

## Advertorial



## NO<sub>x</sub> reduction in a hazardous waste treatment plant via ozone injection and caustic wet scrubbing

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We present the results of a short full-scale trial of the LOTOX<sup>®</sup> technology at the Stade rotary kiln used for hazardous waste incineration. The tested process is a NO<sub>x</sub> reduction technique that can be implemented easily in existing plants, provided a wet scrubber exists. The NO<sub>x</sub> reduction effectivity can be enhanced by caustic scrubbing.

The original assumption that at least stoichiometric ozone feed was necessary to reduce NO<sub>x</sub> emissions still stands for scrubbing with water. The reduction mechanism includes total oxidation of NO and NO<sub>2</sub> to N<sub>2</sub>O<sub>5</sub> with subsequent absorption to water. This necessary ratio was vastly improved by the existing alkaline scrubber providing NaOH to react with NO and NO<sub>2</sub>, thus reducing NO<sub>x</sub> at a lower ozone-to-NO<sub>x</sub> ratio.

### 1 Introduction

The European commission is expected to publish the Best Available Techniques Reference Document (BAT Ref – BRef) for Waste Incineration in September 2019. This document includes Associated Emission Levels (AELs) for pollutants, especially regarding emissions to air and water. After the publication of a BRef there is a four-year transition time to comply with the new regulation. NO<sub>x</sub> is one of the pollutants that will have a lower allowed emission level and partially require plants to upgrade or alter their combustion and flue gas treatment setup. For existing plants, depending on their size, the actual value is 180 or 200 mg/Nm<sup>3</sup> (< 50 MW) respectively [1].

Table 5.4: BAT-associated emission levels (BAT-AELs) for channelled NO<sub>x</sub> and CO emissions to air from the incineration of waste and for channelled NH<sub>3</sub> emissions to air from the use of SNCR and/or SCR

Parameter	BAT-AEL (mg/Nm <sup>3</sup> )		Averaging period
	New plant	Existing plant	
NO <sub>x</sub>	50–120 (*)	50–150 (*)	Daily average
CO	10–50	10–50	
NH <sub>3</sub>	2–10 (*)	2–10 (*)	

(\*) The lower end of the BAT-AEL range can be achieved when using SCR. The lower end of the BAT-AEL range may not be achievable when incinerating waste with a high nitrogen content (e.g. residues from the production of organic nitrogen compounds).  
 (†) The higher end of the BAT-AEL range is 180 mg/Nm<sup>3</sup> where SCR is not applicable.  
 (‡) For existing plants fitted with SNCR without wet abatement techniques, the higher end of the BAT-AEL range is 15 mg/Nm<sup>3</sup>.

The techniques proposed in the BRef include Low-NO<sub>x</sub> burners, flue gas recirculation, selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR).

The addition of SCR in an existing plant can be a difficult task when it comes to space requirements and the addition of an SNCR requires the correct temperature window with a minimum retention

Figure 1. The Waste Incineration AELs according to BRef [1].

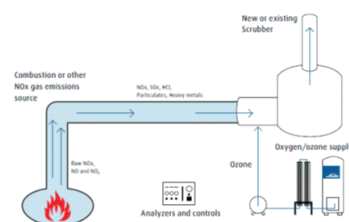


Figure 2. Schematic of the LOTOX<sup>®</sup> process [2]

time. Both technologies also require the addition of a new chemical to the plant's inventory, ammonia or urea. Additionally ammonia emission levels are also being tightened in Europe. This provides another challenge for waste incineration units which may struggle with lower allowed emission levels for  $\text{NO}_x$  and ammonia.

The rotary kiln, used as a test unit, has no dedicated DeNO<sub>x</sub> equipment and at present  $\text{NO}_x$  emissions are only controlled by adjusting the feedstock. The trials were done under the premise that only safe inlet  $\text{NO}_x$  levels were to be created to not exceed emission limits until the effect of LOTOX<sup>®</sup> was understood.

## 2 LOTOX<sup>®</sup> Technology

[2] presents LOTOX<sup>®</sup> as “a patented process for removal of  $\text{NO}_x$  and other pollutants from waste gas streams”. It is described as an end-of-pipe system that reduces  $\text{NO}_x$  emissions through total oxidation of Nitrogen Oxide species, e.g. NO and  $\text{NO}_2$ , to the soluble  $\text{N}_2\text{O}_5$  and absorption in a wet scrubbing system. The relevant theoretical reactions are:

- (1)  $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \text{ (g)}$
- (2)  $2 \text{NO}_2 + \text{O}_3 \rightarrow \text{N}_2\text{O}_5 + \text{O}_2 \text{ (g)}$
- (3)  $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 \text{ (g/l)}$

The first gas phase reaction is very rapid as well as the liquid/gas phase reaction. Previous LOTOX<sup>®</sup> literature and patents thus deem it necessary to first convert all NO to  $\text{NO}_2$  before being able to actually reduce the resulting  $\text{NO}_x$ .

