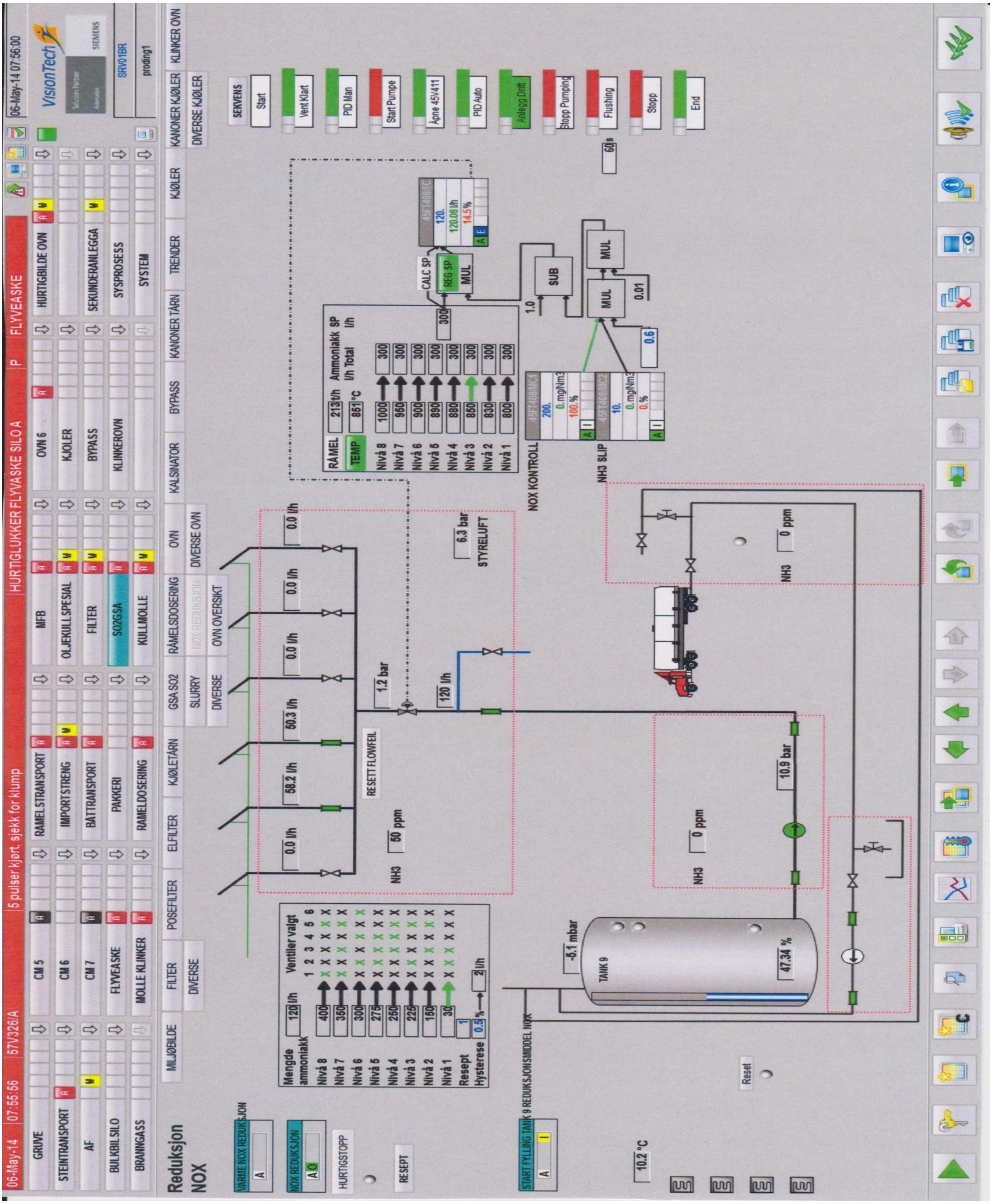
$(HNCO)_3$ = 129g/mol

Molar ratio: $(HNCO)_3/(7/2)NO = 129/105 = \underline{1.23}$

Appendix C: Fuel consumption



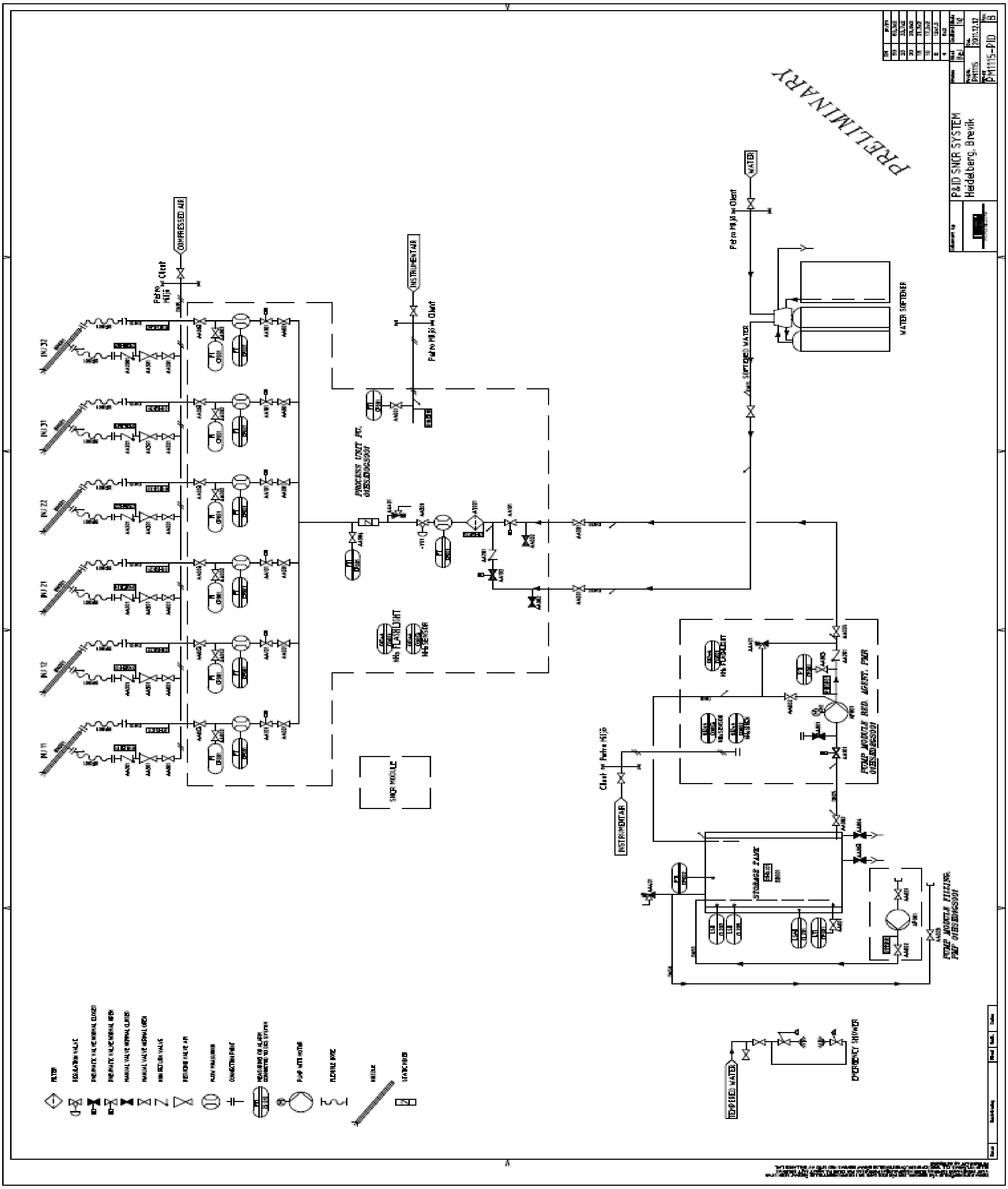
Appendix D: NOx control system (print screen)



Mengde ammoniakk	120 l/h	Ventiler valgt 1	2	3	4	5	6
Nivå 8	400	X	X	X	X	X	X
Nivå 7	350	X	X	X	X	X	X
Nivå 6	300	X	X	X	X	X	X
Nivå 5	275	X	X	X	X	X	X
Nivå 4	250	X	X	X	X	X	X
Nivå 3	225	X	X	X	X	X	X
Nivå 2	150	X	X	X	X	X	X
Nivå 1	30	X	X	X	X	X	X
Resept	1						
Hysterese	0.5 %	2 l/h					

RÅMEL	213 l/h	Ammoniakk SP l/h Total l/h
TEMP	851 °C	
Nivå 8	1000	300
Nivå 7	950	300
Nivå 6	900	300
Nivå 5	890	300
Nivå 4	880	300
Nivå 3	850	300
Nivå 2	830	300
Nivå 1	800	300

Appendix E: P&ID of the NOx reduction system



Appendix F: Information to the operators

Info til driften

Mitt navn er Christine Bregge og jeg er student på Høgskolen i Telemark, avd. Porsgrunn. Her tar jeg en mastergrad i ”Process Technology” og er på mitt siste semester hvor jeg skriver masteroppgave. Denne masteroppgaven skrives i samarbeid med Norcem og heter; ”Fullscale NOx reduction experiments at Norcem Brevik”.

Hensikten med oppgaven er å finne de optimale kjøregrensene for SNCR anlegget som består av å opprettholde dagens NOx grenser (200 mg/Nm^3) samtidig som ammoniakkløsningen skal begrenses mest mulig og unngå en økning av andre utslippskomponenter.

Det er planlagt å kjøre to tester over totalt 4 dager for å få et svar på en rekke hypoteser og for å analysere prosessen. Hvert forsøk skal kjøres i 30 min med en referansetid a 30 min på hver side av forsøket. I denne referansetiden vil NOx anlegget bli slått av. For å oppnå et godt resultat er det nødvendig å kjøre en jevn tilførsel av brensel. Forsøkene blir også lagt til dager hvor det produseres standard klinker. Det tas forbehold om at endringer av mengdene kan forekomme underveis.

Dato for gjennomføring: **Test 1; Torsdag 24/4 og Fredag 25/4**
Test 2; Mandag 5/5 og Tirsdag 6/5

Selve forsøkene skal jeg utføre selv sammen med Arnstein. Det er forventet at utslippsgrenser kommer til å overstige gitte betingelser i perioder og at NOx reduksjonsanlegget vil være veldig ustabilt disse dagene. Håper dere har forståelse for dette og eventuelle konsekvenser det vil få for dere i drift. Nedenfor er deler av forsøksplanen lagt ved så dere får en viss innsikt i forsøkene.

Mvh Christine Bregge

Appendix G: Implementation plan

Implementation plan

The planned experiments are based on series of different combinations of the consumption of reduction agent and nozzles activated and also include a variation of the fuel as a part of it. Each experiment are planned to run for 30 minutes. As a reference there will be 30 minutes on both sides of the experiments with the SNCR system turned off. By implementing the reference the results will be easier to read.

By turning of the system as a reference to all the tests it provides the results to be represented in a clear way. If there should be any time left after the analysis of the test, it could be interesting to compare the results with operational data form Norcem`s database. (If that is so, it have to be taken into account which type of clinker produced, how is the consumption of raw-meal and fuel, etc.)

The experiments are planned to be implemented on days with standard clinker production. Another requirement is stable production. This will provide a stable reference throughout the experiments and then reduce uncertainty.

Implementation date:	**Test 1;**	**Thursday 24/4 and Friday 25/4**
	Test 2;	**Monday 5/5 and Tuesday 6/5**

Below are all the parameters that are monitored during the experiments given. Since the regulator in the NOx-system is only based on levels from string 1 it will be natural to mainly focus on this string. The reason why string 2 is also included is to obtain a so called safety factor to check whether the emission levels are in the same range for both strings. By including both strings it will be possible to observe if there is something wrong with an analyzer.

The aim of the experiment is to find some optimal operating setpoints for the SNCR system in order to achieve a significant reduction of NOx, or maintaining current NOx limits (200 mg/Nm^3), while at the same time minimizing the consumption of reduction agent and avoiding increased emissions of other pollutants.

To monitor the parameters, trends where put up in Aspen Process Explorer:

1.Set: Temperature monitors

2.Set: Raw meal consumptions and produced clinker

3.Set: Reduction agent (Flow of nozzles and total flow)

4.Set: Regulator parameters (NOx control and NH_3-slip)

5.Set: Flow of primary fuel

6.Set: Flow of secondary fuel
7.Set: O_2 /CO monitors (NOx kiln)
8.Set: Emissions 1 string 1; NOx, CO, SO_2 , (mg/Nm^3)
9.Set: Emissions 2 string 1; NO_2, CO_2, $NH_{3,}$ TOC, HCl, HF (mg/Nm^3)
10.Set: Emissions 3 string 1;H_2O, O_2 (%)
11.Set: Emissions 1 string 2; NO (ppm), CO, $SO_{2\,,}$ (mg/Nm^3)
12.Set: Emissions 2 string 2; NO_2, NH_3, TOC, HCl, HF (mg/Nm^3)
13.Set: Emissions 3 string 2; H_2O, O_2, CO_2 (%)
14. Set: Flow of flue gas

These parameters are imported in Aspen Process Explorer and in excel. The graphs in excel shows the same results and are used to present the results in the master thesis report.

Parameters monitored during the experiments:

NOx control	45FT408/MC1.PV_IN
NOx out, string 1	46AT067D/AT01.MV
NO(x) out, string 2	25AT295D/AT.MV
NO_2 out, string 1	46AT067E/AT.MV
NO_2 out, string 2	25AT295E/AT.MV
NH_3-slip	45FT408/MC2.PV_IN
NH_3 out, string 1	46AT067K/AT.MV
NH_3 out, string 2	25AT295K/AT.MV
CO emissions, string 1	46AT067B/AT.MV
CO emissions, string 2	25AT295B/AT.MV
CO before filter 4, string 1	46AT761/AT.MV
CO after filter 3, string 2	46AT754/AT.MV
TOC emissions, string 1	46AT067J/AT.MV
TOC emissions, string 2	25AT295J/AT.MV
O_2 kiln inlet	46AT464/AT.MV
O_2 before filter 4, string 1	46AT760/AT.MV
O_2 after filter 3, string 2	46AT753/AT.MV
O_2 emissions string 1	46AT067I/AT.MV
O_2 emissions string 2	25AT295I/AT.MV
H_2O emissions string 1	46AT067F/AT.MV
H_2O emissions, string 2	25AT295F/AT.MV
HCl emissions, string 1	46AT067A/AT.MV
HCl emissions, string 2	25AT295A/AT.MV
HF emissions, string 1	46AT067H/AT.MV
HF emissions, string 2	25AT295H/AT.MV
CO_2, emissions, string 1	46AT067G/AT.MV
CO_2, emissions, string 2	25AT295G/AT.MV

SO_2, emissions, string 1	46AT067C/AT.MV
SO_2, emissions, string 2	25AT295C/AT.MV
Flue gas 1 string 1 (km^3/h)	46FT046/FT.MV
Flue gas 2 string 1 (kNm^3/h)	46FT046/FX.MV
Flue gas 1 string 2 (km^3/h)	25FT298/FT.MV
Flue gas 2 string 2 (kNm^3/h)	25FT298/FX.MV
Temperature in the calciner	46TT922/TT.MV
Temperature 1 over cyclone 4-1	46TT297/TT.MV
Temperature 2 over cyclone 4-1	46TT297B/TT.MV
Temperature 1 over cyclone 4-2	46TT298/TT.MV
Temperature 2 over cyclone 4-2	46TT298B/TT.MV
Flow of ammonia injection	45FT408/FC.PV_IN
Flow nozzle 1	45FT401/FT.MV
Flow nozzle 2	45FT402/FT.MV
Flow nozzle 3	45FT403/FT.MV
Flow nozzle 4	45FT404/FT.MV
Flow nozzle 5	45FT405/FT.MV
Flow nozzle 6	45FT406/FT.MV
Raw meal Løype 1, string 1	46FT105/FT.MV
Raw meal Løype 2, string 1	46FT106/FT.MV
Raw meal Løype 1, string 2	46FT107/FT.MV
Raw meal Løype 2, string 2	46FT108/FT.MV
Produced clinker	46FT_total_klinkerprod (kalkulert tall)
Raw coal silo 1	*32FT150/FT.MV (kun til forhold)*
Raw coal silo 2	*32FT152/FT.MV (kun til forhold)*
Primary coal meal	46FT955/FT.MV
Secondary coal meal	46FT956/FT.MV
Oil/diesel primary	46FT467/FT.MV
Choice: Oil(0)/diesel(1)	33HS476
Liquid hazard waste	34FT089/FT.MV
Primary solid waste	35FT046/FT.MV (total pfister-system)
M4	35FT050/FT.MV
Plastic	35FT053/FT.MV
Animal meal	Calculated(tot pfister-system-M4-plast)
Secondary solid waste	35FT026/FT.MV
Hot-Mix secondary	35FT010/FT.MV
FAB	Calculated(Solid waste sec.-Hot-Mix)

Test 1; Reduce the consumption of reduction agent:

The first experiment will be carried out by manually operate the amount of reduction agent into the system. That is done by manually adjust the setpoint of the regulator 45FT408/FC while rest of the system operates automatically.

