

Lappeenranta University of Technology

Faculty of Technology

Degree Program of Energy Technology

Master's thesis

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Reduction of nitrogen oxide emissions in lime kiln

Examiners: Prof. (Tech) Esa Vakkilainen

M.Sc. (Tech) Kari Luostarinen

Supervisor: M.Sc. (Tech) Nina Venäläinen

## **ABSTRACT**

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101 pages, 55 figures, 10 tables and 1 annex.

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Keywords: lime kiln, nitrogen oxide emission, Best Available Technology, Selective Non-Catalytic Reduction, Selective Catalytic Reduction, NO<sub>x</sub> scrubber

Different nitrogen oxide removal technologies for rotary lime kiln are studied in this thesis, the main focus being in commercial technologies. Post-combustion methods are investigated in more detail as potential possible NO<sub>x</sub> removal with combustion methods in rotary lime kiln is more limited or primary methods are already in use. However, secondary methods as NO<sub>x</sub> scrubber, SNCR or SCR technologies are not listed as the Best Available Technologies defined by European Union. BAT technologies for NO<sub>x</sub> removal in lime kiln are (1) Optimised combustion and combustion control, (2) Good mixing of fuel and air, (3) Low-NO<sub>x</sub> burner and (4) Fuel selection/low-N fuel.

SNCR method is the most suitable technique for NO<sub>x</sub> removal in lime kiln when NO<sub>x</sub> removal from 50 % to 70 % is required in case primary methods are already in use or cannot be applied. In higher removal cases ammonia slip is an issue in SNCR. By using SCR better NO<sub>x</sub> reduction can be achieved but issues with catalyst materials are expected to arise because of the dust and sulphur dioxide which leads to catalyst poison formation in lower flue gas temperatures. NO<sub>x</sub> scrubbing has potential when simultaneous NO<sub>x</sub> and SO<sub>2</sub> removal is required. The challenge is that NO cannot be scrubbed directly, but once it is oxidized to NO<sub>2</sub> or further scrubbing can be performed as the solubility of NO<sub>2</sub> is higher. Commercial installations have not been made regarding SNCR, SCR or NO<sub>x</sub> scrubbing regarding rotary lime kiln. For SNCR and SCR the closest references come from cement industry.

## TIIVISTELMÄ

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Hakusanat: meesauuni, typenoksidien päästö, paras käytettävissä oleva tekniikka, selektiivinen ei-katalyyttinen reduktio, selektiivinen katalyyttinen reduktio, NO<sub>x</sub>-pesuri

Tässä diplomityössä kartoitetaan erilaiset typenoksidien vähennystekniikat keskittyen pääasiassa kaupallisiin tekniikoihin. Sekundäärisiä menetelmiä tarkastellaan tarkemmin, sillä mahdollisuudet typenoksidien poistoon polttoteknisin keinoin meesauunissa ovat rajallisemmat tai primäärimenetelmillä saavutettavissa oleva reduktio on jo tehty. On huomionarvoista, että SNCR- tai SCR-menetelmät eivät tällä hetkellä edusta Euroopan Unionin määrittelemää parasta saatavilla olevaa teknologiaa. BAT-tekniikkaa ovat (1) optimoitu palaminen ja palamisen hallinta, (2) polttoaineen ja ilman huolellinen sekoittaminen, (3) Low-NO<sub>x</sub>-polttimet ja (4) polttoaineen valinta/vähän typpeä sisältävä polttoaine.

SNCR-menetelmä on soveltuvin tekniikka tavoiteltaessa 50...70 % NO<sub>x</sub>-reduktiota, mikäli primääriset keinot ovat jo käytössä tai niiden käyttö ei ole mahdollista. Haluttaessa suurempi NO<sub>x</sub>-reduktio ammoniakkipäästö kasvaa merkittäväksi SNCR-menetelmässä. SCR-menetelmää käyttämällä voidaan saavuttaa parempi NO<sub>x</sub>-reduktio, mutta soveltuvan katalyyttimateriaalin löytäminen meesauunin pölyisiin olosuhteisiin on haastavaa. Lisäksi savukaasujen rikkidioksidipitoisuus johtaa katalyytille haitallisten yhdisteiden syntyyn. NO<sub>x</sub>-pesuri on potentiaalinen vaihtoehto, kun vaaditaan samanaikaista typen- ja rikinoksidien poistoa. Haasteena NO<sub>x</sub>-pesussa on se, että NO:n liukoisuus on vähäinen ja se tulee hapettaa ensin typpidioksidiksi tai edelleen hapettuneenpiin muotoihin, jotta peseminen on mahdollista. Kaupallisen tason asennuksia ei ole tehty SNCR- tai SCR-järjestelmien eikä NO<sub>x</sub>-pesurin osalta meesauuneille. SNCR- ja SCR-tekniikoiden osalta lähimmät referenssit ovat sementtiteollisuudesta.

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Timo Hakkarainen

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## APPENDIXES

**Appendix I.** Detailed summary of external combustion NO<sub>x</sub> limiting technologies

## **SYMBOLS AND ABBREVIATIONS**

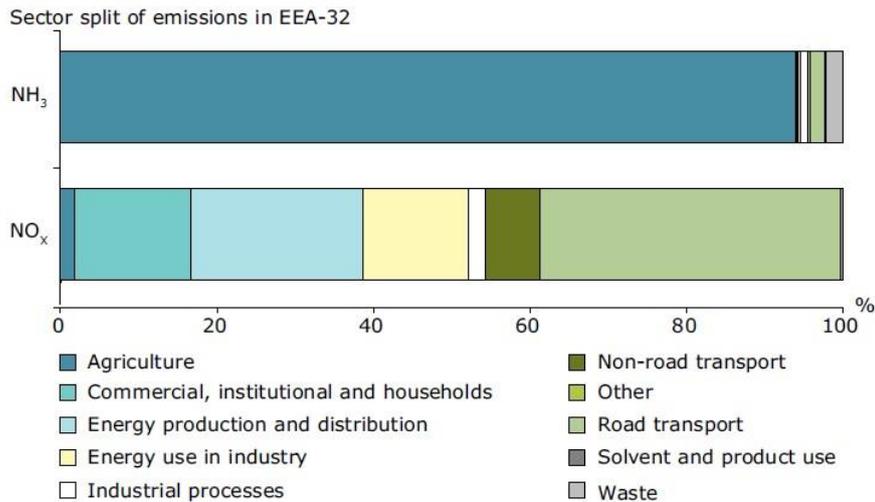
### **Abbreviations**

ABS	Ammonium bisulphate
adt	air dry ton
BAT	Best Available Technology
BREF	Best Available Technology Reference Document
CAPEX	Capital expenditure
CNCG	Concentrated Non-Condensable Gases
DeNO <sub>x</sub>	Nitrogen oxide deletion
DNCG	Dilute Non-Condensable Gases
dscm	dry standard cubic meter
EBFGT	Electronic-beam flue-gas treatment
EU	European Union
EPA	Environmental Protection Agency
ESP	Electrostatic precipitator
FGD	Flue gas desulfurization
FGR	Flue gas recirculation
GHSV	Gas hourly space velocity
HiTAC	High temperature air combustion
ID	induced draft
LEL	Lower Explosion Limit
LMD	Lime mud dryer
LNB	Low NO <sub>x</sub> Burner
LNG	Liquid natural gas
LoTO <sub>x</sub>	Low-Temperature Oxidation
NAAQS	National Ambient Air Quality Standards
NCG	Non-Condensable Gases
NO <sub>x</sub>	Nitrogen oxides
OPEX	Operating expenditure
PM	Particulate matter
ppm	parts per million

rpm	revolutions per minute
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction
SOG	Stripper Off-Gases
TRS	Total reduced sulphur
UEL	Upper Explosion Limit
UV	Ultraviolet light

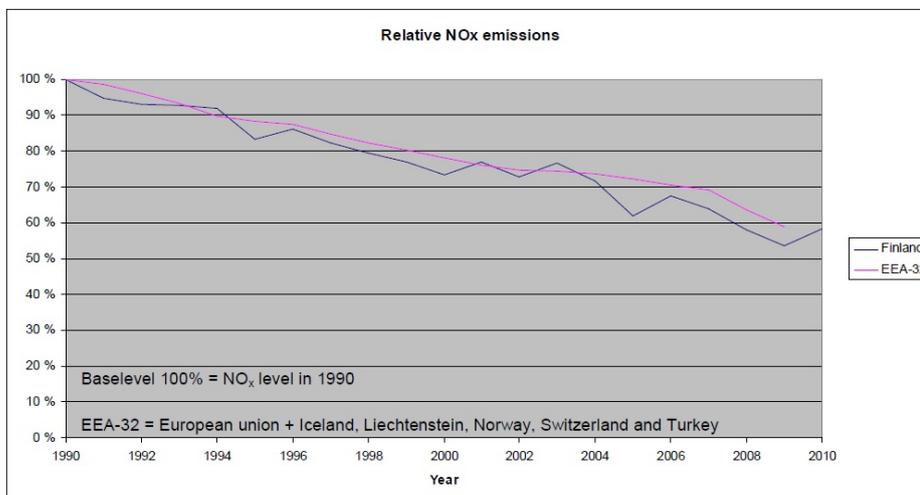
## 1 INTRODUCTION

Nitrogen oxides, also known as NO<sub>x</sub>, are one of the most significant air pollutants. Shares of nitrogen oxide and ammonia emissions by sectors in EEA-32 countries are presented in Figure 1.



**Figure 1.** Sector split of NO<sub>x</sub> and NH<sub>3</sub> emissions (European Environment Agency, 2012)

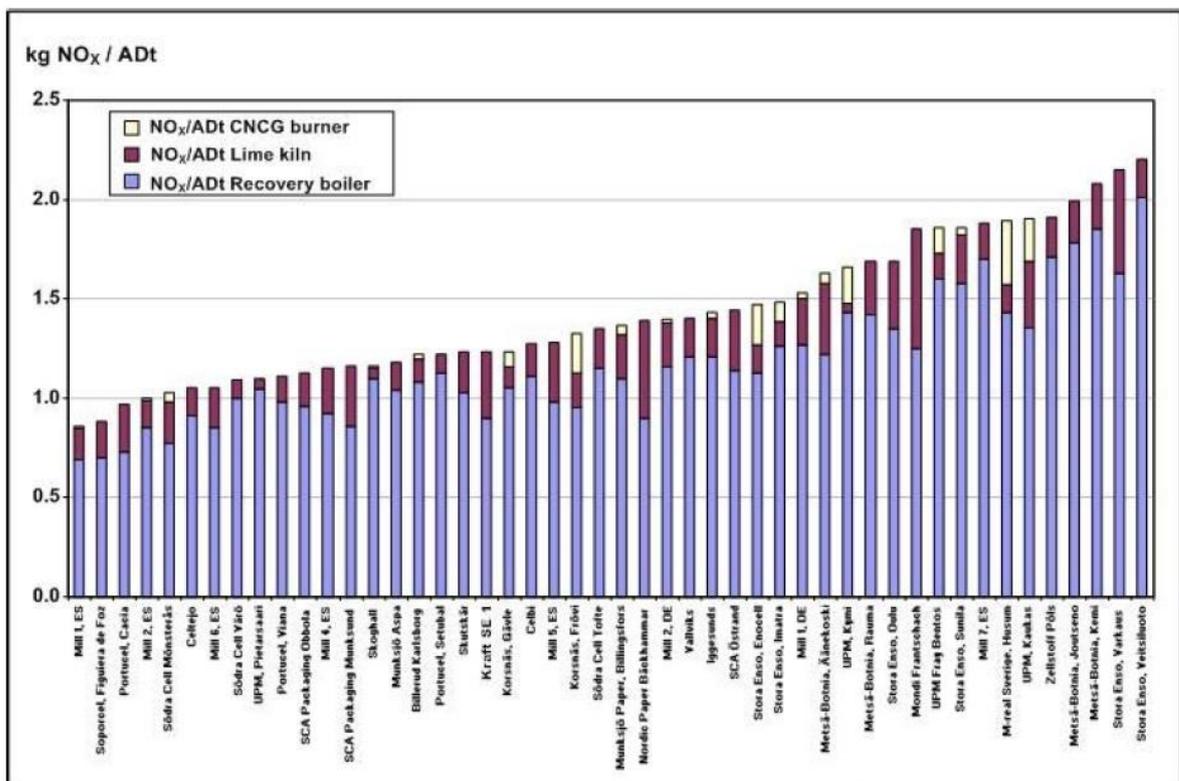
Relative NO<sub>x</sub> emissions in Finland and in EEA-32 countries are presented in Figure 2. Total emission in 2009 was 10.5 million tonnes of NO<sub>x</sub> (as NO<sub>2</sub>). As can be seen the trend in the NO<sub>x</sub> emissions is descending, which is mainly due to tightening emission regulations. (European Environment Agency 2011)



**Figure 2.** Relative NO<sub>x</sub> emissions in Finland and in EEA-32 countries (European Environment Agency 2011)

## 1.1 Background

Nitrogen oxide emission regulations regarding Pulp and Paper industry have been renewed by European Commission. New boundaries have to be considered from the view point of equipment supplier. Nitrogen oxide (NO<sub>x</sub>) emissions are caused mainly by recovery boilers, lime kilns and Non-Condensable Gas (NCG) burners at the pulp mill but also power boilers cause NO<sub>x</sub> emissions. Total NO<sub>x</sub> emission load per air dry ton (adt) of pulp produced from major processes is shown in Figure 3. According to Figure 1, lime kiln is usually the second largest source of NO<sub>x</sub> emissions at the pulp mill. (European Commission 2014)



**Figure 3.** Total NO<sub>x</sub> emission load (as NO<sub>x</sub>/adt) from major processes: recovery boiler, lime kiln & NCG burner at several pulp mills (European Commission 2013a, 248)

Figure 3 does not show NO<sub>x</sub> emission from possible power power at the mill. When separate CNCG burner is used NO<sub>x</sub> emission from other sources is typically smaller. This is possible as CNCGs can be burned in lime kiln or recovery boiler increasing NO<sub>x</sub> emissions.

## **1.2 Purpose and structure of the thesis**

Several nitrogen oxide emission abatement technologies already exist and aim of the thesis is to investigate which one would be the most suitable to use in lime kiln. Chosen NO<sub>x</sub> prevention technology should be both technologically and financially suitable and feasible. Post-combustion methods are investigated in more detail as the NO<sub>x</sub> emission regulations are likely to be tightened in the future. Special focus is in technologies which are at commercial stage.

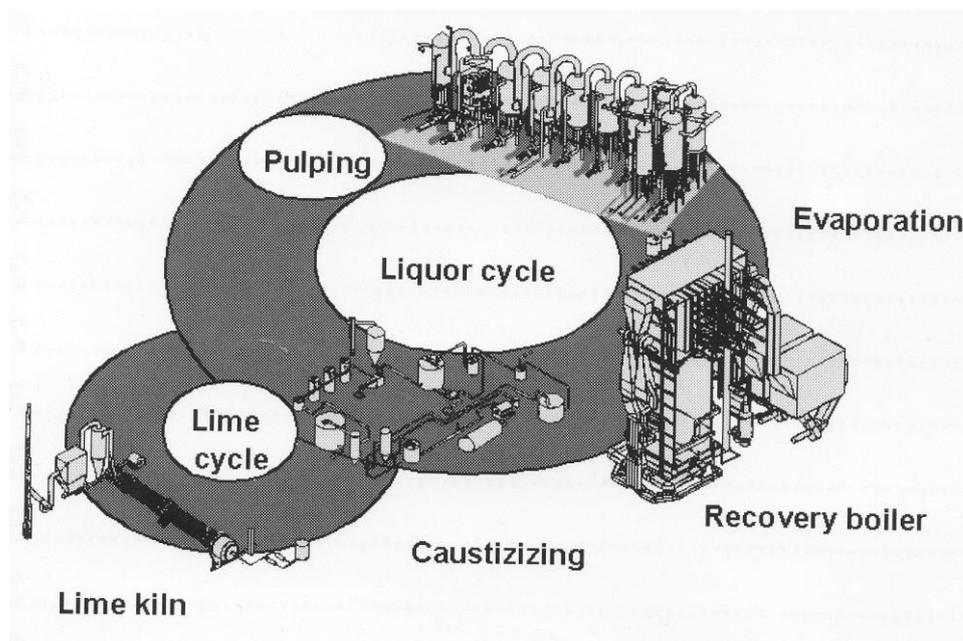
This study consists of 7 chapters. Chapter 2 introduces rotary lime kiln of pulp and paper industry. A review of general nitrogen chemistry in combustion processes. Formation and destruction mechanisms of nitrogen oxide are studied in chapter 3. Chapter 4 expresses NO<sub>x</sub> regulations and data for lime kilns, especially the requirements of European Union. Chapter 5 discusses reducing nitrogen oxides in rotary lime kiln, focus being in removal with combustion methods which are also known as primary methods. Chapter 6 focuses to post combustion i.e. secondary methods in NO<sub>x</sub> removal. Selective Non-Catalytic Reduction, Selective Catalytic Reduction and NO<sub>x</sub> scrubbing are discussed in more detail. Chapter 7 deals with financial analysis of NO<sub>x</sub> reduction, compares different technologies and proposes suitable technologies.

## 2 LIME KILN IN PULP & PAPER INDUSTRY

Lime kiln is part of the chemical pulping process being part of the chemical circuit called lime cycle. In the chemical pulping the chips are cooked together with chemicals. The process is also called the kraft process which is especially advantageous when producing strong and flexible fibres from softwoods. The aim in the pulping process is to remove the lignin that holds the fibres together. Chemical recovery is efficient process thanks to closed loop using only low amount of makeup chemicals. (Arpalahti et al. 2000, 135, 178; Vakkilainen & Kivistö 2010, 31)

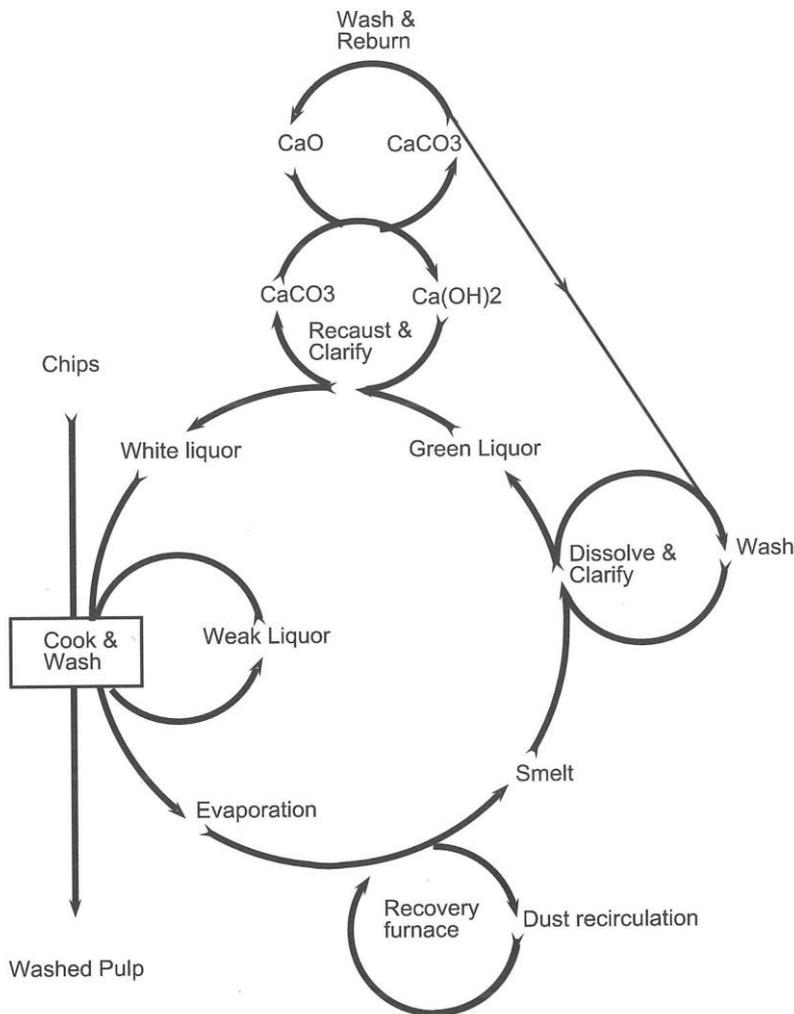
A modern pulp mill is self-sufficient in energy production and it is able to sell significant amount of produced electricity if it is equipped with biomass fired boiler which is connected to the condensing turbine. Also recovery boiler credits significantly to electricity production. At some mills bark and wood waste are used for gasification and direct firing in lime kiln. (Vakkilainen & Kivistö 2010, 106)

Chemical pulp mill consist of a fibre line and a chemical recovery system. Liquor cycle and lime cycle are the main processes of chemical recovery system. Kraft recovery cycles are shown in Figure 4. (Vakkilainen & Kivistö 2010, 31)



**Figure 4.** Kraft recovery process (Vakkilainen 2008, 10)

Another diagram of kraft pulping chemical recirculation loop is presented in Figure 5. Reactions in reburning and recausticizing are introduced in Chapter 2.1.

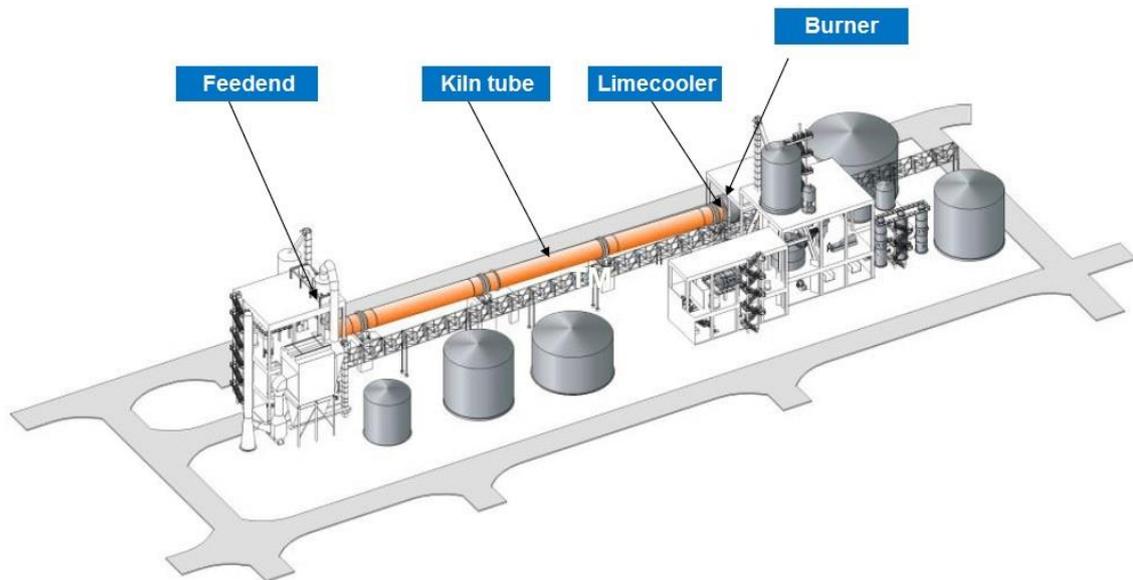


**Figure 5.** Simplified diagram of kraft pulping chemical recirculation loop (Gullichsen & Fogelholm 2000, 40)

Lime kiln is essential part of white liquor plant where the objective of recausticizing process is to produce clean and hot white liquor containing minimum amount of unreactive chemicals for the cooking process. The other function of white liquor plant is lime reburning where clean and white lime mud is burned in lime kiln for reuse as lime. The amount of white liquor needed depends on the effective alkali charge in cooking. This is typically  $3.5\text{-}4.0 \text{ m}^3/\text{adt}$  and the production capacity of a recausticizing plant can be  $8000\text{-}10000 \text{ m}^3$  of white liquor per day. (Arpalahti et al. 2000, 135)

## 2.1 Lime kiln

Lime kiln is a part of chemical pulp mill. Layout of modern rotary lime kiln is presented in Figure 6.

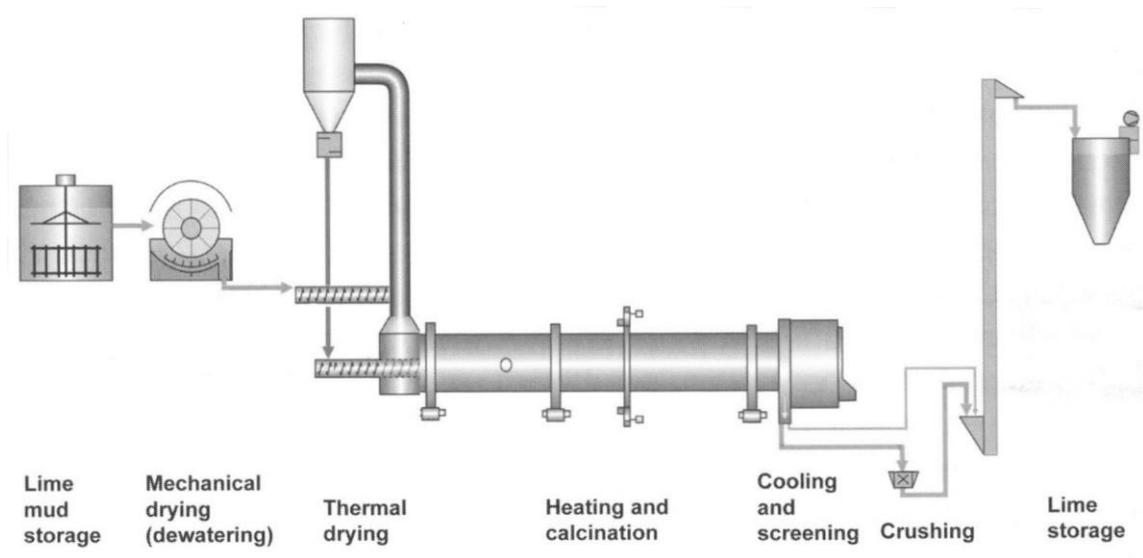


**Figure 6.** Lime kiln layout (after Andritz Oy 2014, 3)

The lime reburning process consists of the following unit operations (Arpalahti et al. 2000, 179):

- Pumping lime mud from lime mud storage
- Mechanical dewatering of lime mud
- Thermal dewatering
- Heating and calcination
- Cooling of product
- Screening and crushing
- Conveying to storage

Unit operations in lime reburning are shown in Figure 7.