Furthermore it is important to note, that the reduction of gaseous  $\text{NO}_x$  emissions comes at the cost of waste water treatment, in that case Nitrate handling ability.

## 3 Stade kiln pilot

The Stade kiln is a thermal treatment asset for hazardous waste with a capacity of 40 kt per year. It handles solids, liquids as well as production off-gases and operates at  $>1,000^\circ\text{C}$ . While the gaseous waste, or vent gases, are solely produced at the Stade site, the liquid and solid wastes are not limited to internal production, but also acquired from third party partners. The flue gas treat-

ment is designed for high chlorine, converted to HCl in the incineration, and particulate matter load.

Maximum utilization of the existing equipment as well as full-scale demonstration were important trial goals. Figure 3 shows a schematic of the kiln process: feed through the rotary kiln barrel and the SCC, steam generation in the boiler, a rapid quench before an HCl absorption column, a caustic scrubber using a scrubbing solution of sodium hydroxide (NaOH) for a resulting pH of 8...9 and an ionizing wet scrubber (IWS) followed by induced draft fan and stack.

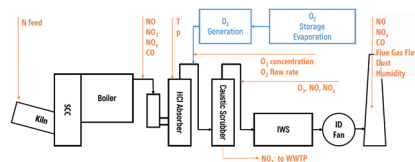


Figure 3. The Stade rotary kiln experimental setup

For the trial, a hand-held  $\text{NO}_x$ -analyzer was used at the boiler outlet. Ozone was injected between the HCl absorber and the caustic scrubber, using the piping between those two as reaction volume, while a second temporary analyzer was installed downstream of the caustic scrubber. The final  $\text{NO}_x$  emission values were retrieved through the continuous emission monitoring system (CEMS) of the plant. Both temporary devices did not include recording capability, limiting the test windows with valid data.

## 4 Equipment and implementation

The trial was set up to last several days with varying parameters in the operation of the kiln and the DeNO<sub>x</sub> equipment:

- Inlet  $\text{NO}_x$  was directly influenced by altering the feed composition
- Reaction time by adjusting the flue gas volume (base  $<1 \text{ s}$  at  $40,000 \text{ m}^3/\text{h}$ )
- Ozone was generated using either high oxygen flow and lower ozone concentration or low oxygen flow and high ozone concentration keeping the resulting mass flow of ozone constant

- Temperature ( $70^\circ\text{C}$ ) and pressure in the injection zone were not to be altered, only the concentration of hydrochloric acid (HCl) in the head space of the absorber was influenced by the absorbers concentration.

Oxygen was delivered as liquid oxygen (LOX) in a mobile pressure tank unit as seen in Figure 4. This tank is connected to an evaporator and a downstream pressure control unit prior to the containerized ozone generator [3] as seen in Figure 5.



Figure 4. Oxygen storage, evaporation and pressure control equipment (Linde AG)



Figure 5. Containerized ozone generator (Xylem Services GmbH)

The ozone generator converts up to 15 % by weight of oxygen to ozone. Data from the ozone generator was retrieved through a temporary connection to the plant's process control system. The ozone generator was supplied with electrical energy and cooling water.

Ozone injection into the piping was done through a mixing lance, consisting of a closed pipe with two rows of 2 mm holes. The reaction time was determined by the length of flue gas pipe from the top of the absorption column to the inlet of the caustic scrubber.

Test setup 01 was implemented on July 4<sup>th</sup> and 5<sup>th</sup>. It included:

- Measurement of inlet NO<sub>x</sub> using hand-held probe at the boiler outlet (downstream kiln, upstream of the HCl absorber and ozone injection)
  - Ozone injection following the HCl absorber upstream of the caustic scrubber
  - Measurement of intermediate NO<sub>x</sub> using ABB EL3020/URAS 26 directly downstream of the caustic scrubber and upstream IWS
  - Prior to 14:30 on July 04<sup>th</sup> intermediate NO<sub>x</sub> measurement downstream of ozone injection but upstream of the caustic scrubber
  - Measurement of O<sub>3</sub> using Teledyne analyzer directly downstream of the caustic scrubber and upstream IWS
  - Measurement of final NO<sub>x</sub> with the existing CEMS in the stack.
- Ozone injection following the HCl absorber upstream of the caustic scrubber
  - Measurement of final NO<sub>x</sub> with the existing CEMS in the stack.



Figure 6. Ozone injection port

Test setup 02 was implemented on July 16<sup>th</sup> and 17<sup>th</sup>. It included:

- Measurement of NO<sub>x</sub> downstream the caustic scrubber for intermediate NO<sub>x</sub> and residual ozone on the 16<sup>th</sup> and before ozone injection above the HCl absorber packing using ABB EL3020/URAS 26

The parameters and their respective impact on the results are found in Table 1.