Before the execution of the experiments, a set of hysteresis where made. This is hysteresis which in theory should be correct and what is planned to be proved. The hysteresis is compared against each other.

The aim with test 1;

- Confirm the hypotheses given below
- This is the most important test according to optimization of the total flow of reduction agent and to observe the NH_3-slip. How small flow is possible to obtain while maintaining the limitations?
- Where to find the highest/lowest emissions of TOC, CO, NOx, NH3-slip and the rest of the components.
- Include analysis of NOx levels/flow of ammonia and produced clinker/flow of ammonia.
- How are NOx and other components dependent on the fuel consumption?

Parameters in the flue gas	**Max reduction agent**	**Min reduction agent**
NOx	Lower	Higher
CO	Higher	Lower
NH_3-slip	Higher	Lower
O_2	Lower	Higher
TOC	Higher	Lower
Other emissions	Higher	Lower

The hysteresis in table (1.1) is expectations with the total reduction reaction in mind. With a very high consumption of the reduction agent it is expected that NOx emissions will be very low because there is “more than enough” reduction agent available. The reduction agent that is left over will cause high emissions of NH_3-slip. O_2 are also consumed in a larger amount and CO is expected to have an opposite effect than NOx. TOC and other emissions are expected to increase parallel to the consumption of reduction agent.

The amounts of reduction agent will cover the usual operating range. Normal amount is approximately 180 l/h and the maximum amount is 300 l/h.

At day 1 there will be one test where the reduction agent is increased from 100 l/h to 300 l/h with a range of 100 l/h. This is done at a constant level of FAB, or more correct the amount of solid waste. This test is repeated to reinforce the result. At the end of these parallel tests the flow of FAB is reduced with a constant amount of reduction agent of 100 l/h.

At day 2 the test is done by increasing the reduction agent from 100 l/h to 300 l/h only now with a wider range, 50 l/h. This will also give a parallel to the two tests from day 1. At the end of this test the flow of FAB is reduced and then gradually increase until it reaches the start value of 15 t/h. At this point it is decreased to 10t/h.

Day 1		
Time	**Reduction agent (l/h)**	**Flow of FAB (t/h)**
08:00	0	12
08:30	100	12
09:00	0	12
09:30	200	12
10:00	0	12
10:30	300	12
11:00	0	12
11:30	100	12
12:00	0	12
12:30	200	12
13:00	0	12
13:30	300	12
14:00	0	12
14:30	0	8
15:00	200	8
15:30	0	8
16:00	200	8
16:30	0	8

Day 2		
Time	**Reduction agent (l/h)**	**Flow of FAB (t/h)**
08:00	0	12
08:30	50	12
09:00	0	12
09:30	100	12
10:00	0	12
10:30	150	12
11:00	0	12
11:30	200	12
12:00	0	12
12:30	250	12
13:00	0	12
13:30	300	12
14:00	0	12
14:30	200	8
15:00	200	9
15:30	200	10
16:00	200	11
16:30	200	12
17:00	200	8

Test 2; Create new prescriptions of the SNCR system:

The second experiment will be carried out by creating new prescriptions that may be more effective in terms of increasing the reduction rate of NOx. The tests will be performed by operating with a constant amount of reduction agent while adjusting the prescriptions. Since the temperature is practically equal upstream and downstream the precalciner, the injection nozzles operating is not dependent. Considering the reaction time it is expected that it should be advisable to inject the reduction agent as early as possible, i.e. at the upstream. It is also interesting to see if there is a difference between using 2 or 3 nozzles with constant injection of reduction agent.

The aim with test 2:

- Confirm the hystereses given below
- Check if the reaction time is important, is it possible to observe better reduction efficiency by only using the upstream nozzles?
- Check if it exist an optimum of 2 or 3 nozzles activated.
- Include analysis of NOx levels/flow of ammonia and produced clinker/flow of ammonia.
- How are NOx and other components dependent on the fuel consumption?
-

Parameters in the flue gas	**Only upstream nozzles**	**Only downstream nozzles**
NOx	Lower	Higher
CO	Higher	Lower
NH_3-slip	Lower	Higher
O_2	Lower	Higher
TOC		
Other emissions		

The hysteresis in table (1.2) is expectations with the reduction time in mind. The parameters are compared against each other. By injecting all reduction agent at only upstream nozzles the NOx emissions should be lower due to a higher effect of the reaction. More reduction agent should be used so less NH_3-slip. The consumption of O_2 should be higher in the reaction resulting in a lower fraction in the flue gas. CO is expected to have an opposite effect than NOx.

At this test the amount of reduction agent will be kept at a constant amount, 100 l/h. This is done because the different combinations of nozzles should be evaluated.

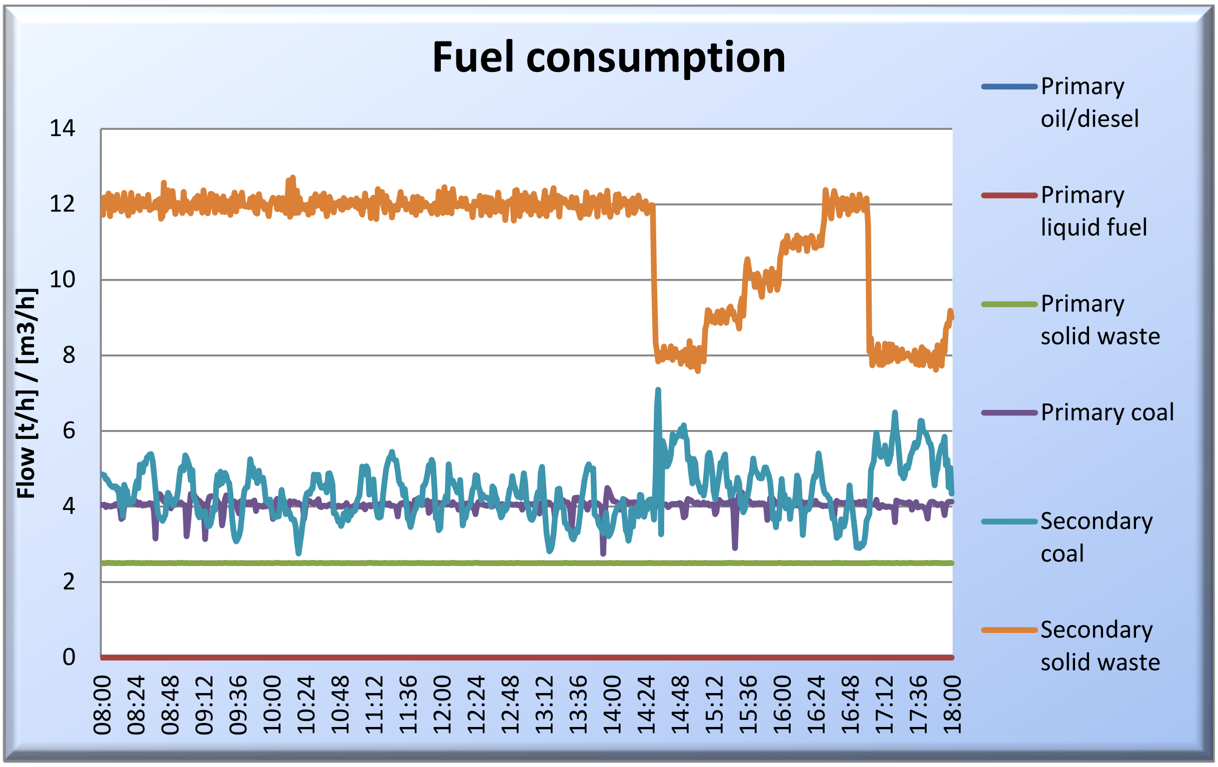
Day 3			
Time	**Reduction agent (l/h)**	**Flow of FAB/ Hot Mix (t/h)**	**Prescription**
08:00	0	12	Off
08:30	200	12	Nozzle 1, 2, 3
09:00	0	12	Off
09:30	200	12	Nozzle 1, 2
10:00	0	12	Off
10:30	200	12	Nozzle 4, 5, 6
11:00	0	12	Off
11:30	200	12	Nozzle 4, 5
12:00	0	12	Off
12:30	200	12	Nozzle 1, 2, 3
13:00	0	12	Off
13:30	200	12	Nozzle 1, 2
14:00	0	12	Off
14:30	200	12	Nozzle 4, 5, 6
15:00	0	12	Off
15:30	200	12	Nozzle 4, 5
16:00	0	12	Off
16:30	200	8	Nozzle 1, 2, 3
17:00	0	8	Off
17:30	200	8	Nozzle 4, 5, 6
18:00	0	8	Off

Day 4			
Time	**Reduction agent (l/h)**	**Flow of FAB/ Hot Mix (t/h)**	**Prescription**
08:00	0	12	Off
08:30	200	12	Nozzle 2, 3
09:00	0	12	Off
09:30	200	12	Nozzle 1, 3
10:00	0	12	Off
10:30	200	12	Nozzle 5, 6
11:00	0	12	Off
11:30	200	12	Nozzle 4, 6
12:00	0	12	Off
12:30	200	12	Nozzle 2, 3
13:00	0	12	Off
13:30	200	12	Nozzle 1, 3
14:00	0	12	Off
14:30	200	12	Nozzle 5, 6
15:00	0	12	Off
15:30	200	12	Nozzle 4, 6
16:00	0	12	Off
16:30	200	8	Nozzle 2, 3
17:00	0	8	Off
17:30	200	8	Nozzle 1, 3
18:00	0	8	Off

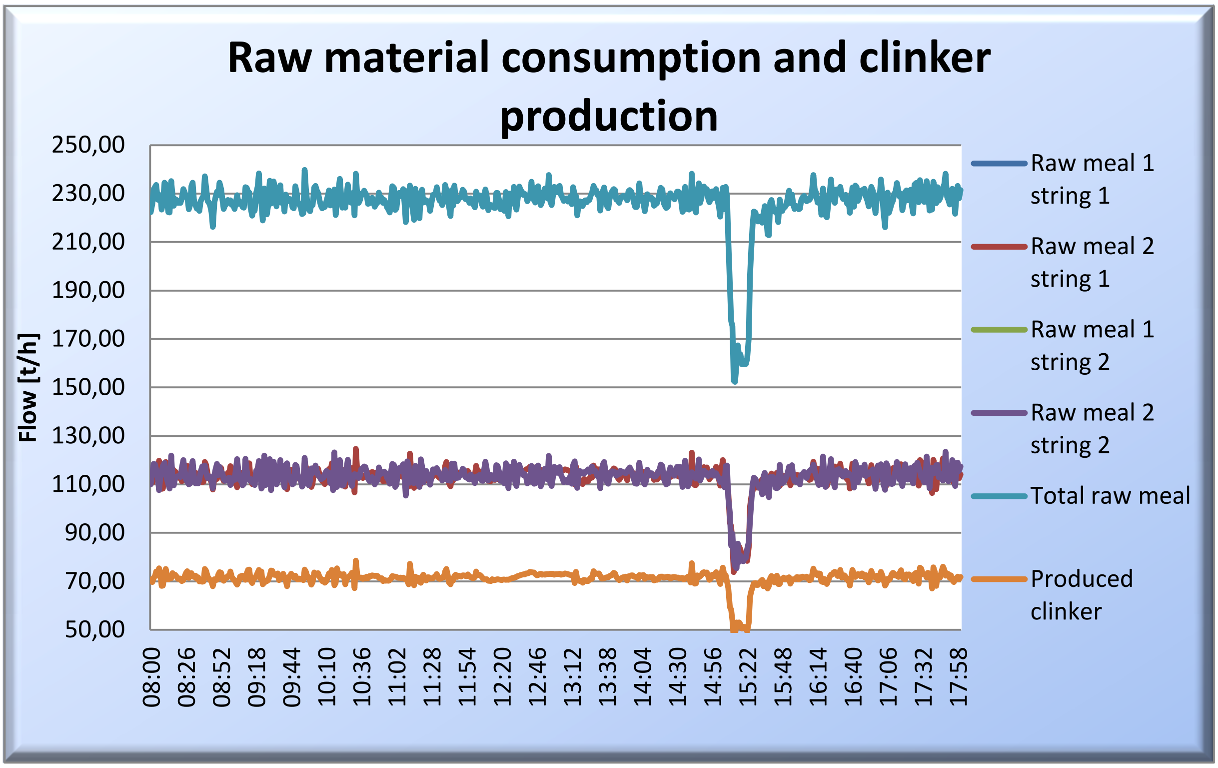
Appendix H: Results test 1

Appendix H1: Day 1 (Thursday 24/4-14)

