Influences of non-SCR De-NO\textsubscript{x} technologies on NO\textsubscript{x} and dioxin emissions in full scale MSW incinerators

Hongquan Zhou \textsuperscript{1,3}, Liu Hong \textsuperscript{1,2*}, Dezhen Chen \textsuperscript{1,2}, Jingtao Lu\textsuperscript{1,4}, Xueding Song \textsuperscript{1,3}

\textsuperscript{1} Thermal & Environmental Engineering Institute; Tongji University, Shanghai 200092, China
\textsuperscript{2} Shanghai Engineering Research Center of Multi-source Solid Wastes Co-processing and Energy Utilization Tongji University, Shanghai 200092, China
\textsuperscript{3} Shanghai Institute for Design & Research on Environmental Engineering Co., Ltd, Shanghai, 200031, China
\textsuperscript{4} School of Civil and Environmental Engineering, Residues and Resource Reclamation Centre, NEWRI, Nanyang Technological University, 1 Cleantech Loop, #06-08, Singapore 637141

* Corresponding author.
E-mail: 96hongliu@tongji.edu.cn; Tel: 0086-21-69584657;
Address: No. 4800, Caoan Road, Jiading District, Shanghai 201804, China.

Abstract

To meet the increasingly stringent NO\textsubscript{x} emission regulations, multi non-selective catalytic reduction (non-SCR) denitrification (De-NO\textsubscript{x}) technologies are adopted in municipal solid wastes (MSW) incineration plants; but their individual or joint impacts on NO\textsubscript{x} and dioxin emissions are not systematically investigated. In this research the emissions of NO\textsubscript{x} and dioxins from three MSW incineration plants were investigated, so that the impact of different non-SCR De-NO\textsubscript{x} technologies including selective none-catalytic reduction (SNCR), De-NO\textsubscript{x} with organic amine-containing compounds as reductants (so-called PNCR), flue gas recirculation (FGR) and air staged combustion (ASC) on NO\textsubscript{x} and dioxin emissions can be evaluated. The emission results are compared and linear regression analysis showed that SNCR is most effective for inhibiting NO\textsubscript{x} and dioxin emissions, therefore SNCR should be primarily chosen. PNCR is an optional technology and its performance should be further improved in order to replace SNCR. FGR level has a strong influence on dioxin emissions, with a lower level being better; ASC level has none decisive effect either for De-NO\textsubscript{x} or for dioxin emission control, but its higher level seems better. The recommended non-SCR De-NO\textsubscript{x} technology combination mode is SNCR + PNCR + FGR25 % + ASC80 %. This study provides valuable suggestion for choosing suitable non-SCR De-NO\textsubscript{x} technologies for cost-effectively controlling NO\textsubscript{x} and dioxin emissions.

Keywords: MSW incinerator, De-NO\textsubscript{x}, dioxin, SNCR, PNCR, FGR, ASC
NOMENCLATURE

MSW, Municipal solid wastes
ASC, Air staged combustion
FGR, Flue gas recirculation
SCR, Selective catalytic reduction
SNCR, Selective none-catalytic reduction
PNCR, Polymer none-catalytic reduction
HSR, High-efficient selective reducing agent
I-TEQ, International toxic equivalence
PCDD, Polychlorinated dibenzo-p-dioxin
PCDF, Polychlorinated dibenzofuran
CEMS, Continuous emission monitoring system
TEF, Toxicity equivalency factor
1 INTRODUCTION

Incineration is one of the most important and widely adopted technologies for municipal solid wastes (MSW) management worldwide. In China there are 248,692,000 tons of MSW generated in the year of 2021 and 72.5% of them were incinerated in 583 incineration plants (China Statistics Press, 2021). Whereas the emission regulations for MSW incineration plant are becoming increasingly stringent, for example, the upper limit for NO\textsubscript{x} emission of 250 mg Nm\textsuperscript{-3} as a daily average is defined in Chinese National Standard GB18485-2014 (AQSIQ and SAC, 2014), and dioxin emissions should be lower than 0.1 ng I-TEQ Nm\textsuperscript{-3}, which is the same as that in Directive 2010/75/EU (European Union, 2010). In many cities the local limitations are even stricter than those in national standard. Therefore, the existing incineration plants must improve their flue gas scrubbing system to meet up with the stricter regulations.

Many technologies have been developed to reduce NO\textsubscript{x} emissions from MSW incinerator, the so-called De-NO\textsubscript{x} technologies are divided into two categories including combustion-correlated De-NO\textsubscript{x} technologies and flue gas scrubbing technologies. Air staged combustion (ASC) and flue gas recirculation (FGR) are typical combustion-correlated De-NO\textsubscript{x} technologies. The widely applied selective none-catalytic reduction (SNCR) and selective catalytic reduction (SCR) technologies using ammonia or urea as reductant to reduce NO\textsubscript{x} (Bing et al., 2018; Isidro et al., 2015; Irfan et al., 2008). SNCR De-NO\textsubscript{x} technology is adopted in each MSW incineration plant and some of them are equipped with SCR facilities as well to achieve high De-NO\textsubscript{x} efficiency.
However, SCR facilities suffer from the arduous maintenance of SCR catalysts, therefore, non-
SCR De-NO\(_x\) technologies are exploited to replace high efficiency SCR De-NO\(_x\) technologies; as
a result, FGR and ASC are widely adopted in MSW incinerators (Liuzzo et al., 2006; Qian et al.,
2011; Vilardi and Verdone, 2020). Another SNCR technology with organic amine-containing
compounds (HSR) as reductants, the so-called PNCR technology (Liu and Pang, 2018; Yang et
al., 2020) is also explored, its wider temperature window of 750-1150 °C is more convenient than
traditional SNCR technology with ammonia/urea as reductants. The reaction is as follows:

\[
NO_x + HSR \rightarrow N_2 + M
\]  
(1)