## 5 Results and findings

Theoretically a molar ratio of 1.5 O<sub>3</sub> to NO is required to oxidize NO to NO<sub>2</sub> and then N<sub>2</sub>O<sub>5</sub>. Due to the temperatures in the rotary kiln NO<sub>x</sub> was expected to be >90 % NO with the remainder being NO<sub>2</sub>. Measurements taken throughout the trial confirmed NO<sub>x</sub> was primarily NO. Due to the reactive environment in the process where ozone is injected it was expected that a molar ratio of between 1.5 and 2 would be required to achieve NO<sub>x</sub> reduction rates in the magnitude of 90 % or higher.

Figure 7 shows the theoretical NO<sub>x</sub> reduction as a function of mass ratio of ozone to NO<sub>x</sub>. This mass ratio is calculated from the molar ratio for practical reasons.

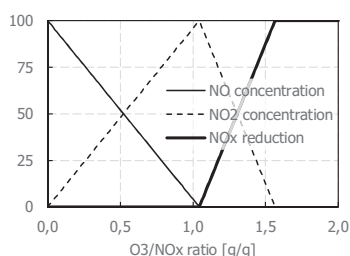


Figure 7. NO<sub>x</sub> reduction according LOTOX<sup>®</sup> mechanism

Initial testing on July 4<sup>th</sup> showed a higher than expected NO<sub>x</sub> reduction, see Figure 9. The stack (outlet) NO<sub>x</sub> was measured

approaching 0 mg/m<sup>3</sup>. The inlet NO<sub>x</sub> was back-calculated based on the measured stack (outlet) NO<sub>x</sub> and according to the ozone mass injected, using a theoretical molar ratio of 1.5. The measured inlet values were significantly higher than the calculated ones (Figure 9 right, “NO<sub>x</sub> boiler LOTOX calc”), indicating that a secondary mechanism had taken place, which improve NO<sub>x</sub> reduction and lowered the required molar ratio.

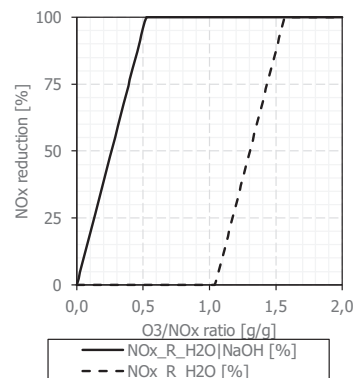


Figure 8. O<sub>3</sub>/NO<sub>x</sub> ratio shift in combined process

[4] proposes alkaline absorption as one method for NO<sub>x</sub> reduction but states that only nitrogen dioxide (NO<sub>2</sub>) has adequate solubility in alkaline solutions. Therefore, according to [4] a flue gas stream with nearly 100 % nitrogen monoxide (NO) must be partially oxidized to NO<sub>2</sub>. During the full-scale trial it was observed, that in fact, with a sub-stoichiometric application of LOTOX<sup>®</sup> (i.e. less than 1.5 moles of O<sub>3</sub> per mole of NO), a percentage of NO is partially oxidized to NO<sub>2</sub>. Now, the absorption reaction not only includes NO<sub>2</sub> but also NO:

Table 1. Test parameters and expected influence on results.

Parameter	Measurement	Control	Expected influence
Inlet NO <sub>x</sub>	01 continuous 02 non-continuous	Manual waste feed control	Increasing inlet concentration requires more ozone
Total flue gas flow	Continuous online	Manual waste feed control	Less total flow increases reaction time and improves NO <sub>x</sub> reduction
Ozone mass flow	Continuous online	Ozone generator setpoint	Increasing ozone injection increases NO <sub>x</sub> reduction up to the point of overdosing
Oxygen flowrate	Continuous online	Ozone generator setpoint	Higher oxygen flow increases mixing of ozone with flue gas and improves NO <sub>x</sub> reduction
Ionizing wet scrubber (stages) operation	Continuous online	Manual control	Additional scrubber volume improves NO <sub>x</sub> reduction if capacity of primary scrubber exceeded

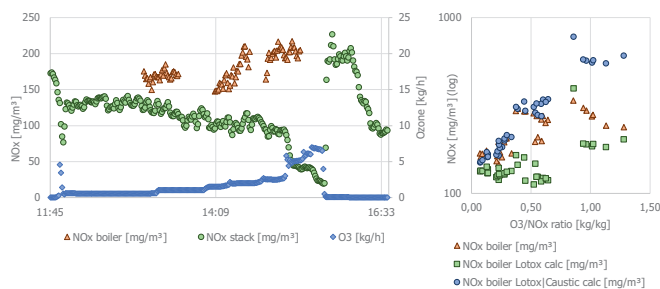
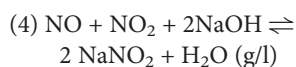
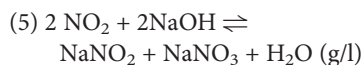