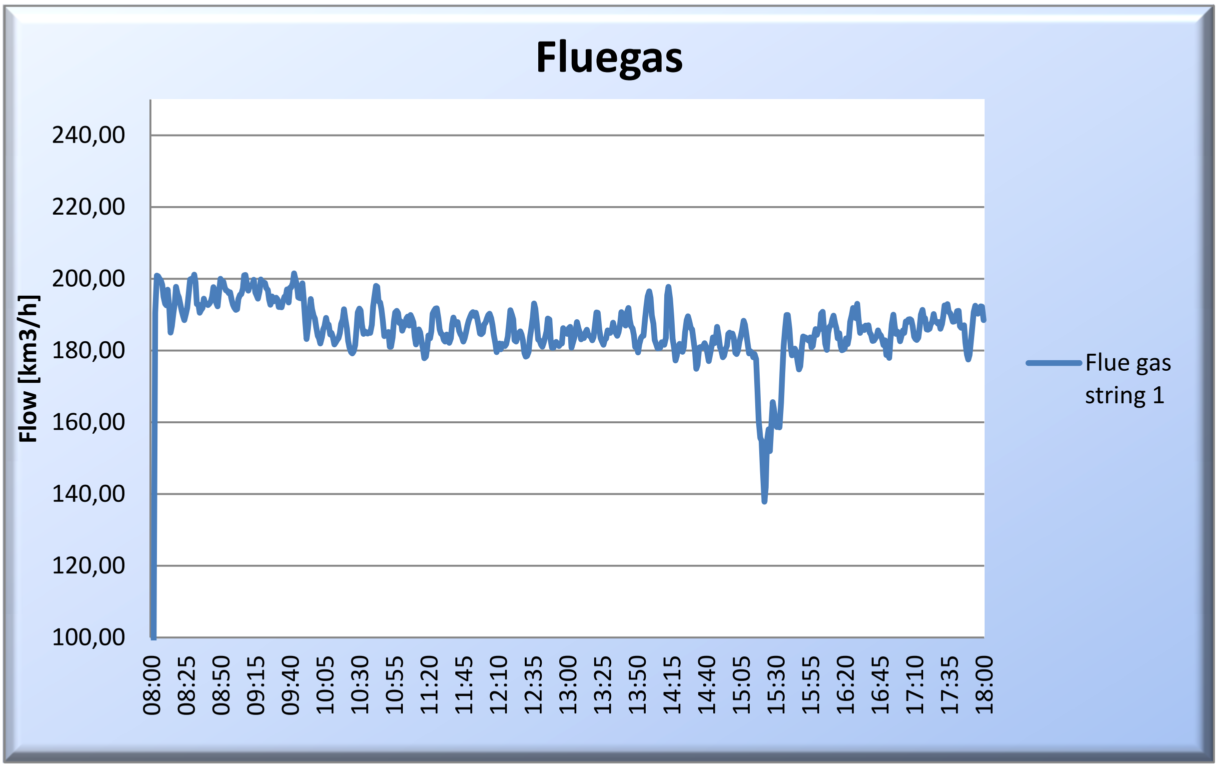
Appendix H1.1: Fuel consumption



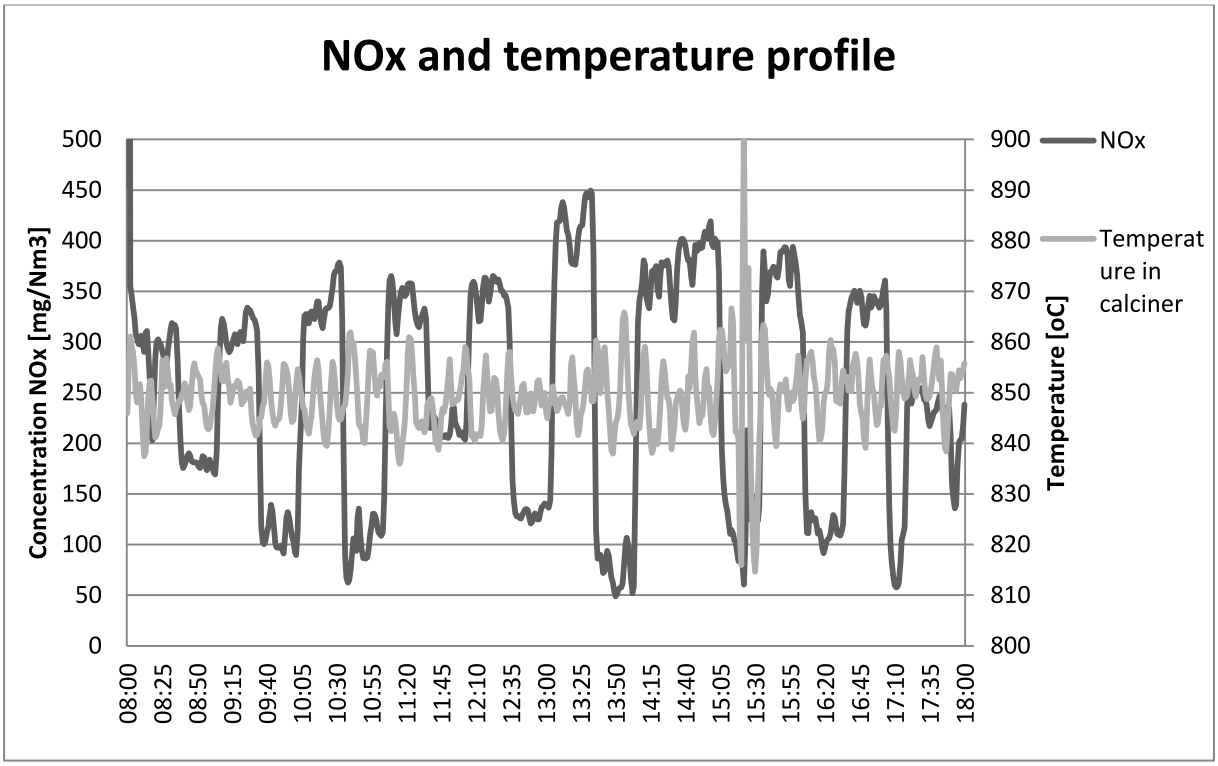
Appendix H1.2: Raw meal consumption and clinker production



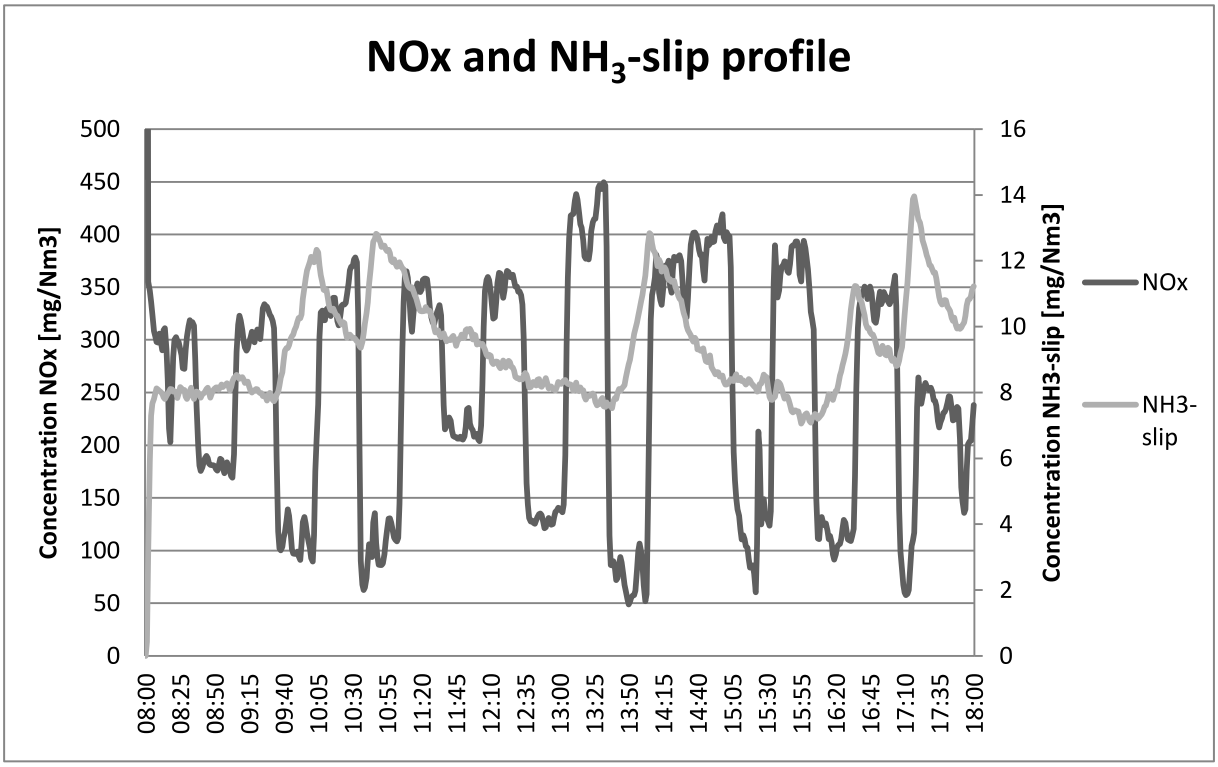
Appendix H1.3: Flue gas stream



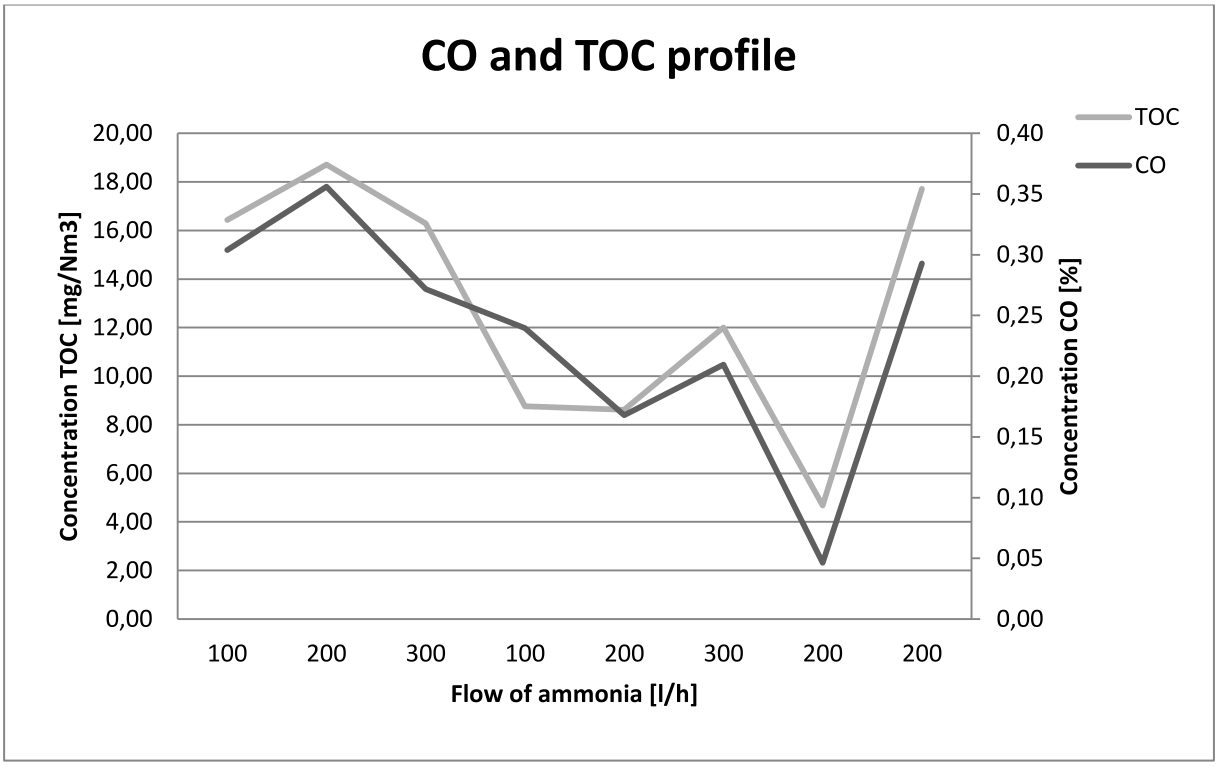
Appendix H1.4: NOx and temperature profile



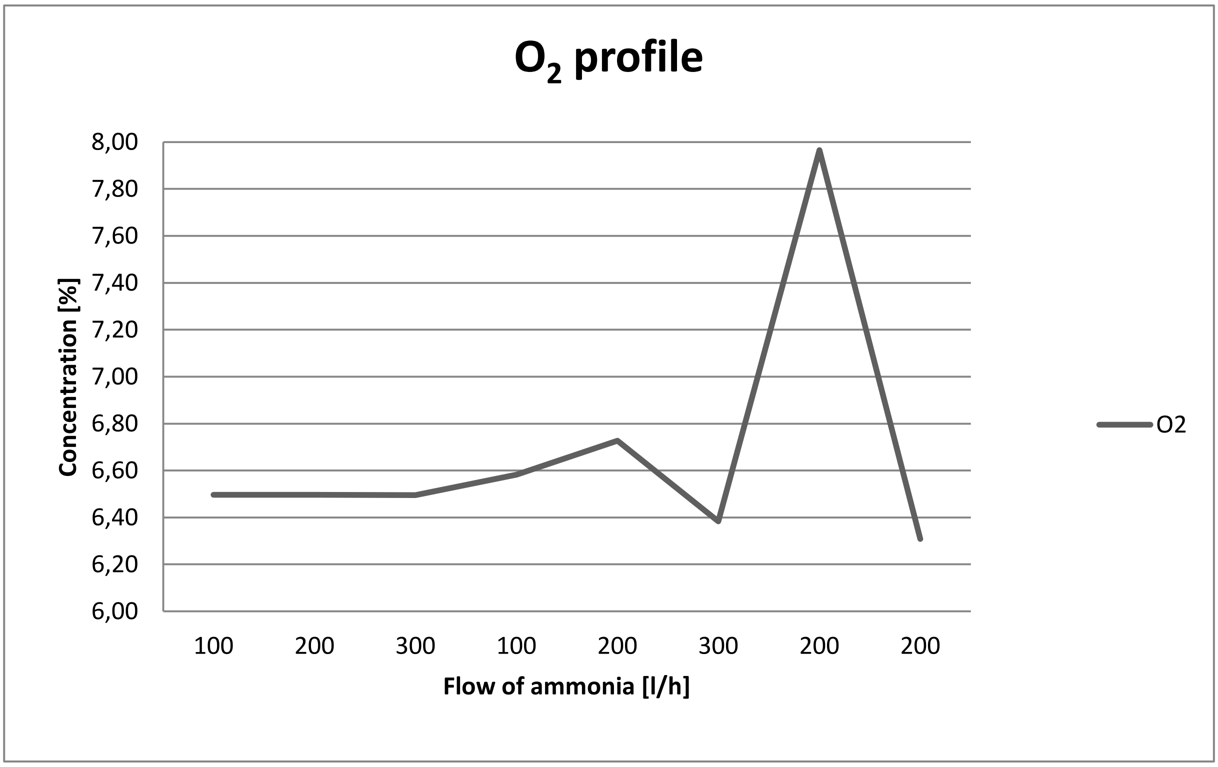
Appendix H1.5: NOx and NH_3-slip profile



