Field test of SNCRDeNOx technology in building ceramic industry and the process optimization

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Abstract. Ceramic industry accounts for considerable amount of NOx emission of industrial sources in China. With stricter air protection act imposed by the Chinese government, many ceramic plants have to install deNOx devices. Among all the de-NOx technologies, selective non-catalytic reduction (SNCR) is barely used in the NOx burning area process-control. In this study, a number of first-hand data focusing on burning area NOx control by using SNCR technology of ceramic roller-hearth kiln were shared, the spraying rate, temperature range, the quantity and arrangement mode of spray guns were studied. Besides, a continuous experiment was carried out. When the spraying rate was 60 L/min, the temperature range was 900-950°C, and two spray guns were used and arranged as opposite spraying mode, the NOx concentration after purification kept below 25 mg/m³, the removal efficiency was steadily higher than 40% with the average about 50%, and the ammonia escape met relevant technical specification.

1. Introduction
Ceramic industry is one of the traditional advantageous industries in China, which plays an important role in the national economy, the output of building ceramic has been ranked the first in the world for many years. At present, there are 3678 ceramic enterprises above designated size and tens of thousands of enterprises below designated size in China. There are about 3350 production lines of building ceramics, and the output of building ceramics was 10.15 billion m², which accounted to 63% of the world’s total output[1]. According to statistics data, the total amount of flue gas produced by ceramic industrial kilns was about 11674 trillion m³ in 2017. If the emission concentration of NOx was processed in keeping with the standard, the total annual emission of NOx in ceramic industry was about 21 thousand tons, which accounted for 1.67% of the national industrial emissions in that year[1].

The national standard of NOx emission concentration in ceramic industry is set to 180 mg/m³, according to the 2014 amending list of national standard(GB 25464-2010). While stricter emission standard has been imposed by the local government. In 2019, Guangdong province brought in a local emission standard of air pollutants for ceramic industry, in which the emission concentration of NOx is set to 100 mg/m³[2]. The NOx emission standard is now set to 80 mg/m³ in the key control area of Shandong province, and will be restrained to 50 mg/m³ in 2021[3]. With stricter protection act, many of the ceramic plants will have to install deNOx devices.
Ceramic raw materials and fuels contain about 0.1% of nitrogen, which generate fuel-NOx through thermal decomposition, oxidation and other ways which accounts for 90-98% of total NOx emission[4,5]. At present, the deNOxmeansfor ceramic kiln are mainly terminal treatment. Based on the fact that desulfurization facilities have been basically built for flue gas control in China, and most of them adopt wet desulfurization, the flue gas wet desulfurization and denitrification which on the basis of existing desulfurization facilities has become a research hotspot. For example, Fang et al[6,7] developed a wet multi-pollutant synergistic control technology by adding additives, which based on the urea wet denitrification technology, can achieve the synergistic removal of NOx, SO2 and heavy metals, and the removal rate of NOx is more than 50%. While the NOx control of burning area process-control according to the characteristics of ceramic kiln is barely reported. In this study, a field test was carried out on a ceramic production burning area, and the optimum condition was obtained.

2. Materials and method

2.1 DeNOx agent and experimental site
In this study, the experimental site is located at a ceramic brick production line of a building ceramic plant in Guangdong Province, China. The production capacity of this line is 20000 m2/d. The experiment was carried out at the burning area of a roller-hearth kiln. During the experiment, the initial NOx concentration was about 45 mg/m3. The deNOx agent used in this experiment was 10% urea (wt/v) with 50 ppm Na-containing additive.

2.2 Analytical methods
The concentration of O2, NO and NO2 before and after de-NOx process were detected by Testo 350 flue gas analyzer (Germany) and the NOx volume concentration (ppm) which directly measured by the flue gas analyzer was converted to mass concentration at 18% standard oxygen content, the equation is as follows:

\[ \text{NOx(mg/m}^3) = (\text{NO + NO}_2)\text{(ppm)} \times \frac{M_r}{22.4} \times \frac{21\% - \varphi_{st}}{21\% - \varphi_m} \]  
(1)

Which, \(M_r\) the relative molecule mass, 46 g/mol; \(\varphi_{st}\) -the standard volume content of oxygen, 18%; \(\varphi_m\)-the volume content of oxygen during the experiment, %.