**Figure 7.** Unit operations in lime reburning (Engdahl et al. 2008, 162)

Lime kiln is divided into four stages (Engdahl et al. 2008, 176):

- Drying: moisture of the lime mud is evaporated
- Heating: lime mud is heated to the reaction temperature
- Calcination: Calcium carbonate dissociates into calcium oxide and carbon dioxide
- Cooling: lime is cooled before it leaves the kiln

Lime kiln operation is based on counter flow principle.  $\text{CaCO}_3$  is fed to the kiln from the feed end. Lime flows due to gravity and rotation of the kiln towards the burner end which is lower down. Flue gases exit the kiln from the feed end. Calcium carbonate, also known as lime, results from causticizing and is fed to the lime kiln where dissociation of  $\text{CaCO}_3$  to  $\text{CaO}$  and  $\text{CO}_2$  begins when temperature goes above  $820\text{ }^\circ\text{C}$ . The reaction is greatly accelerated by temperature increase. Adequate reaction rate for reburning can be reached at temperature of approximately  $1100\text{ }^\circ\text{C}$ . Calcium carbonate decomposes thermally to calcium oxide and carbon dioxide as shown in Equation 1. (Arpalahti et al. 2000, 141)

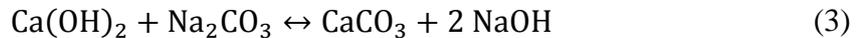


Decomposition temperature of lime mud is a function of  $\text{CO}_2$  partial pressure and also depends on the impurity content of lime mud. According to Tran (2008), the decomposition temperature varies from  $800\text{ }^\circ\text{C}$  to  $820\text{ }^\circ\text{C}$  when  $\text{CO}_2$  concentration varies between 12 % and 25 %.  $\text{CO}_2$  concentration is highest at the feed end flue gas and lowest

at burner end. Temperature begins to increase when calcination of  $\text{CaCO}_3$  in the solids is completed whereas decomposition temperature is nearly constant due to heat absorption. (Tran 2008, 1-2)

Some unreacted lime as  $\text{CaO}$ , water, a small amount of alkali, and impurities enter to the lime kiln in addition to  $\text{CaCO}_3$ , the main component of lime mud. The amount of impurities in lime mud dry solids is typically around 7 % - 10 % and the exact quantity depends on the amount of impurities introduced in to the process with green liquor and makeup lime. (Arpalahti et al. 2000, 141)

Slaking of lime means that calcium oxide reacts with water of green liquor producing calcium hydroxide as shown in Equation 2. Calcium hydroxide reacts further with sodium carbonate of green liquor according to Equation 3. Required green liquor is obtained from recovery boiler. Calcium carbonate and sodium hydroxide are obtained as products. (Arpalahti et al. 2000, 139)



Contributing to lime mud movement rotary kiln slopes slightly toward the firing end. The lime retention time in the kiln depends predominantly on kiln dimensions, rotation speed, and properties of lime mud. The rotation speed is typically between 0.5 to 1.5 rpm and retention time is in the range of 2.5-4 hours. (Arpalahti et al. 2000, 181)

Finally the calcium oxide is cooled in sector cooler. Formerly satellite coolers were used but those were causing greater load for cantilever. Sector coolers are also more practical when the size and capacity of lime kilns have been increased. Both cooling systems are heat exchangers based on direct contact and counter flow principles. (Timonen 1993, 19)

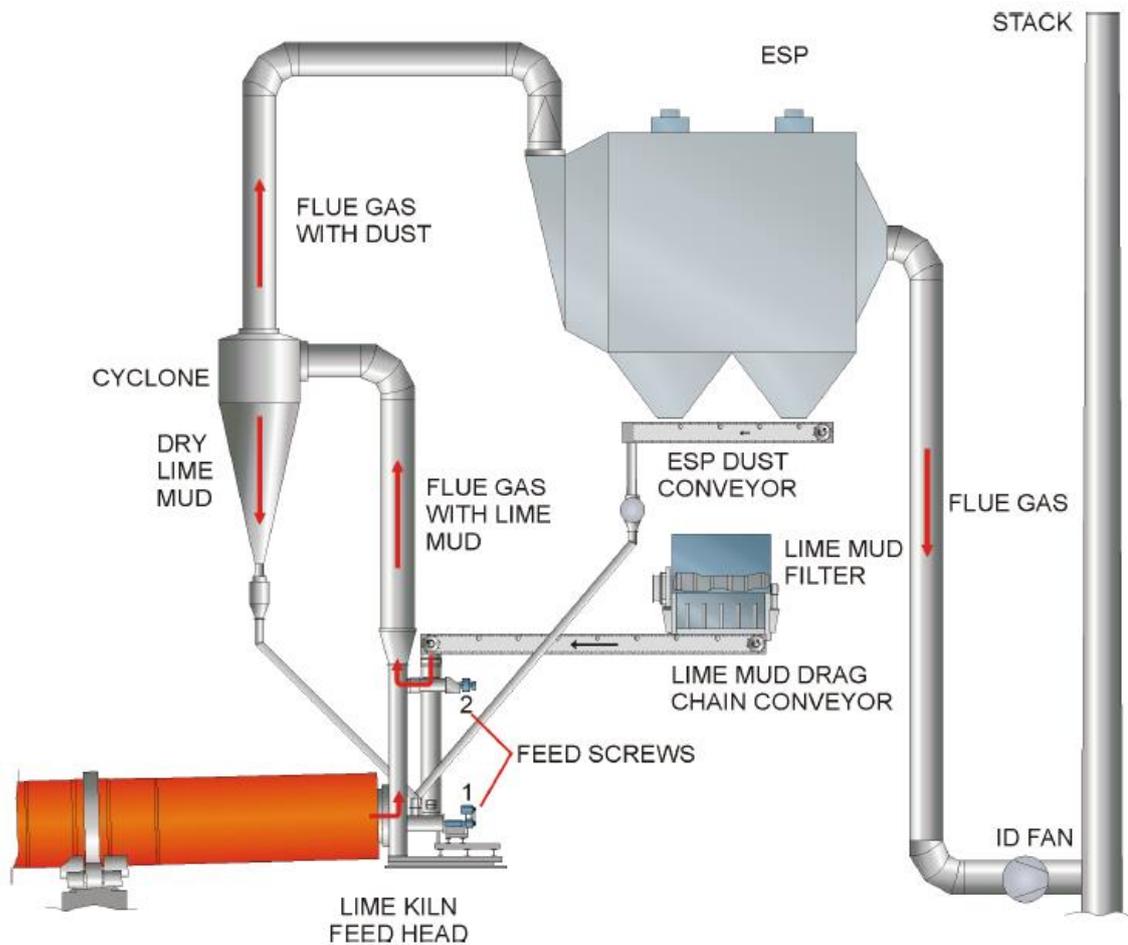
The needed amount of heat for the drying of lime and completing the calcination reaction is produced in the burner head of the kiln. Most of the needed combustion air is secondary air which has a share of approximately 85 %. Drying of the mud is done with the flue gases from the lime kiln. (Vakkilainen & Kivistö 2010, 63; Timonen 1993, 19)

For example, to reach a production capacity of 530 tons reburned lime per day a rotary lime kiln in diameter of 4-4.5 m and 100-140 m in length is needed. Precise dimensions depend on the feed end structure of the kiln. White liquor production of 7000 m<sup>3</sup>/day is typically reached with a kiln of this size. Most of the reburned lime consists of CaO. To be precise, lime reactivity expresses the share of active CaO in the reburned lime which typically ranges from 85 to 95 %. Lime reactivity describes both, the quality of the product and the accumulation of inert materials in the lime cycle. The energy consumption of a modern kiln operating near to nominal capacity is typically in the range of 5.5 to 6.5 GJ per ton of reburned lime. (Arpalahti et al. 2000, 179; Lundqvist 2009, 5; Svedin et al. 2011, 6)

### **2.1.1 Lime kiln equipped with lime mud dryer**

LMD lime kiln is approximately 30 % shorter than conventional lime kiln. Flue gases exit from the feed end releasing heat which is used to dry wet lime in separate Lime Mud Dryer (LMD). Besides, there are typically no chains at the feeding end when compared to a conventional lime kiln. According to the 2010 Lime Kiln Survey, only five of the responded 22 LMD type kilns used chains to assist lime mud drying. Because of the renewed structure flue gas temperature at the feeding end has risen over 700 °C. (Hart et al. 2012, 10; Andritz 2014, 7)

Lime mud drying is done using specific drier. External lime mud dryer of a modern lime kiln is presented in Figure 8. This dryer in question is courtesy of Andritz Oy.



**Figure 8.** Andritz lime mud dryer (Kottila 2009, 5)

In LimeFlash feed system feeded lime mud falls down the chute to the LMD feed screw. Then mud falls off the end of the screw and flows into the LMD riser duct and up to the cyclone due to suction provided by induced draft fan. Dried lime mud returning from the cyclone is conveyed to the kiln. Wet mud also overflows from the LMD feed screw to the lower kiln feed screw and is conveyed directly to the kiln depending on the process temperatures and production rate. Mud is dried in flight and separated from the gases in the cyclone. Usually lime mud is directed to the kiln as dry powder. However, some of the lime dust escapes the cyclone and has to be captured by electrostatic precipitator (ESP). Then mud is directed to the kiln using ESP dust conveyor. After dust removal in the ESP, flue gases flow through the stack to the atmosphere. Induced draft fan (ID fan) is used instead of forced draft fan as it can handle higher temperature gas which may contain erosive particles Advantage of LMD kiln compared to conventional kiln is that all of the

kiln length is available for heating and calcining. (Adams 2008, 4; Hart et al. 2012, 11; Stultz & Kitto 1992, 23-21)

### 2.1.2 Fuels

Natural gas and oil are the most common fuels in lime kiln. Also gasification gas, pet coke, wood powder and tall oil are used as main fuels in lime kilns. Besides, malodorous gases can be burned in lime kiln. When the fossil fuels are being replaced with gasified fuel, lime kiln biomass gasifier can be used. The fuel to be gasified should have moisture content under 15 % in order to avoid excessive flue gas flow that would limit the capacity of lime kiln. (Vakkilainen & Kivistö 2010, 120; Kottila 2014)

The following fuels can be burned as auxiliary fuels (Andritz Oy 2014, 58):

- |                   |                                    |
|-------------------|------------------------------------|
| - liquid methanol | - SOG                              |
| - turpentine      | - petroleum coke from oil refinery |
| - hydrogen        | - gasification gas                 |
| - tall oil        | - wood powder                      |
| - glycerol        | - biogas                           |
| - DNCG            | - gasification gas                 |
| - CNCG            | - LNG (liquid natural gas)         |

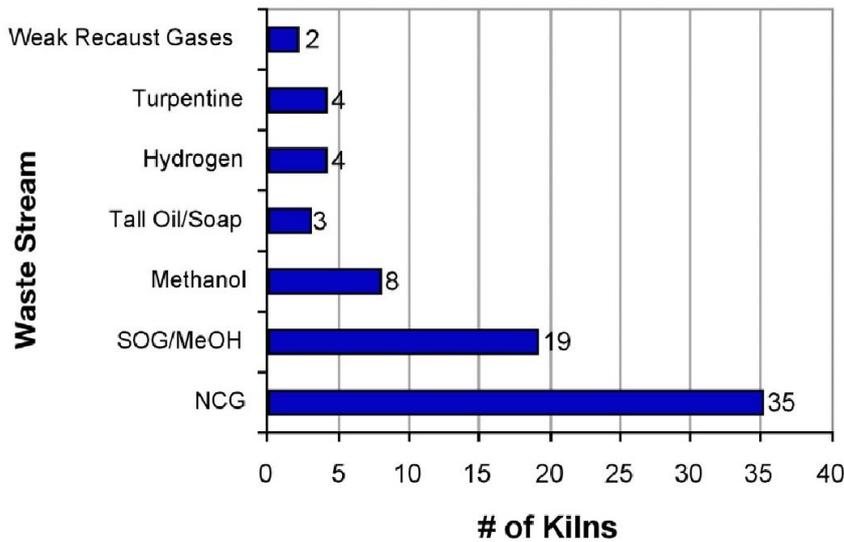
The use of biofuels is increasing for two reasons. Firstly, the increase can be explained by the increase in crude oil price and secondly, because of the tightening environmental policies. Large number of kilns has great fuel flexibility as variety of fuels can be used in the same burner. Therefore, it is possible to use fuels, which are presently available at the mill. The major interest is in biofuels which are available either as a by-product or as an existing raw material at the mill. Tall oil and methanol, both by-products from the kraft process are liquid fuels which are suitable thanks to minor need of process modification. Solid biofuels as bark or lignin require preparation before being fed to the burner. On the other hand, also the use of petroleum coke appears to be increasing as growing number of kilns use it as additional fuel. (Lundqvist 2009, 7; Adams 2008, 7)

Classification of Non-Condensable Gases burned in lime kiln is shown in Table 1.

**Table 1.** Classification of NCG (Higgins et al. 2002, 1)

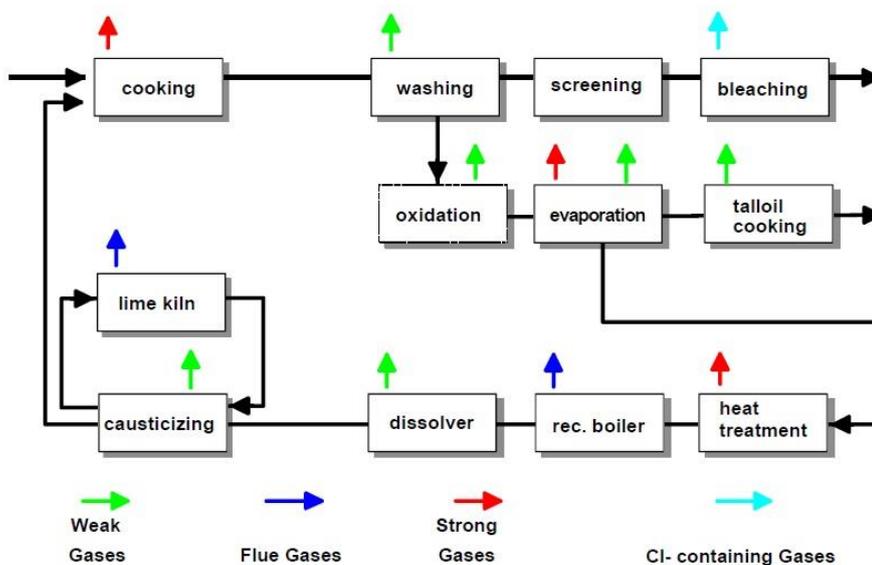
Name	Abbreviation	Definition
Concentrated Non-Condensable Gases	CNCG	Gas containing a concentration of sulfur compounds and/or turpentine, methanol and other hydrocarbons that is above the upper explosion limit (UEL)
Low Volume, High Concentration gases	LVHC	
Dilute Non-Condensable Gases	DNCG	Gas containing a concentration of sulfur compounds that is below the lower explosion limit (LEL)
High Volume, Low Concentration	HVLC	
Stripper Off-Gases	SOG	Methanol, reduced sulfur gases and other volatiles removed by a steam stripping and distillation process from digester and condenser condensates

Waste streams presently burned in lime kilns are presented in Figure 9. The survey was conducted in late 2008. According to Francey et al. (2011), responses were received from 59 pulp mills, and 26 of the kilns were built by Andritz/Ahlström, 17 by F.L. Smidth, 11 by Fuller/Traylor, 5 by Metso Minerals, 2 by Allis Chalmers and rest by others.



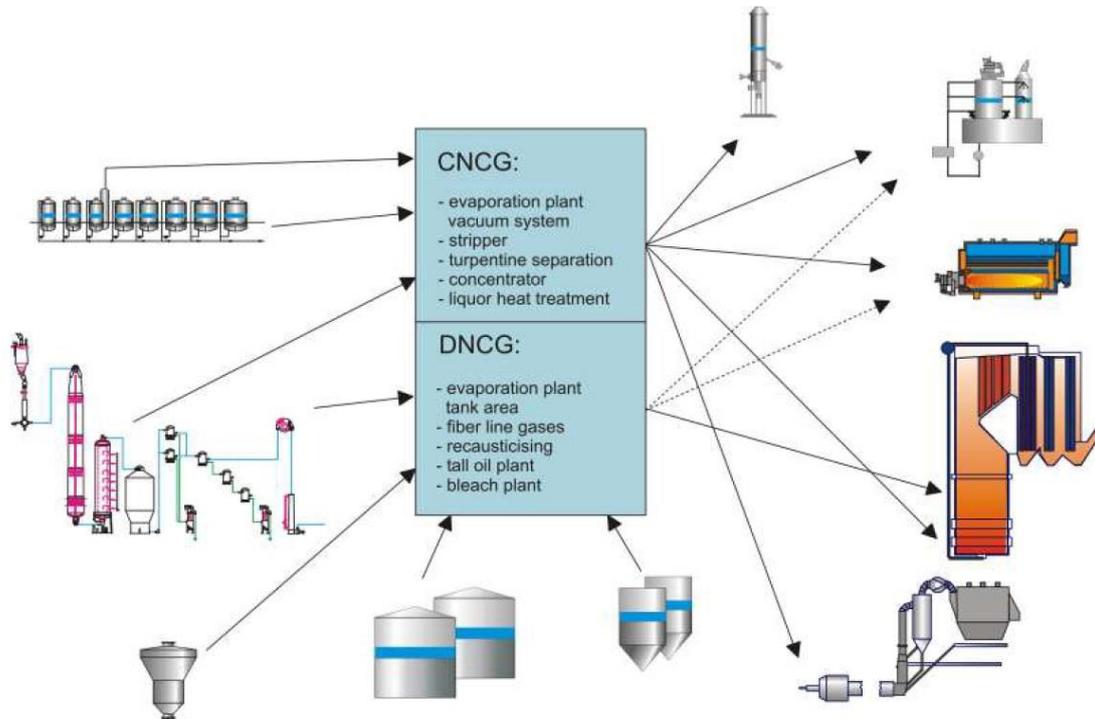
**Figure 9.** Waste streams presently burned in lime kilns (Francey et al. 2011, 22)

Concentrated Non-Condensable Gases (CNCG) include hydrogen sulphide ( $H_2S$ ) and they usually have separate burner in lime kiln or are fired through main burner.  $H_2S$  is very odorous gas and it is formed in the pulping process. As can be seen from the Figure 10, lime kiln can use weak gases originating from causticizing. Weak gases are also called Dilute Non-Condensable Gases (DNCG) which can be fed to the kiln among the combustion air. Also stripper off-gases (SOG) have been burned in lime kilns. (Adams 2008, 8; Kottila 2014)



**Figure 10.** NCG Handling and emission sources of pulp mill (Andritz Oy 2003, 5)

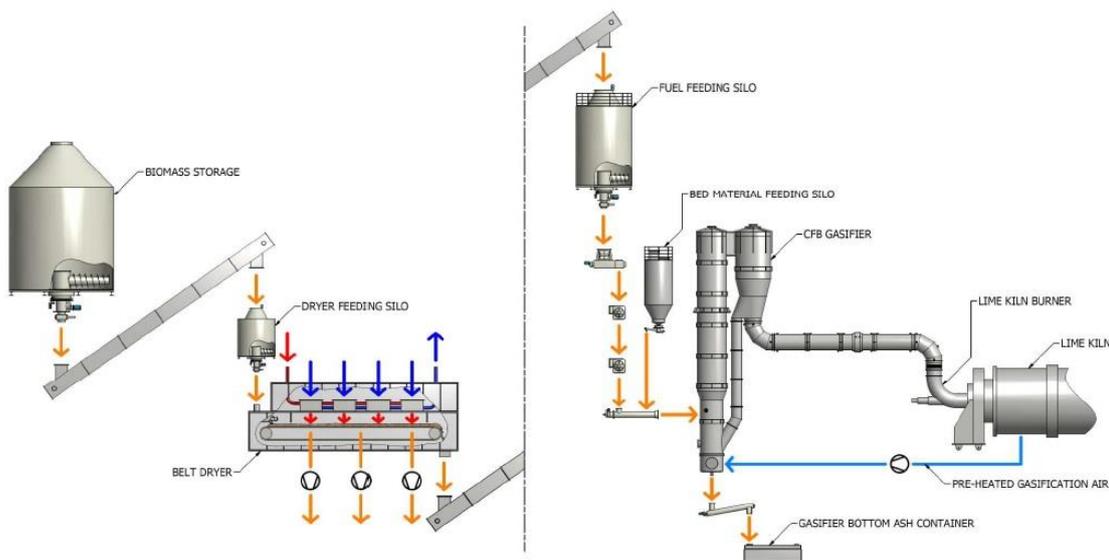
The sources and uses of NCG are shown in Figure 11. On the other hand, also CNCG originating from evaporation plant vacuum system, stripper, turpentine separation, concentrator and liquor heat treatment can be used as a additional fuel. (Andritz 2011, 100)



**Figure 11.** The sources and uses of NCG (Andritz 2011, 100)

Schematic of Andritz's CFB gasifier connected to lime kiln is presented in Figure 12.

According to Rautapää & Pietarinen (2014), gasified biomass can replace all of the natural gas required otherwise.



**Figure 12.** Lime kiln biomass gasifier in Joutseno (Rautapää & Pietarinen 2014, 5)

### 3 NO<sub>x</sub> EMISSIONS IN LIME KILN

Nitrogen oxides are one of the most significant emission components emitted by lime kiln. Other major air emissions from the lime kiln are sulphur dioxide, reduced sulphur compounds (TRS), carbon monoxide (CO) and particulate matter. Additionally requirements for emission of volatile organic compounds (VOC) also exist in some locations. At present NO<sub>x</sub> emissions are mainly dependent on to the kiln burner design and, for a particular burner, to the fuel nitrogen content and combustion temperature. (Dahl 2008, 127; European Commission 2013a, 241)

Nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) are regarded as the most damaging of the hazardous nitrogen compounds formed during combustion. Both, NO and NO<sub>2</sub> are commonly referred to as NO<sub>x</sub>. Usually 95 % or more of NO<sub>x</sub> is in the form of NO, whereas the fraction of NO<sub>2</sub> is less than 5 %. A major part of the nitric oxide is oxidized to nitrogen dioxide in the atmosphere later on. Therefore, the environmental effects of NO and NO<sub>2</sub> emissions are very similar. According to Lövblad et al. (1993), the most significant factors of NO<sub>x</sub> formation in combustion are oxygen availability, combustion temperature, residence time in the combustion zone, fuel nitrogen content and conversion ratio of fuel bound nitrogen. (Kilpinen & Zevenhoven 2004, 4-1)

#### 3.1 Importance of NO<sub>x</sub> reduction

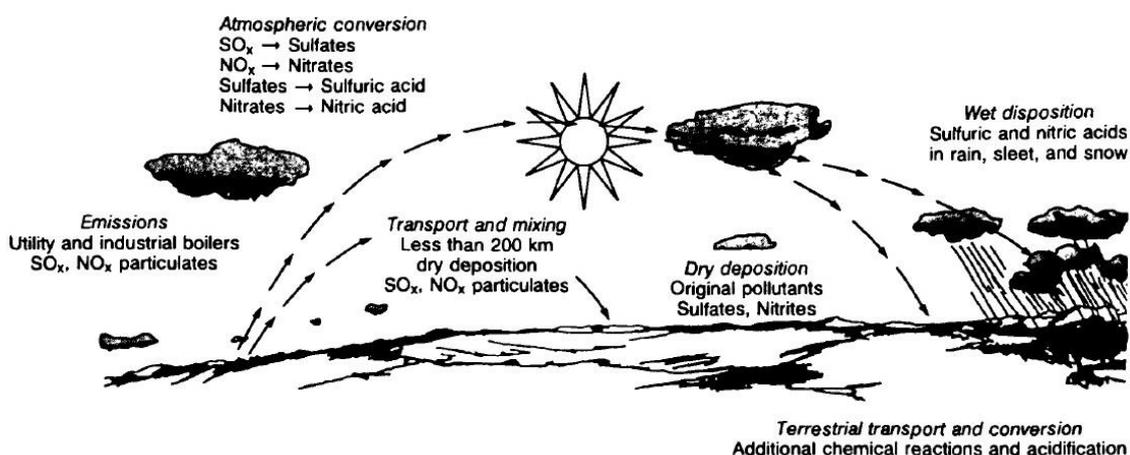
NO<sub>x</sub> as NO or NO<sub>2</sub> is already a significant pollutant but as it reacts further in the atmosphere more harmful compounds will be formed. Most notable pollutants are ozone (O<sub>3</sub>) and acid rain. To be more specific the detrimental ozone is the tropospheric ozone as it is breathed among air. Nitrogen oxide emissions are one of the main reasons for soil acidification, and formation of photochemical oxidants such as ozone, eutrophication and nitrogen saturation. NO<sub>x</sub> forms direct health effects on living organisms and even corrosion damage. Also N<sub>2</sub>O is formed in small extend in combustion. N<sub>2</sub>O has capability to speed up the greenhouse effect by reducing stratospheric ozone. Stratospheric ozone also protects living organisms and troposphere from ionizing radiation emitted by sun. (Ehrhard 1999, 1; Lövblad et al. 1993, 1)

According to De Nevers (2008),  $\text{NO}_2$  and  $\text{O}_3$  are secondary pollutants formed in the atmosphere through complicated reactions, which are summarized in Equation 4.



Furthermore, ultraviolet light (UV) and the presence of air make  $\text{NO}_2$  to react in such a manner that ozone and nitric oxide (NO) is formed. Following this reaction, NO reacts with free radicals in the atmosphere. Also UV acting on volatile organic compounds (VOC) generates radicals. NO is recycled to  $\text{NO}_2$  so that each molecule of NO is able to produce ozone over and over again at certain limit. (Ehrhard 1999, 1)

As described earlier  $\text{NO}_x$  in the atmosphere forms also acid rain. Acid rain has together with cloud and dry deposition strong impact on certain ecosystems and also malign influence on economy. One of the major constituents of acid rain is nitric acid,  $\text{HNO}_3$ , which also forms nitrate particles. Schematic of  $\text{SO}_x$  and  $\text{NO}_x$  transport and conversion is shown in Figure 13. (Ehrhard 1999, 1; De Nevers 2000, 397)



**Figure 13.**  $\text{SO}_x$  and  $\text{NO}_x$  transport and conversion (Frank & Markovic 1994, 8)

A selection of important health effects linked to nitrogen dioxide is summarized in Table 2.

**Table 2.** Related exposure effects of nitrogen dioxide (World Health Organization 2004a, 7)

Short-term exposure effects	Long-term exposure effects
<ul style="list-style-type: none"> <li>- Effects on respiratory function, particularly in asthmatics</li> <li>- Increase in airway allergic inflammatory reactions</li> <li>- Increase in hospital admissions</li> <li>- Increase in mortality</li> </ul>	<ul style="list-style-type: none"> <li>- Decline in lung function</li> <li>- Increased occurrence of respiratory symptoms</li> </ul>

### 3.2 Different type of NO<sub>x</sub> emissions and formation mechanisms

Nitrogen oxides include seven different compounds. Family of nitrogen oxides is introduced in Table 3. (Ehrhard 1999, 1)

**Table 3.** Different nitrogen oxide, NO<sub>x</sub>, compounds (Ehrhard 1999, 2)

Molecular formula	Name	Nitrogen valence	Properties
N <sub>2</sub> O	nitrous oxide	1	colorless gas water soluble
NO	nitric oxide	2	colorless gas slightly water soluble
N <sub>2</sub> O <sub>2</sub>	dinitrogen dioxide		
N <sub>2</sub> O <sub>3</sub>	dinitrogen trioxide	3	black solid water soluble, decomposes in water
NO <sub>2</sub>	nitrogen dioxide	4	red-brown gas very water soluble, decomposes in water
N <sub>2</sub> O <sub>4</sub>	dinitrogen tetroxide		
N <sub>2</sub> O <sub>5</sub>	dinitrogen pentoxide	5	white solid very water soluble, decomposes in water

Nitric acid (HNO<sub>3</sub>) or nitrous acid (HNO<sub>2</sub>) is formed when any of oxides listed in Table 4 dissolve in water and decompose. NO, NO<sub>2</sub> and nitrous oxide (N<sub>2</sub>O) are the most common species of nitrogen oxides in the atmosphere. N<sub>2</sub>O is known for its capability to deplete

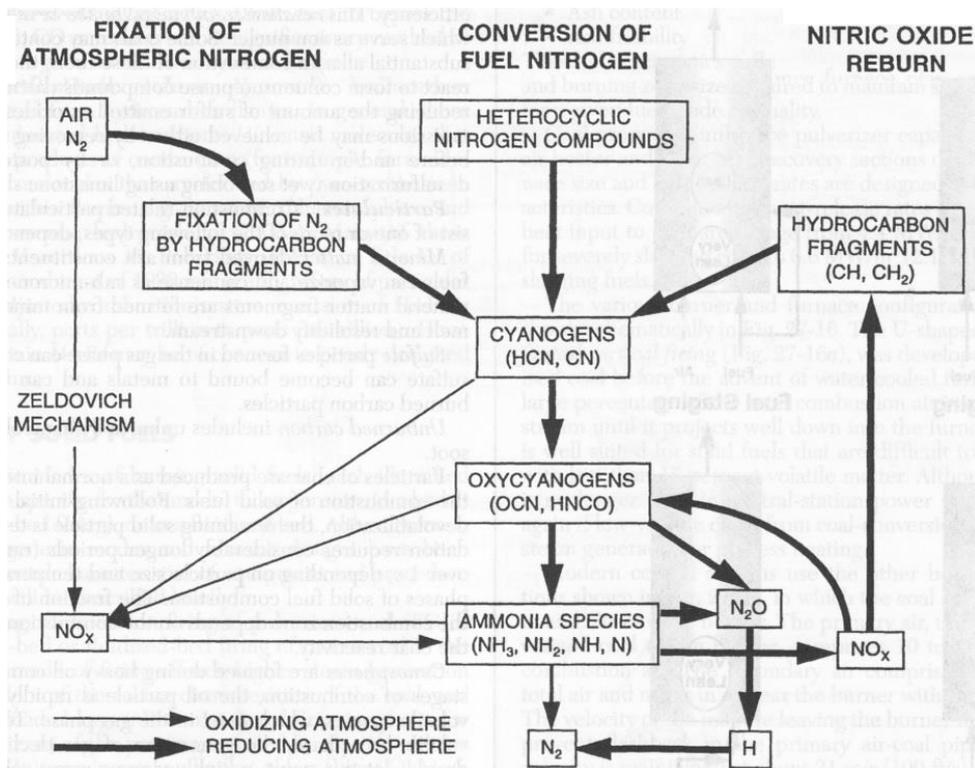
ozone layer. Reactions between  $N_2O$  and  $O_3$  take place in the troposphere and in the stratosphere. Which makes  $N_2O$  problematic is its long half-life, usually varying from 100 to 150 years. Valence state is determined by the number of electrons in the ion compared to the neutral molecule. (Ehrhard 1999, 3)

The formation of  $NO_x$  in coal, gas and oil flames has been extensively studied.  $NO_x$  emissions formed as a result of combustion are for the most part in the form of  $NO$ . One of the key factors in  $NO_x$  formation is temperature of the process. Generation of nitrogen monoxide is non-existent or only slight at temperatures below  $760\text{ }^\circ\text{C}$ . (Ehrhard 1999, 3)

Three principal  $NO_x$  formation mechanisms are recognized:

- thermal  $NO_x$
- prompt  $NO_x$
- fuel  $NO_x$

Nitrogen oxide formation pathways in combustion are presented in Figure 14. As  $NO_x$  formation chemistry is relatively complex all the reactions involved to the  $NO_x$  formation pathways and reactions are not investigated in detail in this study.