Appendix H1.6: CO and TOC profile

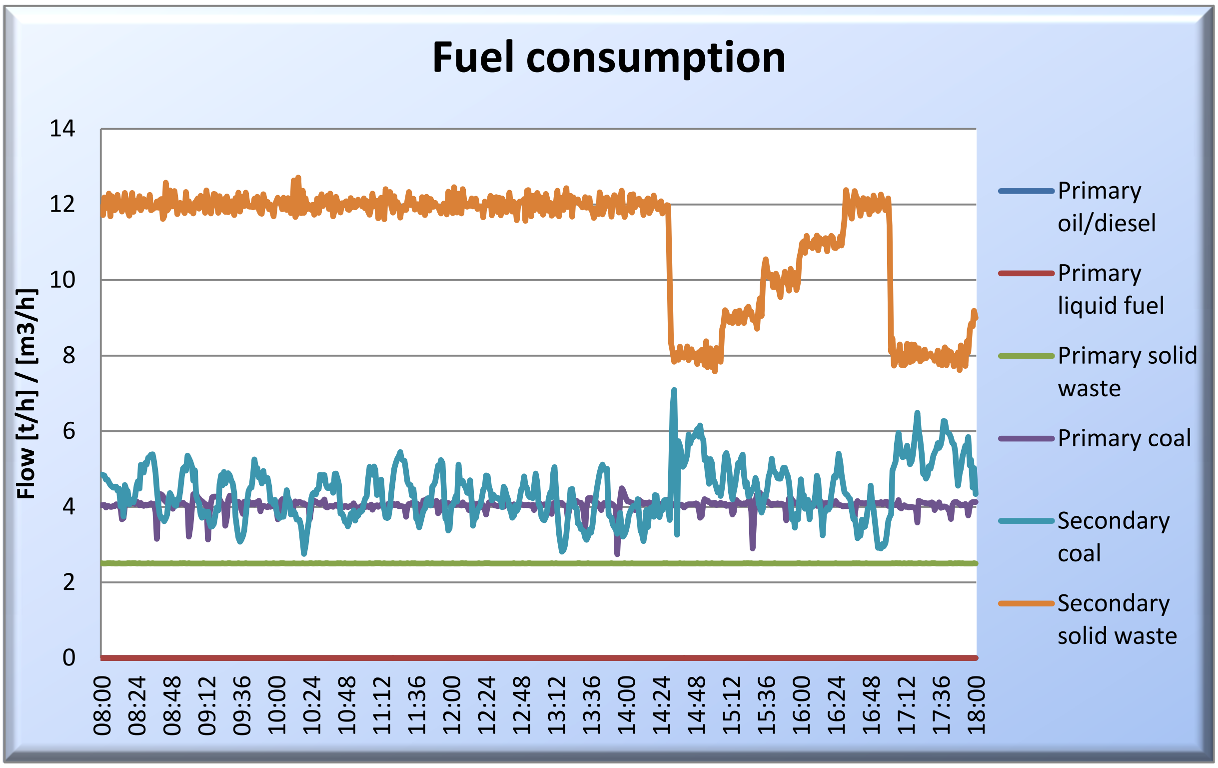


Appendix H1.7: O_2 profile

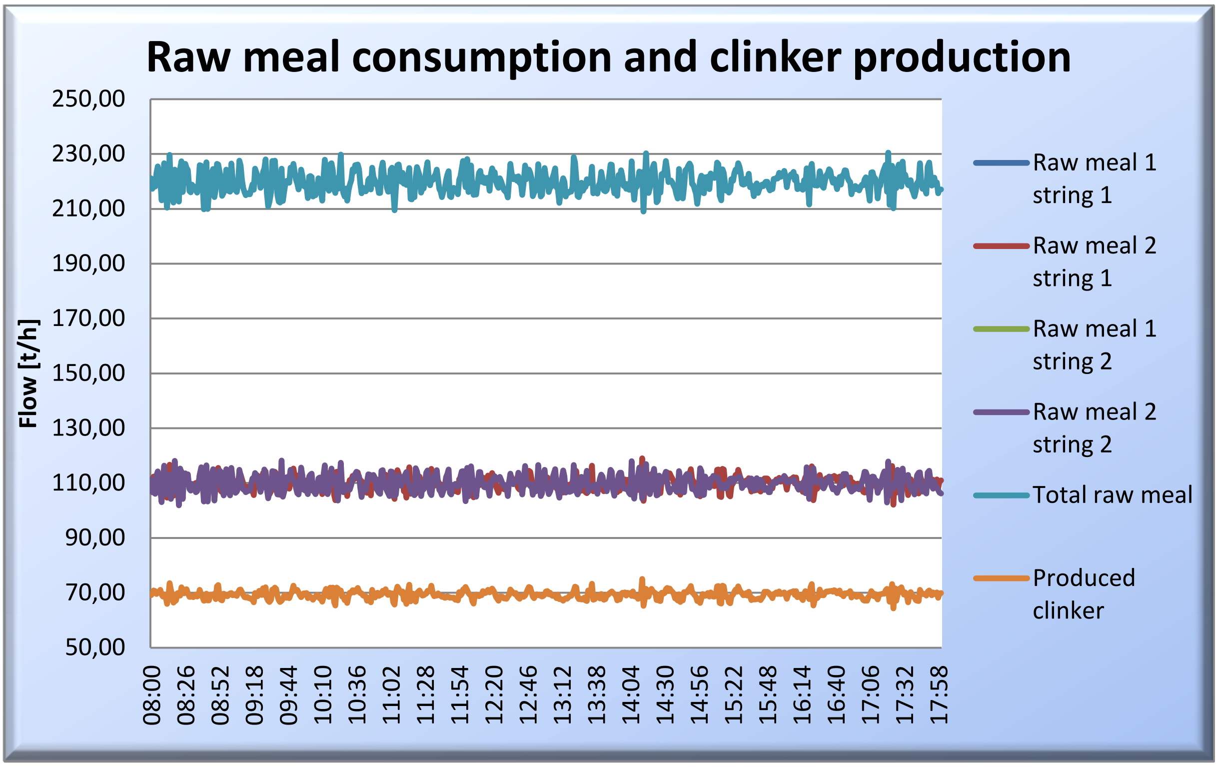


Appendix H2: Day 2 (Friday 25/5-14)

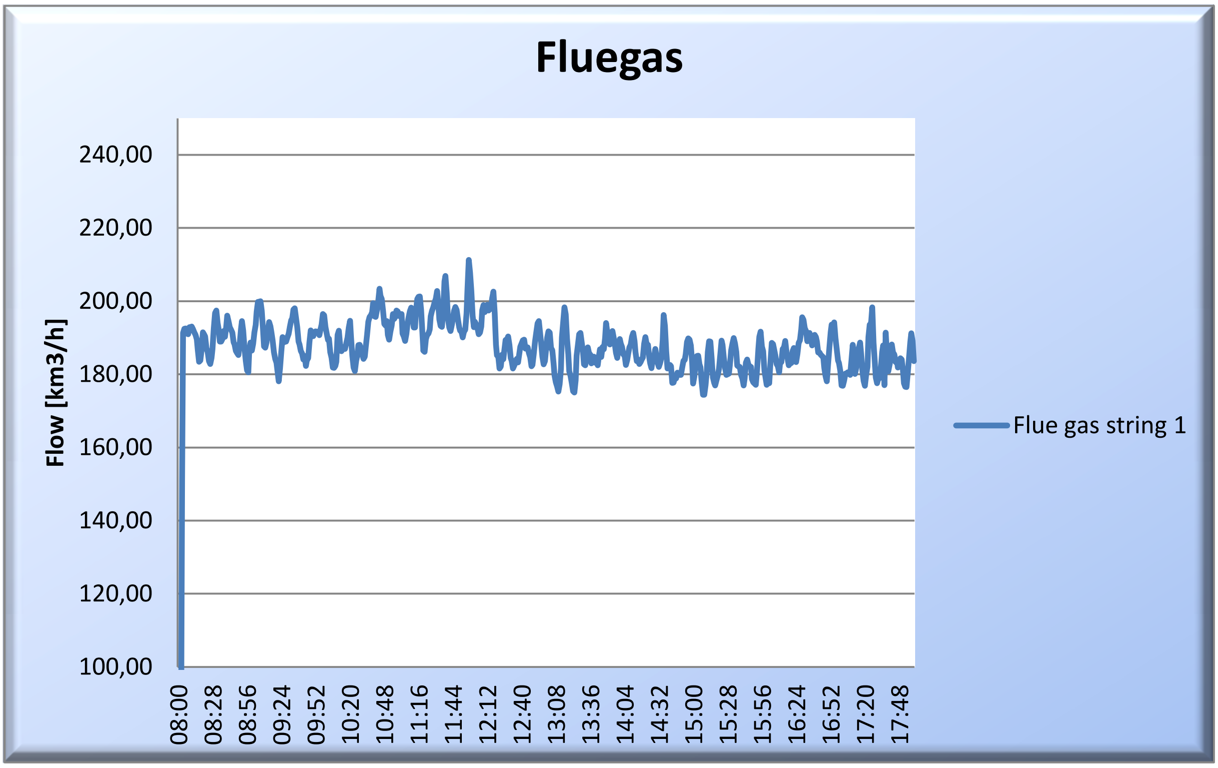
Appendix H2.1: Fuel consumption



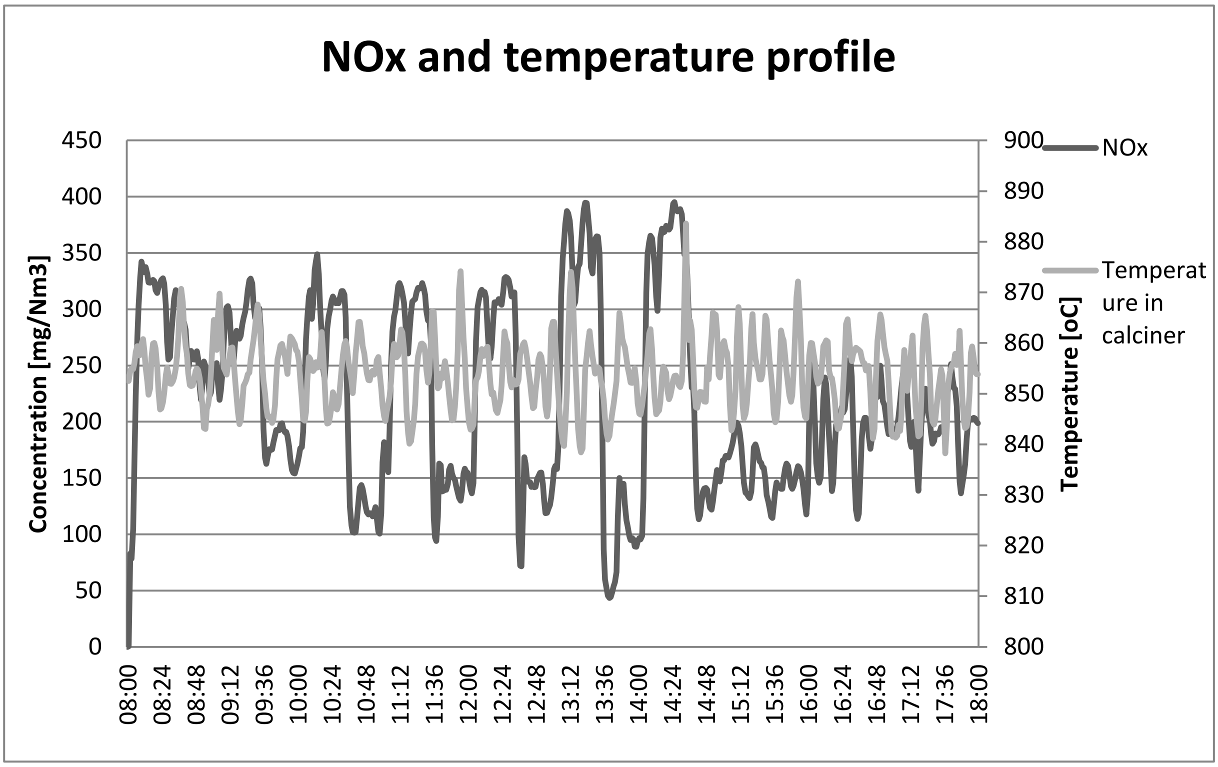
Appendix H2.2: Raw meal consumption and clinker production



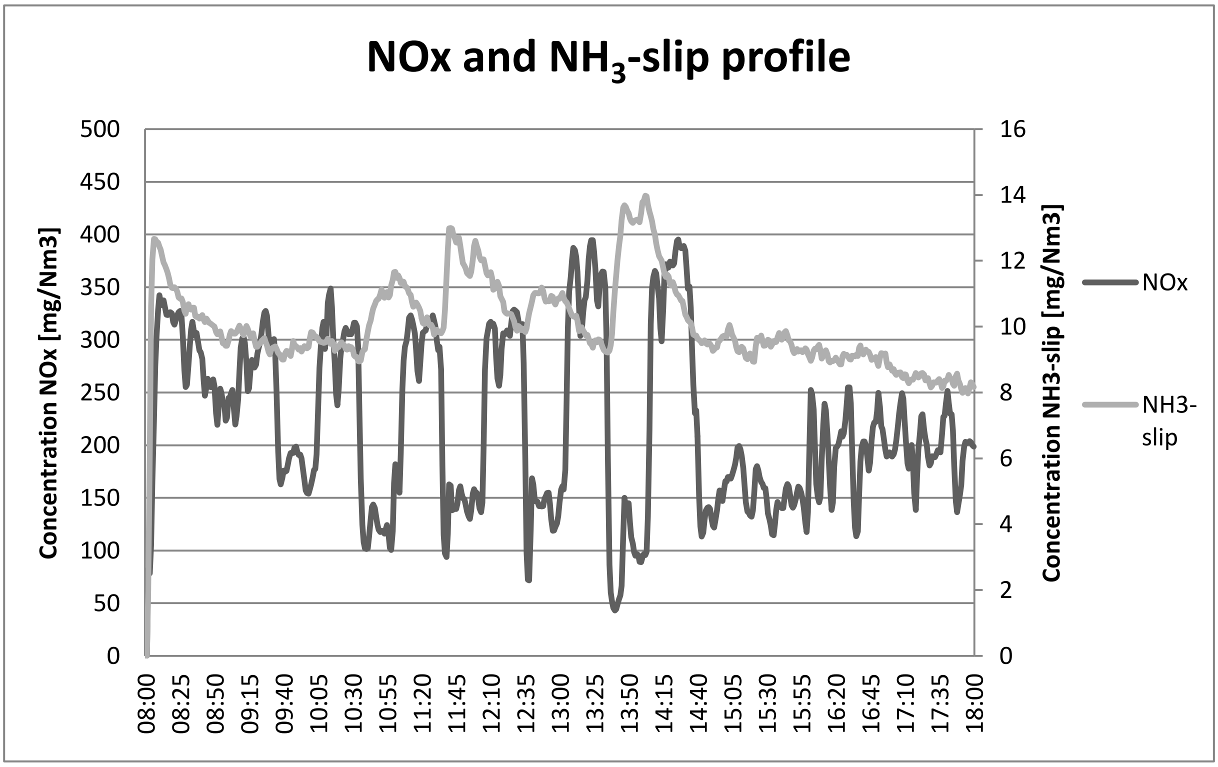
Appendix H2.3: Flue gas stream



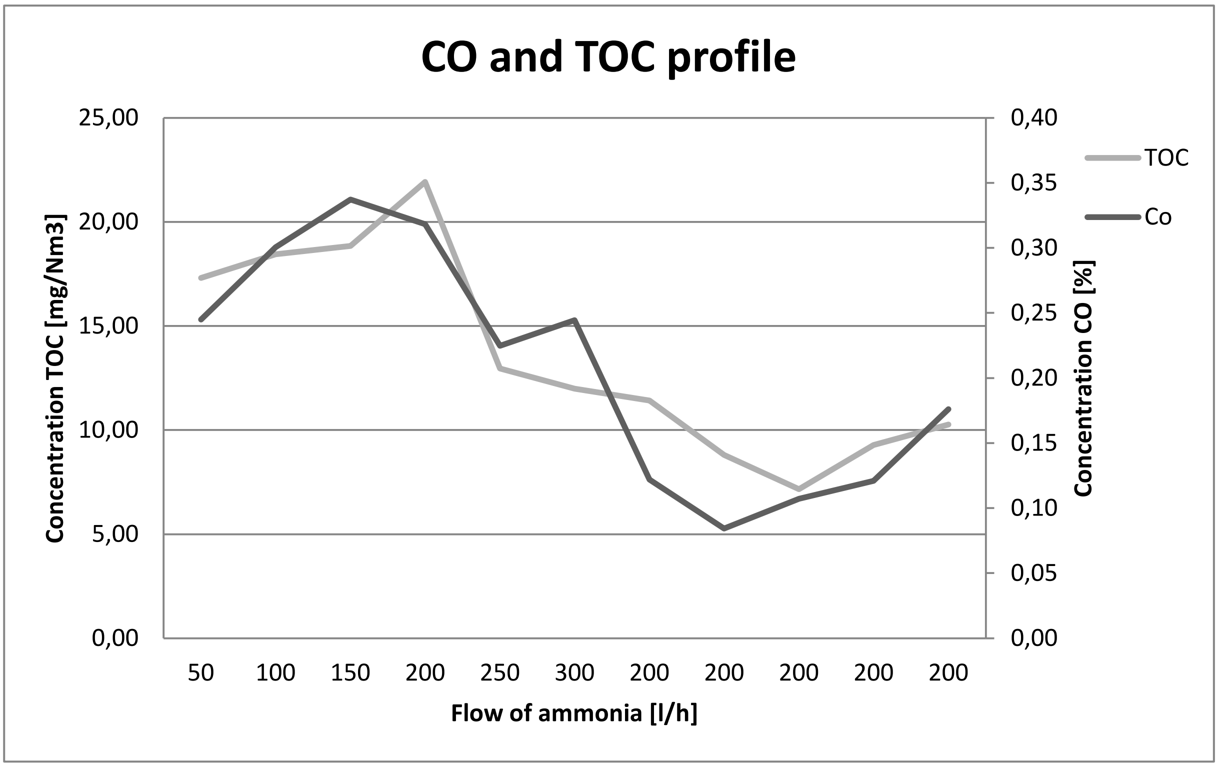
Appendix H2.4: NOx and temperature profile