Figure 9. Initial testing results (left) and significant deviation between measured ( $\Delta$ ) and calculated ( $\square$ ,  $\circ$ ) inlet NO<sub>x</sub> (right)



Therefore, according to the above reaction, up to 50 % of NO should be partially oxidized using ozone to NO<sub>2</sub> to ensure efficient NO<sub>x</sub> removal in combination with a caustic scrubber, using NaOH. The back-calculation for that case (Figure 9 right, “NO<sub>x</sub> boiler LOTOX | Caustic calc”) shows a good fit with the measured values up to a molar Ozone ratio of 0.5 O<sub>3</sub>/NO<sub>x</sub>.

In case of NO excess, this NO will not react and remain in the gas phase. Any NO<sub>2</sub> excess on the other hand will be absorbed as follows:



[4] also states that NaOH is a very good absorption reagent for NO<sub>2</sub>.

Residual Ozone after the caustic scrubber was consistently measured below 5 ppm. On a few occasions 5 ppm was exceeded for a few seconds when O<sub>2</sub> flow rate was increased to 150 kg/h or coinciding with the ozone generator control loop spike when increasing ozone. The subsequent wet scrubbing in the IWS avoided unwanted ozone emission.

A caveat is the creation of Nitrite. Nitrate formation was expected, but not found to significantly increase in the effluent due to the short test time frame (less than 8 hours per day, across 3 weeks) and relatively high dilution rates in the plant. Nitrite needs to be further considered for permanent installation, particularly in regard to the impact on biological waste water treatment.

## 6 Conclusions

The combination of the (incomplete) oxidation of NO and the caustic scrubber results in a theoretical molar ratio of

0.5 O<sub>3</sub>/NO<sub>x</sub>, for 100 % NO<sub>x</sub> reduction. Compared to the LOTOX<sup>®</sup> requirement of 1.5 this not only contributes to energy and oxygen savings but also enables NO<sub>x</sub> reduction beginning at minimum Ozone feed. This enables LOTOX<sup>®</sup> to be used for small reductions without the necessary ‘overspending’ on Ozone (Figure 10).

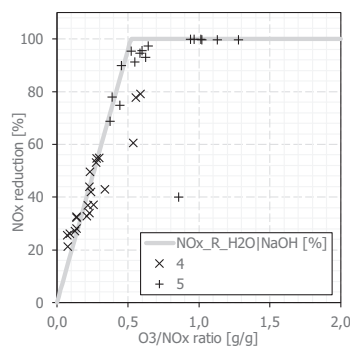


Figure 10. Results of the tests on July 4<sup>th</sup> and July 5<sup>th</sup>

The full-scale trial at Stade rotary kiln confirmed that the LOTOX<sup>®</sup> process worked as advertised and was capable of 100 % NO<sub>x</sub> reduction.

1. For plants that have a caustic scrubber, a low ozone consumption is possible while achieving high NO<sub>x</sub> reduction.
2. For plants that have a wet scrubber with water, a higher ozone consumption is expected, although optimizations like partial stream treatment seem probable and reasonable in terms of efficiency.
3. For plants with an SCR, [5] and [6] report an efficiency increase of SCR catalysts if a 50/50 mixture of NO and NO<sub>2</sub> can be achieved in the flue gas.

The advantage of the tested process is its ease of implementation via modular-

ized equipment and minimal process connection. Compared to the installation of a traditional SNCR/SCR there is no rotating equipment and no additional chemical storage needed. In case of a tail end SCR, which is recommended in high-dust applications, reheating the total flue gas stream would be necessary while LOTOX<sup>®</sup> works in the temperature range of the existing flue gas treatment.

LOTOX<sup>®</sup> is a very flexible process, and the trial demonstrated that ozone can be delivered in seconds to provide almost instantaneous NO<sub>x</sub> reduction.

For permanent operation a continuous online upstream NO<sub>x</sub> measurement is recommended and can be used to optimize ozone consumption and NO<sub>x</sub> removal.

Investment and operating cost comparisons must also be completed to ensure the business case is positive for permanent installation at specific sites. In summary, the LOTOX<sup>®</sup> process is an attractive treatment option for enhanced NO<sub>x</sub> control, particularly in cases with caustic scrubbing.

## Sources

- [1] JOINT RESEARCH CENTRE Directorate B, *Best Available Techniques (BAT) Reference Document for Waste Incineration*, 2018.
- [2] Linde AG, *LOTOX™ System – Low temperature oxidation for NO<sub>x</sub> control*.
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