Where M is the reduction products such as N\(_2\), CO\(_2\) and H\(_2\)O etc.

The reductant used in PNCR technology is usually calcium aspartate C\(_8\)H\(_{12}\)N\(_2\)O\(_8\)Ca power, it
firstly decomposes into C\(_8\)H\(_{12}\)N\(_2\), and then it would react with NO\(_x\):

\[
C_8H_{12}N_2 + 8NO_2 \rightarrow 5N_2 + 5CO_2 + 6H_2O
\]  
(2)

The powder reductant is safer, simpler and cheaper than ammonia without formation of any
other secondary harmful by products, but its blockage could be a problem, and NH\(_3\) escape is
another one. However, with the combination of these non-SCR De-NO\(_x\) technologies, De-NO\(_x\)
efficiency can be comparable to those of SCR De-NO\(_x\) technologies.

To control dioxins simultaneously, many studies investigated the effect of SCR technology on
dioxin removal (Jiang et al., 2019, Gallastegi et al., 2016 and 2017). However, the effective
temperature windows for catalytic decomposition of dioxins and for traditional SCR De-NOx are
different (Yang et al., 2008; Xu et al., 2012; Wang et al., 2016), making the simultaneous NOx
and dioxins removal difficult. In recent years, with the development of V/Ce/Ti SCR catalyst,
removal of NOx and dioxins can achieve high performance at 300-350°C (Yu et al., 2016).
However, the cost of manufacture and maintenance of SCR catalysts is high, and dealing with the
deactivated catalysts is also expensive (Xu et al., 2018; Jin et al., 2019). Therefore, various
combined non-SCR technologies have been developed to achieve high De-NOx efficiencies as
well as controlling dioxin emissions (Chen et al., 2015; Wielgosiński et al., 2020). However,
studies on the impact of non-SCR technologies on dioxin emissions are only available for the
single technology, no reports considered the effect of combined non-SCR De-NOx technologies
on dioxin emissions, therefore the suitable combination mode is undecided and the corresponding
operating parameters are not optimized.

Zhang et al. (2019) studied the effect of FGR technology on dioxin emission; and found that
the FGR can replace the secondary air to blow into the high temperature zone of the combustion
chamber, to fully enhance the turbulivity of the flue gas to ensure complete combustion.
Meanwhile, the residual dioxins from the tail of the incineration system could be sent back into
the combustion chamber for secondary decomposition. However, as the FGR rate was too high, it
would reduce the temperature in the incinerator chamber and be conducive to the CO emission in
Yu et al. (2016) found that by installing SNCR De-NOx device, the emission of dioxins in MSW incineration flue gas can be effectively controlled; they found that the nitrogen-containing compounds in the reducing agent can generate stable chemical bonds with the catalytic transition metals, such as Cu-N bonds, which can inactivate the catalytic effect of Cu in the fly ash for dioxin synthesis, to inhibit the dioxin emission. Meanwhile, H and Cl atoms in dioxins and their precursors were replaced by N-containing groups (NH$_2$, CN, etc.) in reducing agent, thus inhibiting the formation of dioxins. Wielgosiński et al. (2020) proposed a method for the simultaneous removal of both NOx and dioxin pollutants from flue gases by using dioxin synthesis inhibitors as reducing agents in the selective non-catalytic reduction (SNCR) De-NOx process, as a result 63-67% of De-NOx efficiency and 52-80% of PCDD/Fs removal efficiency were achieved. Lv et al. (2021) achieved the reduction in dioxin concentration of fly ash particles by spraying polyacrylamide solution into bag filter, which is also based on the above principle. However, they are seldom used in practice. Furthermore, there are few reports on quantifying and comparing the impacts of different De-NOx methods on dioxin emissions.

In order to understand the individual and joint influences of non-SCR De-NOx technologies on the dioxins’ emissions, in this research, experimental researches were carried out in three full-scale incinerators in Henan province and Shanghai respectively, both with capacity of 500 t d$^{-1}$.
(20.83 t h⁻¹). Combined technologies including two or several of SNCR, PNCR, FGR and ASC were adopted to test their performance for De-NOₓ and dioxins emissions control, so that to recommend most suitable combination mode of De-NOₓ technologies.