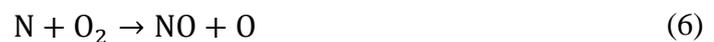


**Figure 14.** Nitrogen oxide formation pathways in combustion (Perry 1997, 27-27)

### 3.2.1 Thermal NO<sub>x</sub>

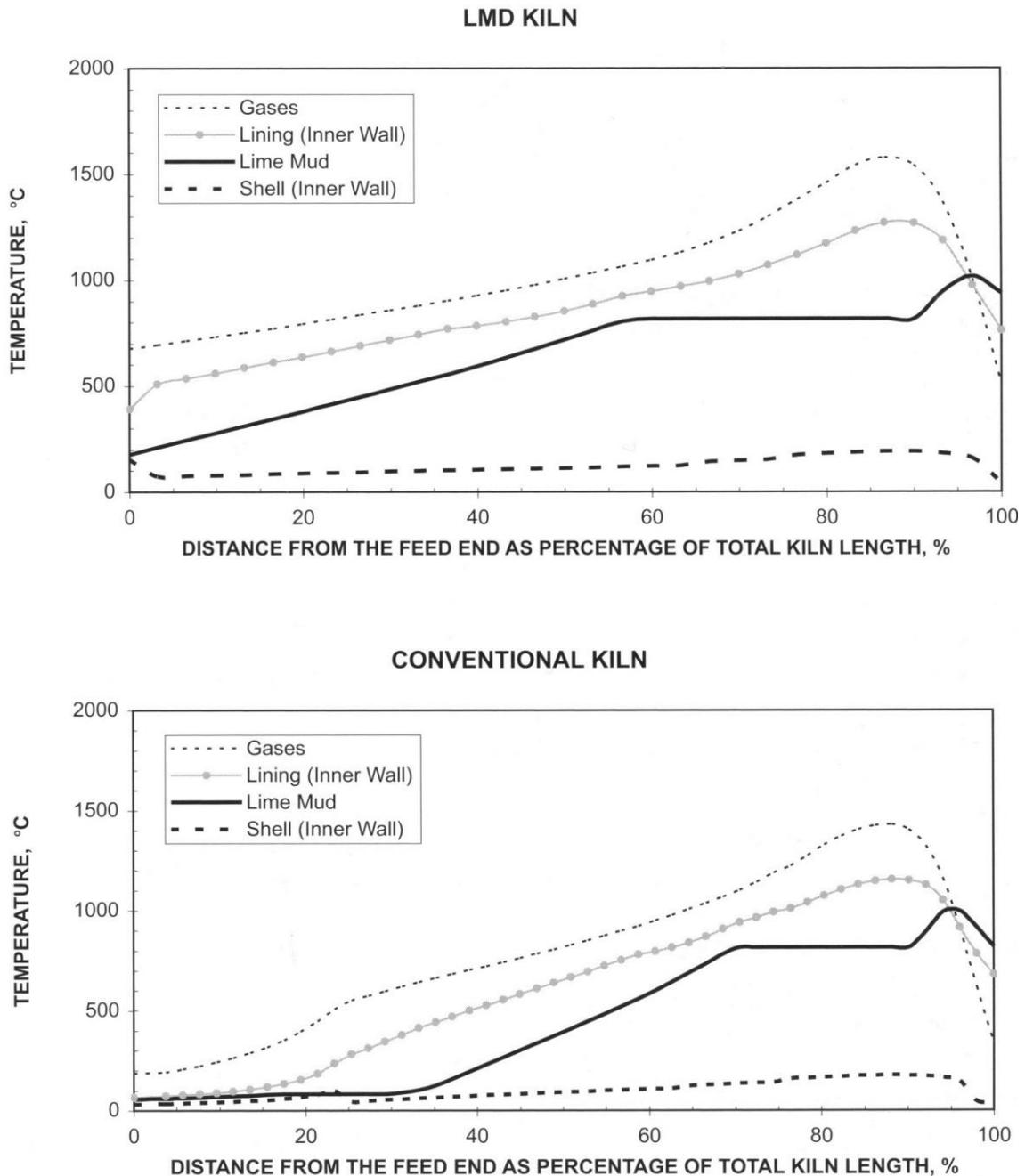
Nitrogen and oxygen molar concentrations and combustion temperature are the main factors relating to thermal NO<sub>x</sub> formation. According to Engdahl et al. (2008), thermal formation of NO begins already at 650 °C, but is not significant until 1300 °C. (Ehrhard 1999, 5)

According to the Zeldovich equations, NO is generated as long as oxygen is available in combustion air at temperatures above 1300 °C. The Zeldovich equations are known as Equations 5, 6 and 7. (Ehrhard 1999, 3)



Reaction by Equation 7 occurs in a fuel-rich environment. (Moreea-Taha 2000, 6)

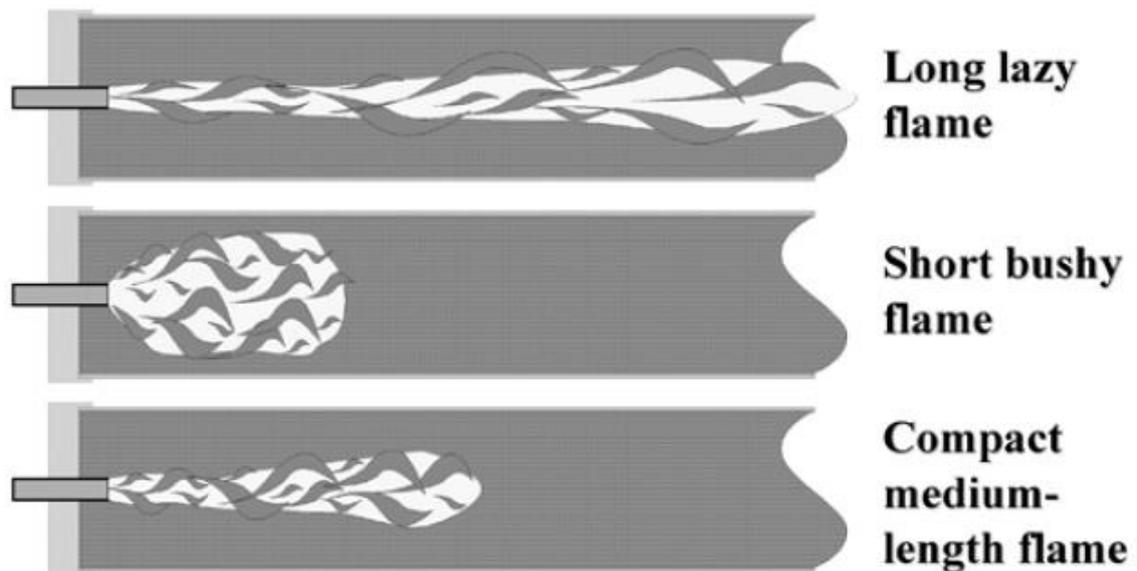
Temperature profiles for LMD kiln and conventional kiln are presented in Figure 15. Regarding formation of NO<sub>x</sub> temperature of gases is of interest. For more accurate analysis also temperature profiles for different fuels should be investigated. For example, combustion of natural gas results in higher peak temperatures of gas compared to heavy fuel oil. (Kottila 2014)



**Figure 15.** Lime kiln temperature profiles (Engdahl et al. 2008, 176)

As can be seen from the Figure 15, peak temperatures for the gas are in the range of 1500-1600 °C. Since the peak temperatures in the process are high, share of thermal NO<sub>x</sub> is significant. Tests performed in three lime kilns at Swedish pulp mills in 1990s suggest that thermal NO<sub>x</sub> is the principal NO formation route in lime kilns. However, the formation of thermal NO<sub>x</sub> occurs in the narrow sector which responds flue gas residence time of 1-2 seconds. (Engdahl et al. 2008, 163, 179; Lövblad et al. 1993, 6)

Flame shape of burner is linked to thermal and prompt NO<sub>x</sub> formation. Rotary kiln flame shapes are presented in Figure 16.



**Figure 16.** Rotary kiln flame shapes (Adams 2008, 2)

Flame length affects to the maximum temperature of flue gas, and thereby also on the formation of thermal NO<sub>x</sub>. Short flames are too hot and they also cause refractory damage and overburning of the lime. Respectively, long flames result in loss in production capacity and efficiency, and they also complicate product quality control. A compact, medium-length flame has roughly length of three kiln diameters providing a tradeoff between efficiency and refractory service life. According to Svedin et al. (2011), lignin gives a different flame shape and a 2-3 m longer flame length compared to fuel oil. On the other hand, lignin has similar temperature profile as fuel oil in case it has been dried to the same low moisture content as the bark powder. (Adams 2008, 2; Wadsborn et al. 2007, vi)

### 3.2.2 Fuel NO<sub>x</sub>

Fuel NO<sub>x</sub> results from oxidation of nitrogen in the fuel. Formation temperature of fuel NO<sub>x</sub> is considerably lower than the formation temperature of thermal NO<sub>x</sub>. Temperature of 1000 °C is sufficient for fuel NO<sub>x</sub> formation. This is explained by the fact that the oxidation of the already-ionized nitrogen contained in the fuel is more effective. (Ehrhard 1999, 5; Lundqvist 2009, 9; Qvintus-Leino 1988, 9)

If fuel contains organic bound nitrogen, as for e.g. heavy fuel oil, are fuel NO emissions typically significantly greater, but total NO<sub>x</sub> emissions are lower due to lower combustion temperature. Certain fuels contain about 0.1-5 % of organic bound nitrogen which typically is in forms of aromatic rings like pyridine or pyrrole. In the conventional fuel burning great share of fuel bound nitrogen, 20-80 %, is oxidized to nitrogen oxide. Respectively only 0.1 % of nitrogen in the air is oxidized to NO. Also conversion ratio of fuel bound nitrogen over NO and N<sub>2</sub> has effect to NO<sub>x</sub> emission. (IFRF 2014; Lövblad et al. 1993, 3; Qvintus-Leino 1988, 9)

### 3.2.3 Prompt NO<sub>x</sub>

Prompt NO<sub>x</sub> is formed when molecular nitrogen in the air combines with fuel in fuel-rich environment. Favourable conditions for prompt NO<sub>x</sub> formation are present almost in all combustion. Molecular nitrogen oxidizes in fuel-rich condition as the nitrogen in the fuel, and forms NO<sub>x</sub> in the course of combustion. (Ehrhard 1999, 5)

Occurrence of radicals in flame zone is followed by formation of different cyanide compounds. According to Fenimore, prompt NO<sub>x</sub> forms through cyanide compounds. Formation of radicals is described by Equations 8, 9 and 10. Reaction between cyanide and molar nitrogen occurs only at high temperature, between 1600 °C to 1800 °C, in the flame zone. (Timonen 1993, 28; Qvintus-Leino 1988, 8-9)



Cyanide compounds react then in the presence of oxygen through multiple transitional phases to NO. Prompt NO<sub>x</sub> portion of the total amount of NO<sub>x</sub> is relatively small. For example, when burning oil and coal, it is estimated to be 10 %. (Timonen 1993, 28; Qvintus-Leino 1988, 9)

## 4 NO<sub>x</sub> EMISSION REGULATIONS AND DATA

Emission regulations refer to NO<sub>x</sub> calculated as NO<sub>2</sub>, because NO is oxidized to NO<sub>2</sub> in the ambient atmosphere in short period of time. This time is approximately one day. Also according to Ehrhard (1999) some specialists state that NO<sub>2</sub> is a valid surrogate for NO<sub>x</sub> since NO reacts relatively rapidly to NO<sub>2</sub>, and N<sub>2</sub>O has a long lifespan but appears in minor concentrations. Therefore, the share of NO and N<sub>2</sub>O could be neglected. (Kilpinen & Zevenhoven 2004, 2-10)

Typical nitrogen oxide emissions to air from a lime kiln are presented in Table 4.

**Table 4.** Typical nitrogen oxide emissions to air from a lime kiln (Dahl 2008, 126)

Nitrogen oxides (as NO <sub>2</sub> )		
- oil firing	240-380	mg/m <sup>3</sup> n
	130-200	mg/MJ
	0.2-0.3	kg/Adt
- gas firing	380-600	mg/m <sup>3</sup> n
	200-320	mg/MJ
	0.3-0.4	kg/Adt

Higher NO<sub>x</sub> emissions occurring from gas-fired kiln can be explained by the higher combustion temperatures of gas firing. According to De Nevers (2000) NO<sub>x</sub> emissions are commonly reported and regulated also in the following units: ppm, lb/10<sup>6</sup> Btu, g/GJ or µg/kcal.

NO<sub>x</sub> emissions can also be announced as kg per produced ton of CaO. In 2005 NO<sub>x</sub> emission from gas-fired lime kilns were reported to be 0.77 kg/t<sub>CaO</sub> (1.69 lb/t<sub>CaO</sub>) and from oil-fired kilns 0.54 kg/t<sub>CaO</sub> (1.18 lb/t<sub>CaO</sub>) in the US. In 2005 the total NO<sub>x</sub> emission from kraft lime kilns was 9000 tons of NO<sub>x</sub> in the US. In comparison NO<sub>x</sub> emissions from three lime kilns at Swedish pulp mills in 1990s were in the range of 1-3 kg/t<sub>CaO</sub> according to the measurements performed. The reason for higher values can be explained by the fact that all

those three Swedish kilns fired malodorous gases during normal operation. (Lövblad et al. 1993, 1; Pinkerton 2007, 3-4)

#### 4.1 Regulations set by European Union

Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control) establishes demand for controlling NO<sub>x</sub> emissions. The European IPPC Bureau has been founded to organize the matter and it produces Best Available Techniques. BAT Conclusion 2014/687/EU is legally binding document and it is made based to the BAT Reference document. (European Commission 2014, 1)

The emissions levels are presented in Table 5 according to BAT Conclusion document for the Production of Pulp, Paper and Board.

**Table 5.** BAT-associated emission levels for NO<sub>x</sub> emissions from a lime kiln (European Commission 2014, 26)

Parameter		Long-term average mg/Nm <sup>3</sup> at 6 % O <sub>2</sub>	Yearly average kg NO <sub>x</sub> /ADt
NO <sub>x</sub>	Liquid fuels	100-200 <sup>(1)</sup>	0.1-0.2 <sup>(1)</sup>
	Gaseous fuels	100-350 <sup>(2)</sup>	0.1-0.3 <sup>(2)</sup>

<sup>(1)</sup> When using liquid fuels originating from vegetable matter (e.g. turpentine, methanol, tall-oil), including those obtained as by-products of the pulping process, emission levels up to 350 mg/Nm<sup>3</sup> (corresponding to 0,35 kg NO<sub>x</sub>/ADt) may occur.

<sup>(2)</sup> When using gaseous fuels originating from vegetable matter (e.g. non-condensable gases), including those obtained as by-products of the pulping process, emission levels up to 450 mg/Nm<sup>3</sup> (corresponding to 0,45 kg NO<sub>x</sub>/ADt) may occur.

According to European Commission (2014), NO<sub>x</sub> emission limits are given as both source specific (mg/Nm<sup>3</sup>) and mill specific (kg NO<sub>x</sub>/ADt) for new pulp mills. Mill emission limits are expected to be set according to the renewed BAT regulations.

There is also specific emission levels determined for the lime kiln in cement industry and those emissions levels differ considerably from the ones of lime kiln in pulp and paper industry. This could be explained so that there is more thermal NO<sub>x</sub> in cement kiln due to higher required process temperature. (European Commission 2013b)

According to European Commission (2014), Best Available Technologies for NO<sub>x</sub> removal in lime kiln are (1) Optimised combustion and combustion control, (2) Good mixing of fuel and air, (3) Low-NO<sub>x</sub> burner and (4) Fuel selection/low-N fuel. Best Available Techniques are listed and described in Table 6 as announced by European Commission. These techniques are further discussed in Chapter 5.

**Table 6.** Best Available Technologies to reduce NO<sub>x</sub>-emissions in lime kiln (European Commission 2014, 100,119)

Technique	Description
Optimised combustion and combustion control	Based on permanent monitoring of appropriate combustion parameters (e.g. O <sub>2</sub> , CO content, fuel/air ratio, unburnt components), this technique uses control technology for achieving the best combustion conditions. NO <sub>x</sub> formation and emissions can be decreased by adjusting the running parameters, the air distribution, excess oxygen, flame shaping and temperature profile
Good mixing of fuel and air	
Low-NO <sub>x</sub> burner	Low-NO <sub>x</sub> burners are based on the principles of reducing peak flame temperatures, delaying but completing the combustion and increasing the heat transfer (increased emissivity of the flame). It may be associated with a modified design of the furnace combustion chamber
Fuel selection/Low-N fuel	The use of fuels with low nitrogen content is applied to reduce the amount of NO <sub>x</sub> emissions from the oxidation of nitrogen contained in the fuel during combustion. The combustion of CNCG increases NO <sub>x</sub> emission, as CNCG contain more nitrogen than oil and natural gas. Firing biomass or biomass based fuels will also slightly increase NO <sub>x</sub> emissions, as all wood derived fuels contain more nitrogen than oil and natural gas. Due to higher combustion temperatures, gas firing leads to higher NO <sub>x</sub> levels than oil firing

According to European Commission (2014), BAT in lime kiln is to use combination of technologies listed in Table 6. Description for “Good mixing of fuel and air” was not given in the BAT conclusion document, therefore it is blank. However, it should be noted that SNCR and SCR technologies or NO<sub>x</sub> scrubbing are not among the Best Available Technologies defined by European Union. Nevertheless, BAT document designates the emission limits but the selection of technology for how the emission target is to be reached should be optional. (Vakkilainen 2014a)

## **4.2 Regulations set by U.S. Environmental Protection Agency**

U.S. Environmental Protection Agency has established National Ambient Air Quality Standards (NAAQS) for NO<sub>2</sub> and tropospheric ozone. According to standard, the primary and secondary limit for NO<sub>2</sub> is 0.053 parts per million (ppm). However, this describes concentration in the ambient air, not in the exhaust flue gas. Limit is given for annual arithmetic mean concentration. (Ehrhard 1999, 1)

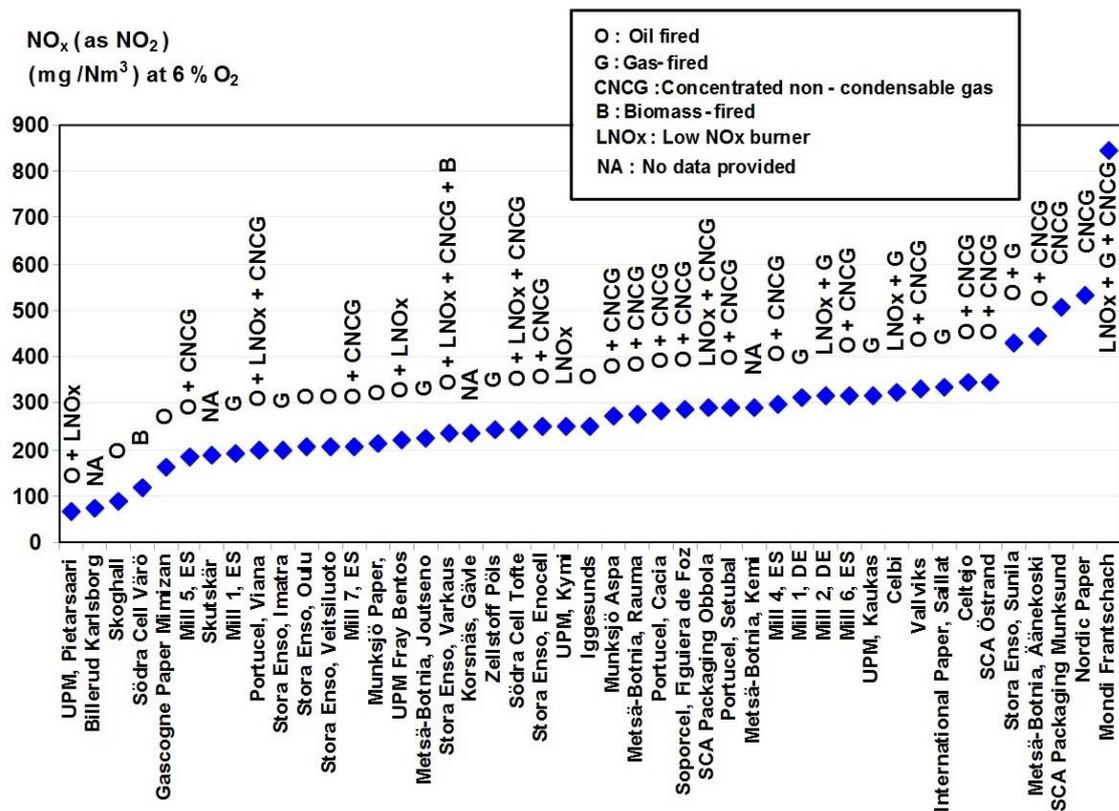
Limits for lime kiln are given regionally. For example, San Joaquin Valley Air Pollution Control District located in California has verified the following nitrogen oxide emission limits for a specific lime kiln:

- 43 mg/MJ (0.10 pound per million Btu) when burning gaseous fuel
- 51 mg/MJ (0.12 pound per million Btu) when burning distillate fuel oil
- 85 mg/MJ (0.20 pound per million Btu) when burning residual fuel oil

In the above limits NO<sub>x</sub> is given as NO<sub>2</sub>. When comparing these emission limits to common emission levels given in Table 4, it can be noticed that they are very strict. However, this represents only an individual case. (San Joaquin Valley Air Pollution Control District 2003)

### 4.3 NO<sub>x</sub> emission data according to the BAT survey

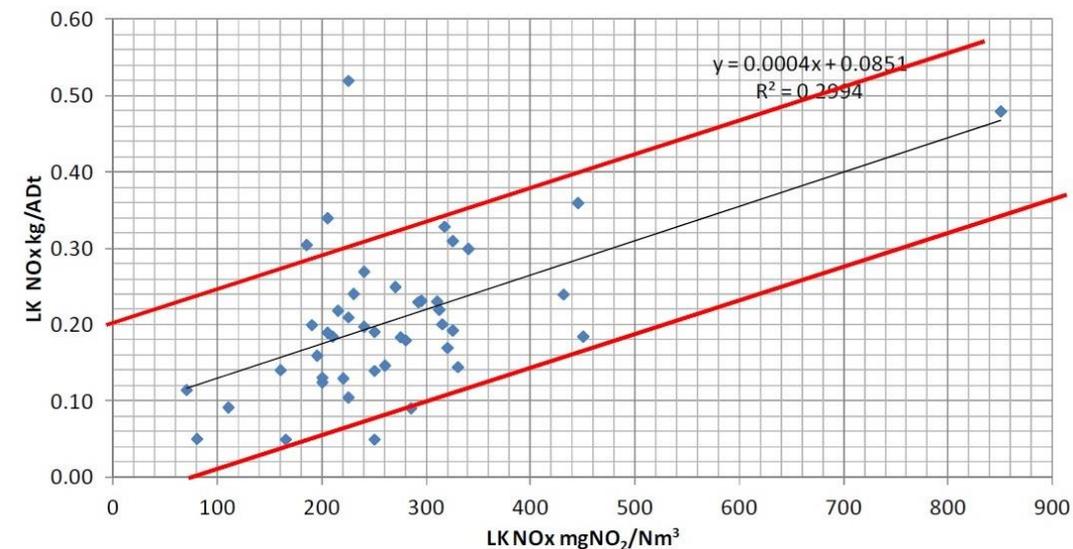
Data from survey conducted by European Union is shown in Figure 17. The used fuel is also shown in Figure. For example, O+LNO<sub>x</sub>+CNCG means that kiln is oil-fired, it has a Low NO<sub>x</sub>-burner and Concentrated Non-Condensable Gases are burned.



**Figure 17.** NO<sub>x</sub> emission concentrations from lime kilns for various fuels (European Commission 2013, 336)

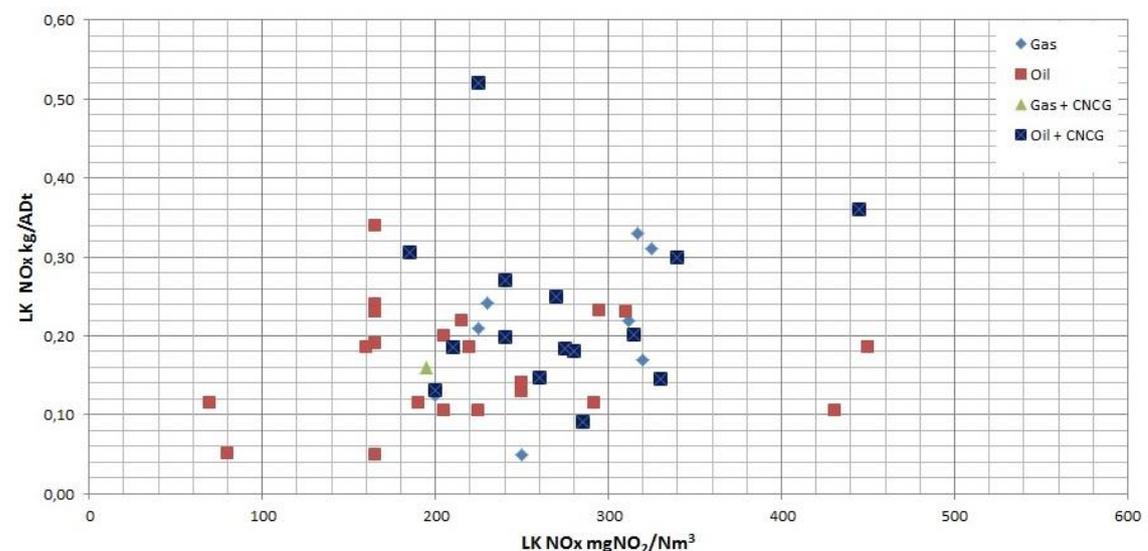
In the survey it was also requested if the mill used ESP, scrubber or both for flue gas cleaning. It should be noticed that the emission data between mills is not comparable unless it is reduced to the similar flue gas moisture and oxygen concentration. Because the moisture of the flue gases affects to the emission measurement value, measurements are tend to be reported always in dry flue gases. (Finnish Recovery Boiler Committee 2007, 4)

The operator can affect emission as  $\text{mg NO}_2/\text{Nm}^3$  but not as  $\text{kg NO}_2/\text{ADt}$ .  $\text{NO}_x$  emission in unit  $\text{kg NO}_2/\text{ADt}$  is the flue gas flow multiplied by concentration. Flue gas flow depends on wood species, yield and sulfidity.  $\text{NO}_x$   $\text{kg}/\text{ADt}$  emission as a function of  $\text{NO}_x$  emission measured in  $\text{mg NO}_2/\text{Nm}^3$  is shown in Figure 18. (Vakkilainen 2012, 39)



**Figure 18.**  $\text{NO}_x$   $\text{kg}/\text{ADt}$  emission as a function of  $\text{NO}_x$  emission measured in  $\text{mg NO}_2/\text{Nm}^3$  at dry flue gas in 6 % oxygen (Vakkilainen 2012, 39)

$\text{NO}_x$   $\text{kg}/\text{ADt}$  emission as a function of  $\text{NO}_x$  emission measured in  $\text{mg NO}_2/\text{Nm}^3$  shown by different fuel types is presented in Figure 19.