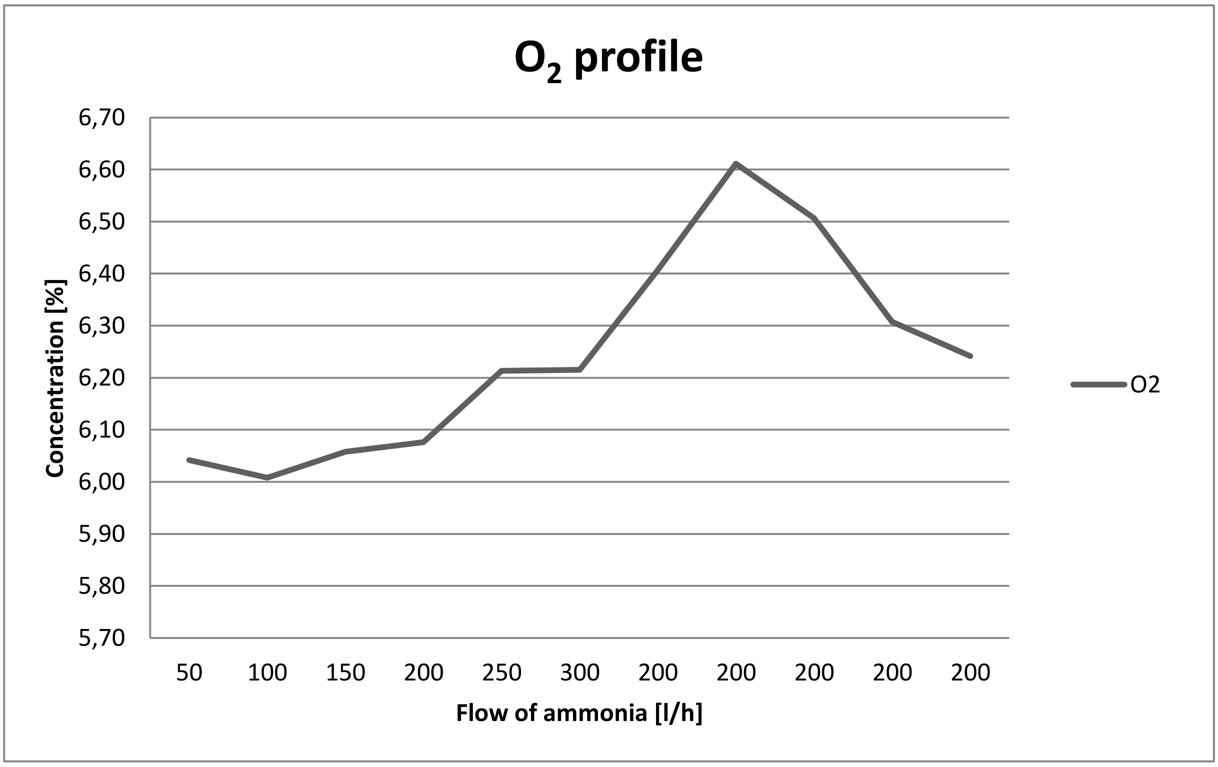
Appendix H2.5: NOx and NH_3-slip profile



Appendix H2.6: CO and TOC profile



Appendix H2.7: O_2 profile



Appendix H3: Calculated reduction efficiency

Flow of ammonia [l/h]	NOx emissions [mg/Nm^3]	Reduction efficiency relative to mean reference [%]	Reduction efficiency relative to reference time before/after [%]
50	265	15.4	2.5
100	213	32.1	30 (32.9/27/30)
150	151	51.8	46.2
200	154	50.8	49.8 (53.3/54.1/42.1)
250	158	49.4	47.6
300	132	57.9	59.2 (54.7/62.2/60.8)

Appendix H4: Cost calculation and Interpolation of ammonia consumption

The price of ammonia is taken as average price from all the “truck-fillings” bought from Yara, documented by Norcem. According to the operational time it was decided to copy the 2013 operating hours.

Table 0-1 Basic parameters

Ammonia price	1.54	NOK/l
Operating hours	7513	h/y

Table 0-2 Resulting ammonia prices

Flow of ammonia (l/h)	50	100	150	200	250	300
Consumption per year (l/y)	375650	751300	1126950	1502600	1878250	2253900
Cost per year (NOK/y)	578501	1157002	1735503	2314004	2892505	3471006
Cost per year (kNOK/y)	578.501	1157.002	1735.503	2314.004	2892.505	3471.006

General formula of interpolation:

$$f(x) = f_1 + (f_2 - f_1)\frac{(x - x_1)}{(x_2 - x_1)}$$

Based on average values of NOx, found in the excel file NOx mean values-results:

3 parallels at 100 l/h and 1 parallel at 150 l/h

F(x) = 150 + (100-150) * (200-151.4)/ (212.81-151.4)

F(x) = 110.42 l/h

Based on average values of NOx, found in the excel file NOx mean values-results:

3 parallels at 100 l/h and 3 parallels at 150 l/h (estimated)

F(x) = 150 + (100-150) * (200-174)/ (212.81-174)

F(x) = 116.50 l/h

Appendix H5: Mean values of NOx concentration, test 1.

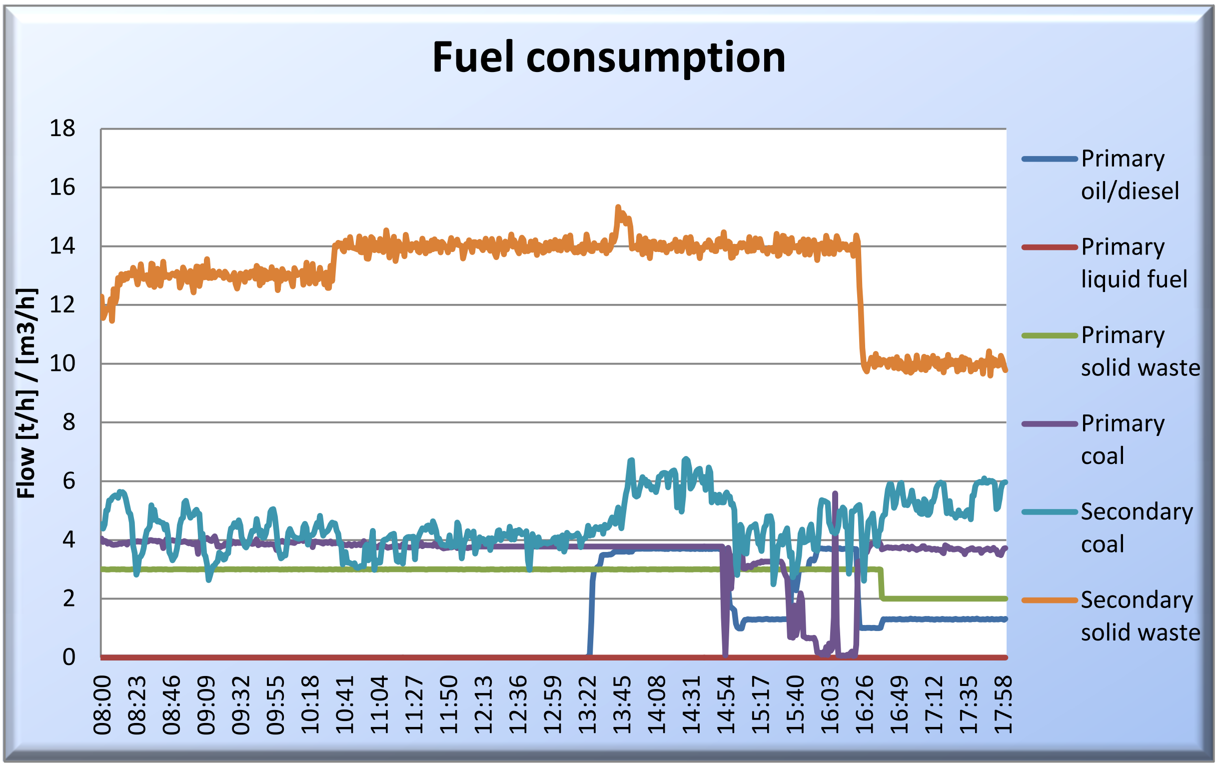
Flow of ammonia (l/h)	Trial number	NOx concentration, mean value [mg/Nm3]
100	1	209,50
200	2	138,98
300	3	138,46
100	4	232,70
200	5	161,61
300	6	130,40
200	7	165,47
200	8	147,24
50	9	265,06
100	10	196,22
150	11	151,14
200	12	161,92
250	13	158,46
300	14	127,28
200	15	192,12
200	16	166,35
200	17	141,82
200	18	201,74
200	19	193,59

Flow of ammonia (l/h)	**Average of the 3 parallels [mg/Nm3]**
100	212,8074665
200	149,2748526
300	132,0470228

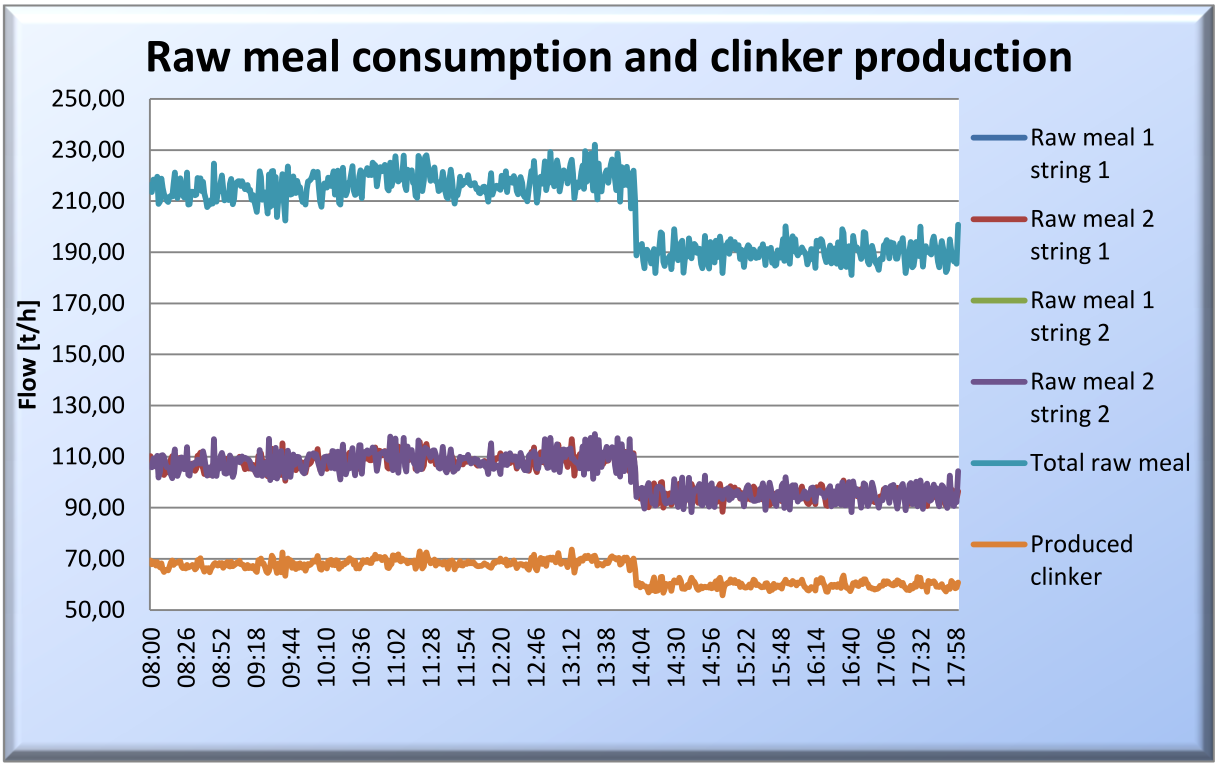
Appendix I: Results test 2

Appendix I1: Day 3 (Monday 5/5-14)

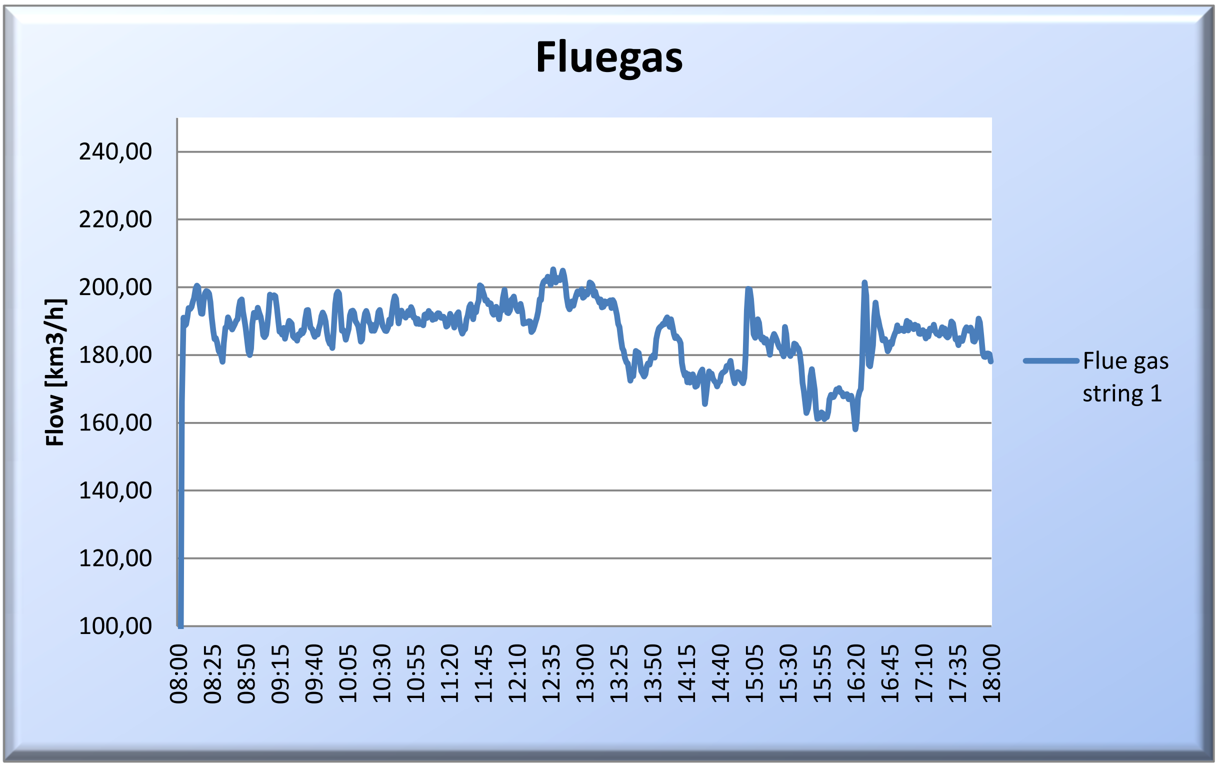
Appendix I1.1: Fuel consumption



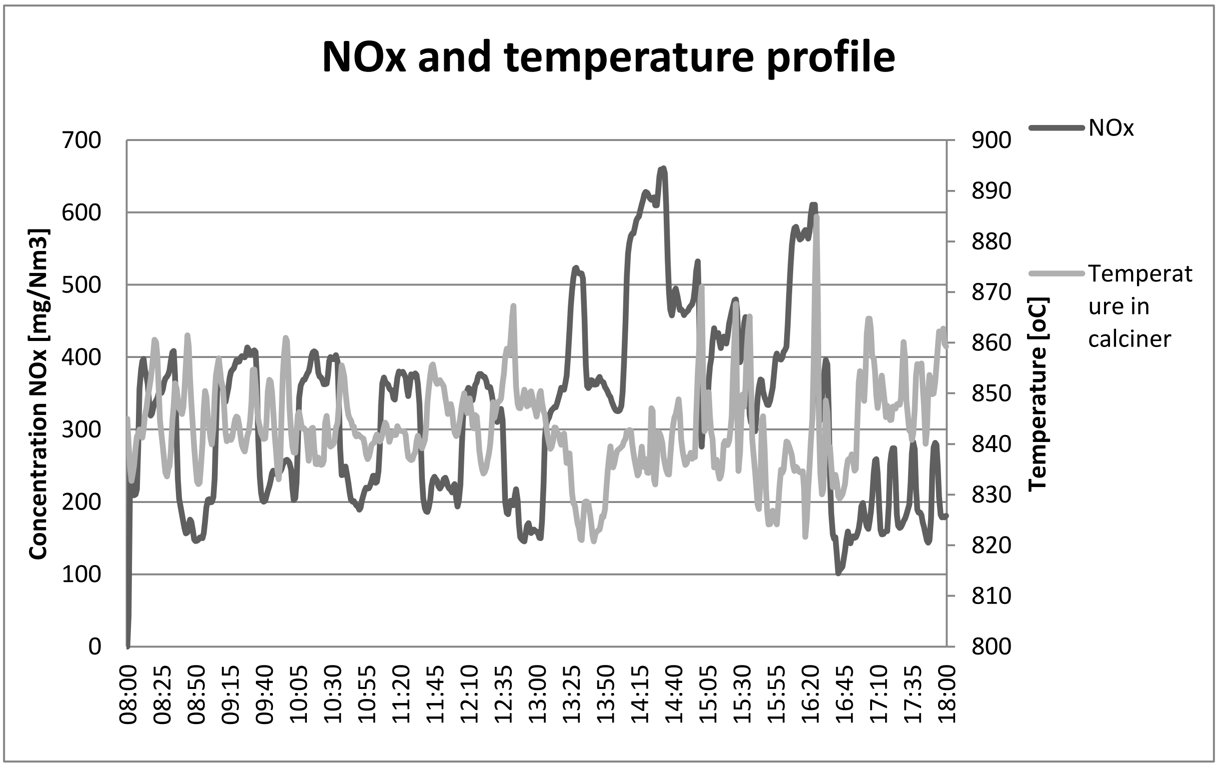
Appendix I1.2: Raw meal consumption and clinker production