2 MATERIALS AND METHODS

2.1 Incineration plants

Three full-scale incinerators were investigated in this research. The three incinerators are of the same type with capacity of 500 t d⁻¹; as shown in Fig. 1. They are installed with the similar flue gas scrubbing system, consisting of a SNCR system, a PNCR system, a FGR system, a semi-dry scrubber and a dry scrubber using NaHCO₃ as neutralizer for removing acidic gases; finally, there was a bag filter with activated carbon spraying before it. ASC was realized by providing secondary air in the furnace throat (position 3 in Fig. 1); while the secondary air can be replaced by the recirculated flue gas, which constituted the FGR technology. SNCR De-NOₓ was carried
out by spraying urea solution from the front wall and side walls on the top of the furnace in the temperature range of 850~900 °C; to operate PNCR De-NOₓ technology the HSR powder was sprayed from the front wall and side walls above the SNCR nozzles; to carry out FGR, the flue gas discharged from bag filter was recirculated into the furnace through the nozzles of secondary air installed in the furnace throat (position 3 in Fig.1).

2.2 Experimental scenarios

22 scenarios were investigated in this research, as shown in Table 1. Scenarios 1-6 are based on a MSW incineration plant in Henan province (herein noted as Henan incineration plant); Scenarios 7-9 are based on an incineration plant in Shanghai (noted as Shanghai (I)); and Scenarios 10-22 are based on another incineration plant in Shanghai (noted as Shanghai (II)), of which Scenarios 10-19 were carried out before MSW source segregation policy implementation and Scenarios 20-22 were performed after the policy. During the experiments, non-SCR De-NOₓ technologies including SNCR, PNCR and FGR or ASC were combined in different ways. Averaged characteristics of MSW during experimental periods are shown in Table 2.

For the scenarios in Table 1, the percentage behind SNCR is based on urea consumption; the maximum consumption is assumed to 100% and other consumptions were the percentages of the maximum, as shown in Table S1. The percentages behind ASC and FGR are based on the opening of valves; 100% means that the regulating valve for FGR or the secondary air is fully
Table 1. Design of experimental scenario

<table>
<thead>
<tr>
<th>Region</th>
<th>Scenario</th>
<th>De-NOx Technology</th>
<th>First Air supply (Nm³ h⁻¹)</th>
<th>Secondary air supply (Nm³ h⁻¹)</th>
<th>Recircuiting flue gas (Nm³ h⁻¹)</th>
<th>Secondary air ratio (%)</th>
<th>Recircuiting rate (%)</th>
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<tr>
<td>Henan Incineration Plant</td>
<td>1</td>
<td>SNCR41%+PNCR42%+FGR100%+ASC25%</td>
<td>52274.8</td>
<td>2133.8</td>
<td>12094.8</td>
<td>3.92</td>
<td>18.19</td>
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<tr>
<td></td>
<td>2</td>
<td>SNCR44%+PNCR70%+FGR65%+ASC60%</td>
<td>57178.8</td>
<td>5138.4</td>
<td>8817.5</td>
<td>8.25</td>
<td>12.40</td>
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<td>3</td>
<td>SNCR58%+FGR90%+ASC90%</td>
<td>69787.3</td>
<td>9959.1</td>
<td>12893.9</td>
<td>12.49</td>
<td>13.92</td>
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<tr>
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<td>4</td>
<td>SNCR87%+FGR60%+ASC80%</td>
<td>68085.4</td>
<td>8160.1</td>
<td>8763.9</td>
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<td>7129.0</td>
<td>3598.1</td>
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<td>55901.9</td>
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<td>SNCR89%+FGR80%+ASC25%</td>
<td>39080.9</td>
<td>2297.9</td>
<td>7288.0</td>
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<td>8</td>
<td>SNCR89%+FGR50%+ASC15%</td>
<td>37986.4</td>
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<td>SNCR89%+FGR20%+ASC18%</td>
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<td>1297.0</td>
<td>2596.2</td>
<td>3.14</td>
<td>5.23</td>
</tr>
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<td>Shanghai (II) and (II*)</td>
<td>10</td>
<td>SNCR55%+ASC30%+FGR48%</td>
<td>44970.2</td>
<td>3259.2</td>
<td>4813.3</td>
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<td>SNCR55%+ASC28%+FGR60%</td>
<td>47955.3</td>
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<td>2996.3</td>
<td>7477.3</td>
<td>7.39</td>
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<td>3437.3</td>
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<td>3270.3</td>
<td>7437.1</td>
<td>7.92</td>
<td>13.94</td>
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<tr>
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<td>40980.2</td>
<td>2891.2</td>
<td>7415.3</td>
<td>6.59</td>
<td>13.08</td>
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<td>42306.3</td>
<td>3406.1</td>
<td>7410.5</td>
<td>7.45</td>
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<td>Plant</td>
<td>Proximate analysis (%)</td>
<td>Ultimate analysis (%)</td>
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<td>M_ar</td>
<td>A_ad</td>
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<td>F_ad</td>
<td>C_ar</td>
<td>H_ar</td>
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<tr>
<td>A(Henan)</td>
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<td>12.72</td>
<td>72.29</td>
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<td>22.47</td>
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<td>B(Shanghai-I)</td>
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<td>12.06</td>
<td>75.15</td>
<td>12.79</td>
<td>16.65</td>
<td>2.84</td>
<td>12.64</td>
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<td>C(Shanghai-II)</td>
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<td>12.50</td>
<td>77.06</td>
<td>10.45</td>
<td>18.85</td>
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<tr>
<td>C(Shanghai-II*)</td>
<td>43.50</td>
<td>10.72</td>
<td>76.51</td>
<td>12.78</td>
<td>19.85</td>
<td>3.91</td>
<td>9.78</td>
</tr>
</tbody>
</table>