**Figure 19.**  $\text{NO}_x$   $\text{kg}/\text{ADt}$  emission as a function of  $\text{NO}_x$  emission measured in  $\text{mg NO}_2/\text{Nm}^3$  at dry flue gas in 6 % oxygen (after Vakkilainen 2012, 39)

#### **4.4 Incentives and sanctions relating to NOx emissions**

In the cement industry some incentives exist for NOx reduction. For example in Taiwan the NOx emission fee is reduced 50 % when a NOx removal method is applied and kiln is operated with emissions at least 25 % lower than the requested emission level. The fee is further reduced to 12.5 % when the kiln reaches a 70 % NOx reduction compared to the standard requirement. (Lin & Knenlein 2000, 2)

For example, NOx emission fee of 4.3 € (40 SEK) per kg NOx was introduced for the power boilers in Sweden. However, these regulations did not concern process combustion units, such as lime kilns and recovery boilers in the pulp industry. The share of NOx emission caused by the pulp and paper industry was estimated to be approximately 3 % of the total national emission in Sweden. (Lövblad et al. 1993, 2)

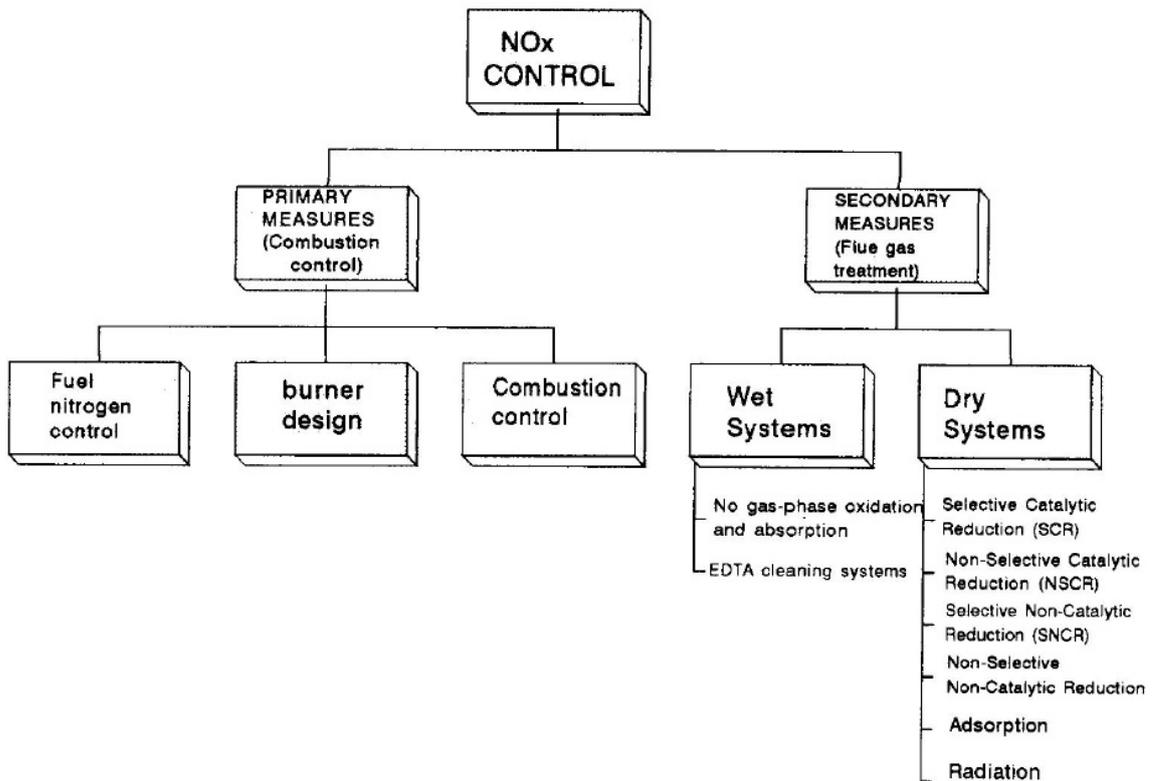
This kind of incentives and sanctions would encourage suppliers and plant owners to develop and invest in NOx removal equipment. For example China has started to fight against air pollutants and very strict aims to reduce NOx exist.

## 5 NO<sub>x</sub> REMOVAL BY COMBUSTION CONTROL

Extensive range of NO<sub>x</sub> abatement and control technologies exist. NO<sub>x</sub> reduction methods can also be divided in primary methods and secondary methods. Primary methods are related to combustion technology and secondary methods are related to flue gas handling usually at lower temperature but exception to the rule is for example SNCR. In general flue gas handling is more expensive than NO<sub>x</sub> reduction at the combustion zone but the process will not allow applying of primary methods beyond certain limit. Applying secondary method provides usually more efficient reduction of NO<sub>x</sub> than single primary method. On the other hand when using a combination of primary methods, achievable NO<sub>x</sub> reduction can be of high magnitude. For example, according to Engdahl et al. (2008), NO<sub>x</sub> emissions in lime kiln can be reduced by 50 % using primary methods. (Ehrhard 1999, 8)

When comparing NO<sub>x</sub> destruction or removal efficiencies, it is important to know real or reduced concentrations for NO<sub>x</sub> in the flue gas. Often new lime kilns incorporate NO<sub>x</sub> prevention methods into their design and generate less NO<sub>x</sub> than otherways similar but older systems. Therefore, when comparing NO<sub>x</sub> removal efficiencies given as relative values, the results are not often comparable. (Timonen 1993, 30; Ehrhard 1999, 8)

Also combination of different NO<sub>x</sub> removal methods can be applied when pursuing greater NO<sub>x</sub> removal. By combining different methods better NO<sub>x</sub> reduction can be achieved. NO<sub>x</sub> reduction techniques for stationary applications according to Forzatti & Lietti (1996) are presented in Figure 20. (Ehrhard 1999, 11)



**Figure 20.** NO<sub>x</sub> reduction techniques for stationary applications (Forzatti & Lietti 1996, 2)

Secondary measures for NO<sub>x</sub> control will be discussed in Chapter 6 and detailed list of external combustion NO<sub>x</sub> limiting technologies according to Ehrhard (1999) is presented in Appendix I. Values are given as relative removal which means NO<sub>x</sub> generation with reduction compared to NO<sub>x</sub> generation without any abatement technologies. (Ehrhard 1999, 8)

## 5.1 Reducing Temperature

According to Ehrhard (1999) combustion temperature may be reduced by:

1. Using mixtures rich in fuel to limit the amount of oxygen available
2. using fuel lean mixtures to limit temperature by reducing energy input
3. injecting cooled low oxygen content flue gas into the combustion air
4. injecting cooled flue gas with added fuel
5. injecting water or steam

As discussed in Chapter 3, flame temperature has significant impact on formation of thermal NO<sub>x</sub>. Reducing peak values of temperature in the kiln is effective method to reduce NO formation. One of the key parameters is the local oxygen concentration in the flame field. During low oxygen concentration, NO is formed through OH-radical which reacts to NO significantly slower than free oxygen. Hereby, the oxidation rate of fuel nitrogen to NO is low when the oxygen content is low and reduction rate of formed NO to molecular nitrogen is increased at the same time. (Timonen 1993, 31; De Nevers 2000, 464)

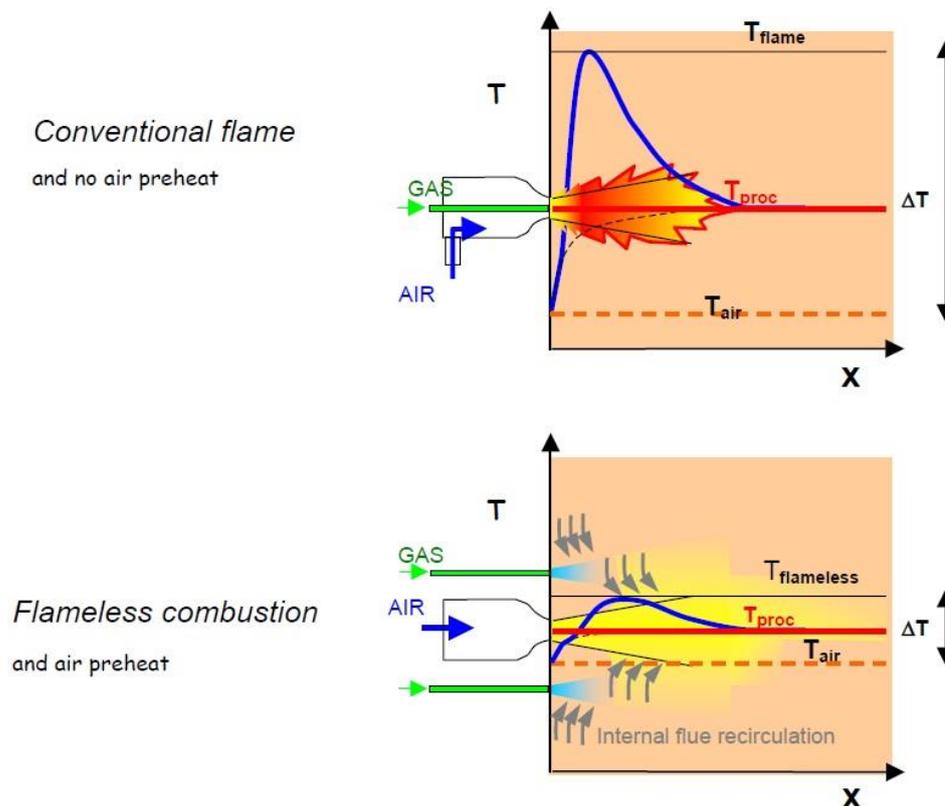
As the calcination reactions in lime kiln require high temperature and certain residence time at high temperature, the kiln sizing should be changed if temperatures were to be reduced significantly.

#### **5.1.1 Staging of combustion air**

Controlling of NO<sub>x</sub> emissions can be treated by adjusting primary air distribution and splitting burning air to primary, secondary and tertiary air. These actions regulate lime kiln temperature distribution. Also internal staging of air can be done in Low-NO<sub>x</sub> burner which is discussed Chapter 5.3. (European Commission 2013, 242)

#### **5.1.2 Flameless combustion**

Flameless combustion could be applied to reducing peak temperatures. The technology is called high temperature air combustion (HiTAC). Despite the name of technology, in HiTAC the temperature profile is smoother as the combustion occurs gradually and internal flue gas recirculation is utilized. The idea of flameless combustion is introduced in Figure 21. Burner applying flameless combustion can be considered as Low-NO<sub>x</sub> burner which is further discussed Chapter 5.3. (Roiha 2012, 12)



**Figure 21.** High velocity gas burner: flame and flameless firing (Milani & Wüning 2012, 4)

Provided that air preheating is used in flameless combustion, temperature of the air is higher but the flame peak temperatures are significantly lower compared to conventional combustion without air preheating. Therefore, formation of thermal  $\text{NO}_x$  could be significantly avoided by using HiTAC.

### 5.1.3 Steam/water injection

In the Finnsementti Oy's cement factory in Lappeenranta, water injection was used to reduce the combustion temperature. The system was installed in the summer 1999. In the kiln number 4 the initial  $\text{NO}_x$  emission level was  $2759 \text{ mg NO}_x / \text{m}^3 \text{ n}$ . As a result of water spraying energy consumption of the kiln was risen  $90 \text{ kJ/kg}$  produced clinker as the spraying water was heated and steamed. It should be also noticed that the sprayed water was sewage water having water content of 90%. The mixture contained also for instance propanol and glycol. The reduction level achieved is not mentioned in the publication. (Koskinen 2000, 54, 119)

Steam or water injection has also been used in power boilers where achieved NO<sub>x</sub> reduction has been between 60 % and 80 %. However, when the aim is to reach simultaneously low CO emissions, achievable reduction rates are in the range of 40 % to 60 %. (European Commission 2013, 94)

Reducing peak temperatures using water spray increases heat consumption of the kiln. Therefore, reduction with water spray is not economical in the long run when considering the increased fuel cost. Also increased CO emissions might occur due to incomplete burning caused by water spraying. According to European Commission (2013b), steam/water injection is BAT for cement kilns, but it is not considered as BAT technology for lime kilns.

#### 5.1.4 Flue gas recirculation

Flue gas recirculation (FGR) reduces NO<sub>x</sub> emission by evening out temperature fluctuations, reducing peak temperatures and lowering oxygen content of the combustion gas. Cooled flue gas should be redirected to burner end of the kiln. As the calcination reactions require high temperature and certain residence time in lime kiln, the kiln sizing should be changed if temperatures were to be reduced significantly. Also the stack is often in the opposite end compared to burner. Flue gas recirculation would be more economical to put into practice at the mill where flue gases already flow next to the burner end. Both fuel and thermal NO<sub>x</sub> could be reduced using FGR. (Cottrell 2003, 8-9)

Applying flue gas recirculation to lime kiln is hindered by the following issues:

- proper lime formation would be prevented due to excessive peak flame temperature reduction
- lime quality would weaken due to presence of a long and lazy flame
- often a lot additional ducting would be required from the stack to the burner end
- there has never been a FGR application in lime kiln (Cottrell 2003, 8-9)

According to Cottrell (2003), FGR is considered a technically infeasible control technology for lime kilns because of the above-mentioned factors.

## 5.2 Reducing Residence Time

Reducing residence time can be done by restricting the flame to a short region in which the combustion air becomes flue gas. The short residence time at peak temperature keeps the vast majority of nitrogen from becoming ionized. On the other hand NO emission can be reduced when increasing the delay time of the combustion in NO reducing conditions. (Ehrhard 1999, 10; De Nevers 2000, 464; Timonen 1993, 31)

This technology has similar requirements as reducing temperature. As the calcination reactions require high temperature and certain residence time in lime kiln, the kiln sizing should be changed if residence time were to be reduced significantly.

## 5.3 Low-NO<sub>x</sub> burner

Low-NO<sub>x</sub> burner (LNB) technology stages combustion in the high temperature zone of the flame and different burner types are available. For example, it is possible that LNB has three stages that each contribute to NO<sub>x</sub> reduction. Primary combustion can be done in the first stage, second stage can be fuel reburning and the combustion can be finished in third stage in low excess air. According to Finnish Environment Institute (2001), flame should be located as close to the burner tip as possible, flame size should be small and flame temperature high. In addition to primary air it is possible to use also secondary and tertiary air in LNB. Secondary air has usually a swirling motion enabling high-speed ignition as it passes the hot combustion gases from the flame close to the burner tip. Burner is often provided with a flame stabilizer if pulverized fuel is used so that ignition can be accelerated. (Ehrhard 1999, 15; Finnish Environment Institute 2001, 52)

According to Hart et al. (2012) burner installed in a lime kiln upgrade had a primary air coming on the inside of the flame. Lower NO<sub>x</sub> emission can be achieved by using this type of burner as it results in better mixing of staged air. Thanks to both, the new kiln feed and low-NO<sub>x</sub> burner, NO<sub>x</sub> emissions are considerably lower compared to the old LMD feed system and the conventional burner. (Hart et al. 2012, 12)

As discussed in Chapter 3, the burner flame shape has influence on calcining efficiency and NO<sub>x</sub> emission. Therefore, calcining capacity of the kiln is decreased if burner design is not proper which also leads to increased energy consumption. In consequence of these technical restrictions, the conversion of a standard lime kiln burner to low-NO<sub>x</sub> burner is

challenging. According to Cottrell (2003), there was no commercially available LNB for lime kiln application in the early 21st century. However, concepts have been developed to suit lime kiln and functional application exists. Also according to BAT survey multiple kilns had applied Low-NO<sub>x</sub> burners. NO<sub>x</sub> removal with LNB is typically around 30 % according to literature. Therefore, only adding a Low-NO<sub>x</sub> burner might not be sufficient technique to achieve tightening NO<sub>x</sub> emission limits in the future. However, according to Engdahl et al. (2008), emission measurements for lime kiln have shown that NO<sub>x</sub> emissions can be reduced by 50 % by adjusting primary air distribution. (Cottrell 2003, 8)

### 5.3.1 Burning in separate chamber

This method can be utilized in LNB. Idea of this technique is lower the oxygen content of the primary air by pre-burning. In case separate gas generator is applied, NO<sub>x</sub> emission is effected by gas generator power and combustion chamber pressure. (Kottila 2014)

## 5.4 Fuel reburning

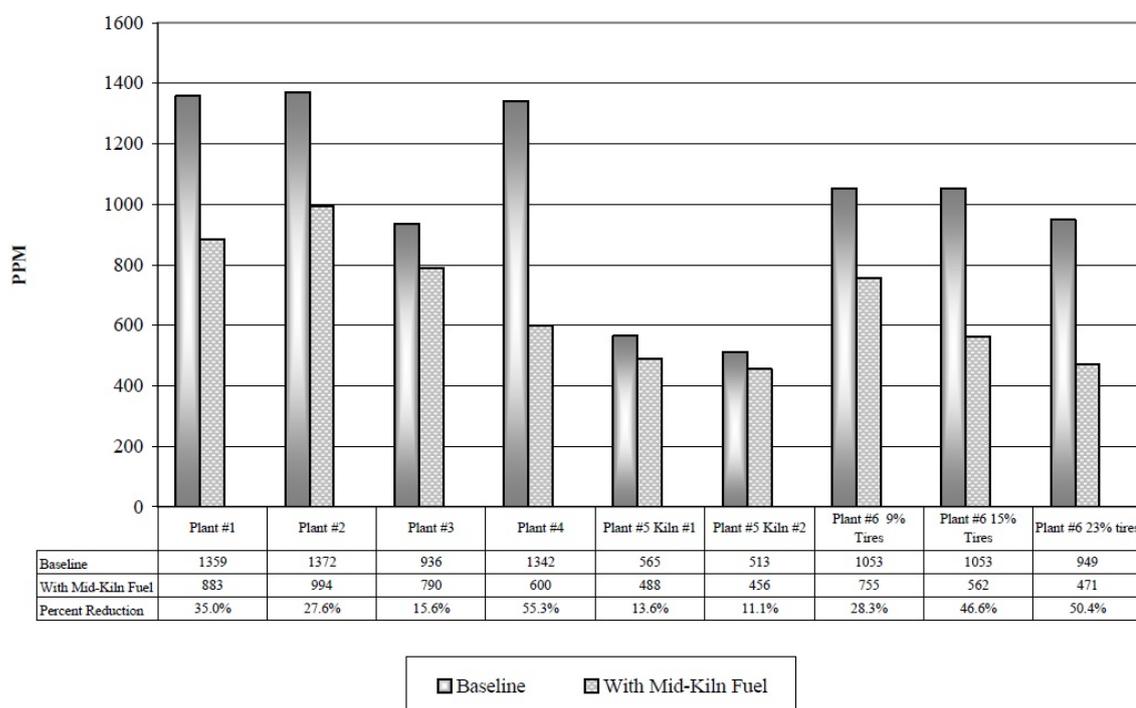
Fuel feeding is challenging in the other parts of the rotary kiln than in the burner end since the kiln is rotating. However, if part of the fuel is burned in reduced temperature, some of the thermal NO<sub>x</sub> formation can be avoided. This could be explained by the interaction between local reducing atmospheres located at secondary firing point and NO<sub>x</sub> formed in earlier combustion. Another explanation to lower overall NO<sub>x</sub> emissions could be higher excess air in primary combustion producing cooler main flame. (Hansen 2002, 1)

Following critical parameters impacting NO<sub>x</sub> reduction are listed:

- concentration of NO<sub>x</sub> entering the reburning zone
- stoichiometry in fuel-lean reburn zone
- temperature and residence time at fuel-lean reburn zone
- distribution of the fuel-lean reburn into the kiln gases (Le et al. 2010, 3)

According to Le et al. (2010), first three objects can be achieved by control operators or process control but additional mixing is needed to accomplish a decent distribution.

Results of NO<sub>x</sub> reduction on nine cement kilns using mid-kiln firing are presented in Figure 22.

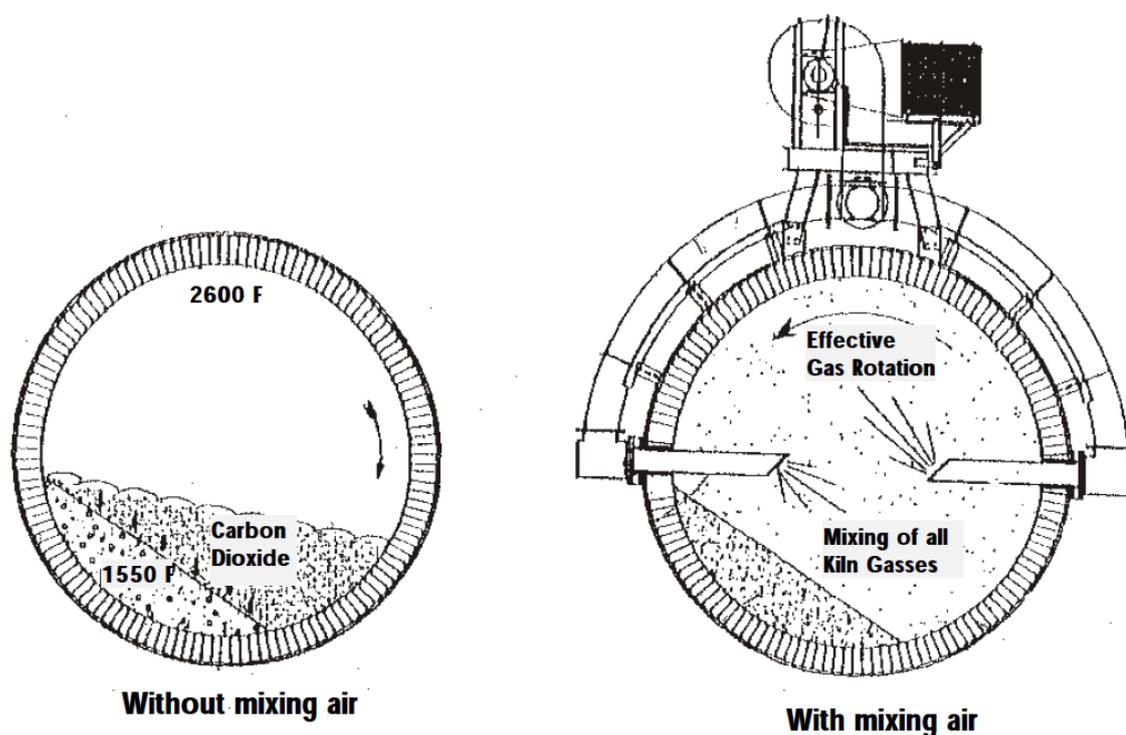


**Figure 22.** NO<sub>x</sub> reduction at cement kilns feeding whole tires using the Cadence mid-kiln technology (Hansen 2002, 9)

However, it should be noticed that similar mid-kiln firing of tires would not probably be possible in lime kiln as it would cause impurities to be congregated to the desired product, calcium oxide. Use of another type of fuels than tires could be possible. Staging of fuel feeding is similar to fuel reburning. On the other hand excessive fuel staging can be the reason to incomplete combustion which results in poor efficiency and other emissions as unburned fuel. (Jalovaara et al. 2003, 72)

## 5.5 Improving mixing of fuel and air

According to European Commission (2014), good mixing of fuel and air is considered as BAT technology for lime kiln. Commercial application to mix lime kiln flue gas along tube length exists. Illustration of the stratification of gases in the calcining zone and the effect of mixing air is shown in Figure 23.



**Figure 23.** Illustration of the stratification of gases in the calcining zone and the effect of mixing air (Hansen 2002, 10)

Temperature contrast is high in the unmixed condition. According to Figure 23, flue gas located in the upper part of the kiln has temperature of 1427 °C (2600 °F) and the opposite section has a temperature of 843 °C (1550 °F). When air mixing is used, gas rotation can smooth temperature fluctuations and peak temperatures, and thus reduce NO<sub>x</sub>.

## 5.6 Removal of nitrogen from combustion

It is possible to remove nitrogen from combustion by

- using oxygen instead of air in the combustion process
- controlling excess air
- using ultra-low nitrogen content fuel to form less fuel NO<sub>x</sub> (Ehrhard 1999, 10)

According to Ehrhard (1999), combination of ultra-low-nitrogen content fuels and oxygen can virtually eliminate fuel and prompt NO<sub>x</sub>.

### 5.6.1 Controlling excess air

Amount of excess air used in combustion has clear impact to the NO<sub>x</sub> emissions. NO<sub>x</sub> emission can be significantly limited by reducing excess air flow to 2 % or less. Even though overall net excess air is limited, fuel-rich and fuel-lean zones still exist in the combustion region. However, if NO<sub>x</sub> is reduced by using reduced excess air or lower oxygen concentration in combustion, higher CO emissions will follow. NO<sub>x</sub> emissions might be slightly lowered when at the same time emission of CO grows prominently. Therefore, an accurate process control is essential to achieve balance between CO and NO<sub>x</sub> emissions. (Ehrhard 1999, 15; European Commission 2013, 240)

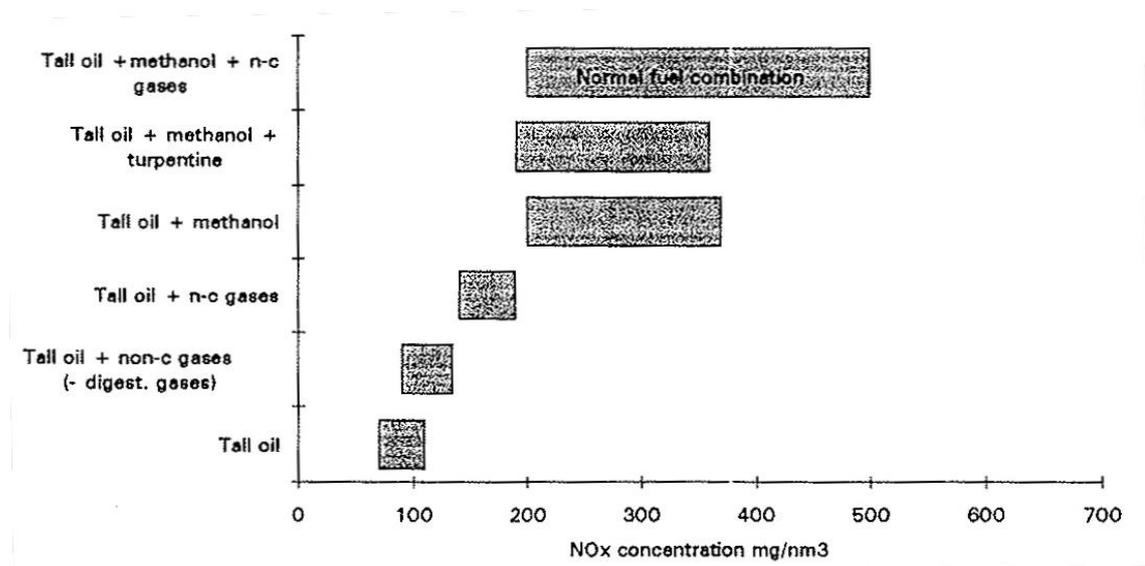
### 5.6.2 Fuel selection

Significant reductions in NO<sub>x</sub> emissions from lime kiln can be achieved by avoiding combustion of non-condensable gases and their derivatives. On the other hand, in one of the kilns studied in the article “NO<sub>x</sub>-emission characteristics for lime kiln in the pulp industry”, virtually no fuel dependence on the NO<sub>x</sub> emissions was observed. The measures for NO<sub>x</sub> reduction have to be specified separately for the lime kiln in question. (Löfblad et al. 1993, 1)

Heavy fuel oil has nitrogen content in the range of 0.3-0.4 % in dry solids. Respectively, biogas has greater nitrogen content, 0-25 %, than natural gas (<1 %). Nitrogen content of wood powder, depending if it originates from woodchips, bark or sawdust, is 0.1-0.8 % in dry solids. Avoiding use of high nitrogen content fuels results in lower fuel NO<sub>x</sub> emissions. According to European Commission tall oil as a fuel lowers NO<sub>x</sub> emissions. NO<sub>x</sub> emissions are usually lower when firing wood powder instead of bark powder, which is most likely possible because of the lower nitrogen content in wood powder. (Alakangas 2000, 152, 155, 156; Francey 2009, 52)

Use of petcoke increases NO<sub>x</sub> emissions. One lime kiln has been using petcoke since September 2006 at pulp mill located in the south eastern US. Testing data indicated that this particular mill would be exceeding their NO<sub>x</sub> permit limit, 16 kg NO<sub>x</sub>/h, if they burned petcoke at substitutions higher than 16 %. Therefore, they applied for regulatory approval to burn petcoke at higher substitutions and new permit of 55 kg NO<sub>x</sub>/h was issued in 2007. After the increase in petcoke burning actual measurement showed 26 kg NO<sub>x</sub>/h. (Francey 2009, 48-49)

The effect of NO<sub>x</sub> reduction with fuel selection was investigated in Sweden in 1990s. In a single lime kiln NO<sub>x</sub> concentrations for the normal operating case were 200-500 mg/Nm<sup>3</sup>, and were greatly reduced down to 80-100 mg/Nm<sup>3</sup> by eliminating addition of the auxiliary fuels. These NO<sub>x</sub> concentration intervals for different fuels at the Mörrum lime kiln are introduced in Figure 24. Especially methanol had significant impact on NO<sub>x</sub> emission, while turpentine, which was added in smaller amounts, had little influence on the NO<sub>x</sub> levels. (Lövblad et al. 1993, 4)



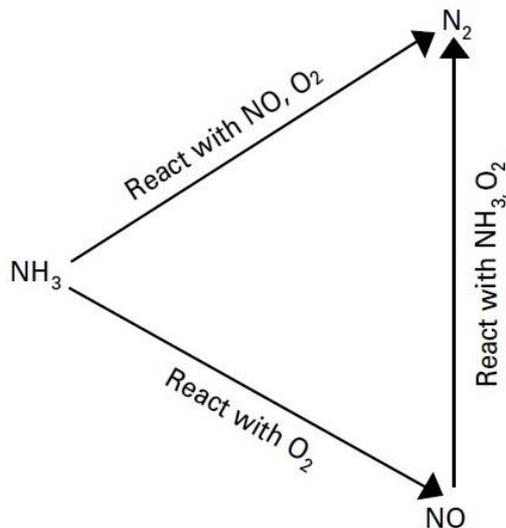
**Figure 24.** NO<sub>x</sub> concentration intervals for different fuels at the Mörrum lime kiln (Lövblad et al. 1993, 10)

As can be seen from the Figure 25 fuel selection has strong impact to NO<sub>x</sub> emissions. Effect of the stripper of gases to NO<sub>x</sub> emission has also been studied by Crawford & Jain (2002) at two separate mills. Lime kiln at unnamed mill, Mill A, used natural gas as a fuel and another lime kiln at unnamed mill, Mill E, burned fuel oil. Both NO<sub>x</sub> emission increase and share of ammonia converted to NO<sub>x</sub> in three different cases are shown in Table 7.