NOx removal efficiency is defined as follow:

\[ \text{NOx Removal efficiency} = \frac{(\text{NOx}_{in}-\text{NOx}_{out})}{\text{NOx}_{in}} \times 100\% \]  
(2)

3. Results and discussion

3.1 DeNOx condition process optimization
In this study, a field test of urea+Na-containing additive used as denitrification agent of SNCRdeNOx technology in the burning area of a ceramic roller kiln was conducted. The influence of different process conditions on de-NOx efficiency was studied, the denitrifier spraying rate, temperature range, quantity and arrangement mode of spray guns were determined, and the results are shown in figure 1-4.

3.1.1 Effect of spraying rate on NOx removal efficiency.
It can be seen from figure 1 that when the spraying temperature range was 900-950°C and the spray mode was two spray guns facing each other, the NOx removal rate rose with the increase of the spraying rate. When the spraying rate was 40 L/h, the NOx removal rate was less than 30%, and the NOx outlet concentration was about 30 mg/m3. And when the spraying rate increased to 120 L/h, the NOx removal rate reached 70%, and the NOx outlet concentration was about 12 mg/m3. Some studies have shown that when the ammonia nitrogen molar ratio (NSR) is less than 1.6, the denitrification efficiency of SNCR will increase significantly with the increase of NSR, but when NSR is more than 1.6, the increase trend of denitrification efficiency of the system will tend to be slow[8]. It can be seen from figure 1 that when the spraying rate of denitrification agent increased from 40 L/h to 60 L/h, the denitrification efficiency of the system increased significantly,
while when the spraying rate was further increased, the increase speed of denitrification rate of the system slowed down. In consideration of the limited amount of NOx in the kiln, increasing the spraying quantity can promote the denitrification reaction under certain mixing conditions, while excessive spraying amount would increase the amount of ammonia escape, so the spraying rate of denitrification agent in this study was set to 60 L/h.

3.1.2 Effect of temperature range on NOx removal efficiency. Figure 2 shows the effect of temperature range on denitrification efficiency. It can be seen from figure 2 that when the spraying rate was 60 L/min and the spraying mode was two guns facing each other, the system has a some deNOx effect in the temperature range of 750-1000°C, among which the denitrification efficiency of the system was stable at about 50% in the temperature range of 850-1000°C. When the temperature was lower or higher than that, the denitrification efficiency of the system reduced. Besides, it can be seen that under the current process conditions, a better denitrification efficiency can be obtained near 950°C, which was also consistent with the literature that the optimal reaction temperature of SNCR with urea as reducing agent is 960°C[9]. In the synthesis all the factors, the temperature range in this study was set to 900-950°C.

![Figure 1. Effect of spraying rate on NOx removal efficiency.](image1)

![Figure 2. Effect of temperature range on NOx removal efficiency.](image2)

3.1.3 Effect of the quantity of spray gun on NOx removal efficiency. The effect of the number of spray guns and the arrangement mode on the deNOx efficiency were shown in figure 3 and 4. It can be seen from figure 3 that when the spray temperature range was 900-950°C and the total spraying rate was 60 L/min, the denitrification efficiency of the system rose with the increase of the quantity of spray guns. When one spray gun was used, the denitrification efficiency of the system was only 37.33%, and the NOx concentration after purification was 25.68 mg/m³, while when the quantity of spray gun increased to four, the denitrification efficiency of the system rose to 56.67%, and the outlet NOx concentration also dropped below 20 mg/m³. As more spray guns were used, larger the spraying coverage area obtained. Therefore, the spray area determines the denitrification rate of the system to some extent. In this study, the quantity of spray gun was set to two.