1^ar: as received;
2^ad: air dried;
3^the tests performed in the same Shanghai (II) plant after the source segregation policy implemented.
opened and the other percentages are based the opening graduation. However, as the feeding MSW are fluctuating in components, density and heating value, the primary air supply and its pressure are fluctuating accordingly, the same valve opening percentage would correspond to different secondary air ratio or FGR rate, the relationship between the valve opening and ASC/FGR ratios are shown in Figure S1. The reason for using valve opening percentages as the level of variable is that the valve opening percentage is the direct and easiest tool for adjusting FGR and ASC. During the experimental process, the capacity of the incinerator was tried to maintain its full mechanical load or close to the full load. For Scenarios 1-6, the amount of recirculating flue gas was adjusted to be different levels of its full designed amount by adjusting the regulating valve, which accounts 5.27-18.19% of the total air supply to the furnace. For Scenarios 20-22, the valve opening was adjusted to let the secondary air ratio changing from 25% to 100% of its full amount, which accounts 4.15-25.18% of the total air supply, but no FGR was adopted. When adjusting FGR and ASC levels, the O₂ pressure at the exit of economizer should be maintained relatively stable (Table S1), therefore a higher FGR ratio would correspond to a higher amount of flue gas inside the furnace chamber. The amount of first air, the secondary air and the FGR are affecting each other, and their total amounts are also influenced by the fluctuation in the calorific value of the MSW. So, neither FGR nor ASC level can be freely varied without impact on other parameters. Another constraint is that for a full-scale incinerator, the
emissions of all pollutants should be below their limitations during the whole testing periods, which confines the variation levels of different technologies.

2.3 **Analysis methods**

NOx emissions data are obtained from continuous emission monitoring system (CEMS), which is installed to sample flue gas from Position B in Fig.1, so that NOx concentrations are the mean values during the whole text time of a certain scenario. Dioxins are measured by sampling the flue gas after the economizer (Position A in Fig.1) following the standard GB 17378.3-2007 (AQSIQ and SAC, 2007), and dioxins measurements were performed according to the standard HJ-77.2-2008 (MEP, 2008). According to the standards, the sampled flue gas first went through the filter thimbles (Mucunjinling, Shanghai) and then passed through a miniature circulating chiller (MC450LSA, Qingdao, China) during the sampling operation. The condensed water in the flue gas was then collected in a brown flask. Finally, the flue gas flowed through an XAD-2 resin (SigmaAldrich, Shanghai) layer. Three parallel samples were collected for each scenario, and each sample was collected over a period of 2 h, 66 samples were collected in total. The prepared samples were sent to the authorized laboratory to be measured within 14 days. The samples (filter thimble, XAD-2 resin, and condensed water) were maintained in a cooler at a temperature lower than 4 °C during transportation and storage. Their dioxins’ concentrations were determined by using a high-resolution gas chromatography and a high-resolution mass spectrometry.
(HRGC/HRMS, Thermo Fisher DFS, America) with a chromatographic column (Agilent DB-5ms, 60m × 0.25mm × 0.25μm). The recoveries and the extraction of the internal standard recoveries were determined based on the standard HJ 77.2-2008 (MEP, 2008).

All of the results are expressed in international toxicity equivalents (I-TEQ). I-TEQ values were obtained from the PCDD/Fs mass concentration under the standard conditions and the toxicity equivalency factor (TEF), and the total TEQ of the 17 toxic 2,3,7,8-substituted PCDD/F congeners was calculated per Equation (3):

\[
I\text{-TEQ} = \sum (PCDD_i \times I\text{-TEFi}) + \sum (PCDF_i \times I\text{-TEFi})
\]

Where, PCDD\(_i\) and PCDF\(_i\) are 17 toxic 2,3,7,8-substituted congeners; I-TEFi is the toxicity equivalency factor (dimensionless) of a certain PCDD/F congener.

The mass concentrations were converted into values under the condition of 1 atm and 0°C and corrected referring to an 11% oxygen content, according to Equation (4):

\[
\rho = (21 - 11)/(21 - O_2) \times \rho_i
\]

Where \(\rho\) is the standard concentration (ng I-TEQ Nm\(^{-3}\)), \(O_2\) is the averaged O\(_2\) concentration of the sampling process. \(\rho_i\) is the measured mass concentration under practical conditions.