**Table 7.** NO<sub>x</sub> emission increase in lime kiln from burning SOGs (Crawford & Jain 2002, 3-4)

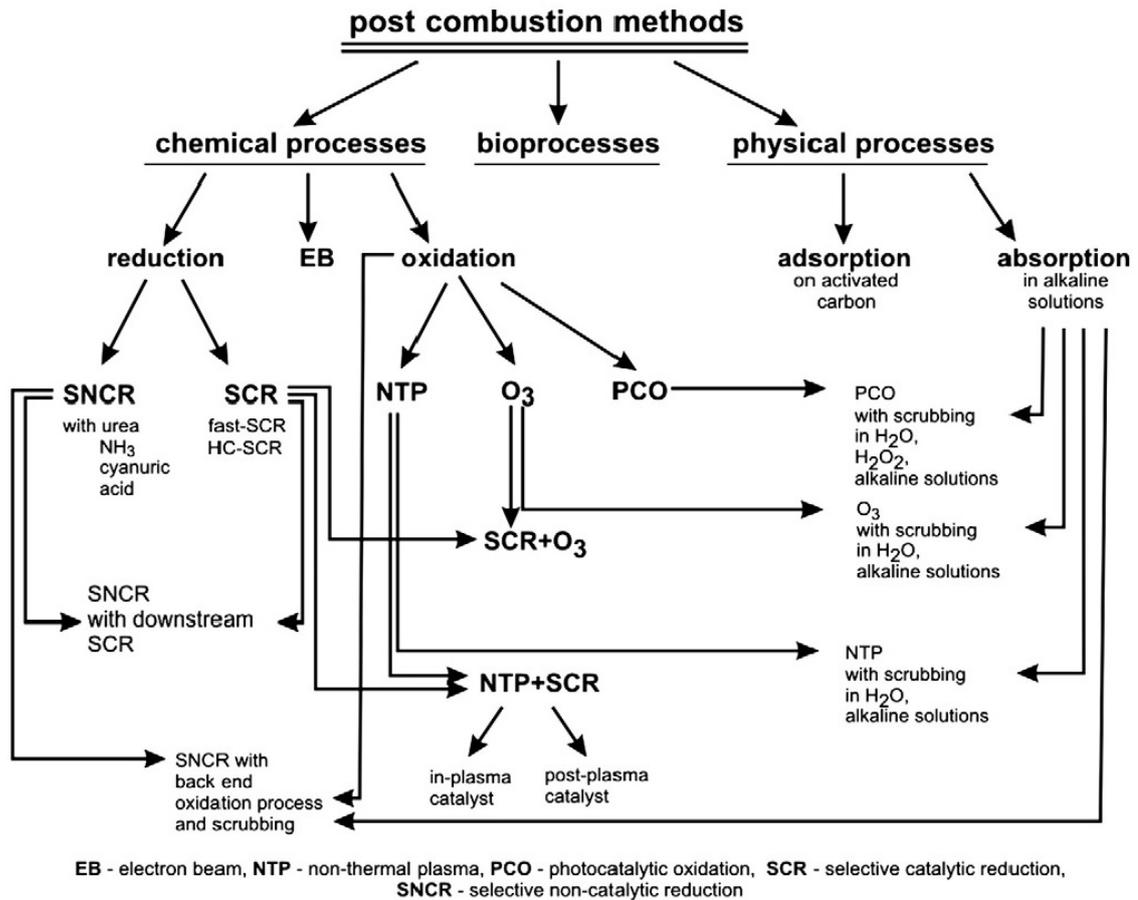
	NO <sub>x</sub> emission increase	Share of NH <sub>3</sub> converted to NO <sub>x</sub>
Mill A, 760 °C	2.26 kg/h	12.3 %
Mill A, 1093 °C	2.25 kg/h	10.8 %
Mill E, 1010 °C	6.35 kg/h	23.3 %

Difference in NO<sub>x</sub> emission increase could be explained by the difference in main fuel, temperature, oxygen content or SOG mixing efficiency in combustion gas. Lime kiln at Mill E had also greater oxygen content during post combustion which could also credit to greater NO<sub>x</sub> conversion at Mill E. It is crucial which reaction route ammonia goes through. Reactions of ammonia and nitric oxide are presented in Figure 25. (Crawford & Jain 2002, 3-4)

**Figure 25.** Reactions paths for ammonia and nitrogen monoxide (Crawford & Jain 2002, 2)

## 6 NO<sub>x</sub> REMOVAL BY POST COMBUSTION METHODS

Post combustion methods are presented in Figure 26. Post combustion methods are also known as secondary methods for NO<sub>x</sub> removal.

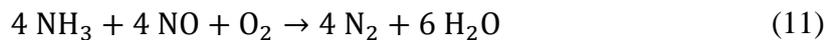


**Figure 26.** Schematic presentation of described NO<sub>x</sub> abatement post-combustion methods (Ledakowicz et al. 2010, 7)

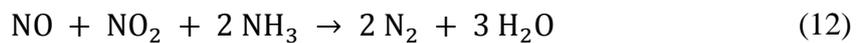
This Chapter focuses to chemical processes such as SNCR and SCR. NO<sub>x</sub> scrubbing is a combination of chemical process and physical process, but is discussed under one section. Bioprocesses are discussed shortly under the NO<sub>x</sub> scrubbing where they can be applied to remove NO<sub>x</sub> from scrubbing waste water.

## 6.1 Chemical Reduction of NO<sub>x</sub>

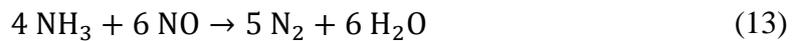
Chemical reduction uses chemical to remove oxygen from nitrogen oxides. In this field SNCR and SCR are the two most common technologies which have been both tried on a large scale and result in good reductions. However, neither SNCR nor SCR have been fitted to rotary lime kiln. In both technologies, the main reaction of NO with NH<sub>3</sub> and oxygen is presented in Equation 11. (De Nevers 2000, 462; Ehrhard 1999, 10)



The reaction can be also expressed as in Equation 12 when there is NO<sub>2</sub> present (Koskinen 2013, 7):

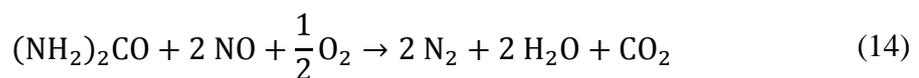


The desired reaction is shown in Equation 13. (De Nevers 2000, 462)



However, some oxygen always exists which leads to reaction 11. (De Nevers 2000, 462)

When ammonia is used as a reagent the above equations are to be used. When urea is used as a reagent the reaction is as shown in Equation 14. (Stultz & Kitto 1992, 34-4)



Normal stoichiometric ratio (NSR) describes the molar ratio of the reagent injected to NO in the flue gas. According to Equation 11, one mole of ammonia reacts with one mole of NO so NSR is one. If urea is used NSR is two as one molecule of urea includes two ammonia radicals. If NSR is increased greater NO<sub>x</sub> reduction can be reached. It has to be noted that increasing reagent dosing beyond certain point results in increased ammonia slip and higher reagent cost. (ICAC 2008, 5)

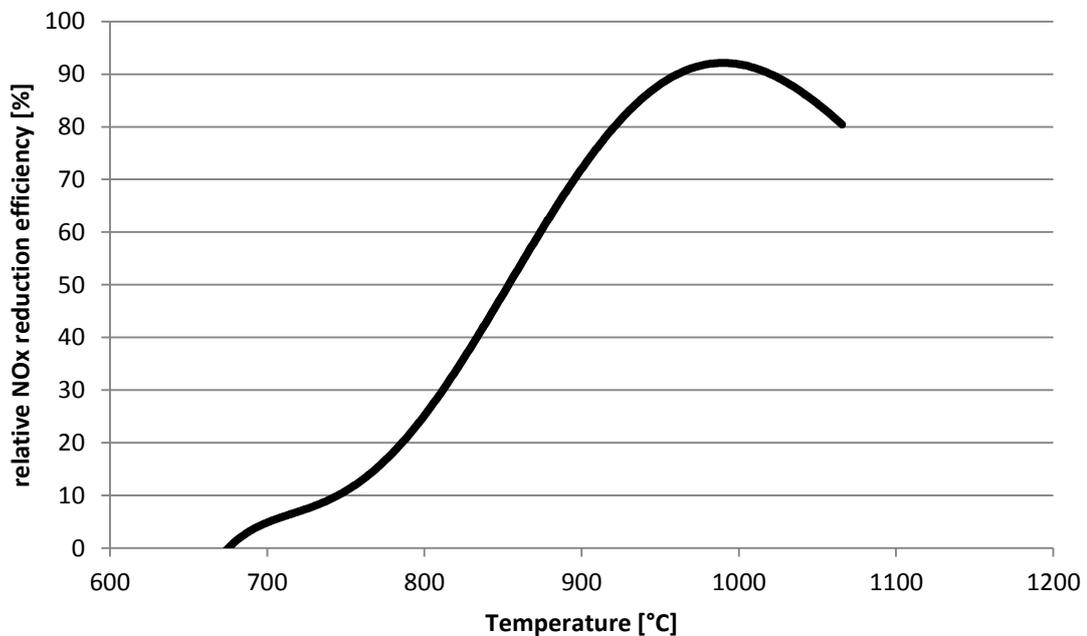
Chemical reduction of NO<sub>x</sub> has not been applied yet in lime kilns due to emission limits achievable with primary methods. Cement kilns have already applied both SNCR and SCR. This can be explained by the fact that required process temperature in clinker production is higher than the one in lime kiln for lime production, and therefore, more

thermal NO<sub>x</sub> will form in cement kiln. However, installations will be also likely seen in lime kilns if the trend for low NO<sub>x</sub> emission requirement continues further in the future.

### 6.1.1 Selective Non-Catalytic Reduction

Selective Non-Catalytic Reduction (SNCR) is a chemical reduction of NO<sub>x</sub> and it usually uses ammonia or urea. Ammonia or urea is injected in a region where temperature is between 900 and 1100 °C. Ammonia solution can be injected as a liquid to the lime kiln due to high temperature but it is possible to use also gaseous form.

NO<sub>x</sub> reduction efficiency as a function of temperature for SNCR is presented in Figure 27.

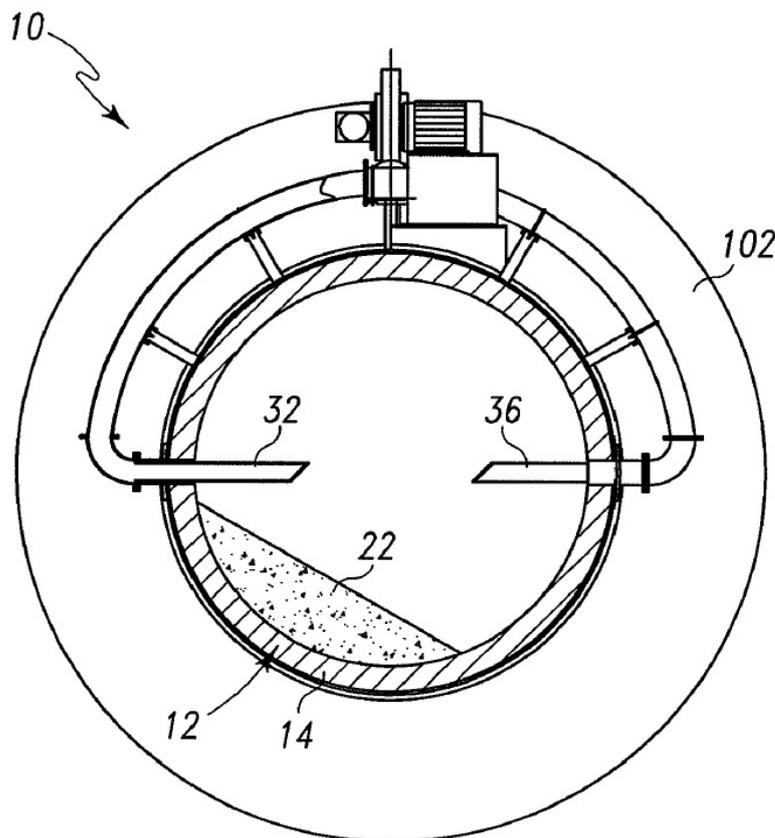


**Figure 27.** Typical SNCR efficiency as a function of temperature (after ICAC 2008, 5)

If too high temperature is present NO content is increased instead of NO<sub>x</sub> being removed. According to De Nevers (2000), the dominant reaction above temperature of 980 °C (1800 °F) is as shown in Equation 15. However, according to Figure 27, SNCR has good efficiency still at 1050 °C which is possible when urea is used.



Applicable temperature range is located in the kiln tube which means that injection has to take place in the rotating part of the lime kiln. Schematic of SNCR system patented to rotary lime kiln is presented in Figure 28. This system has injection piping and fan attached to kiln tube.

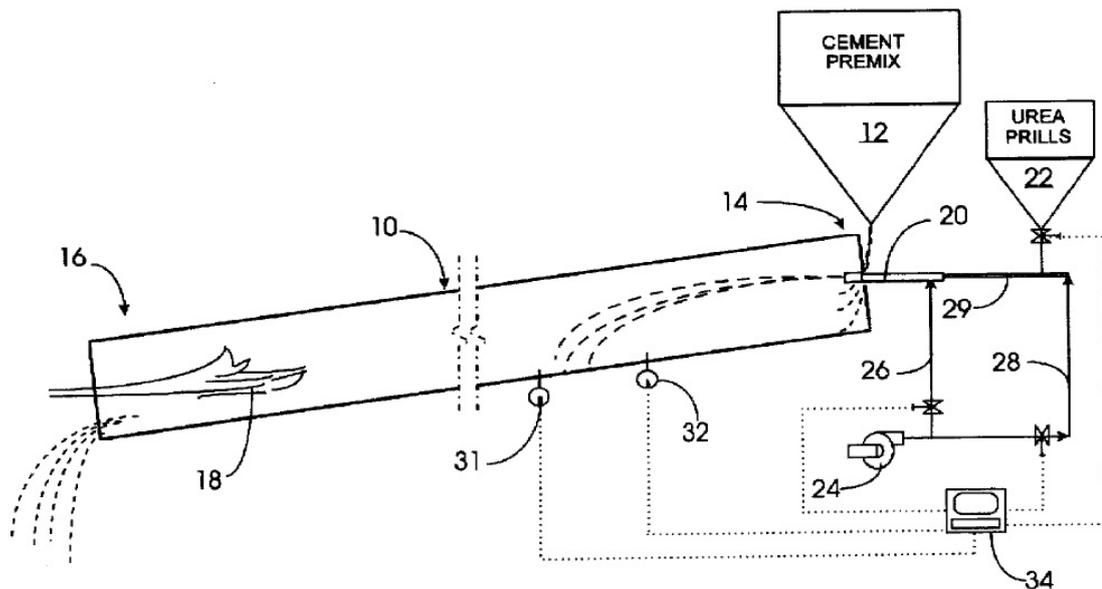


**Figure 28.** Schematic of SNCR system applied in rotary lime kiln (Blankenship et al. 2011, 12)

By using SNCR in power boilers usually a NO<sub>x</sub> reduction of 40-60 % is achieved. Transient reduction varies in the best case between 60-70 % and in the worst case between 30-40 %. The possible achievable reduction depends on the initial NO<sub>x</sub> level. 80 % reduction from uncontrolled emissions of 1.6-2.7 kg NO<sub>x</sub> per ton clinker (3.5-6.0 lb NO<sub>x</sub> per ton of clinker) have been reached using SNCR in cement kiln in a demonstration. (ICAC 2008, 6; Jalovaara et al. 2003, 68)

Patented urea prill feeding system for cement kiln is presented in Figure 29. In this system spherical type of urea prills about 1.6 millimeters in median diameter are injected through a venturi-type injector into the kiln. Urea prills are injected at an initial velocity of approximately 140 m/s and about 90 % of the prill fall into a zone located 9-12 meters

from injection point. By this kind of arrangement NO<sub>x</sub> removal of 75% down to concentration of 140 ppm can be reached. In general, baseline NO<sub>x</sub> concentration in combustion gases is within the range of from about 300 to about 1000 ppm and is reduced by at least 50%. (von Harpe 1998, 5)



**Figure 29.** SNCR using urea prill feeding system in cement kiln (von Harpe 1998, 1)

For the time being there is no installed SNCR application for reburning lime kilns. (European Commission 2013, 242)

#### 6.1.1.1 Controlling technology in SNCR

Since no installation has been made for rotary lime kiln other applications can be investigated. According to Oksman (2012), typical arrangement in BFB-boiler is that NO<sub>x</sub>-emission in flue gases is measured in stack and ammonia is dosed according to the measurement of NO<sub>x</sub> emission and boiler load. As lime kiln load usually does not vary as much as in BFB-boiler adjustments might not needed in such a large-scale. Ammonia injection level can be fixed during commissioning of the SNCR system. Controlling of the system is also possible based on ammonia slip measurement which might be viable option in lime kiln since high NH<sub>3</sub>-slip is expected. (Oksman 2012, 52)

### 6.1.1.2 Ammonia slip in SNCR

Since SNCR is not BAT for lime kiln, ammonia slip emission levels are not given for lime kilns. The BAT-associated NH<sub>3</sub> emission levels for cement industry when SNCR is applied are presented in Table 8. Oxygen concentration of the flue gas is not given for NH<sub>3</sub> emission levels.

**Table 8.** BAT-associated emission levels for NH<sub>3</sub>-slip in the flue gases when SNCR is applied for cement kiln (European Commission 2013b, 18)

Parameter	Unit	BAT-AEL (daily average value)
NH <sub>3</sub> -slip	mg/Nm <sup>3</sup>	< 30-50 <sup>(1)</sup>
<sup>(1)</sup> The ammonia slip depends on the initial NO <sub>x</sub> level and on the NO <sub>x</sub> abatement efficiency. For Lepol and long rotary kilns, the level may be even higher		

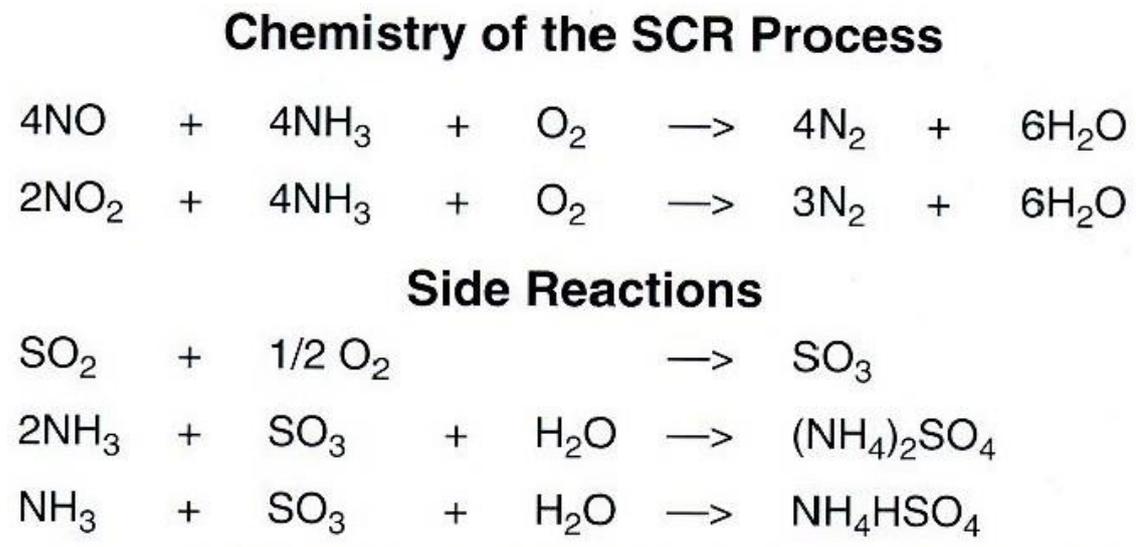
NH<sub>3</sub>-slip values guaranteed for the SNCR system depend on the required NO<sub>x</sub> removal. If high reduction is required, NH<sub>3</sub>-slip will be higher. Operation of SNCR in lower temperature, as at 840 °C, leads to increased NH<sub>3</sub>-slip. Also inaccurate injection of the reagent causes greater slip. According to the results of 14 tests performed in cement plants with a precalcination cyclone tower, the average ammonia slip were 24 mg/Nm<sup>3</sup> at 10 % oxygen. The average NO<sub>x</sub> reduction during that period was 86 %, NO<sub>x</sub> baseline of 1124 mg/Nm<sup>3</sup> were reduced to 152 mg/Nm<sup>3</sup> with injection, both values given at 10 % O<sub>2</sub>. However, these results are not directly comparable to lime kiln as injection was not done in the rotating part of the cement kiln. (Yara Miljö 2011, 2)

According to European Commission (2013b), when SNCR is applied to cement kiln, BAT is to reach as low ammonia slip as possible by using the following techniques:

- to reach sufficient NO<sub>x</sub> reduction efficiency simultaneously with a stable process operation
- to apply a decent stoichiometric distribution of ammonia
- to acknowledge the correlation between the NO<sub>x</sub> removal efficiency and the NH<sub>3</sub>-slip

### 6.1.2 Selective Catalytic Reduction (SCR)

Selective Catalytic Reduction uses typically ammonia, ammonium solution or urea. Used ammonium solution is typically ammonium hydroxide (NH<sub>4</sub>OH). If ammonium solution is used it has to be evaporated and used in gaseous form due to lower temperature at injection point. According to Kilpinen & Zevenhoven (2004), SCR is usually operated at temperature of 350-400 °C. However, operation is also possible at lower temperatures. Chemical reactions taking place in SCR are presented in Figure 30.

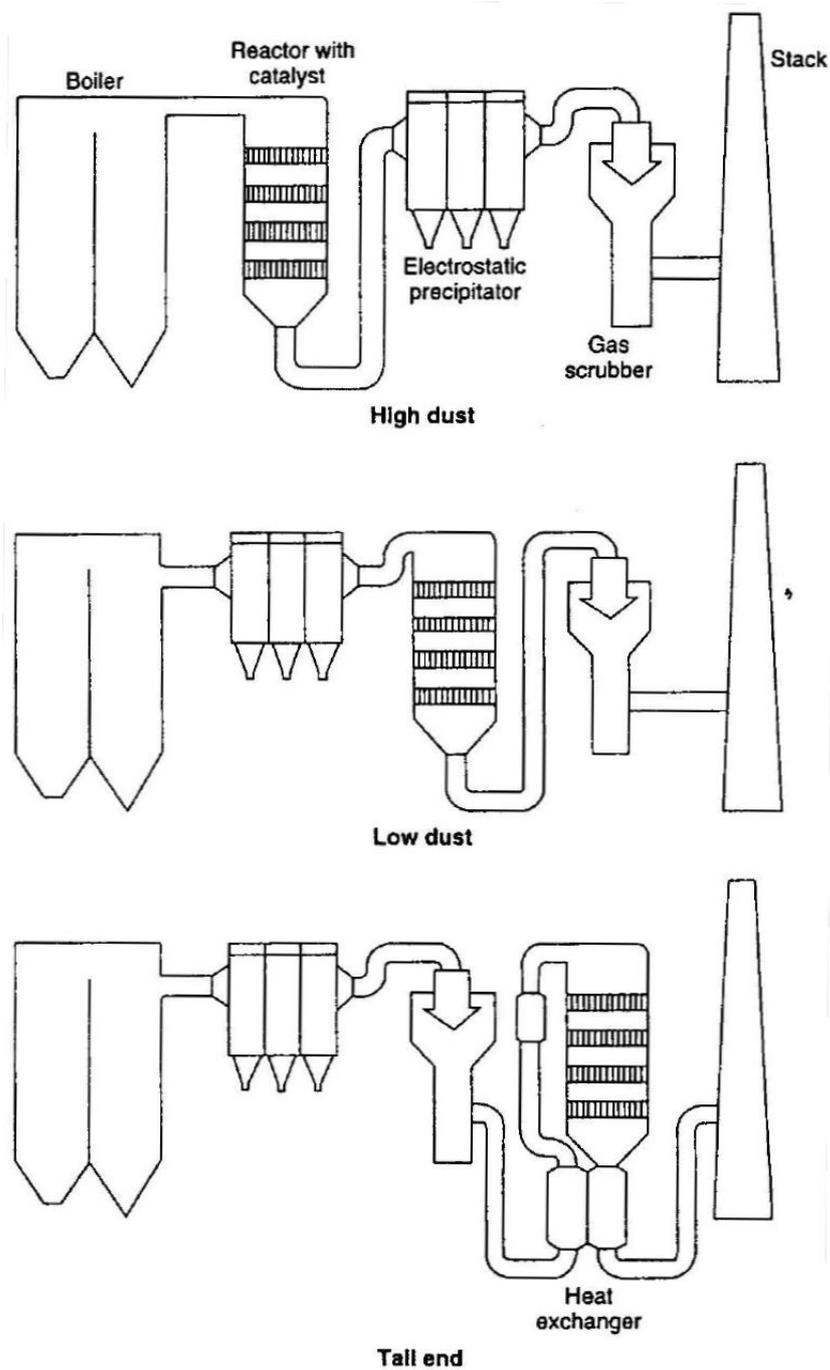


**Figure 30.** Simplified SCR reactions, picture from US DOE 1997 (Kilpinen & Zevenhoven 2004, 4-30)

SCR reactor can be placed before or after the ESP or scrubber. Three different methods are recognized:

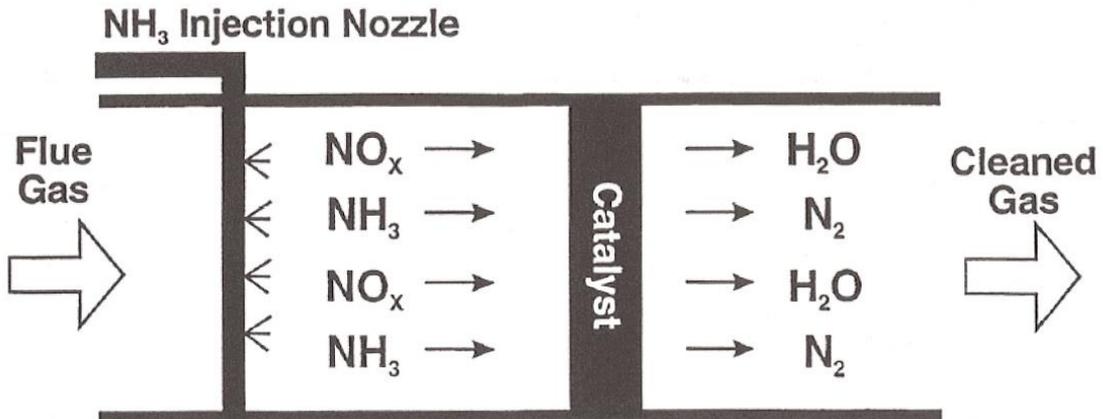
- High dust –method
- Low dust –method
- Tail end –method (Horvath 2003, 309)

SCR process configurations are presented in Figure 31.