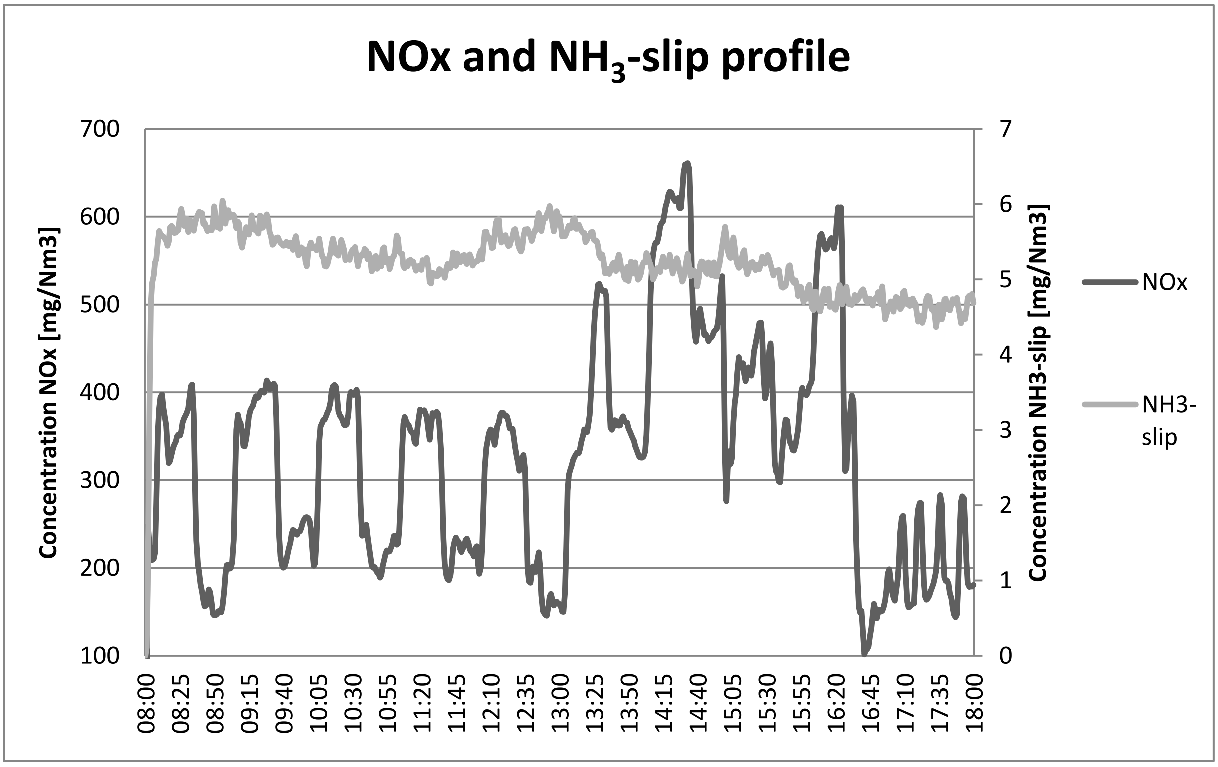
Appendix I1.3: Flue gas stream



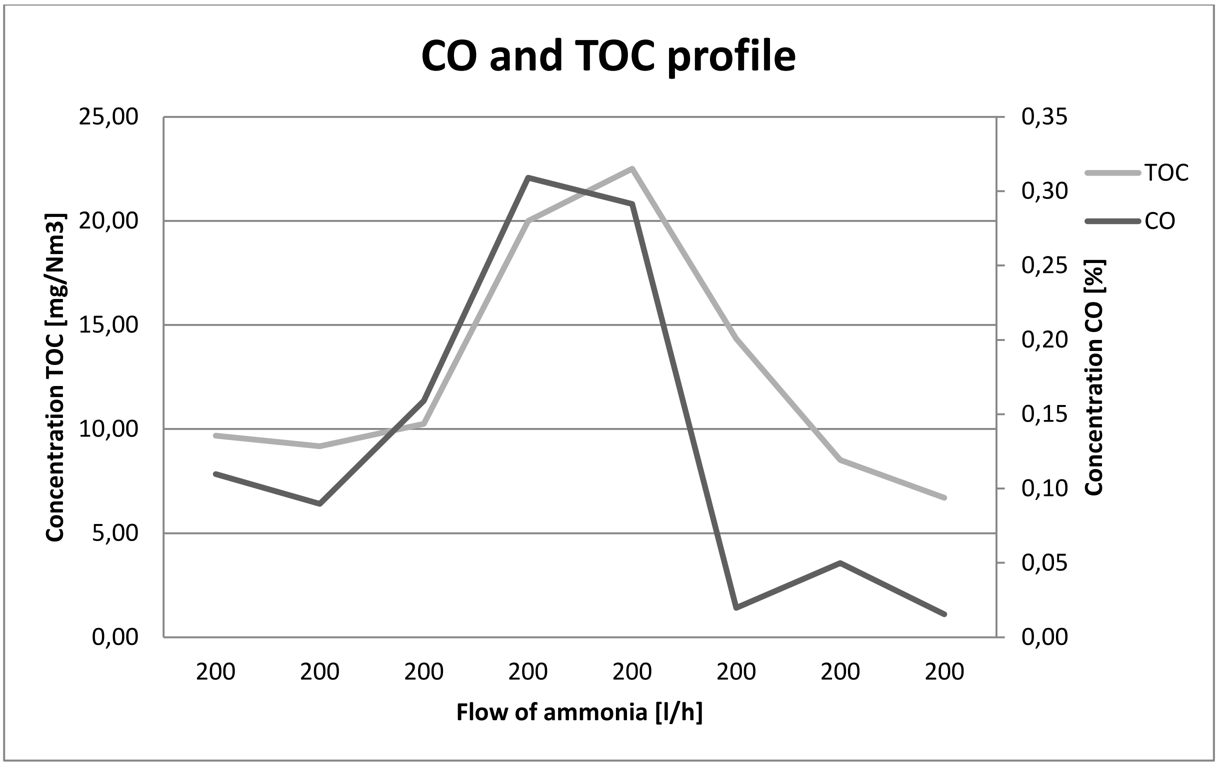
Appendix I1.4: NOx and temperature profile



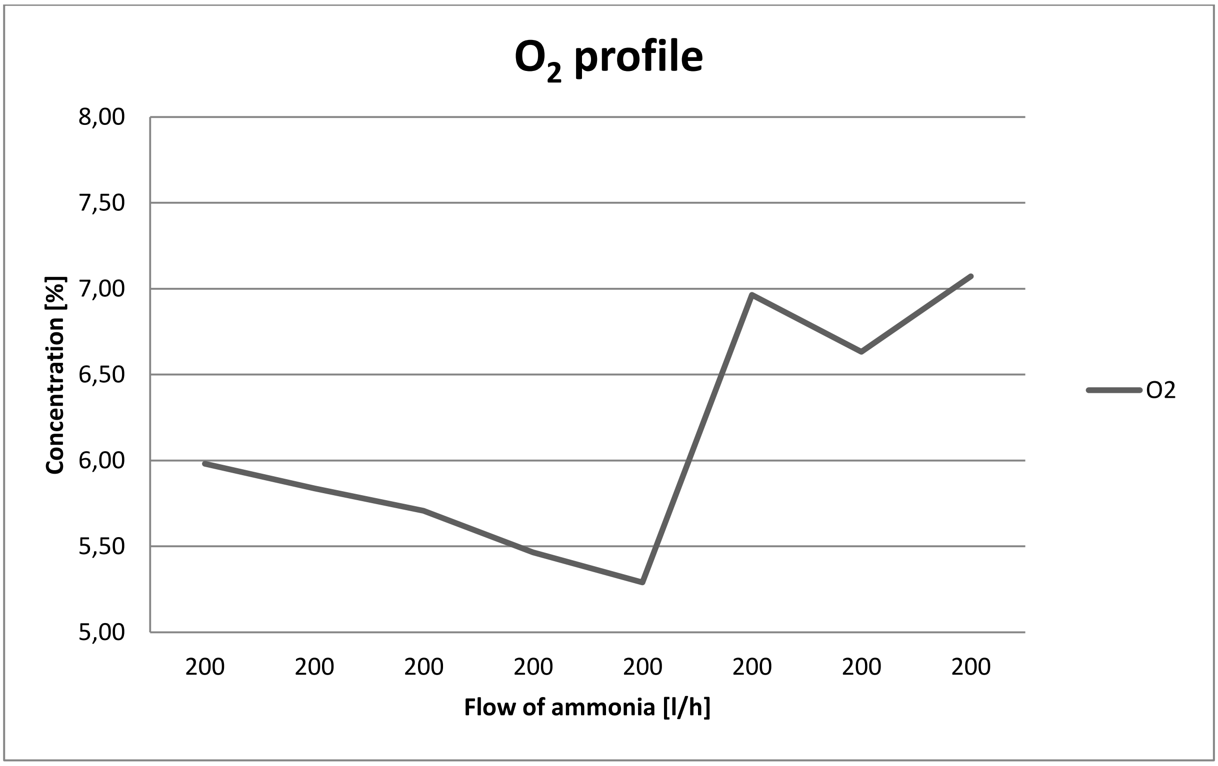
Appendix I1.5: NOx and NH_3-slip profile



Appendix I1.6: CO and TOC profile

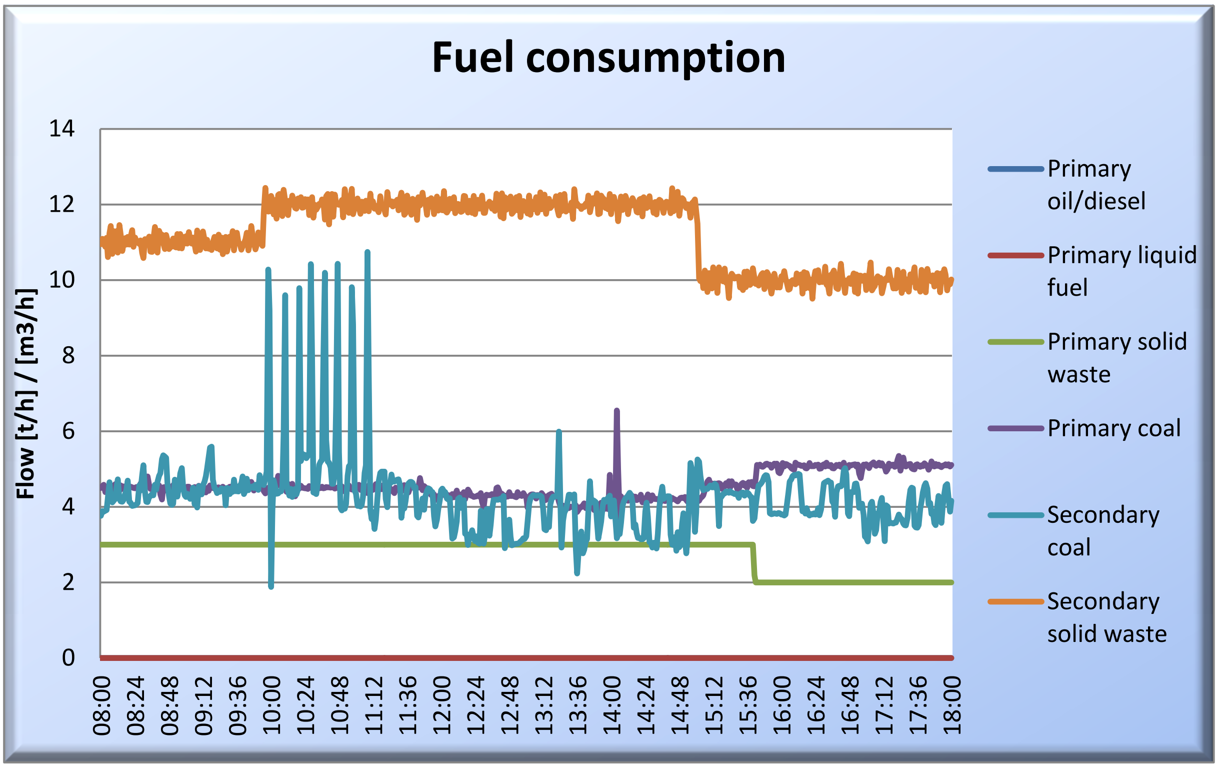


Appendix I1.7: O_2 profile

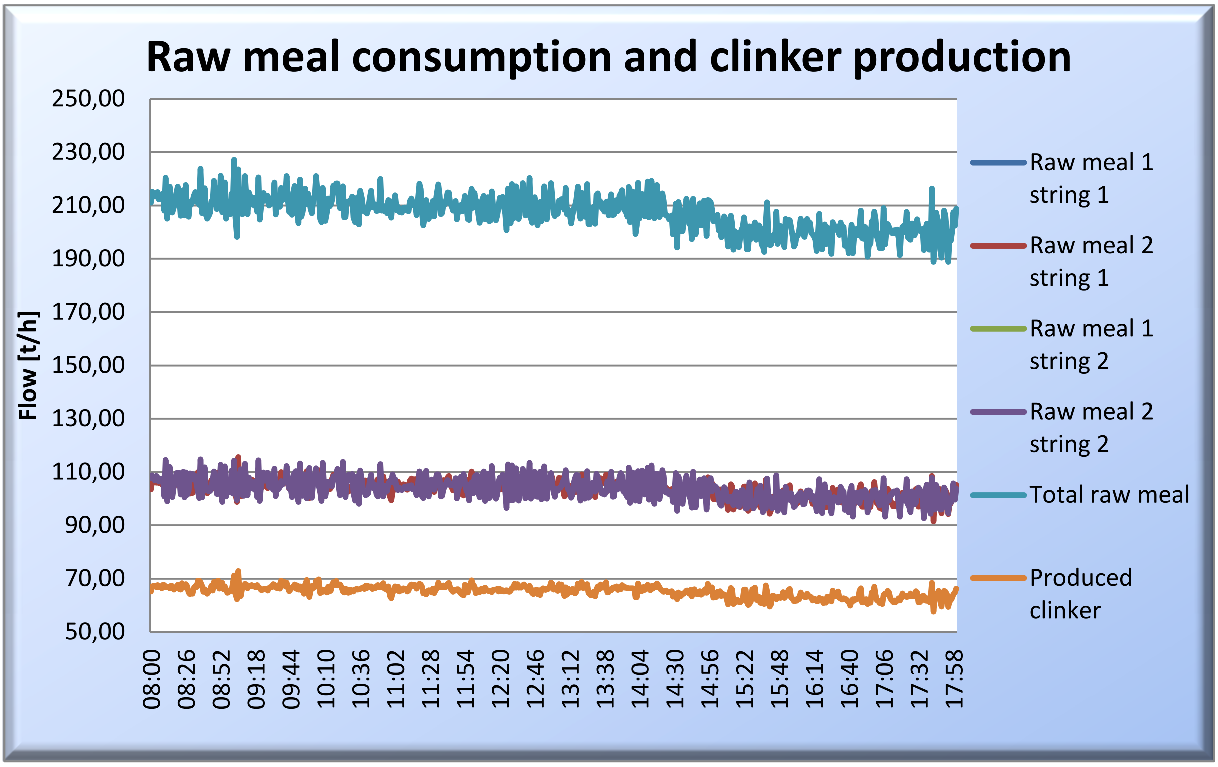


Appendix I2: Day 4 (Tuesday 5/5-14)