As the experiments were carried out in the three full scale incinerators which should ensure their emissions below the limitations even during the experiments, therefore it is very difficult to regulate the operation parameters freely to identify the so-called background conditions, namely,
the measures for controlling the emissions are all stopped. To quantify the influence of various factors on the final NO\textsubscript{x} and dioxins emissions, the experimental data collected from three MSW incinerators are fitted and analyzed by using multi-factor linear regression method when one or multiple non-SCR technologies were simultaneously used in the incineration system. Multi-factor linear regression method is suitable for mathematical problems that contain multiple independent variables and one dependent variable. By fitting a line to the observed data to describe the relationship between variables, the quantitative relationship between two or more independent variables and one dependent variable is obtained when reaching the minimal variance. The formula of multi-factor linear regression for predicting the dependent variable (NO\textsubscript{x} or dioxins’ emission) is:

\[ \hat{y} = \beta_0 + \beta_1 X_1 + \cdots + \beta_n X_n \]  

Where \( \hat{y} \) is the predicted mean value of the dependent variable, here it refers NO\textsubscript{x} or dioxin concentration, \( X_1, \ldots, X_n \) are the independent variables including SNCR, PNCR, ASC and FGR levels. \( \beta_0 \) is the y-intercept, \( \beta_1, \ldots, \beta_n \) are the regression coefficient of the respective variables \( X_i \).

When different incinerators were tested, \( \beta_0 \) is changed, the strategy is shown in Supplementary materials.

### 3 RESULTS AND DISCUSSIONS

During the experiment periods, air supply and temperature in the furnace are shown in Table S1, CO emissions were always below 20 mg Nm\textsuperscript{-3}, much lower than its emission limitation of 80 mg
Nm$^{-3}$ defined in standard GB 18485-2014, suggesting that the MSW incinerators were running efficiently under their normal conditions.

### 3.1 NO\textsubscript{x} emissions

Fig. 2 shows that the hourly averaged NO\textsubscript{x} emissions during the experimental periods were all below 250 mg Nm$^{-3}$, the limitation defined in standard GB 18485-2014, it can be also seen that NO\textsubscript{x} emissions from different incinerators are different. The highest NO\textsubscript{x} emission was 207.7 mg Nm$^{-3}$ corresponding to Scenario 7 for incinerator Shanghai (I) with the combination mode of SNCR89%+FGR80%+ASC25%; and the lowest NO\textsubscript{x} emission was 67 mg Nm$^{-3}$ corresponding to Scenario 5 from Henan incinerator by mode SNCR100%+FGR25%+ASC80%.

#### 3.1.1 Comparison of SNCR and PNCR on De-NO\textsubscript{x}

Comparing Scenarios 1-6 in Fig. 2, it can be seen that when PNCR and FGR technologies are combined, adding SNCR has an obviously promoting role on De-NO\textsubscript{x} performance, the NO\textsubscript{x} emission can be reduced from 90.4 mg Nm$^{-3}$ for Scenario 6 to 80.0 mg Nm$^{-3}$ for Scenario 1. However, when comparing Scenario 3 (SNCR58%+FGR90%+ASC90%) with Scenario 1 and 2 (PNCR involved), the addition of PNCR and reducing the urea consumption slightly, the NO\textsubscript{x} emissions only slightly changed, meaning that PNCR is not a decisive technology for De-NO\textsubscript{x}. In addition, increasing PNCR powder consumption did not show a better De-NO\textsubscript{x} effect when comparing Scenarios 1-2 and 6. Therefore, it can be concluded that PNCR is not as effective as
SNCR technology. The main reason is that the solid powder used in the PNCR technology cannot contact flue gas as perfectly as the atomized urea solution does in SNCR. But the temperature window (750-1150°C) for PNCR is much wider than that of SNCR technology (900-1100°C), so PNCR can be combined with SNCR technology as an auxiliary measure to achieve better De-NO\textsubscript{x} effect. Presently effective PNCR agent is under development to improve its performance (Zhu et al., 2023), but its full-scale application was not reported.

3.1.2 Comparison of SNCR, FGR and ASC on De-NO\textsubscript{x}

When comparing Scenarios 7-9, the NO\textsubscript{x} emissions showed a slightly decreasing trend with decrease in FGR level when SNCR and FGR were combined and urea consumption was kept the same. In addition, for Scenarios 3-5, when FGR level decreased from 90 to 25%, NO\textsubscript{x} emission decreased from 82.8 to 67.0 mg Nm\textsuperscript{-3}; simultaneously the urea consumption was increasing;
similar to the behaviors of Scenarios 7-9. Therefore, it can be concluded that FGR is inferior to SNCR for De-NO\textsubscript{x}, and lower FGR level seems better. The comparison of Scenarios 10 and 13 also shows a lower level of FGR is more helpful for De-NO\textsubscript{x}. Based on Fig. 2, FGR level around 20-25\% can be recommended, which corresponds to the flue gas recirculating rate of 5.23-5.46\%.

When ASC level varies, NO\textsubscript{x} emission does not change significantly. For Henan Incinerator (Scenarios 1-6), as ASC ratio increases from 25\% (Scenario 1) to 90\% (Scenario 3), NO\textsubscript{x} emissions changed slightly from 80 to 82.8 mg Nm\textsuperscript{-3}. For incinerator of Shanghai (II*), ASC level decreased from 100\% (Scenario 20) to 25\% (Scenario 22), NO\textsubscript{x} emissions decreased slightly with the lowest emission of 174 mg Nm\textsuperscript{-3} corresponding to urea consumption of 94\% and ASC level of 80\%. Meanwhile, for incinerator Shanghai (II), as the urea consumption increases from 52\% (Scenario 13) to 100\% (Scenario 15) but maintains the same ASC level, the NO\textsubscript{x} emission significantly reduced from 163.3 to 111.2 mg Nm\textsuperscript{-3}. Therefore, SNCR is also more important than ASC for De-NO\textsubscript{x}.

