INTRODUCTION

Sustainable urban development needs a reliable supply of heat and power as well as efficient treatment of Municipal Solid Waste (MSW). New technologies for generating Energy from Waste (EfW) will be of central importance in providing solutions in order to meet these needs. In Europe, the more progressive cities use EfW as source of energy and district heating. The emissions from EfW plants are strictly limited by the EU Incineration Directive, which sets the limit on NOx emissions, for example, to 200 mg/m$^3$. Moreover the need for further improvement is reflected by new German legislation effective as of 27 January 2009, requiring 100 mg/m$^3$ (Umweltministerium, 2009), which at an $O_2$ of 7.5% is equivalent to a NOx of 74 mg/m$^3$ (referred to 11% $O_2$). In the Netherlands, there has long been a limit of 80 mg/m$^3$. In France, a TGAP tax reduction has been granted since 2009 provided that NOx values of less than 80 mg/m$^3$ are reached in combination with high energy efficiency. Other countries are expected to follow due to the national emission ceilings stipulated in the Gothenburg protocol and the resultant EU directive 2001/81/EC.

Figure 1: German EfW plants sorted by DeNOx technology and yearly average emission (Lahl, 2007)
As shown in Figure 1, Selective Catalytic Reduction (SCR) technologies were used in most cases to achieve the above-mentioned reduced NOx limits. However, there are drawbacks to SCR systems such as high investment costs and the energy consumption necessitated by the reheating of flue gas as well as the increased pressure loss.

Consequently, SCR falls short of the efforts to increase energy efficiency encouraged by the EU Waste Framework Directive and its R1 requirement of 0.65 for new plants. New technologies are therefore required to make it possible to reconcile both requirements: reduced emissions and increased energy efficiency.

This presentation will describe and assess three promising EfW technologies that comply with these requirements:

- SNCR technology (SNCR = Selective Non Catalytic NOx Reduction)
- SNCR with boiler integrated slip catalyst (reduced pressure loss and no pre-heating necessary)
- VLN system (Very Low NOx combustion system: “VLN gas” is drawn off at the rear end of the grate and is reintroduced into the upper furnace just below the SNCR injection positions)

**FORMATION OF NOX IN EfW PLANTS**

NOx is the generic term for nitrogen oxides. The oxides emitted during the combustion of waste are nitric oxide (NO), nitrogen dioxide (NO\(_2\)) and nitrous oxide N\(_2\)O.

The NOx limit value is given as a converted NO\(_2\) value, even though more than 95% of nitrogen oxides are emitted in the form of NO. NO is formed mainly in the furnace, while NO\(_2\) is formed mainly after emission into the atmosphere by the oxidation of NO with the air oxygen or ozone (O\(_3\)). The latter process occurs slowly and plays a minor role in the hot flue gas.

In principle, the current standard of knowledge differentiates between three mechanisms for the formation of NO depending on the nitrogen source and the reaction medium:

- **“Thermal NO”** is produced by oxidation of atmospheric molecular nitrogen and notably occurs at very high temperatures above 1500 °C (Weichert, 2000; Zeldovich, 1946). Due to the relatively low flue gas temperature levels usually present in EfW, the formation of thermal NO can be regarded as negligible.
- **“Prompt NO”** appears in the area of the flame front (reaction zone) under fuel-rich conditions at lower temperatures. However, it is generally accepted that prompt NO represents an insignificant part in the overall NO formation, especially for the combustion of solid fuels such as coal or waste.
- **“Fuel NO”** is by far the most predominant mechanism in the case of EfW. Municipal waste contains chemically-bound nitrogen in the form of organic (e.g. amine, amide, nitrile) or inorganic nitrogen compounds NH\(_3\) and HCN. Depending on the combustion conditions, either N\(_2\) or NO is formed with NH\(_i\) as an intermediate product.

Based on the predominant fuel NOx mechanism, the N content in the waste as well as combustion conditions such as temperature, air distribution and residence time will be crucial for predicting the NOx levels in the flue gas. According to Seifert (2003), the NOx content of MSW is around 1%. The origin of the Nitrogen in the waste is further detailed in Table 1.
### Table 1: Contributions to total Nitrogen content in MSW (Seifert, 2003)

<table>
<thead>
<tr>
<th>Carrier of N</th>
<th>% of N in carrier (referred to total N in waste)</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proteins</td>
<td>&gt;30</td>
<td>Food waste, garden waste, leather, fine fraction, paper</td>
</tr>
<tr>
<td>Polyamides</td>
<td>20</td>
<td>Textiles, plastics</td>
</tr>
<tr>
<td>Polyurethanes</td>
<td>&lt;10</td>
<td>Plastics, hard and soft foams (e.g. in shoes)</td>
</tr>
</tbody>
</table>