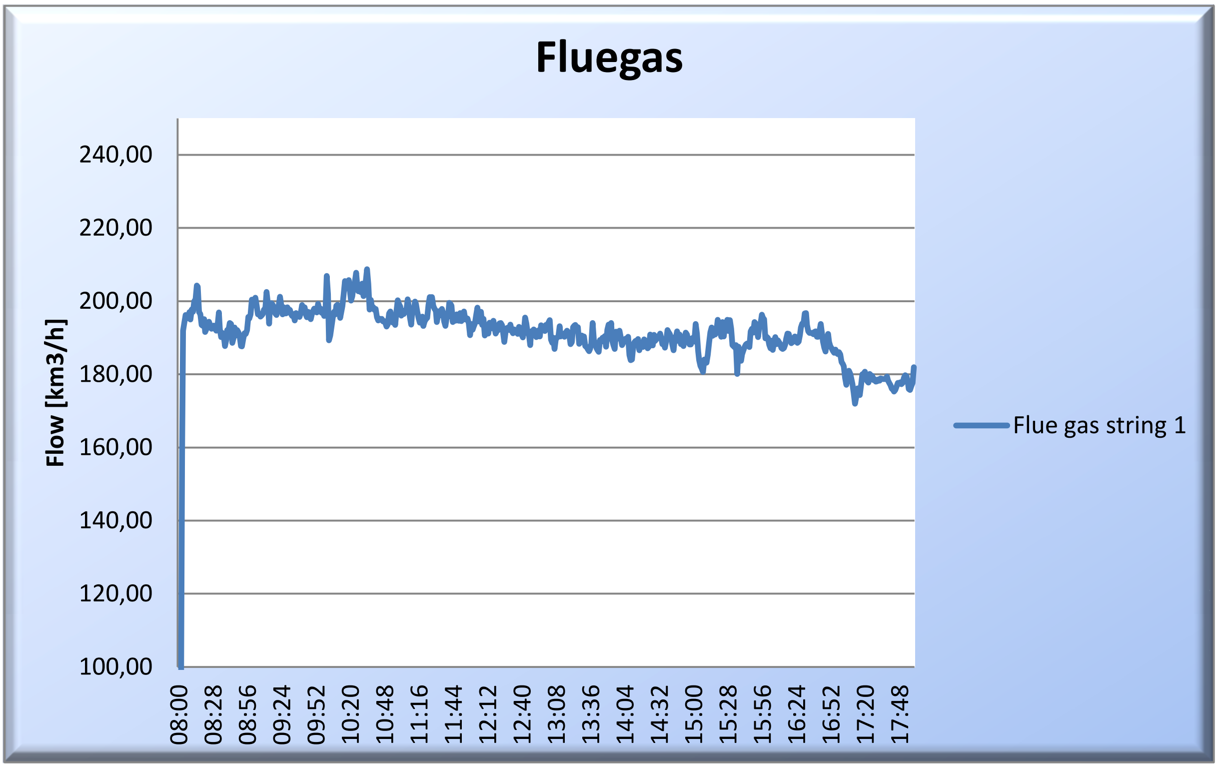
Appendix I2.1: Fuel consumption



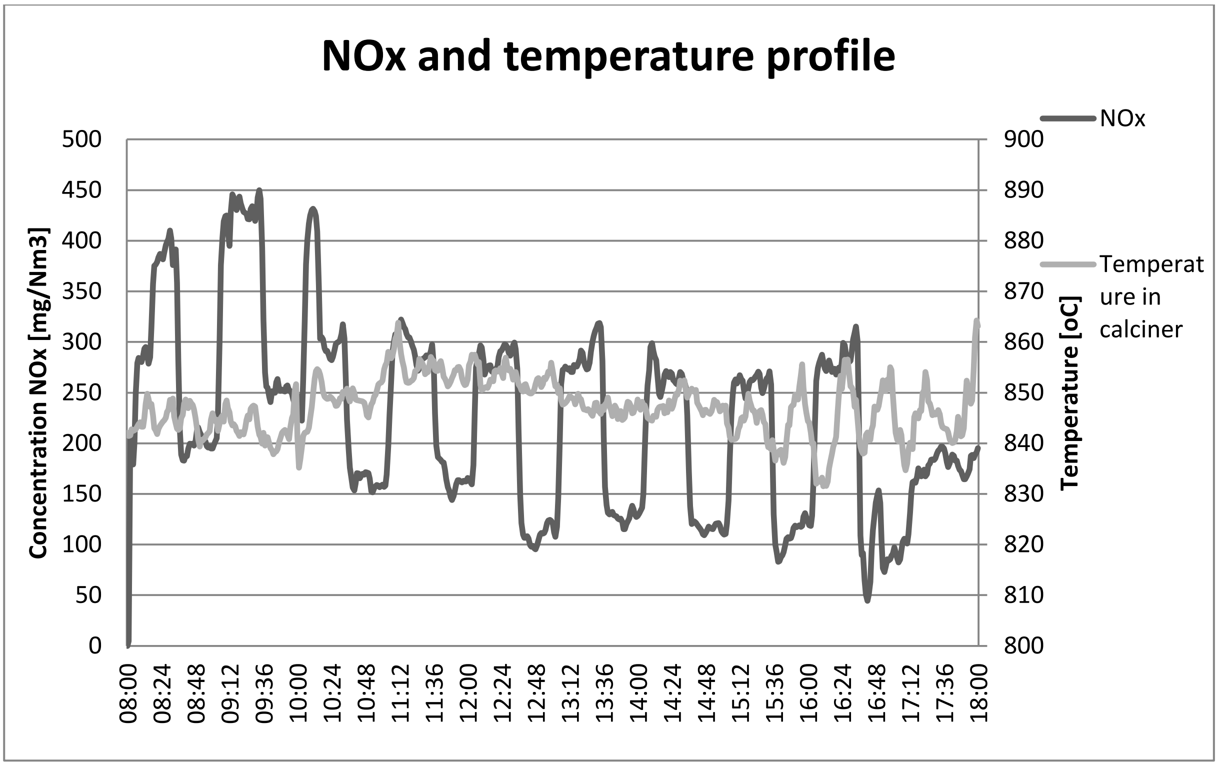
Appendix I2.2: Raw meal consumption and clinker production



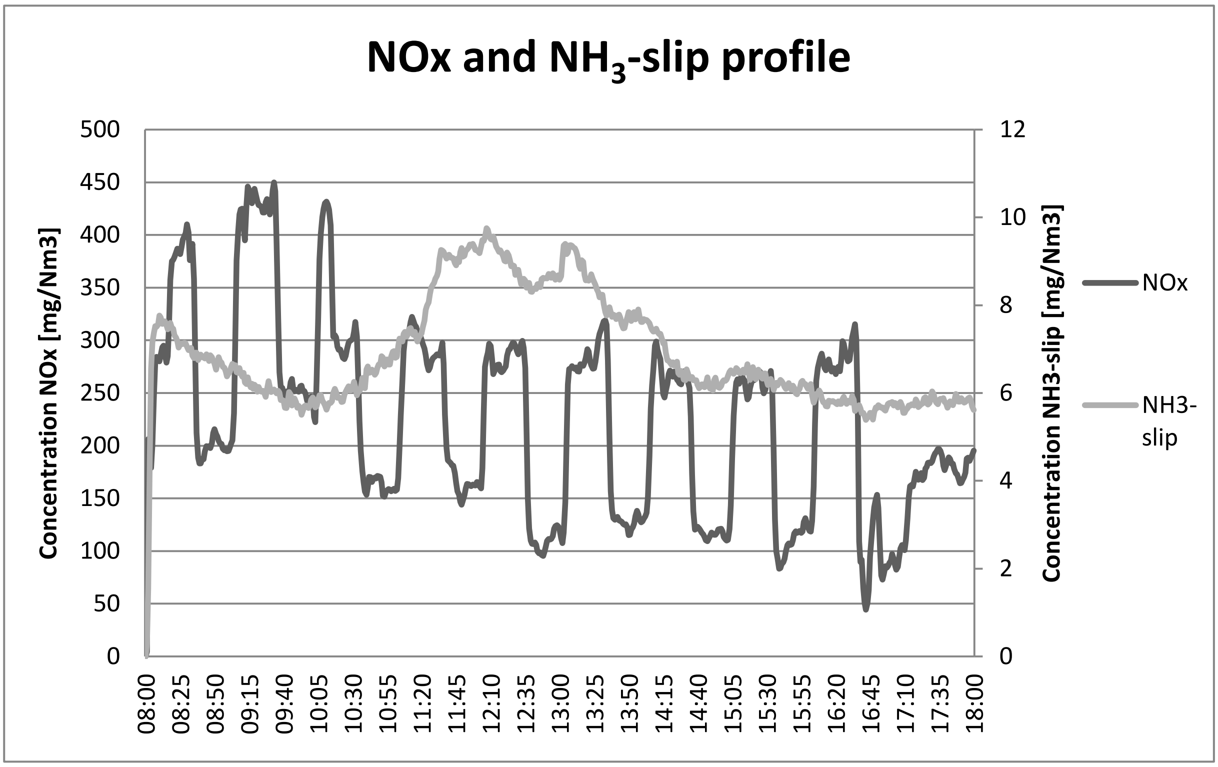
Appendix I2.3: Flue gas stream



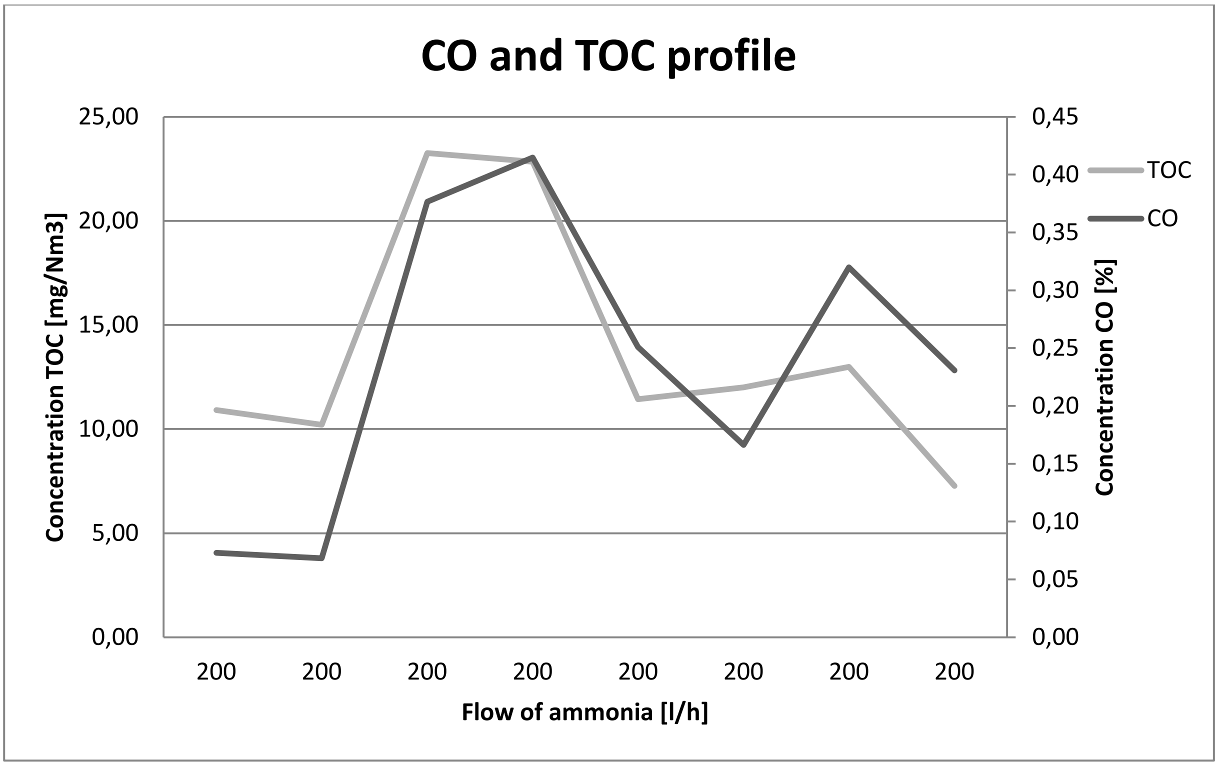
Appendix I2.4: NOx and temperature profile



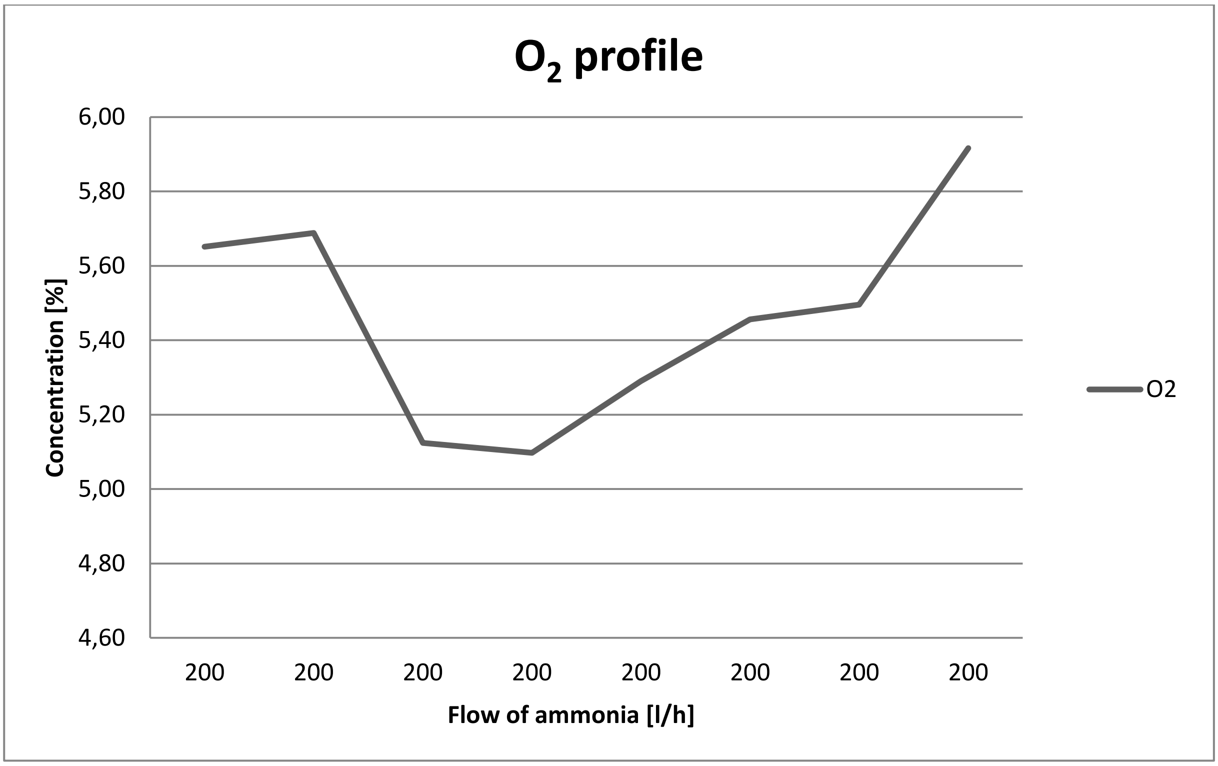
Appendix I2.5: NOx and NH_3-slip profile