When comparing Scenarios 21 and 22 with similar urea consumption, NO\textsubscript{x} emission increases from 174 to 182.5 mg Nm\textsuperscript{-3} when ASC level decreases from 80 to 25\%, suggesting a higher ASC level is better. When comparing Scenarios 14 and 16 with close urea consumption and the same FGR level, higher ASC level of 52\% corresponds to a lower NO\textsubscript{x} emission. Whilst the comparison of Scenarios 17 and 18 also proves that the application of ASC helps to decrease
NO\textsubscript{x} emission. But it is difficult to decide whether ASC is more effective than FGR or not.

### 3.1.3 Influence of individual incinerator on NO\textsubscript{x} emissions

When comparing NO\textsubscript{x} emissions from different incineration plants, from Fig. 2 it can be seen that NO\textsubscript{x} emissions in Henan Incinerator were much lower than those from Shanghai (I) and Shanghai (II and II*), which may be caused by differences in MSW composition and temperature distribution in the furnace. For example, Scenarios 11 and 18 correspond to the highest furnace temperature (Table S1), thus correspond to the relatively higher NO\textsubscript{x} emissions. The scenarios for incinerator Shanghai (I) all exceeded 1030 °C and they correspond to the highest NO\textsubscript{x} emissions; therefore, high furnace temperature could contribute to higher NO\textsubscript{x} emissions. However, the influencing laws of SNCR, ASC and FGR on De-NO\textsubscript{x} performance does not change when comparing the results within different incinerators. For all incinerators, SNCR is the most important De-NO\textsubscript{x} measure. The quantitively comparison of PNCR, ASC and FGR will be carried out with help of linear regression analysis.

### 3.2 Influence of non-SCR De-NO\textsubscript{x} technologies on dioxins emissions

Fig. 3 shows the hourly averaged PCDD/Fs emissions, which were sampled before bag filter (Position A in Fig. 1) in order to estimate the influences of different non-SCR De-NO\textsubscript{x} technologies. When sampled from the chimney (Position B in Fig. 1), the dioxin emissions can be decreased to less than 0.1 ng I-TEQ Nm\textsuperscript{-3} by activated carbon spray before bag filter.
3.2.1 Influence of SNCR and PNCR on dioxins’ emissions

As indicated by Scenarios 1, 2, 3 and 6 in Fig. 3, it can be seen that when PNCR and FGR technologies are combined, adding SNCR can significantly inhibited the formation of dioxins. When comparing Scenarios 1 and 6, it is found that involvement of SNCR can reduce the dioxins’ emission from 0.708 to 0.561 ng I-TEQ Nm$^{-3}$. But when comparing Scenarios 1 and 3, it can be found that by adding PNCR the dioxins’ emission also decreased from 0.722 to 0.561 ng I-TEQ Nm$^{-3}$, showing the inhibition effect of PNCR for dioxins. However, when FGR level is 60-65%, involvement of PNCR only slightly reduces PCDD/Fs from 0.721 to 0.663 ng I-TEQ Nm$^{-3}$ (scenarios 2 and 4). Yu et al. (2018) reported that PNCR had a lower inhibition effect on PCDD/Fs formation than that of SNCR technology, which is consistent with the results of this
research. However, the combination of PNCR and SNCR always achieve better dioxins inhibition effect, as proved by scenarios 1 and 2.

Combined the results in Fig. 2 and 3, it can be seen that for Scenario 6 (PNCR100%+FGR100%+ASC60%), the only scenario without adoption of SNCR, both NOx and dioxin emissions reached their peaks, SNCR technology seems essential when choosing the combination mode of non-SCR technologies.

3.2.2 Influences of FGR and ASC

When SNCR+FGR is combined, the dioxin emissions showed a decreasing trend with the decreasing FGR level, as proved by comparing scenarios 3-5, and scenarios 7-9, as FGR level decreased from 80 to 20%, the PCDD/Fs emissions decreased from 0.675 to 0.223 ng I-TEQ Nm$^{-3}$; and the results for other comparisons (Scenarios 10 and 12, Scenarios 18 and 19) showed the similar trend when the FGR level changed. The reason could be that, as FGR ratio decreased, more urea solution was consumed as SNCR reducing agent (Table S1), and the increase in urea consumption could lead to inhibition of PCDD/Fs emission (Kuzuhara et al., 2005; Yan et al., 2013). The exceptions are scenarios 1-3, when FGR level decreased, emission of the PCDD/Fs increased, which can be explained by the increased amount of flue gas in the furnace chamber (Table 1), Scenario 1 corresponded to less flue gas (66504.4 Nm$^3$ h$^{-1}$) than Scenario 2 (71134.7 Nm$^3$ h$^{-1}$) and Scenario 3 (92639.3 Nm$^3$ h$^{-1}$); a higher amount of flue gas in the chamber resulted
in a lower residence time inside the chamber, that might cause the incomplete combustion of carbon particles and lead to higher PCDD/Fs emission. In general, SNCR+FGR25% mode is preferred under the premise of stable operation of the incinerator for achieving lower NOx and dioxin emissions.