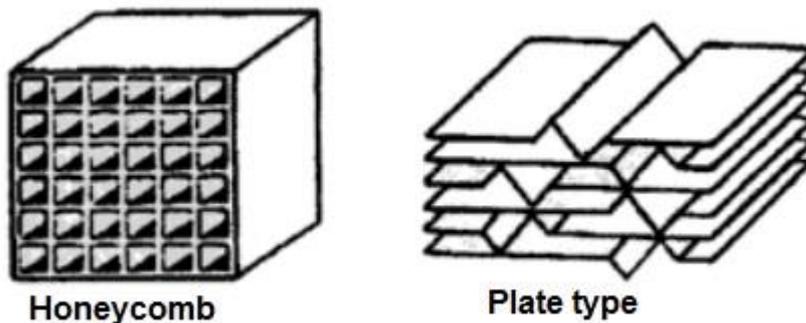
**Figure 31.** SCR process configurations: high dust, low dust and tail end (Horvath 2003, 309)

Schematic diagram of a general SCR DeNO<sub>x</sub> process is presented in Figure 32. Injection nozzle can be placed to injection grid which is located in the flue gas duct.



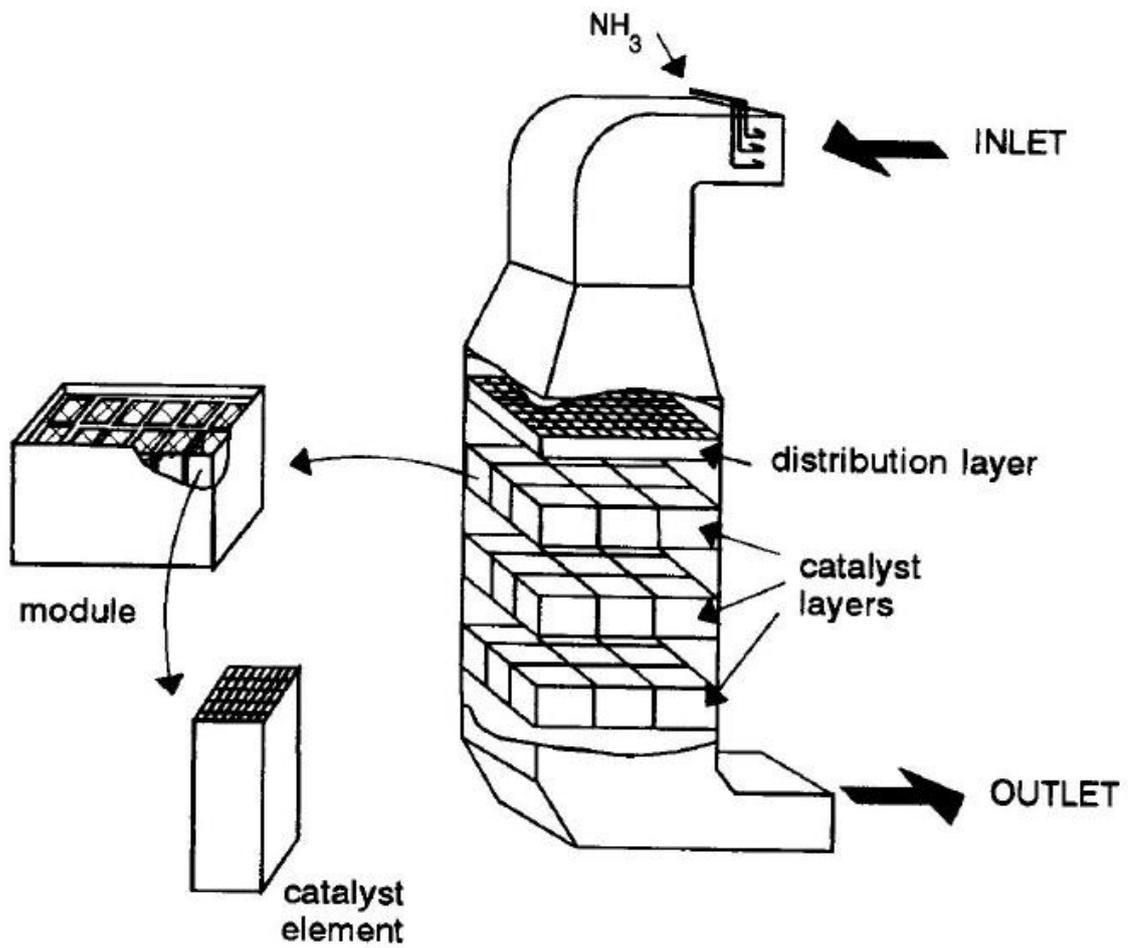
**Figure 32.** Schematic diagram of SCR system (ICAC 2009, 6)

Monolith honeycomb catalysts have typically a square channel section and they are constructed by extruding paste-like material. Plate-type catalysts consist of stainless steel net or a perforated metal plate coated with a catalytic material. Plate-type catalysts are recommended for high-dust and high-sulfur applications like coal-fired power plants. Types of monolithic SCR catalyst are presented in Figure 33. (Cybulski & Moulijn 2006, 181)



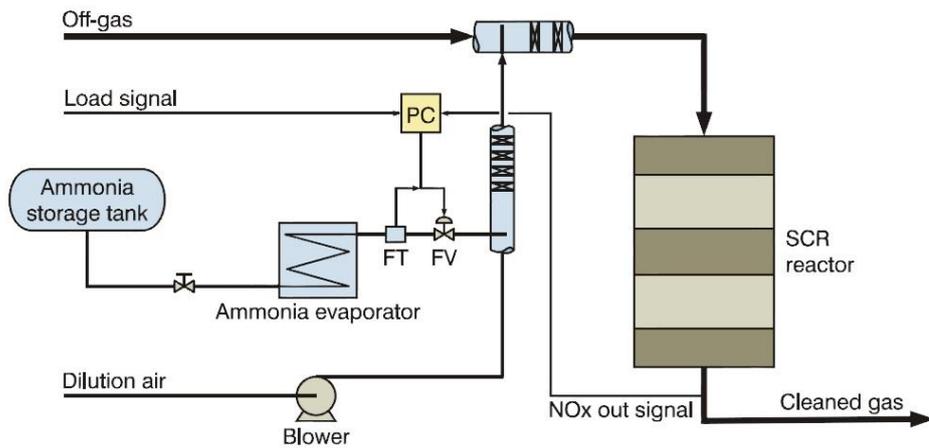
**Figure 33.** Types of monolithic SCR catalyst: honeycomb monolith and plate-type catalyst (Cybulski & Moulijn 2006, 180)

In the reactor catalyst material is assembled into steel-cased modules. Example of SCR reactor is shown in Figure 34. Typical dimensions for the modules are for example 150 mm x 150 mm x 600 mm, length ranging from 350 mm to 1000 mm. Dimensions and geometry depends on the process arrangement i.e. whether high dust, low dust or tail end configuration is in question. Plate-type catalysts are inserted to the reactor in multiple layers in similar manner as the honeycomb catalysts. (Cybulski & Moulijn 2006, 181)



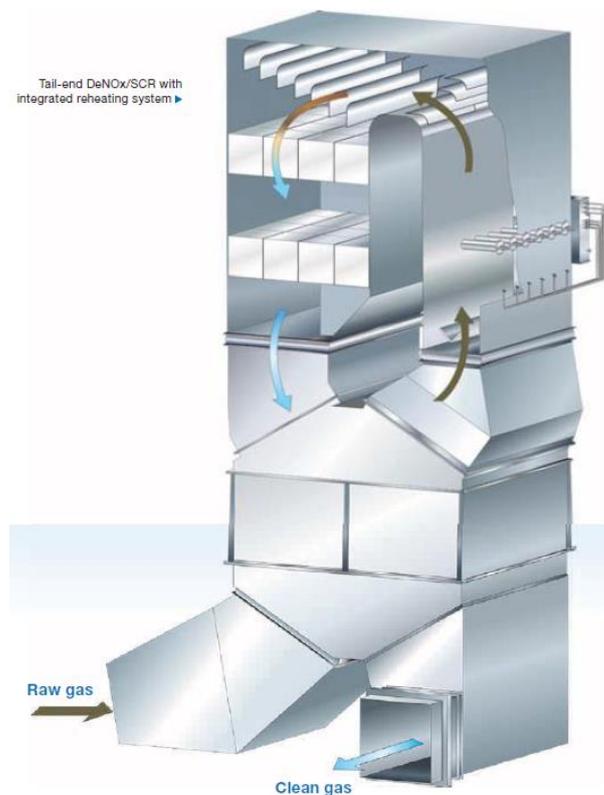
**Figure 34.** DeNOx SCR reactor (Forzatti & Lietti 1996, 4)

Figure 35 introduces a typical flow sheet for the SCR DeNOx process which includes ammonia storage tank, ammonia evaporator, blower, SCR reactor, controlling units and NOx emission measurement.



**Figure 35.** Typical flow sheet for the SCR DeNO<sub>x</sub> process based on anhydrous ammonia as reducing agent (Haldor et al. 2000, 4)

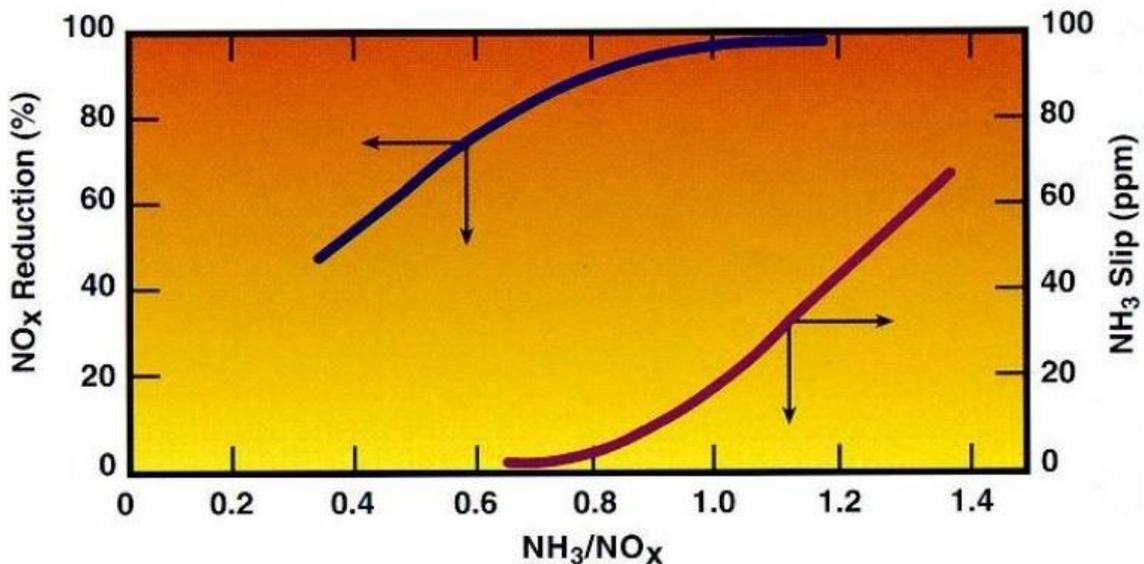
Especially tail end arrangement requires reheating of flue gas in order to reach the required operating temperature for SCR. Figure 36 introduces SCR system offered by Andritz Energy & Environment.



**Figure 36.** Tail-end DeNO<sub>x</sub>/SCR with integrated reheating system. (Andritz Energy & Environment 2014, 12)

### 6.1.2.1 Ammonia slip in SCR

Both effectiveness of SCR and ammonia slip depend of the proportions of ammonia and NO<sub>x</sub>. According to Cottrell (2003), ammonia is typically injected to produce a NH<sub>3</sub>/NO<sub>x</sub> molar ratio of 1.05-1.1/1 to achieve NO<sub>x</sub> conversions of 80 to 90 percent with an ammonia slip of about 10 ppm. On the other hand, according to Kilpinen & Zevenhoven (2004), by using SCR a 90-95 % NO<sub>x</sub> reduction at an NH<sub>3</sub> slip below 5 ppm corresponding 3.8 mg/m<sup>3</sup> can be reached. Increasing NH<sub>3</sub>/NO molar ratio leads to significantly higher ammonia slip. Ammonia slip and NO<sub>x</sub> reduction efficiency for SCR as function of NH<sub>3</sub>/NO<sub>x</sub> input is presented in Figure 37.



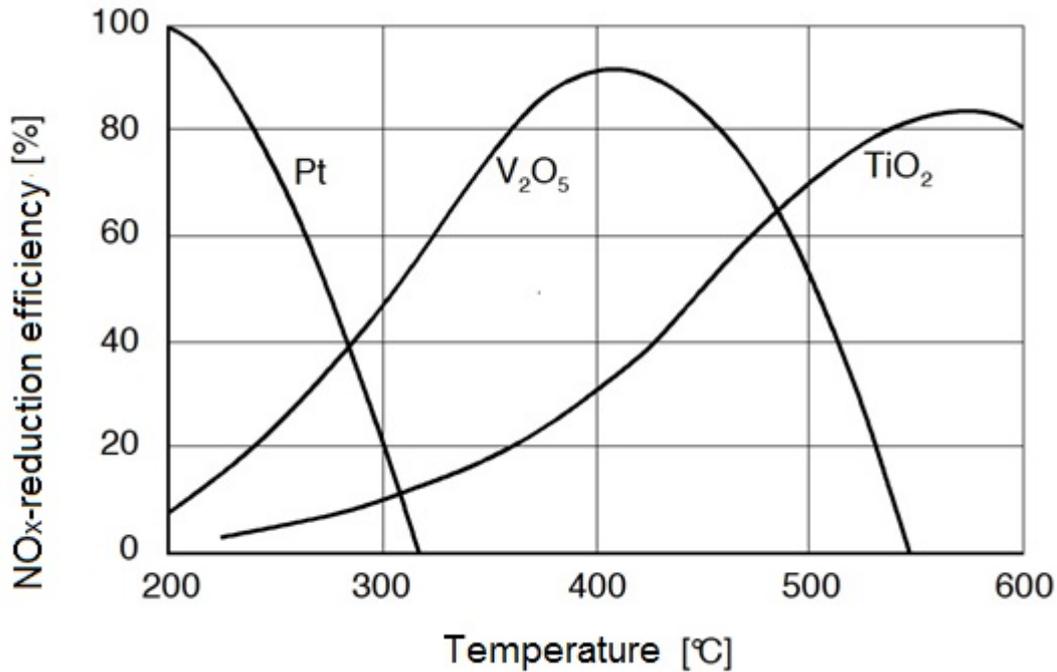
**Figure 37.** Ammonia slip and NO<sub>x</sub> reduction efficiency for SCR as function of NH<sub>3</sub>/NO<sub>x</sub> input, picture from US DOE 1997 (Kilpinen & Zevenhoven 2004, 4-30)

### 6.1.2.2 Catalyst materials used in SCR

Typically vanadium oxide (V<sub>2</sub>O<sub>5</sub>) or tungsten trioxide (WO<sub>3</sub>) supported by titanium dioxide (TiO<sub>2</sub>) is used. Previously, also platinum (Pt) was used but it caused formation of ammonium nitrate which is explosive compound. A drawback of the SCR catalyst used at the present time is that it catalyses also the oxidation of SO<sub>2</sub> to SO<sub>3</sub>. SO<sub>3</sub> is expected to cause sulphuric acid corrosion downstream in the flue gas channel and in the stack at lower temperatures. Side reactions form also ammonium sulphates as shown in Figure 31, which is followed by formation of corrosive deposits both in the SCR unit and downstream. Also

catalyst deactivation occurs at the presence of ammonium sulphates, this is further discussed in the next subsection. (Kilpinen & Zevenhoven 2004, 4-30)

NO<sub>x</sub> reduction efficiencies as a function of operating temperature for different catalyst types are presented in Figure 38.



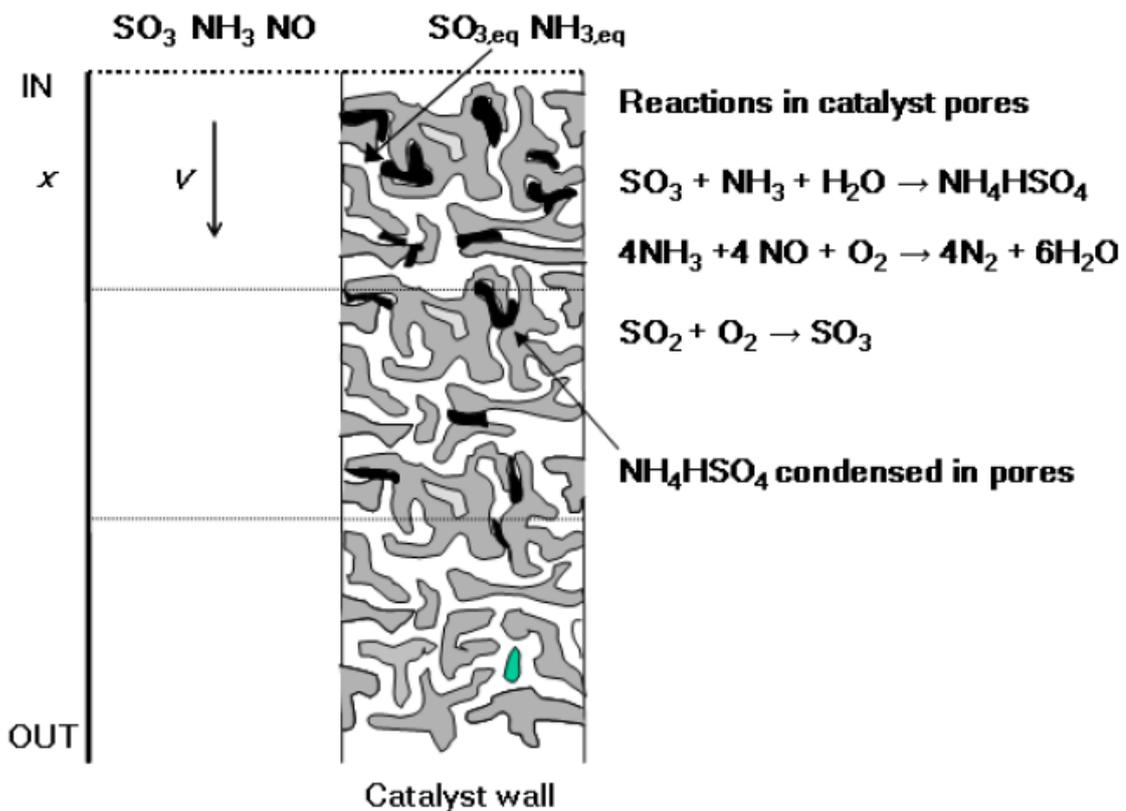
**Figure 38.** relative NO<sub>x</sub> reduction efficiency as a function of temperature for different catalyst types (after Modigell 2012, 222)

### 6.1.2.3 Catalyst poisoning

It is predominantly high sulfur content in the flue gases which causes problems in SCR catalyst materials. During combustion most of the sulfur in the fuel will be oxidized to sulfur oxides. Additionally, some sulfur will accumulate the lime cycle from the lime mud. SO<sub>2</sub> concentration of the flue gases is mainly determined by the sulphur content of the fuel. Equation 16 shows the oxidation reaction of SO<sub>2</sub> to SO<sub>3</sub>, which occurs in the catalyst pores. Further sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) is formed in the reaction between sulphur trioxide (SO<sub>3</sub>) and water. (Heck & Farrauto 2001; Lundqvist 2009, 9):



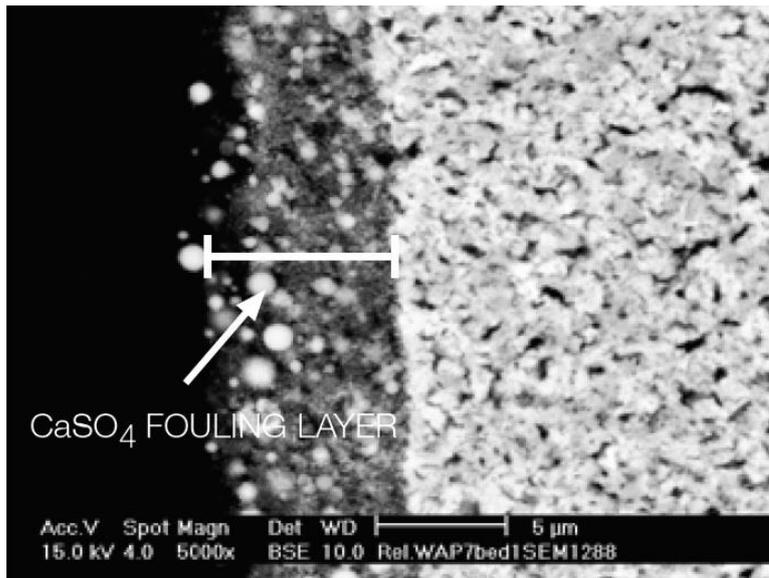
Sulphur trioxide reacts further with injected ammonia and moisture forming salts which determine the required minimum process temperature. Most notable ammonium salts are ammonium chloride ( $\text{NH}_4\text{Cl}$ ), ammonium bisulphate ( $\text{NH}_4\text{HSO}_4$ ) and ammonium nitrate,  $(\text{NH}_4)_2\text{NO}_3$ . Usually ammonium bisulphate (ABS) has the highest dew point but for example in chlorine and sulphur free flue gases the minimum temperature is determined by the  $(\text{NH}_4)_2\text{NO}_3$  dew point. ABS will condense to both, inside the catalyst pores and at the catalyst surface, which leads to formation of sticky surface. In the long run this can cause plugging of the catalyst. ABS catalyst dew points are typically between 280 °C and 320 °C. Ammonium bisulphate deactivation mechanism is presented in Figure 39. (Thøgersen et al. 2008, 3-4)



**Figure 39.** Ammonium bisulphate deactivation mechanism (Thøgersen et al. 2008, 10)

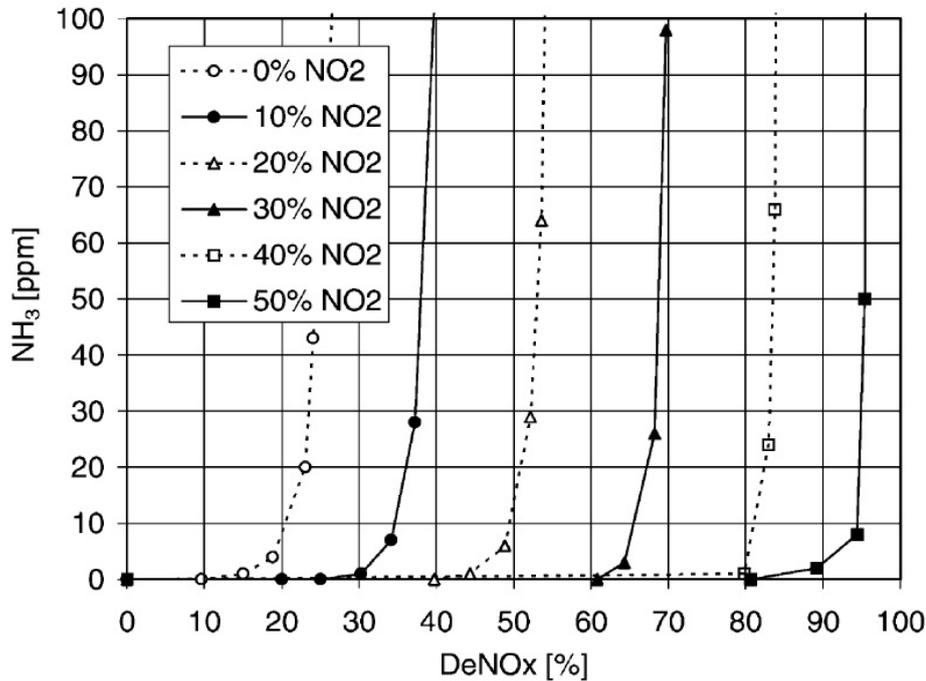
According to Haldor Topsøe (2014), a specific fouling layer forms on the catalyst surface in case high-calcium content coals are fired in the boiler. Scanning electron microscopy is introduced in Figure 40 showing usual  $\text{CaSO}_4$  fouling layer in such SCR units. That might

prove to be a problem in lime kiln as the calcium oxide concentration is relatively high, therefore, it should be further investigated which catalyst types are vulnerable. It is also possible that calcium sulfate is formed as the lime reacts with the sulfur in flue gas. Calcium sulfate layers, in addition to other dusts, will block the catalyst pores in similar manner as ABS. (Cottrell 2003, 11)



**Figure 40.** High content of calcium in coal can cause deactivation of the catalyst in the SCR unit. (Haldor Topsøe 2014, 1)

The presence of NO<sub>2</sub> has a significant effect on the activity of an SCR catalyst at low temperatures. Figure 41 shows performance of monolithic catalyst sample at the temperature of 200 °C. (Koebel et al. 2002, 241)



**Figure 41.** Performance of monolithic catalyst sample at temperature of 200 °C for varying ratios of NO<sub>2</sub>/NO<sub>x</sub> at GHSV=52,000 h<sup>-1</sup> (Koebel et al. 2002, 242)

The GHSV stands for Gas hourly space velocity and it is defined as volumetric flow rate per space volume.

Long-lasting steady activity has been reported for SCR catalysts regardless of the possible deactivation mechanisms. According to Cybulski & Moulijn (2006) catalyst suppliers can usually guarantee an operation time of 16000 to 24000 hours for high dust and tail end arrangements but longer catalyst lifetime have been experienced in practice. However, the main issue regarding the low temperature catalysts is their poor dust and catalyst poison resistance which explains why they are not suitable for lime kiln application.

#### 6.1.2.4 High dust SCR

As noted plate-type catalysts are preferentially used for high-dust and high-sulfur applications, as in coal-fired power plants. The following reasons favor plate-type catalysts for high dust applications (Cybulski & Moulijn 2006, 181):

- with respect to honeycombs, plate-type monoliths are less prone to blockage owing to their structure which permits slight vibration of the individual plates

- the metal support makes the plates more resistant to erosion than the all-ceramic materials as the inlet section of the channel exposes the metal sheet, erosion does not further proceed
- the plates are very thin, so that only a small area of the cross-section is obstructed and pressure drops are very low

Commercial installations regarding SCR systems have been made in cement industry. The conditions in cement kiln are somehow very similar to the conditions in lime kiln after the rotating part of the kiln. For example, in both applications very high dust loading is present in the flue gas before PM removal.

According to Zurhove (2014), when cement kiln SCR installation is compared to a normal, e.g. power boiler, SCR installation the main differences are:

- dust concentration is higher
- dust stickiness is much higher
- dust contains clays and often salts
- dust abrasiveness is lower
- deactivation mechanisms are different

Monolithic catalysts designed for high dust applications have channel openings of a larger size and thicker wall structure in order to reduce erosion and catalyst plugging. Also, when compared to low dust or tail end SCR catalyst, the high dust SCR catalyst requires greater volume and has therefore usually higher investment cost. (Cybulski & Moulijn 2006, 180-181)

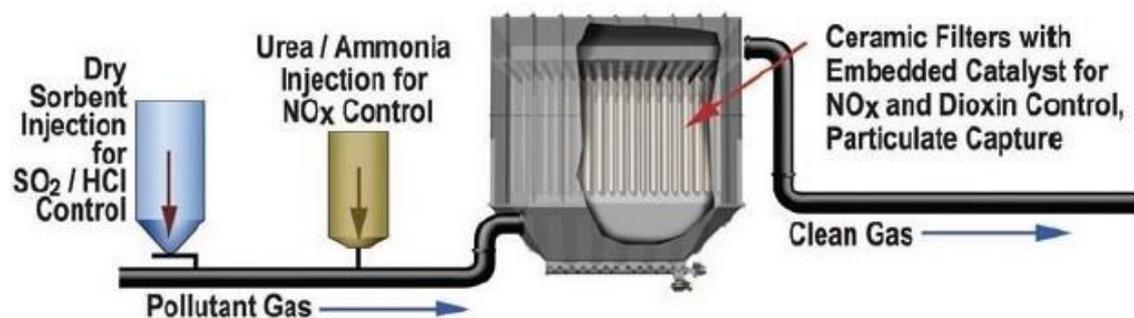
One example of high-dust SCR system installed to cement kiln is located at the Cementeria di Monselice in Padova Province, Italy. This was second installation to cement kiln regarding high-dust SCR and the system has been operated since 2006. NO<sub>x</sub> emissions were reduced to less than 200 mg/Nm<sup>3</sup> reduced to oxygen concentration of 10 % and less than 0.50 kg per metric ton (1 pound per short ton, lb/ston) of clinker in the continuous operation. The system had also capability to achieve 50 mg NO<sub>x</sub>/Nm<sup>3</sup> and less than 0.09 kg/ton (0.20 lb/ton). Furthermore, emissions of volatile organic compounds (VOC) and ammonia were reduced. (Linero et al. 2007, 1)

SO<sub>3</sub> formed could be absorbed by the lime mud of flue gases in the high dust SCR arrangement so that SCR system could be operated at lower temperature and higher SO<sub>2</sub> concentration. Also the injection of reagent could be done in the cyclone in order to achieve more efficient mixing.