Appendix I2.6: CO and TOC profile



Appendix I2.7: O_2 profile

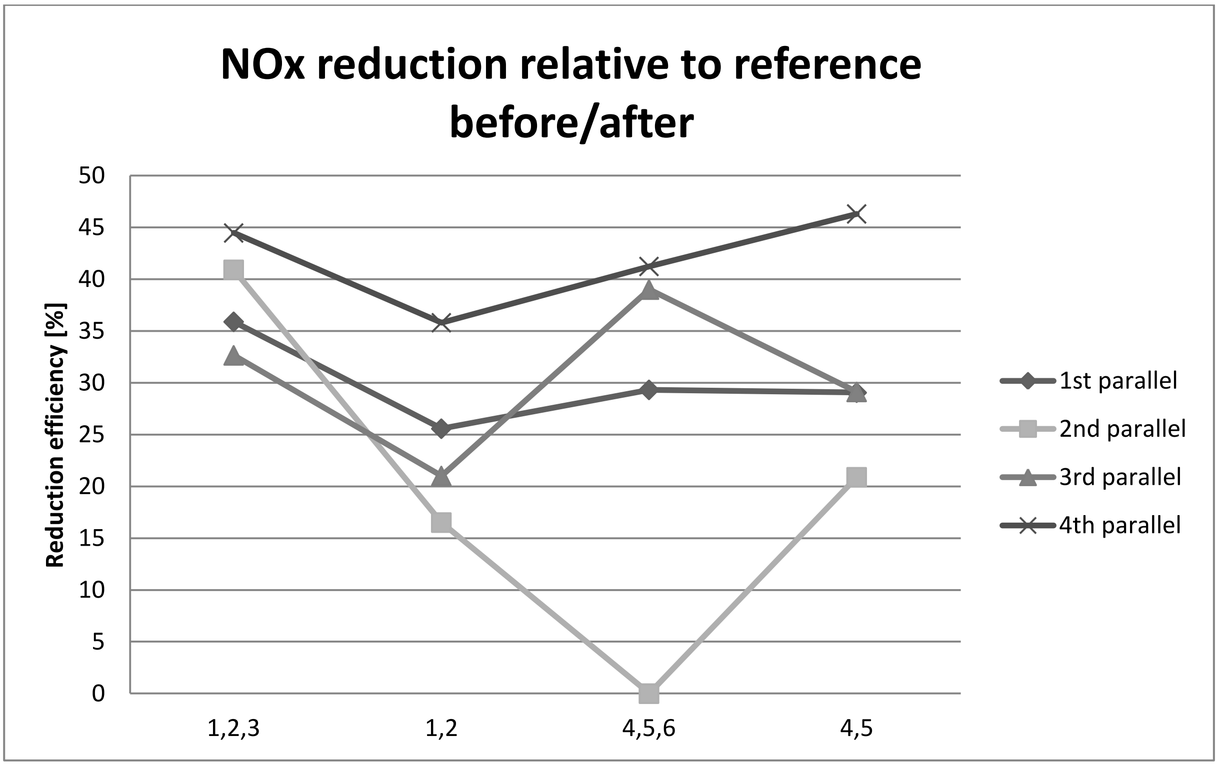


Appendix I3: Calculated reduction efficiency

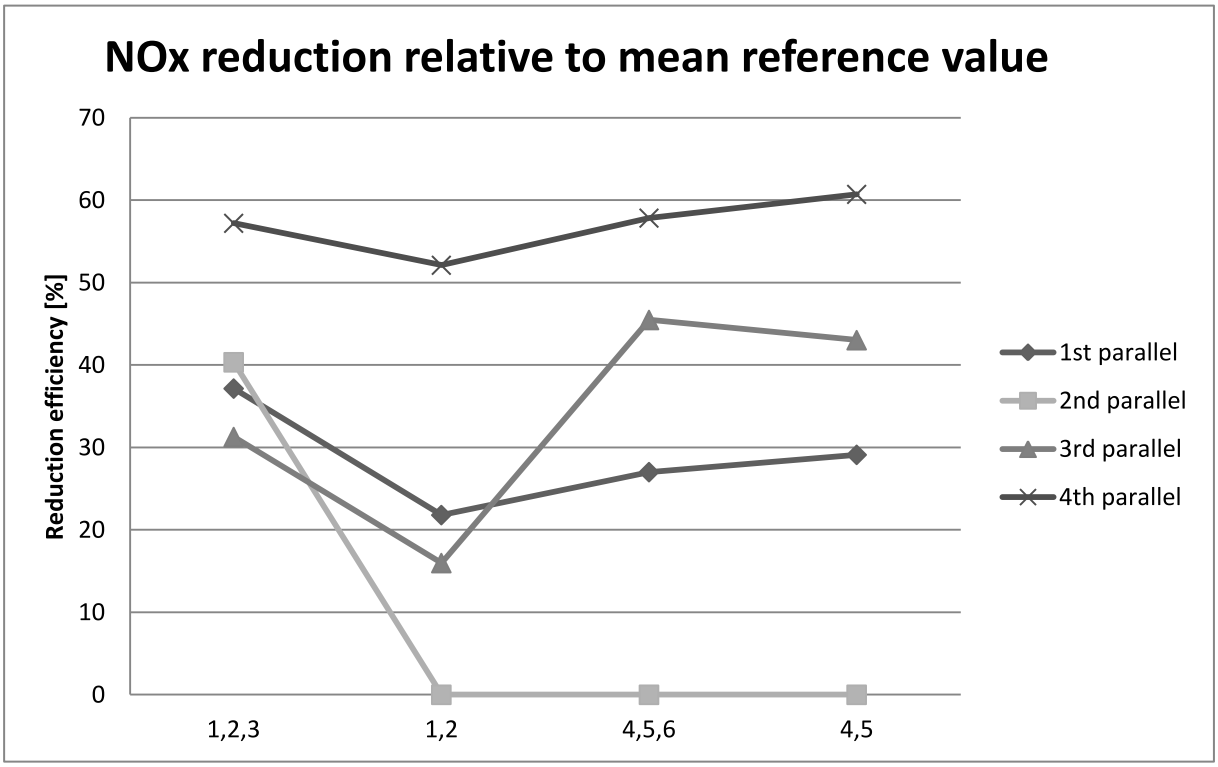
	Nozzle 1,2,3	Nozzle 1,2	Nozzle 4,5,6	Nozzle 4,5
Flow of ammonia [l/h]	200	200	200	200
NOx concentration [mg/Nm^3]				
1st parallel	212	264	246	239
2nd parallel	201	379	502	365
3rd parallel	232	283	184	192
4th parallel	144	161	142	132
Reduction efficiency relative to mean reference [%]				
1st parallel	37.1	21.8	27	29.1
2nd parallel	40.3	0	0	0
3rd parallel	31.3	16	45.5	43
4th parallel	57.2	52.1	57.8	60.7
Reduction efficiency relative to the references before/after [%]				
1st parallel	35.9	25.5	29.3	29
2nd parallel	40.9	16.5	0	21
3rd parallel	32.6	21	39	29.1
4th parallel	44.6	35.8	41.2	46.3

Appendix I4: Reduction efficiency

Appendix I4.1: NOx reduction relative to reference before/after

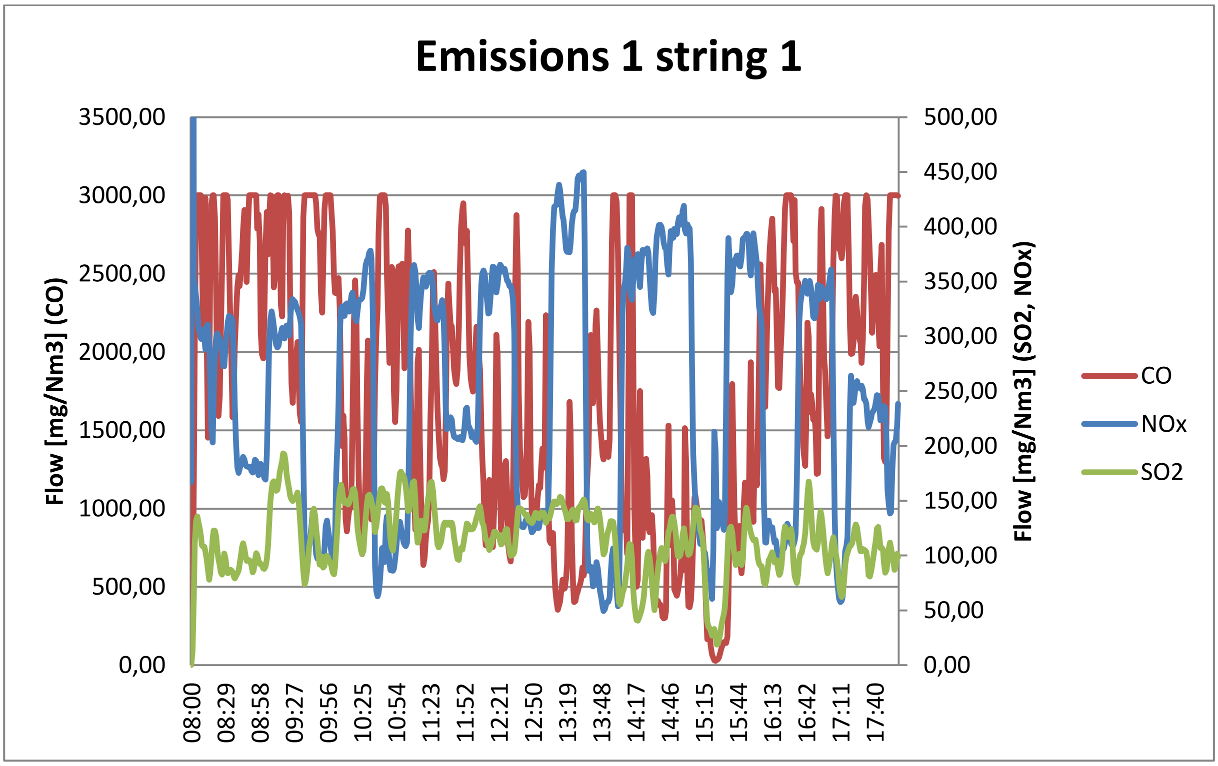


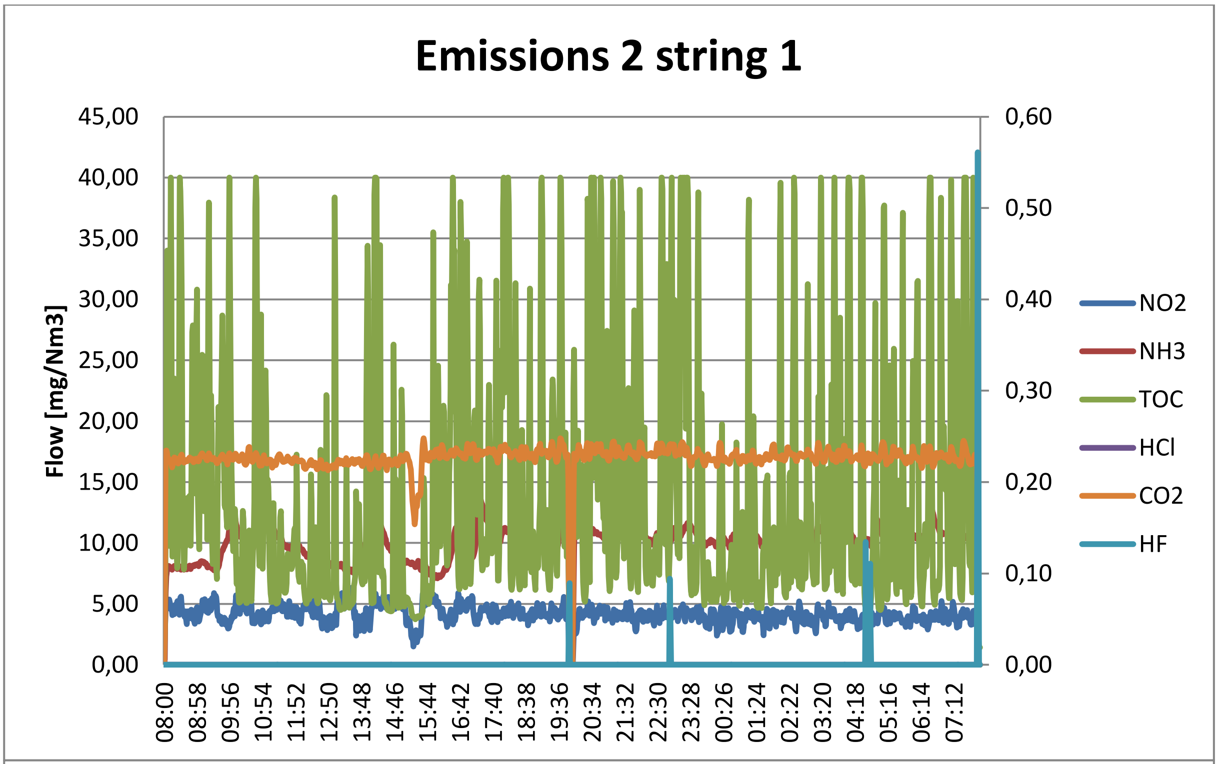
Appendix I4.3: NOx reduction relative to mean reference value

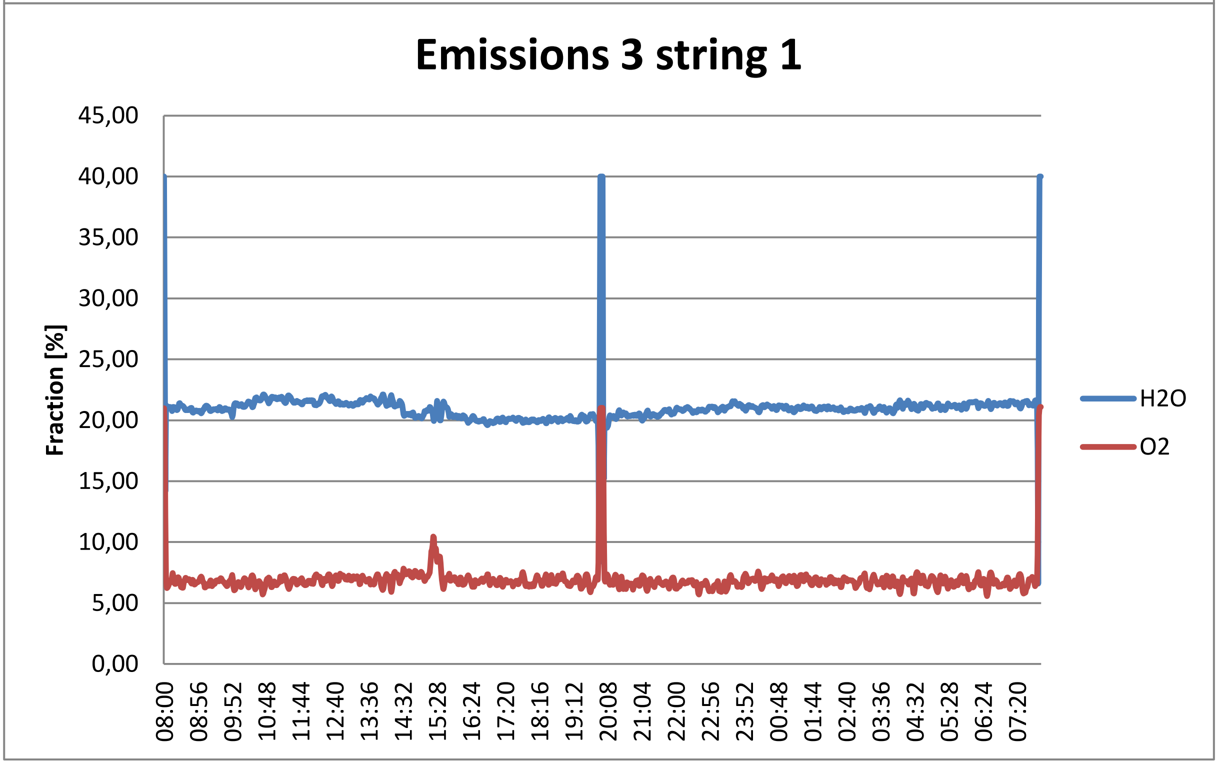


Appendix J: Emission control

Example of the measured emissions in string 1 during the first test, day 1.




Emissions 2 string 1
Flow [mg/Nm3]
45,00
40,00
35,00
30,00
25,00
20,00
15,00
10,00
5,00
0,00
0,60
0,50
0,40
0,30
0,20
0,10
0,00
08:00
08:58
09:56
10:54
11:52
12:50
13:48
14:46
15:44
16:42
17:40
18:38
19:36
20:34
21:32
22:30
23:28
00:26
01:24
02:22
03:20
04:18
05:16
06:14
07:12
NO2
NH3
TOC
HCl
CO2
HF


Emissions 3 string 1
Fraction [%]
45,00
40,00
35,00
30,00
25,00
20,00
15,00
10,00
5,00
0,00
08:00
08:56
09:52
10:48
11:44
12:40
13:36
14:32
15:28
16:24
17:20
18:16
19:12
20:08
21:04
22:00
22:56
23:52
00:48
01:44
02:40
03:36
04:32
05:28
06:24
07:20
H2O
O2