When ASC level varied, the changes in dioxins did not show a regular trend, except for scenarios 20-22, and no obvious influence pattern can be inferred.

3.2.3 Influence of individual incinerator

Fig.3 also shows that the dioxins emissions change from incinerator to incinerator. That’s because each incinerator has its own operation history and it is widely reported that dioxins emissions have “memory effect” (Chang and Lin, 2001; Wu et al., 2014). In addition, MSW treated in different incinerators have different components and Cl contents. However, the influences of SNCR and FGR show the similar patterns for different incinerators, therefore scenarios from different incinerators can be considered together to estimate the influencing laws.

3.2.4 Changes in dioxin congeners

The formation mechanism for the two congener categories of PCDDs and PCDFs are different. More than 90% of the toxicity equivalents (TEQ) of PCDD/Fs are derived from precursor synthesis and de novo synthesis (McKay, G., 2002), both are low-temperature heterogeneous catalytic reactions; and precursor synthesis is inclined to generate PCDDs, while
the *de novo* synthesis tends to generate PCDFs (Kuzuhara et al., 2005). Fig. 4 shows the
distribution of PCDDs and PCDFs congeners when different non-SCR technologies are adopted.

Fig. 4 (a) shows the influences of SNCR and PNCR. Comparing scenarios 1, 2 and 6, it is
proved that SNCR application can effectively reduce TEQ for both PCDDs and PCDFs;
additionally, TEQ of both PCDDs and PCDFs decreased for Scenario 5 when compared with
Scenario 6, showing the significance of SNCR on dioxin control. By comparing the ratio of
PCDFs/PCDDs (scenarios 1-6), it can be seen that the ratio is relatively stable for all scenarios,
indicating that SNCR can simultaneously inhibit the formation PCDDs and PCDFs. While PNCR
has no obvious effect on reducing TEQ of either PCDDs or PCDFs.
Fig. 4 Influences of non-SCR technologies on dioxin congeners
Fig. 4 (b) shows the influence of FGR, it is shown that the TEQs decrease significantly with the decreasing FGR level, especially the TEQs of 2,3,4,7,8-P$_5$CDF, 1,2,3,7,8-P$_5$CDD, 1,2,3,6,7,8-H$_6$CDD showed most obvious decreases. Meanwhile, it can be seen that the ratio of PCDFs/PCDDs presents an increasing trend with the decreasing FGR level (scenarios 7-9), indicating that when FGR level is reduced, formation of PCDDs is more inhibited than that of PCDFs. This is because higher level of FGR means more amount of flue gas inside the furnace chamber, which leads to the decreased residence time of the flue gas in the furnace and more particulates entrainment; there could be more chance for de novo synthesis, so higher FGR level corresponds to higher PCDFs emission. At the same time, the decrease in FGR level leads to the decreases in total flue gas volume and urea solution has longer contact time with flue gas inside the furnace, the N-containing compounds can inactivate the transition catalytic metal such as Cu which catalyzed PCDDs synthesis (Lippert et al., 1991). In addition, the N-containing radicals in the flue gas can also replace H and Cl atoms in PCDDs and their precursors, so to inhibit the precursor synthesis of PCDDs congeners (Kuzuhara et al., 2005).

Fig. 4 (c) shows the influence of ASC level, which indicates that TEQs of PCDFs increase significantly as ASC level decreases; and the TEQs of PCDDs increase too when ASC level decreases from 100 to 80%, but ceases to increase when ASC level drops from 80 to 25%. By comparing the ratio of PCDFs/PCDDs when ASC level decreases (scenarios 20-22), it can be
found that the ratio fluctuates a little but basically maintains stable. Higher ASC level improves the turbulence in the chamber thus enhances the complete combustion. So, the precursors and carbon content in particulates decreased for Scenario 20, inhibiting both precursor synthesis and *de novo* synthesis. The Scenario 21 corresponded to the lowest furnace temperature, that’s could be the reason for its highest PCDDs TEQ, as the precursors may exist. The increase in TEQs of PCDFs for Scenarios 20-22 is generally consistent with the results of Li et al. (2017) and could attribute to the enhanced *de novo* synthesis; of which 2,3,4,7,8-P$_5$CDF congener increased most significantly, so it is necessary to explore the detailed mechanism for this in future. In conclusion, higher ASC level is recommended to combine with SNCR technology.

3.3 Influence of different non-SCR technologies and their combination mode

3.3.1 Comparing the influence of different non-SCR technologies on both NO$_x$ and dioxin emissions

The multi-factor linear regression method was used to analyze the total 22 scenarios, as well as the impacts of different incinerators. The dependent variable was NO$_x$ or dioxin emissions, and the independent variables were the 4 non-SCR technologies (SNCR, PNCR, ASC and FGR) and the incinerator.