#### 6.1.2.5 Embedded SCR

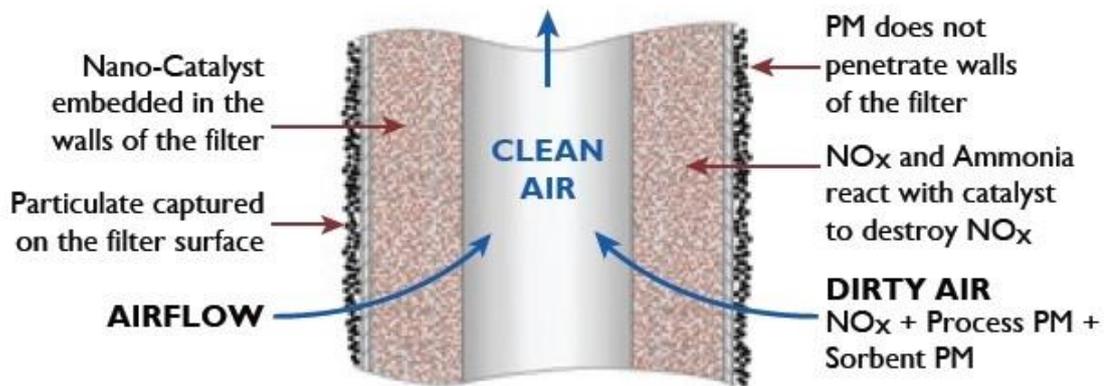
Embedded SCR can be considered as high dust SCR in which catalyst is placed inside ceramic filter tubes. When using this application, ESP is not needed to remove particulate matter separately. Ceramic filter technology has potential in applications where both particulate and NO<sub>x</sub> removal are needed. It can be seen as alternative option for electrostatic precipitators and standard selective catalytic reactors, particularly in the power generation, glass and cement industries. (Startin & Elliott 2009, 39)

Ceramic filter with embedded SCR system offered by Tri-Mer is presented in the Figure 42. The system provides combined PM, SO<sub>2</sub> and NO<sub>x</sub> removal. (Moss 2012, 26)



**Figure 42.** Ceramic filter with embedded SCR system for PM+SO<sub>2</sub>/HCl+NO<sub>x</sub> removal (Moss 2012, 26)

Ceramic fiber filter tube with embedded nano-catalysts is presented in Figure 43.



**Figure 43.** Ceramic fiber filter tube with embedded Nano-catalysts (Moss 2012, 23)

However, earlier experience from ceramic filters indicates that issues due to temperature and pressure gradients are expected to arise. This should be investigate using a pilot plant if ceramic filter could be considered instead of ESP. (Vakkilainen 2014b)

### 6.1.3 Reagents used in SCR and SNCR methods

In general ammonia in different forms is used as a reagent but also urea, cyanuric acid or ammonium sulfate can be used. SNCR usually uses ammonia-water as a solution typically delivered as 24.5 or 24.7 m-%. Transportation of more concentrated solutions is more restricted, and railway transportation should be chosen instead of tank truck delivery. Also ammonia in anhydrous form can be used but it is the most hazardous option. Ammonia as a chemical is water-soluble, colourless liquid and has a sharp smell. In case of heating ammonia solution ammonia gas can be released. Therefore, also flammable limits of anhydrous ammonia in air have to be taken into account in system design: lower limit is 16 % and upper limit is 25 %. (Oksman 2012, 50; Praxair 2012, 5; Stultz & Kitto 1992, 34-8)

Properties of urea make it more stable than ammonia-water solution. Besides, storing and transporting of urea are not under such a stringent regulation than the ones of ammonia-water solution. Handling of urea is also possible as solid granules and it can be dissolved at the plant. According to Oksman (2012), measurements have shown that urea dosage must be approximately doubled compared to ammonia dosage when using SNCR in BFB-boiler which is due to lower reactivity of urea. However, temperatures are higher in lime kiln and kiln tube could be long enough to improve reactivity. Another disadvantage of using urea solution in SNCR process is possible increase in N<sub>2</sub>O emission level. Urea also requires higher temperature compared to ammonia which is a challenge in SCR system designed for lime kiln. Depending on the SO<sub>2</sub> concentration in flue gas, SCR already requires reheating of flue gases to reach appropriate temperature when using ammonia. (Oksman 2012, 51)

## 6.2 Scrubbing of NO<sub>x</sub>

Scrubbing of NO<sub>x</sub> is based on the higher solubility of NO<sub>x</sub> at higher valence. Oxidation step is needed to increase solubility of NO<sub>x</sub> which is required in scrubbing. According to Kilpinen & Zevenhoven (2004), using a caustic solution with added oxidant is recommended. First solubility of nitrogen oxides is discussed, then oxidation of NO and scrubbing in more detail. (Ehrhard 1999, 10)

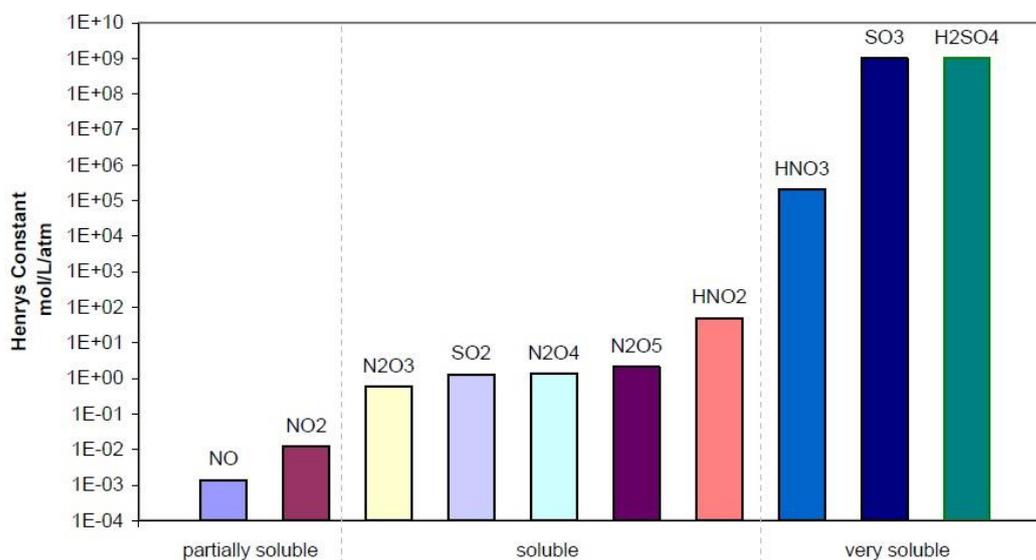
### 6.2.1 Solubility of nitrogen oxides

Solubility of the emission component is one of the key factors in scrubbing. Relative solubilities of NO<sub>x</sub>, SO<sub>2</sub> and further oxidized forms of nitrogen oxide are presented in Table 9.

**Table 9.** Relative solubilities of NO<sub>x</sub>, SO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub> (Confuorto & Suchak 2002, 5)

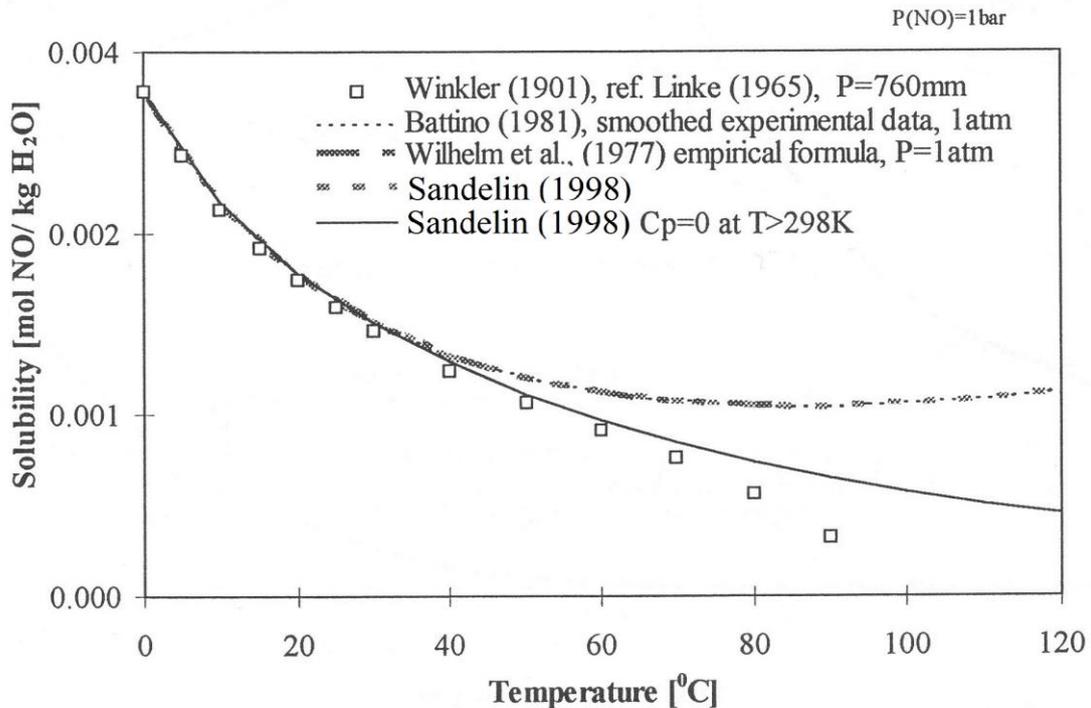
	Relative solubility (25 °C)
NO	1
NO <sub>2</sub>	20
SO <sub>2</sub>	2000
N <sub>2</sub> O <sub>5</sub>	>> 2000
HNO <sub>3</sub>	absolutely soluble

Solubilities of NO<sub>x</sub> and SO<sub>x</sub> gaseous species in water using Henry's Constant are presented in Figure 44.



**Figure 44.** Comparison of solubilities of NO<sub>x</sub> and SO<sub>x</sub> gaseous species in water using Henry's Constant at 25 °C. SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> values are given as infinite by Sander (1999) but expressed here as a value. (Stanger et al. 2012, 23)

Solubility of nitric oxide (NO) in water at 1 bar partial pressure shown as function of temperature is presented in Figure 45. Solubility of NO decreases as temperature increases which is typical for gases.

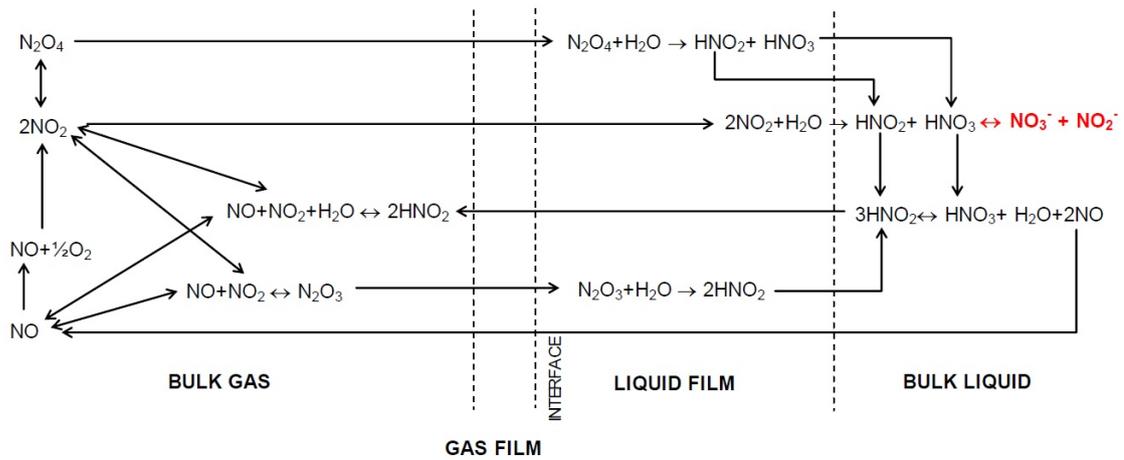


**Figure 45.** Solubility of nitric oxide (NO) in water at 1 bar partial pressure (Sandelin 1998, 4-27) As can be seen from the Figures 45 and 46, solubility of NO in water is very low. Also NaOH does not scrub NO significantly which is experienced from SO<sub>2</sub>-scrubbers. This indicates the importance of oxidation step in the process.

### 6.2.2 Oxidizing of NO

As earlier describer, in order to scrub NO<sub>x</sub> it needs to be oxidized first as solubility has to be increased. Oxidation can be done by injecting strong oxidizing agent, such as ozone (O<sub>3</sub>), chlorine dioxide (ClO<sub>2</sub>) or chlorine (Cl<sub>2</sub>) into the flue gas. Another way to oxidate NO is to add oxidant, such as sodium chlorite (NaClO<sub>2</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), sodium hypochlorite (NaClO) or potassium permanganate (KMnO<sub>4</sub>) to the scrubbing solution. Also non-thermal plasma can be used to oxidize NO<sub>x</sub> when no reducing agent is used, besides, use of catalyst is possible. (Chen et al. 2002, 1; Ehrhard 1999, 10)

The oxidation process in which NO is converted to NO<sub>2</sub> and absorbed in an aqueous phase is presented in Figure 46.

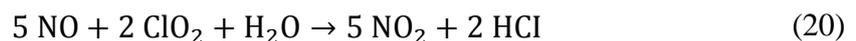


**Figure 46.** NO<sub>x</sub> oxidation and absorption mechanisms, re-drawn from Counce and Perona with added ionisation step marked in red (Stanger et al. 2012, 23)

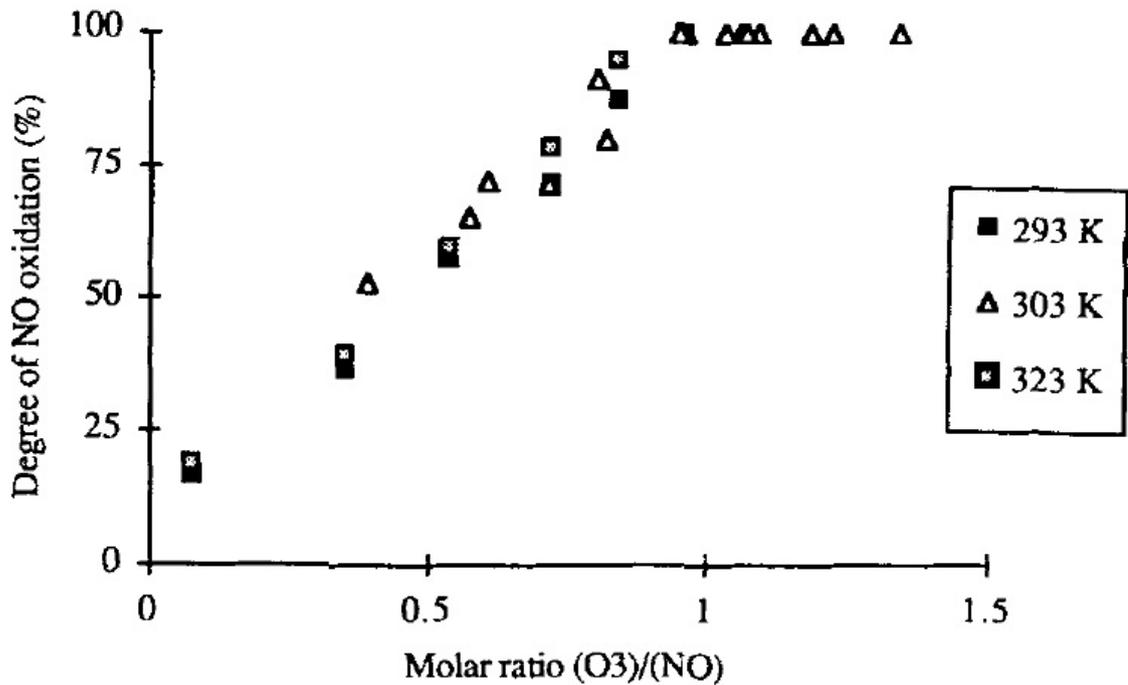
When using ozone as oxidizer, the main product of oxidation is N<sub>2</sub>O<sub>5</sub> which is very soluble as discussed in Chapter 6.2.1. Therefore, rapid NO<sub>x</sub> reduction is possible already in moist flue gases and wet scrubber is necessarily not needed. Main reactions are described by the Equations 17, 18 and 19. (Confuorto & Suchak 2002, 5)



According to Deshwal & Lee (2009), oxidation of NO can be performed using euchlorine, which is a mixture of chlorine dioxide and chlorine. Molar ratio of the compounds is 2:1 and both the constituents are capable to oxidize NO. Deshwal & Lee (2009) suggest that oxidation reaction of NO using ClO<sub>2</sub> can be written as in Equation 20.



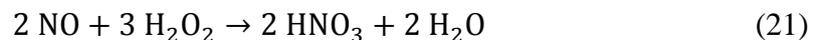
Oxidation stage of NO as a function of molar ratio of ozone and nitrogen monoxide at three different temperatures is presented in Figure 47.



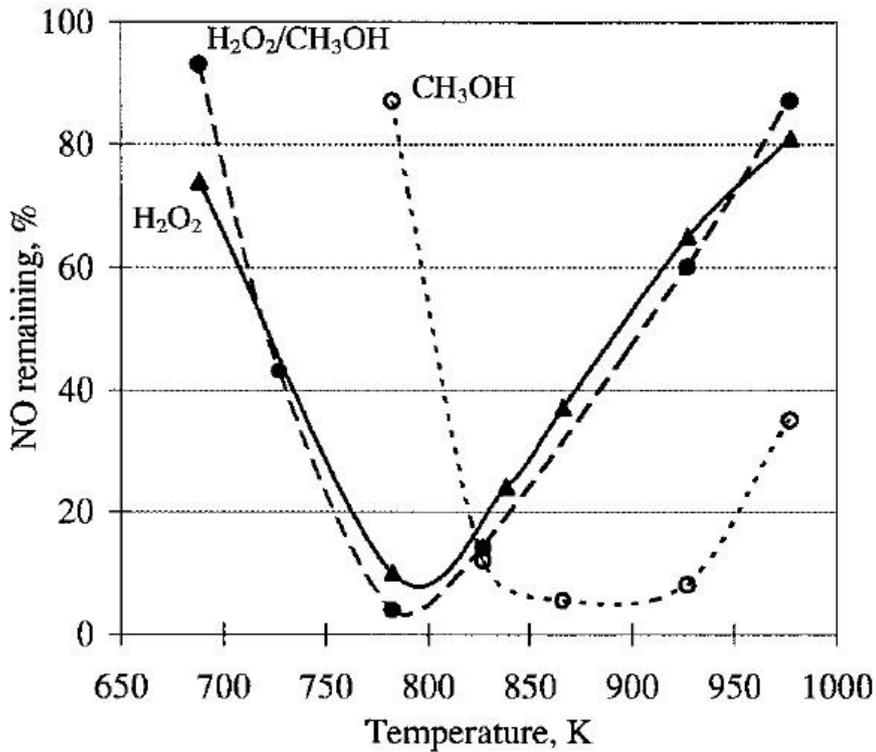
**Figure 47.** Degree of oxidation of NO as a function of molar ratio  $O_3/NO$  at temperatures of 293 K, 303 K and 323 K (Leskelä et al. 1997, 2)

Based on the test results, molar ratio should be at least one if ozone is used for oxidation of NO in case full oxidation degree of NO is pursued.

According to Yangxian et al. (2012), in case hydrogen peroxide is used for oxidation, the reaction is as shown in Equation 21. UV/ $H_2O_2$ /CaO process had reached a NO reduction between 40 % to 60 % when  $H_2O_2$  concentration ranged from 0.5 to 2.5 mol/l. (Yangxian et al. 2012)



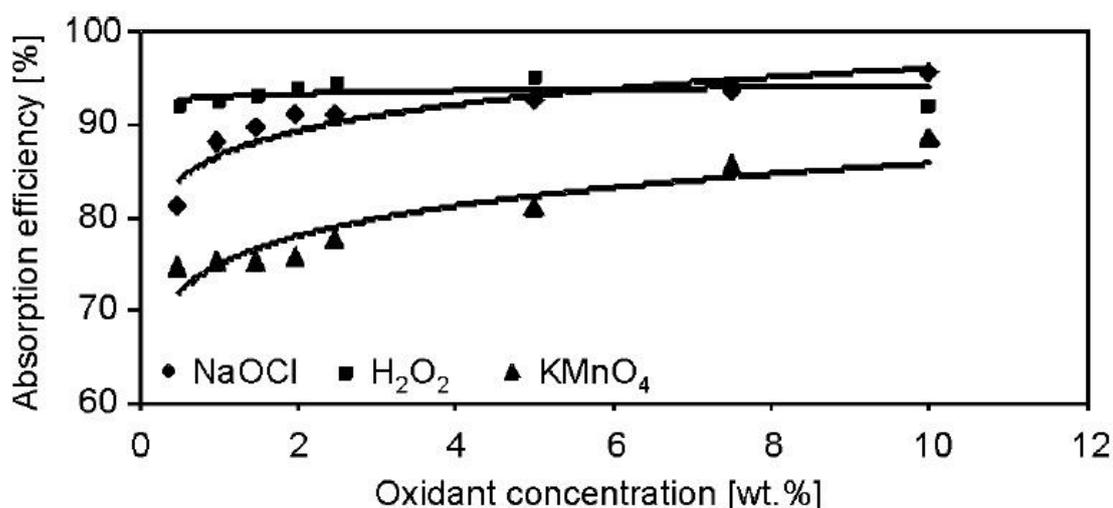
Temperature windows of NO removal by injection of hydrogen peroxide, methanol and their mixture in the molar ratio of 1:1 are presented in Figure 48, which shows that  $H_2O_2$  is most effective at the temperature range of 480-580 °C. Use of  $CH_3OH$  is not recommended since it results in increased CO emission. (Zamansky et al. 1996, 1, 3)



**Figure 48.** Temperature windows of NO removal by injection of H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>OH and their mixture of 1:1 molar ratio (Zamansky et al. 1996, 3)

According to Kiiskilä et al. (2000), introduction of the peroxide results in the conversion of the majority of NO<sub>x</sub> in the flue gases to N<sub>2</sub>O<sub>2</sub>, typically 60-90% and even more than 90%. The US patent 6146604A introduced a NO<sub>x</sub> removal method for recovery boiler where for example NO<sub>x</sub> content 100-150 ppm could be reduced to about 30-40 ppm.

Absorption efficiencies of NO as a function of oxidant concentrations for sodium hypochlorite (NaClO), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and potassium permanganate (KMnO<sub>4</sub>) are presented in Figure 49.



**Figure 49.** Effect of the addition of oxidant into 5 wt. % solution of NaOH on the absorption of nitrogen oxides at constant initial concentration of NO<sub>x</sub> of 3.5 g/m<sup>3</sup> gas, gas velocity of 0.2 m/s and spraying density of 20 m<sup>3</sup>/(m<sup>2</sup>h) (Kuroпка 2011, 16).

### 6.2.3 Scrubbing of oxidized NO<sub>x</sub>

Oxidized NO<sub>x</sub> can be removed in scrubber. The required scrubbing arrangement depends on the oxidation stage of nitrogen oxide. NO<sub>2</sub> is an acid gas that produces nitric acid by reaction with water as shown in Equation 22. Since the reaction rate is slow for NO<sub>2</sub>, use of scrubbing chemical is preferred. According to Kilpinen & Zevenhoven (2004), caustic solution can be used. Alkaline scrubbing solution can remove acid gases as NO<sub>2</sub> but since NO is not an acid gas, it cannot be removed with an alkaline solvent. (De Nevers 2000, 403)



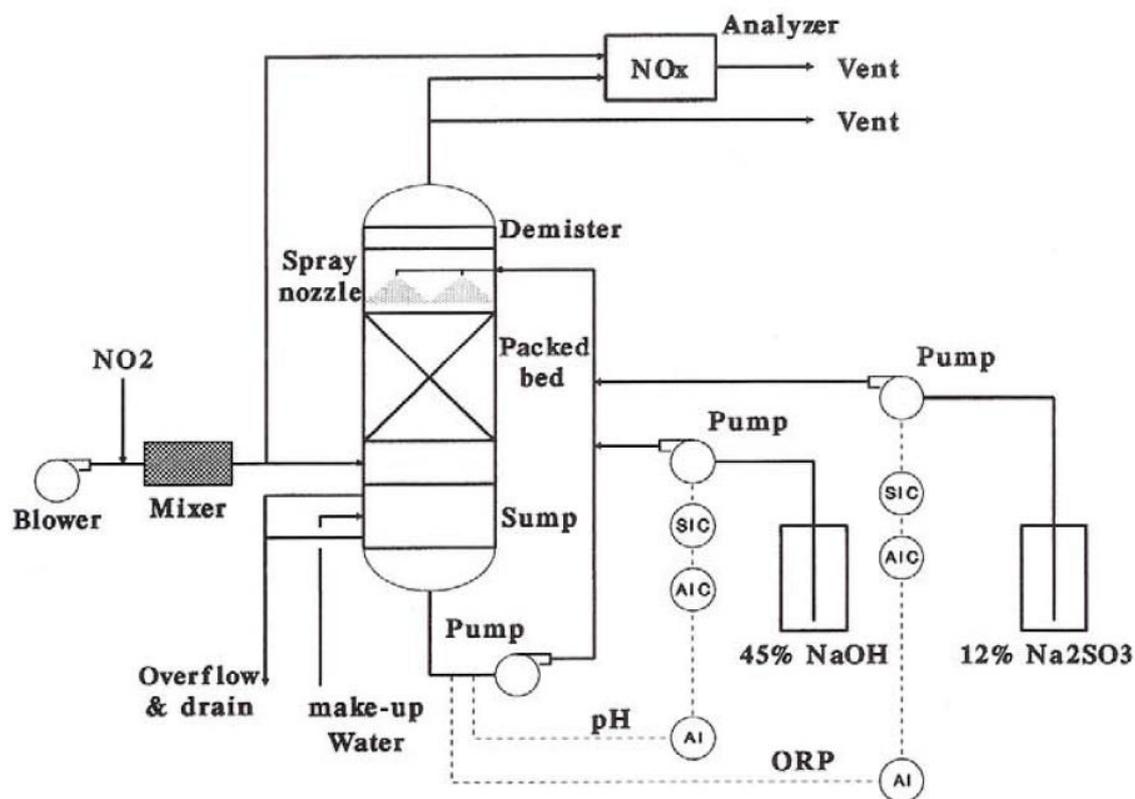
However, according to Kuroпка (2011), the NO reacts with similar molar ratio as NO<sub>2</sub> with NaOH as shown in Equation 23, but only as long as NO<sub>2</sub> is present and the remainder NO does not react with NaOH, but remains in the gas phase. Considering the majority of NO<sub>x</sub> in the flue gas is in the form of NO, NO<sub>x</sub> cannot be reduced significantly this way without oxidation step.



According to Deshwal & Lee (2009), NO<sub>2</sub> is also absorbed by chlorine dioxide as shown in Equation 24.

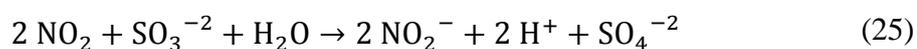


Schematic of the pilot  $\text{NO}_2$  scrubbing plant is presented in Figure 50.

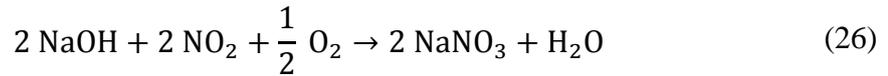


**Figure 50.** Schematic of the pilot plant gas scrubbing system (Chen et al. 2002, 4)

According to Chen et al. (2002), the overall reaction in the packed tower scrubber may be described by the Equation 25 and sulfate ion is the principal end product in the solution after complex reaction mechanism.



According to Cottrell (2003), when nitrogen and sulfur oxides are absorbed in a wet scrubber vapor forms produce nitric and sulfuric acid solution which has to be neutralized and recovered by using caustic solution. Reactions in caustic scrubbing introduced by Cottrell (2003) are described by the Equations 26 and 27. Formed nitrate solution could be then discharged to sewer system. Reaction according to Equation 27 occurs also in scrubber using ozone as oxidizer.