The key to drawing conclusions from the NOx mechanism is to understand that under oxidizing conditions, the NH\textsubscript{i} components released from the fuel react with molecular oxygen and oxygen containing radicals O and OH to nitric oxide NO:

\[
\text{NHi} + \text{O}_2 \leftrightarrow \text{NO} + \text{HiO} \quad \text{Equation 1}
\]
\[
\text{NHi} + \text{OH} \leftrightarrow \text{NO} + \text{H}_{i+1} \quad \text{Equation 2}
\]
\[
\text{NHi} + \text{O} \leftrightarrow \text{NO} + \text{H}_i \quad \text{Equation 3}
\]

Under oxygen-poor conditions, NO formation is inhibited because of the low concentration of oxidizing radicals and the NH\textsubscript{i} radicals are converted preferentially with a nitrogenous component to molecular nitrogen N\textsubscript{2} (Fenimore, 1976):

\[
\text{NHi} + \text{NO} \leftrightarrow \text{N}_2 + \text{HiO} \quad \text{Equation 4}
\]

Figure 2 shows a summary of the most important reaction steps in the fuel NO formation process.

#### Figure 2: Overview of the most important steps of fuel NO formation (NO recycle only relevant in fuel-rich conditions; simplified reaction from HCN to NH\textsubscript{i}: HCN + OH \rightarrow NH\textsubscript{2} + CO)

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**SELECTIVE NON CATALYTIC NO\textsubscript{X} REDUCTION (SNCR)**

SNCR systems are based on the selective reaction of ammonia [NH\textsubscript{3}] or urea [CO(NH\textsubscript{2})\textsubscript{2}] at temperatures of 850 to 1100\textdegree C. At the right temperature, these reactants reduce the NO to N\textsubscript{2} in a sufficiently reactive way without being oxidized by the excess oxygen of the combustion gases (Lyon 1987). Today’s research focuses on the development of simplified reaction mechanisms to be implemented in Computational Fluid Dynamics (CFD) codes. With these tools it will be possible to describe the interaction between turbulent mixing, radiation and chemical reaction rates.
Figure 3: Reaction paths of NH$_3$ and NO (Baumbach, 1990)

From the mechanism in Figure 3 it can be concluded that efficient SNCR is based on the combination of different factors:

- sufficient stoechiometry of injected reactants
- efficient mixing of reactants with flue gases
- sufficient retention time (at temperature level)
- optimal excess oxygen content

The stoechiometry is defined by

$$\beta = \frac{\dot{n}_{NH_3}}{\dot{n}_{NO}}$$

($\dot{n}_{NO}$ being the difference of NO before and after the SNCR reaction)

In an ideal case of mixing and reactivity, the best results could be attained with a $\beta = 1$. In practice only 50 - 60% of NOx reduction is reached with the addition of ammonia or other reductants at a stoechiometry of 2 (Dittrich, 2002).

Laboratory experiments show that retention times of 50 ms are sufficient for the SNCR reaction. In practice it is necessary to obtain retention times at suitable temperatures of up to 1 s in order to reach reasonable reduction rates. This is mainly due to the fact that the mixing and turbulence is insufficient in incineration furnaces.
An example of a typical EfW plant with emission value limits according to the European Waste Incineration Directive (WID) is shown in Figure 5 (Spliethoff 2009). The WID requires a NOx value of 200 mg/Nm$^3$ (EU commission, 2000). These systems also reach ammonia slip values of below 10 mg/m$^3$s as often required in permits according to the BREF (EU commission, 2006; if not mentioned otherwise: all emission values are meant to be daily average values referred to 11% O$_2$).
SNCR WITH SLIP CATALYST

In many cases SNCR technologies are limited by the ammonia slip which increases in case of severe NOx requirements. According to the BREF, a limit of 10 mg/Nm$^3$ is generally required at stack (EU commission, 2006). In order to achieve reduced NOx values of 70 to 100 mg/Nm$^3$, it is necessary to implement measures to reduce ammonia slip, as indicated in Figure 7, by means of either a wet scrubber (shifting the ammonia problem to the waste water) or a slip catalyst.

As shown in Figure 6, the operation point of the SNCR is preferably shifted to lower temperatures in SNCR systems with slip catalyst. This results in a reduced stoechiometry with a higher NH$_3$ slip.

![Figure 6: SNCR operation with slip catalyst. Injection position preferably shifted to lower temperatures](image)

EfW plants in Mainz (Germany) and Brescia (Italy) are examples of operational plants which use SNCR with a slip catalyst.