The regression results (Table 3S and Table 4S) are consistent with the phenomena in above discussions. The negative test statistics T value means that the mean value of the previous group
of samples is lower than that of the latter group; or vice versa. The larger absolute test statistics $T$ values of SNCR technology (3.27) for NO$_x$ and FGR (3.6625) for dioxin emissions indicate their stronger correlation with NO$_x$ or dioxin emissions and the smaller probability of the result being accidental. The smallest p value (0.0056) of SNCR shows its most significant influence on NO$_x$ emission, and the smallest p value (0.0026) of FGR shows its most significant influence on dioxin emission. However, p values of the other non-SCR technologies are higher than 0.05 and they fail to reflect the absolute impact on the dependent variables; suggesting that none of them can play an important role on dioxin and NO$_x$ emissions.

For NO$_x$ emission, the absolute value of $T$ value (3.27) corresponding to SNCR is much higher than those of PNCR (1.63), FGR (0.81) and ASC (1.30), and its p value is lower than those of PNCR (0.126), FGR (0.434) and ASC (0.214), which all prove that SNCR is currently the most effective non-SCR technology for De-NO$_x$. The ranking of regression coefficients is: SNCR > PNCR > ASC > FGR. Therefore, it can be inferred that their influence on NO$_x$ emission is in the same order; when ASC and FGR are kept unchanged within the same incinerator, one percentage increase in SNCR is associated with 0.60 mg Nm$^{-3}$ decrease in NO$_x$.

While for dioxin emission, the regression results show that FGR and SNCR are more significant than PNCR and ASC; meanwhile, the absolute $T$ value (3.6625) corresponding to FGR is slightly higher than that of SNCR (2.2415). The ranking of regression coefficients is:
FGR > SNCR > PNCR > ASC. When PNCR, ASC and FGR are kept at constant levels within the same incinerator, one percentage increase in SNCR is associated with 0.0027 ng I-TEQ Nm$^{-3}$ increase in dioxin emission.

The formula for predicting the mean values of NO$_x$ and dioxin emissions obtained through multi-factor linear regression are as follows:

For NO$_x$ emission:

$$\hat{\gamma}_{\text{NOx-Henan}} = 147.37 - 0.60 \cdot X_{\text{SNCR}} - 0.31 \cdot X_{\text{PNCR}} - 0.19 \cdot X_{\text{ASC}} - 0.12 \cdot X_{\text{FGR}}$$

And for dioxin emission:

$$\hat{\gamma}_{\text{Dioxin-Henan}} = 0.1489 + 0.0027 \cdot X_{\text{SNCR}} + 0.0010 \cdot X_{\text{PNCR}} + 0.0010 \cdot X_{\text{ASC}} + 0.0037 \cdot X_{\text{FGR}}$$

The above two formulas are only for Henan incinerator. For the other alternative incinerators, only the intercept of formula should be changed, as shown in Supplementary materials.

### 3.3.2 Recommendation of non-SCR technology combination mode

Base on the above discussions, it has been found that SNCR is most important for both NO$_x$ and dioxin emission control. When FGR is used, lower NO$_x$ and dioxins emissions can be achieved at the level of 25% (flue gas recirculating rate of around 5.3-5.5%), In addition, PNCR technology can be used as a supplement to assist reducing NO$_x$ and dioxin emissions with a relatively lower urea consumption. ASC has negligible influence on both NO$_x$ and dioxin emissions, but ASC and FGR are important measures for ensuring the turbulence in the furnace.
chamber and the burnt out of the dioxin precursors, and ASC and FGR may use the same nozzles, therefore, the combination mode of ASC and FGR can be chosen to preferentially satisfy the complete combustion but to control FGR level around 25%, and Scenario 5 with the mode of SNCR100%+FGR25%+ASC80% corresponded to lower NOx emission and lower dioxin emission; which could be a good choice. Considering the possible benefit of PNCR, non-SCR technologies can be recommended as: SNCR+PNCR+FGR25%+ASC80%.

4 CONCLUSIONS

In this paper, the joint impacts of different non-SCR De-NOx technologies on NOx and dioxin emissions have been evaluated in full scale incinerators. The conclusions are drawn as follows:

(1) SNCR technology is most effective for inhibiting NOx and dioxin emissions, it is suitable to be combined with FGR and other De-NOx technologies. PNCR is a potential supplement to SNCR without negative influence on dioxin control.

(2) FGR has negligible inhibition effect on De-NOx but strongly influences dioxin emission, especially through PCDDs congeners’ generation. FGR level around 25% is recommended. But higher ASC levels seem to benefit De-NOx and reducing dioxin emissions.

(3) The multi-factor linear regression analysis results suggested that the ranking of regression coefficients for De-NOx is: SNCR > PNCR > ASC > FGR; while for dioxin emissions: FGR > SNCR > PNCR > ASC. The recommended combination mode of non-SCR technology is
SNCR+PNCR+FGR25%+ASC80%.

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DISCLAIMER

No potential conflict of interest was reported by the author(s).

Data availability statement

The data used to support the findings of this study are available from the corresponding author, Liu Hong, upon reasonable request. No potential conflict of interest was reported by the author(s).

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