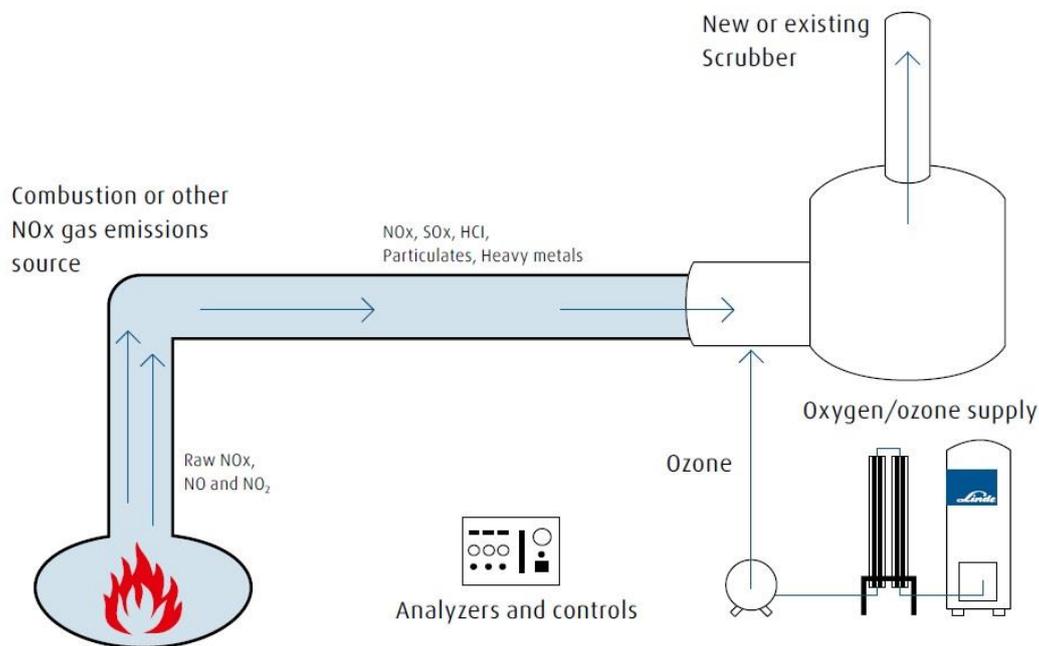


According to Sohlberg (2007), second stage of pilot NO<sub>x</sub> scrubber in Gruvön recovery boiler absorbed NO<sub>2</sub> by Equation 28. Sodium sulphate was used as a scrubbing solution and it can be formed when SO<sub>2</sub> is first scrubbed using NaOH.



However, reaction according to Equation 28 was not completed successfully as gaseous NO<sub>2</sub> formed nitrate, NO<sub>2</sub><sup>-</sup>, in aqueous solution instead of gaseous nitrogen. (Sohlberg 2007)

Commercial LoTOx process is presented in Figure 51. In this process ozone is used to oxidize NO. Since ozone is not very stable molecule it is required to be produced shortly before injection which requires ozone generator consuming oxygen and electricity.



**Figure 51.** Illustration of LoTOx technology (Linde 2014, 2)

#### 6.2.4 Other challenges in NO<sub>x</sub> scrubbing

It is not only the required oxidation step which makes NO<sub>x</sub> scrubbing a demanding task. Oxidizer or scrubbing liquid is possibly consumed to by other pollutants in certain conditions. This should be avoided since increase in chemical consumption will result in high operating costs. For example, according to Yi et al. (2011), about 1.38 kg of NaClO<sub>2</sub> is needed to remove 1 kg of NO<sub>x</sub>, which indicates high absorbent cost. According to Deshwal & Lee (2009), ClO<sub>2</sub> is also supposed to scrub SO<sub>2</sub> via Equation 29.



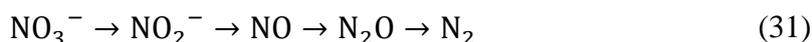
Therefore, SO<sub>2</sub> should be scrubber before NO<sub>2</sub>-scrubbing stage using for example NaOH so that ClO<sub>2</sub> would not be consumed for crubbing of SO<sub>2</sub> .

Exhaust gases from lime kiln contain more CO<sub>2</sub> than other combustion sources. Typical concentration of CO<sub>2</sub> in other combustion sources is around 12% which is 120 times the concentration of SO<sub>2</sub>. The problem is that CO<sub>2</sub> as an acid gas uses up sodium hydroxide as shown in Equation 30. (De Nevers 2000, 413)



Any sodium hydroxide consumed according to Equation 30 cannot be used for scrubbing of SO<sub>2</sub> or NO<sub>2</sub>. (De Nevers 2000, 413)

As was discussed earlier, nitrogen emissions turn into aqueous form. Then, for example biological denitrification should be applied to turn nitrate back into nitrogen. Biological denitrification is based on the capability of specific bacteria to use nitrate for respiration. This requires anaerobic conditions i.e. lack of oxygen. In the complete process reduction of nitrate to nitrogen gas occurs according to Equation 31. Also other denitrification methods are available. (World Health Organization 2004b, 108)



Scrubbing of NO<sub>x</sub> is preferably performed after the ESP due to the heavy dust concentration in the flue gas after cyclone. On the other hand, if flue gases reached dew point in the scrubber, they would require reheating before exiting through the stack to

avoid condensing of acid gases in the stack. Therefore, removing also SO<sub>2</sub> and other emission components would be advisable in the same scrubbing unit. (Cottrell 2003, 10)

In addition to scrubber itself, flue gas cooling is essential to reach suitable scrubbing temperatures. Flue gas cooler as heat exchanger, use of bleed air or water spray cooling tower would be required to cool the flue gases. This leads to higher pressure loss especially when multiple scrubbing stages are needed for scrubbing. Then higher power consumption results from increased size of the ID fan. (Cottrell 2003, 10)

According to Cottrell (2003), NO<sub>x</sub> scrubbing system designed for lime kiln or a similar source has never been demonstrated and, therefore, NO<sub>x</sub> scrubbing is not a technically suitable control technology for the lime kiln. However, if simultaneous removal of SO<sub>2</sub> and NO<sub>x</sub> is required scrubbing might prove to be effective method. Also, according to Richardson (2014), size of scrubber can be significantly reduced when NO<sub>x</sub> scrubbing is done in mist or gas phase using ClO<sub>2</sub> as rapid reaction is achieved. Besides, if mill has need for supplementary low value heat, which could be used e.g. to biomass drying, purchasing a flue gas cooling unit is not directly an additional cost.

### **6.3 Sorption**

Both adsorption and absorption are considered. When sorbents are injected to flue gas NO<sub>x</sub> and other pollutants can be removed. Known possible sorbents are ammonia, powdered limestone, aluminum oxide or carbon. Besides, zeolite can be used as sorbent and also other transition metal compounds and transition metals have given good results. Use of aluminum oxides has been studied for simultaneous SO<sub>2</sub> and NO<sub>x</sub> removal, and it was observed that alkalizing of Al<sub>2</sub>O<sub>3</sub> increases SO<sub>2</sub> removal efficiency. Sorption can be used in combustion chamber and flue gas zone. Usually dry sorbent is preferred, but slurries also have been used. Filtration or electrostatic precipitation (ESP) is used to remove the sorbent. (Ehrhard 1999, 11; Qvintus-Leino 1988, 23, 30)

In the 1990s NO<sub>x</sub>SO process was known for simultaneous removal of nitrogen oxides and sulfur dioxide. According to Black (1993), the NO<sub>x</sub>SO process is a dry, post-combustion flue gas treatment technology which uses regenerable sorbent to simultaneously adsorb sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>). In the process, the SO<sub>2</sub> is converted to sulfur by-product which is in the form of elemental sulfur, sulfuric acid, or liquid SO<sub>2</sub>.

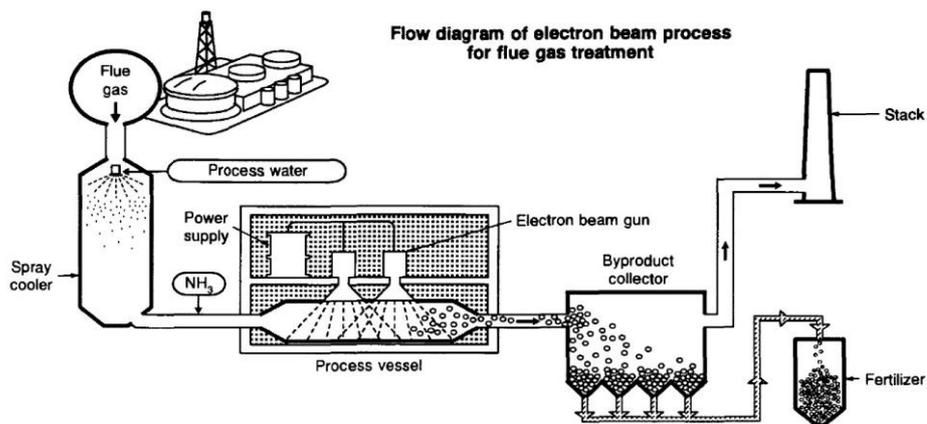
Respectively, NO<sub>x</sub> is converted to nitrogen and oxygen in the process. Activated carbon can be used with ammonia injection and the commercial technology is known as C-SCR. Using ammonia was introduced in chapter 6.1 when SNCR and SCR methods were discussed.

Moisture content of the flue gases limits the usage of sorbents because in the wet flue gas H<sub>2</sub>O will be absorbed instead of NO. Because flue gases of lime kiln are rich in moisture especially after LMD unit, absorption cannot be readily applied. Moisture content of the flue gases could be reduced for example by diluting flue gases with ambient air. (Qvintus-Leino 1988, 23)

#### 6.4 Electron-beam flue gas treatment

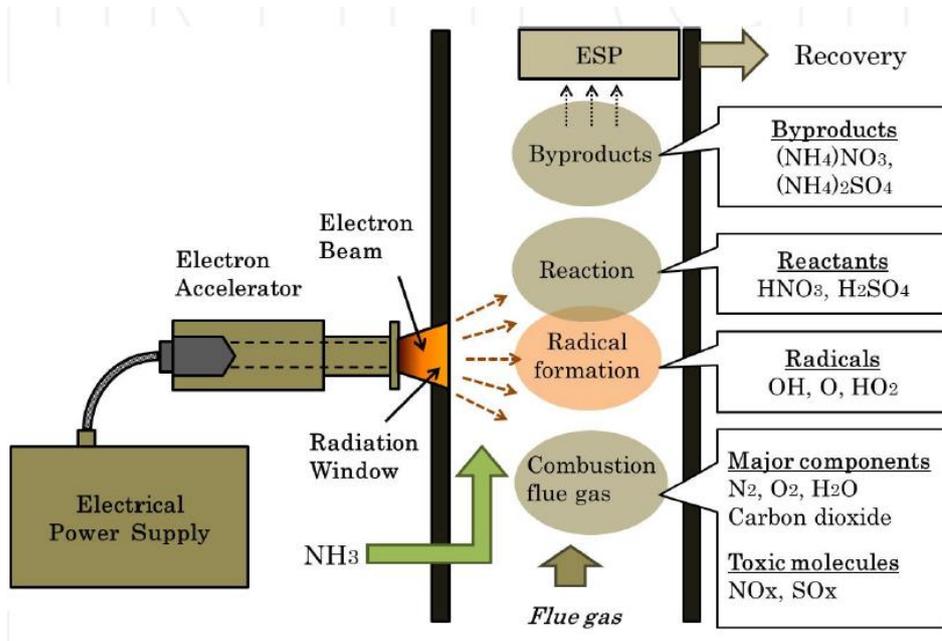
Electronic-beam flue gas treatment (EBFGT) is a dry-scrubbing process of simultaneous NO<sub>x</sub> and SO<sub>2</sub> removal. EBFGT technology is usually applied as a combination of ammonia based SCR and wet flue-gas desulfurization (FGD). Fertilizer can be gained as a by-product of the process. EBFGT allows also removal of VOCs. (Doutzkinov et al. 2011, 1; Basfar et al. 2010, 1)

Flow diagram of the electron beam process for flue gas treatment is presented in Figure 52.



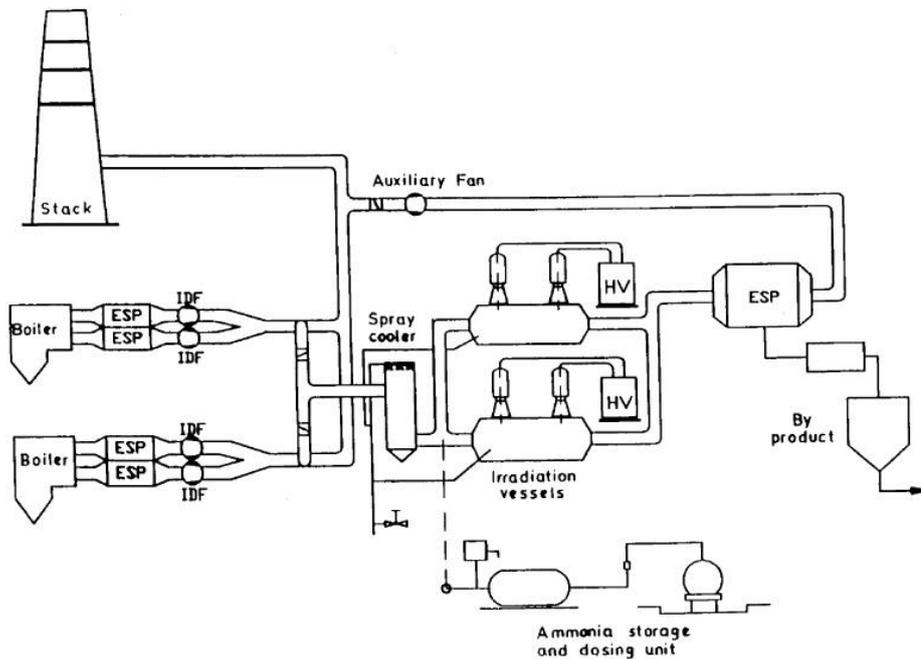
**Figure 52.** Flow diagram of electron beam process for flue gas treatment (Frank & Marcovic 1994, 3)

Principle of combustion flue gas treatment by electron beam is presented in Figure 53.



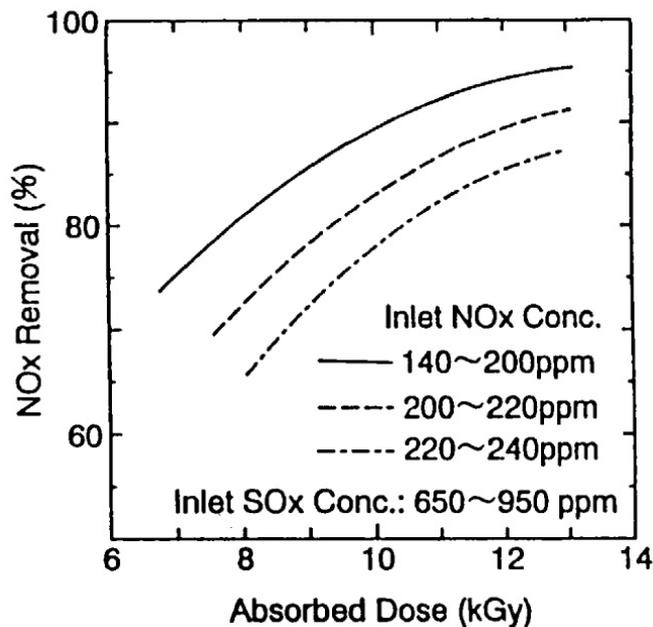
**Figure 53.** Principle of combustion flue gas treatment by electron beam (Matsumoto et al. 2012, 218)

According to Edinger (2008), seven installations regarding EBFGT have been done in the scale of  $20\,000\text{ Nm}^3/\text{h}$  or larger. For example, two Benson type boilers have applied EBFGT at the EPS Pomorzany in Poland. Process arrangement is introduced in Figure 54. Flue gases have a maximum flow rate of  $270\,000\text{ Nm}^3/\text{h}$  and the total electron beam power is equal to 1 MW. Two electron accelerators are installed in series to two separate process vessels. Power of each accelerator is 260 kW and voltage 700 keV. Removal efficiency is between 50–70 % for  $\text{NO}_x$  and 85–95 % for  $\text{SO}_2$ , which requires dose in the range of 7–12 kGy (kJ/kg). Additional ESP collects the formed fertilizer which is the by-product of the process. Fertilizer is transported to fertilizing plant. (Basfar et al. 2010, 2)



**Figure 54.** Scheme of industrial-demonstration plant at EPS Pomorzany (Licki 2003, 8)

According to Licki et al. (2003), NO<sub>x</sub> removal efficiency is affected mainly by irradiation dose, gas temperature, ammonia injection, multi-stage irradiation and flue gas humidity. Dose dependence of the NO<sub>x</sub> removal efficiency is presented in Figure 55.



**Figure 55.** Dose dependence of the NO<sub>x</sub> removal efficiency (Licki et al. 2003, 6)

According to Licki et al. (2003), flue gases should be cooled down to 50-80 °C. Also additional ESP would be required to collect the formed by-product and the occasional heavy dust concentration might cause problems. Applying EBFGT is not profitable unless there is a need or market for fertilizer. Therefore, EBFGT is not competitive for NO<sub>x</sub> removal in lime kiln.

## 7 FINANCIAL ANALYSIS FOR NO<sub>x</sub> REDUCTION

When comparing NO<sub>x</sub> reduction methods, both capital expenditure (CAPEX) and operating expenditure (OPEX) should be noted in the total cost. The investment cost is the most significant part of capital expenditure but also installation cost and interest payables have an effect on the CAPEX. In general, most of the operational expenditure consists of chemical consumption in NO<sub>x</sub> removal systems but also electricity consumption and other consumables have to be taken into account.

### 7.1 NO<sub>x</sub> removal cost for lime kiln

Environmental Protection Agency introduces NO<sub>x</sub> removal methods to fulfill the local emission regulations in the other words Menu of Control Measures for NAAQS implementation. NO<sub>x</sub> removal methods and costs for lime kiln are presented in Table 10 according to U.S. Environmental Protection Agency (2013).

**Table 10.** Menu of Control Measures and cost for NO<sub>x</sub> removal in lime kiln (U.S. Environmental Protection Agency 2013)

Emission Reduction Measure Name	Control Efficiency (%)	Cost * (€/ton)	Applicable to
Selective Catalytic Reduction	90	2560	Bituminous coal-fired cement kilns and coal-fired lime kilns
Selective Non-Catalytic Reduction - Urea	50	930	Bituminous coal-fired cement kilns and lime kilns
Low NO <sub>x</sub> Burner	30	900	Lime kilns
* unit converted to 2014€/ton (metric) from 2006\$/ton (short), conversion is based on the currency ratio 1 € = 1.25 \$ and the cost is rounded to closest ten.			

Cost given by EPA includes both capital and operational expenditures and the basis for the cost estimate is the annual NO<sub>x</sub> removal cost. Costs are applicable with uncontrolled NO<sub>x</sub> emissions greater than 10 tons per year. (U.S. Environmental Protection Agency 2013)

## **7.2 NO<sub>x</sub> removal costs compared to other applications**

As there is no SCR or SNCR installations made in rotary lime kilns, NO<sub>x</sub> removal costs from other units could give understanding of the removal costs. Typical cost for SNCR in power boilers has been 1500-2000 €/ton NO<sub>x</sub> removed including the investment, operating and maintenance costs. Typical cost for SCR in power boilers has been 3000-4000 €/ton NO<sub>x</sub> removed including the investment, operating and maintenance costs. With the SCR in power boilers usually a NO<sub>x</sub> reduction of 80-90 % is achieved. Cost for SNCR ranges widely depending on the process category. According to ICAC small rotary lime kiln would represent a high cost application and the lower cost applications are typically large hazardous waste incinerators and large bubbling bed/fluidized bed boilers and large wood-fired stokers. (ICAC 2008, 7; Jalovaara et al. 2003, 68)

The NO<sub>x</sub>SO process was introduced in Chapter 6.3. According to Black (1993), cost for NO<sub>x</sub> removal was estimated to be 1090 €/ton NO<sub>x</sub> consisting investment, operating and maintenance costs for the 500 MW power plant burning 3% sulfur coal where cost of sorbent represented 41 % of the total costs. It can be concluded that in the large scale installations the cost per removed NO<sub>x</sub> ton is lower.

## 8 CONCLUSION

Current status of NO<sub>x</sub> emission levels and requirements were investigated, especially in the European Union. Also different nitrogen oxide removal technologies for rotary lime kiln were studied in this thesis. Post-combustion methods were investigated in more detail as potential possible NO<sub>x</sub> removal with combustion methods in rotary lime kiln is more limited. As many of the introduced methods were used in different application than lime kiln, the suitability of each technology had to be considered case by case. At present NO<sub>x</sub> emissions are mainly dependent on to the kiln burner design, to the fuel nitrogen content and combustion temperature. According to EU, Best Available Technologies for NO<sub>x</sub> removal in lime kiln are (1) Optimised combustion and combustion control, (2) Good mixing of fuel and air, (3) Low-NO<sub>x</sub> burner and (4) Fuel selection/low-N fuel. However, emission regulations are expected to tighten globally in the future. Therefore it is essential to investigate the effectiveness and costs of post-combustion methods for NO<sub>x</sub> removal.

When NO<sub>x</sub> reduction is discussed it is important to know the initial NO<sub>x</sub> level, NO<sub>x</sub> concentration after NO<sub>x</sub> removal and the oxygen content to which the concentration are reduced, otherwise the results are not comparable. SNCR method appears to be the most suitable technique for NO<sub>x</sub> removal in lime kiln when NO<sub>x</sub> removal from 50% to 70% is required. SNCR is a small-scale installation compared to SCR or NO<sub>x</sub> scrubbing. By using SCR better NO<sub>x</sub> reduction can be achieved but issues with catalyst materials are expected to arise because of the dust and sulphur dioxide content of the flue gases. On the other hand, when using a combination of primary methods, as low NO<sub>x</sub>-burner and low nitrogen content fuel low NO<sub>x</sub> emission can be achieved. However, then lime kiln fuel selection is more limited.

SNCR or SCR technologies are not recognized as BAT technologies for lime kiln which is due to fact that there is no SNCR or SCR installations made for rotary lime kiln so far. Therefore, limit for ammonia slip has not been defined for the lime kiln in the pulp and paper industry. However, both SNCR and SCR are BAT for cement kiln. The experiences from the commercial SNCR and SCR installations are so far from the cement industry. If SNCR or SCR became common technology for lime kilns, the upcoming emission limit for ammonia slip influences to the decision between SCR and SNCR technologies. Current legislation allows reasonably high limits for NH<sub>3</sub>-slip in cement kiln.

NO<sub>x</sub> scrubbing was also investigated and it has potential when simultaneous NO<sub>x</sub> and SO<sub>2</sub> removal is required. NO cannot be scrubbed directly, but once it is oxidized to NO<sub>2</sub> scrubbing can be performed as the solubility of NO<sub>2</sub> is higher. Scrubber only for NO<sub>x</sub> removal was not recognized as a potential option due to both high investment and operating costs. Operating cost consist mostly of the oxidizing agent like ozone or chlorine dioxide. High occasional particulate matter concentration in the flue gas is challenging for the scrubber. Also flue gases have to be cooled down significantly which means basically that flue gas cooler and for further cooling spraying tower need to be installed. On the other hand, flue gases rich in SO<sub>2</sub> could be used so that, NaSO<sub>3</sub>, a chemical for NO<sub>2</sub> scrubbing could be produced in one scrubber stage. Also, if there is use for the lower temperature heat stream at the mill, flue gas cooler would be needed in any case which would be favourable considering scrubbing.

There is no universal solution if secondary NO<sub>x</sub> removal is wanted to fit rotary lime kiln. Applying of SCR is more or less limited by SO<sub>2</sub> and dust content of flue gases. Applying SCR successfully as universal NO<sub>x</sub> removal method would require reheating of flue gas because of ammonia bisulfate or other catalyst poison formation in lower flue gas temperature. Also applying SNCR requires kiln modification and the challenging part is the installation due to rotation of kiln. NO<sub>x</sub> scrubbing requires flue gas to be cooled down significantly. However, regarding current legislation, sufficient NO<sub>x</sub> removal can be achieved using presently available abatement technologies but then fuels resulting in high NO<sub>x</sub> formation cannot be necessarily burned in all locations or permission limits have to be reapplied. Some of secondary methods could be seen as commonly applied technology for lime kiln in the future, for example, during the time span of ten years. Most likely SNCR is applied first due to lower capital cost and the fact that emission regulations do not require very high degree of NO<sub>x</sub> reduction at present. But state of affairs can be changed for example after five years favouring SCR or NO<sub>x</sub> scrubbing.

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Technique	Description	Advantages	Disadvantages	Impacts	Applicability
Less Excess Air (LEA)	Reduces oxygen availability	Easy modification	Low NOx reduction	High CO Flame length Flame stability	All fuels
Off Stoichiometric: Over Fire Air (OFA)	staged combustion	Low cost	Higher air flow for CO	Flame length	All fuels
Flue Gas Recirculation (FGR)	<30% flue gas recirculated with air, decreasing temperature	High NOx reduction potential for low nitrogen fuels	Moderately high capital cost and operating cost Affects heat transfer and system pressures	Fan capacity Furnace pressure Burner pressure drop Turndown stability	All fuels Low nitrogen fuels
Water/Steam Injection	Reduces flame temperature	Moderate capital cost NOx reduction similar to FGR	Efficiency penalty Fan power higher	Flame stability Efficiency penalty	All fuels as Low nitrogen fuels
Reduced Air Preheat	Air not preheated, reduces flame temperature	High NOx reduction potential	Significant efficiency loss (1% per 22°C)	Fan capacity Efficiency penalty	All fuels Low nitrogen fuels
Selective Catalytic reduction (SCR)	Catalyst located in the air flow, promotes reaction between ammonia and NOx	High NOx removal	Very high capital cost High operating cost Catalyst siting Increased pressure drop Possible water wash required	Space requirements Ammonia slip Hazardous waste Disposal	All fuels
Selective Non-Catalytic Reduction (SNCR) a. urea b. ammonia	Inject reagent to react with NOx	a. Low capital cost Moderate NOx removal Non-toxic chemical b. Low operating cost Moderate NOx removal	a. Temperature dependent NOx reduction less at lower loads b. Moderately high capital cost Ammonia storage, handling, injection system	a. Furnace geometry Temperature profile b. Furnace geometry Temperature profile	All fuels
Fuel Reburning	Inject fuel to react with NOx	Moderate cost Moderate NOx removal	Extends residence time	Furnace temperature profile	All fuels (pulverized solid)
Combustion Optimization	Change efficiency of primary combustion	Minimal cost	Extends residence time	Furnace temperature profile	Gas Liquid fuels
Catalytic Combustion	Catalyst causes combustion to be at low temperature	Lowest possible NOx	Very high capital cost High operating cost Catalyst siting	Space requirements Disposal	Gas Liquid fuels

Detailed summary of external combustion NOx limiting technologies (Ehrhard 1999) - Appendix I (2/2)

<b>Technique</b>	<b>Description</b>	<b>Advantages</b>	<b>Disadvantages</b>	<b>Impacts</b>	<b>Applicability</b>
Non-Thermal Plasma	Reducing agent ionized or oxidant created in flow	Moderate cost Easy siting, High NOx removal	Fouling possible Ozone emission possible	Uses electrical power	All fuels
Inject Oxidant	Chemical oxidant injected in flow	Moderate cost	Nitric acid removal	Add-on	All fuels
Oxygen instead of Air	Uses oxygen to oxidize fuel	Moderate to high cost Intense combustion	Eliminates prompt NOx Furnace alteration	Equipment to handle oxygen	All fuels
Ultra-Low Nitrogen Fuel	Uses low-nitrogen fuel	Eliminates fuel NOx No capital cost	Slight rise in operating cost	Minimal change	All ultra-low nitrogen fuels
Use Sorbents (add-on technology) in: a. Combustion b. Duct to Electrostatic Precipitator	Use a chemical to absorb NOx or an adsorber to hold it	Can control other pollutants as well as NOx Moderate operating cost	Cost of handling sorbent Space for the sorbent storage and handling	Add-on	All fuels
Air Staging	Admit air in separated stages	Reduce peak combustion temperature	Extend combustion to a longer residence time at lower temperature	Adds ducts and dampers to control air Furnace modification	All fuels
Fuel Staging	Admit fuel in separated stages	Reduce peak combustion temperature	Extend combustion to a longer residence time at lower temperature	Adds fuel injectors to other locations Furnace modification	All fuels