Table 1: Performance of SNCR with slip catalyst at the Brescia plant (Rossignoli, 2010)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Slip catalyst</th>
<th>Unit</th>
</tr>
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<tbody>
<tr>
<td>NO$_x$</td>
<td>Without</td>
<td>With</td>
</tr>
<tr>
<td></td>
<td>80 - 90</td>
<td>60 - 70</td>
</tr>
<tr>
<td>NH$_3$ slip</td>
<td>10-30</td>
<td>2-6</td>
</tr>
<tr>
<td>NH$_3$ consumption</td>
<td>0,22</td>
<td>0,18</td>
</tr>
</tbody>
</table>
VERY-LOW NOX PROCESS

Another option for achieving NOx values below 100 mg/m³, without the necessity of additional scrubbers or catalytic converters for removing excess ammonia is the Very-Low NOx process (VLN), which has recently been developed by MARTIN GmbH with its cooperation partners CNIM, COVANTA and Mitsubishi Heavy Industries (MHI).

The VLN process is based on a classical grate-based combustion system for municipal waste, where the so-called “VLN gas” is drawn off at the rear end of the grate and is reintroduced into the upper furnace just below the ammonia injection positions (White et al., 2009). The positive effect of this patented process is twofold: On the one hand, drawing off the VLN gas leads to combustion conditions which promote the inherent NOx reduction processes such that fuel NOx is to a large extent reduced to nitrogen. On the other hand, the reinjection of the VLN gas cools the flue gases down and enforces their mixing with injected ammonia or urea. This leads to improved efficiency of the SNCR system (Gohlke, 2010; see also Figure 9).

The VLN gas has a temperature of below 300 °C. It is re-injected at a position where the furnace temperature is around 1000 °C. This typically corresponds to a level of 8 to 12 m above the grate, depending on the capacity of the unit and the type of waste. The overfire air pressures are reduced to around 10 mbar and are thus considerably less than in conventional EfW plant design. Nevertheless, superstoichiometric conditions are reached at the overfire air level, which is an advantage compared to air-staged or fuel-staged combustion systems. The residence time from the last combustion air injection at the overfire air level to the 850 °C level in the furnace is significantly increased. A further advantage of the VLN system is the reduced flue gas velocity in the lower furnace due to internal recirculation via the VLN duct. This leads to a reduction in the fly ash carried over to the boiler.
The VLN gas is re-injected into the front and rear side of the upper furnace, where the space between front and rear wall is narrowed. This leads to an intensive barrier of turbulence, which reduces the flue gas temperature and blocks the passage of flames or unreacted material. Given test plant results, corrosion is expected to be significantly reduced in the furnace above the VLN level as well as in the superheaters. However, temperatures between the overfire air and the VLN level are higher than in conventional combustion and higher grades of furnace protection material should be used there. Another advantage of the VLN system is the reduced excess air rate, which allows cost reduction in the boiler and flue gas cleaning and improves boiler efficiency.

The influence exerted on the SNCR efficiency by the temperature and excess oxygen content is illustrated in the diagram of Figure 9.
NOx values of 80 mg/m$^3_s$ with an NH$_3$ slip of less than 10 mg/m$^3_s$ have been reached in the test plant in Bristol/USA. Further test plants in Thiverval/France and Oita/Japan have confirmed these results. At the Thiverval plant, which has a municipal solid waste throughput of 12 t/h, NOx was reduced from 190 mg/Nm$^3$ to 80 mg/Nm$^3$ during test operation with the VLN components in 2008 (see Figure 10). Dry urea is used as the SNCR reagent in Thiverval.

Figure 9: NO$_x$ conversion with SNCR depending on temperature and excess oxygen content in the flue gas (Spliethoff 1999)

Figure 10: NOx reduction with the VLN process at the Thiverval EfW plant (results from 2008 testing)
CONCLUSIONS

Energy from waste systems have attained a high technological standard. In the EU, emissions from EfW plants are largely reduced by applying the Waste Incineration Directive (EU Commission, 2001) with its limit values for dioxins (PCDD/F), dust, NOx and many other pollutants. The new German legislation laid down in the 17. BImSchV requiring 100 mg/m$^3$s for future EfW plants indicates that further improvements are needed. The problem is that although more stringent emission value may become compulsory, an increase in energy efficiency will be encouraged by the Waste Framework Directive (EU Commission, 2008). Consequently, new technologies enabling the achievement of both requirements (reduced emissions and increased energy efficiency) are needed. Both SNCR with slip catalyst and the VLN technology described in this paper offer promising solutions to achieve these goals.

REFERENCES


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