3.1.4 Effect of the spraying mode on NOx removal efficiency. The spray guns arrangement mode of denitrification agent has a great influence on NOx removal rate. As can be seen in figure 4, when the spraying rate was 60 L/min, the spraying temperature range was 900-950°C, and two spray guns in the same side (mode A) were used, the denitrification efficiency of the system was only 36.17%. When the opposite spraying mode (B) was applied, the deNOx efficiency was 50.54%. The denitrification efficiency of the system was about 55%, when the diagonal pattern was used (mode C and D), which was slightly higher than that of mode B, and the difference between the NOx removal efficiency of the two diagonal arrangements was not significant. During the experiment, denitrifier mixed with the flue gas,
the water of denitrifier evaporated, denitrifier decomposed and reacted with NOx in the flue gas, the selection of denitrifiers spraying location not only determines the contact time between flue gas and denitrifier, but also affects the coverage of denitrifier in the furnace to some extent. When mode A was applied, the contact time of flue gas and denitrifier was longer than that of mode B. However, due to the limited coverage area, part of NOx in the flue gas far away from the spray gun was not in good contact with denitrifier, resulting in the low denitrification rate of the system as a whole. When the spray gun was arranged into a diagonal pattern, the contact time of denitrifier and NOx was well balanced. Therefore, the denitrification efficiency of the system was the highest. Taking all the factors into account, the arrangement pattern of spray guns was chosen as mode B.

![Figure 3. Effect of the quantity of spray guns on NOx removal efficiency.](image)

3.2 Trend of NOx concentration and removal rate.
The results of continuous deNOx experiments are shown in figure 5. As can be seen from figure 5, when the spraying rate was 60 L/min, the temperature range was 900-950 °C, and two spray guns were used and arranged as opposite spraying mode, the NOx concentration after purification kept below 25 mg/m³, and the 6-day average concentration of NOx was 22.51 mg/m³. Besides, the NOx removal rate was stable >40.0% during the continuous experiment, and the average removal rate was above 50%.

![Figure 4. Effect of the spraying mode on NOx removal efficiency.](image)

![Figure 5. The concentration and removal efficiency of NOx and ammonia escape.](image)

When urea or ammonia water was used as denitrifier and cannot be fully utilized in SNCR denitrification process, ammonia will escape and cause new environmental pollution. At the same time, ammonia escape is easy to combine with SO₃ in flue gas to form ammonia hydrogen sulfate or ammonia sulfate, which adhere to dust, resulting in pipelines blockage and corrosion [10]. Therefore,
the lower ammonia escape value of SNCR denitrification system, the better. During the continuous experiment, it was found that the amount of ammonia escape was stable at 3.29-4.11mg/m³, which met the relevant technical specification[11].

4. Conclusion
In this study, urea with 50 ppm Na-containing additive was used as denitrifier of SNCR technology in burning area of ceramic roller kiln for NOx control. The main conclusions are shown as follows:

(1) The NOx removal rate rose with the increase of the spraying rate. Considering the NOx removal efficiency and NH₃ escape, the spraying rate was set as 60 L/h. The proper temperature range for burning area denitrification in the ceramic roller-hearth kiln was 850-1000 °C, and a better deNOx efficiency can be obtained at 900-950 °C.

(2) The quantity and the arrangement mode of spay gun can both affect the removal rate of NOx. The more spray guns used, the better denitration rate of the SNCR system obtained. The arrangement mode affected both the spaying area and the contact time, which influenced the NOx removal efficiency. When the spray guns were arranged into a diagonal pattern, the deNOX efficiency can reached to 55%.

(3) During consecutive experiment, when the spraying rate was 60 L/min, the temperature range was 900-950 °C, and two spray guns were used and arranged as opposite spraying mode, the 6-day average concentration of NOx was 22.51 mg/m³, and the average removal rate was 50.54%.

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References
[1] Fang P, Tang Z.J., Tang Z.X., Chen X.B., Cen C.P.(2014) Emission characteristics and its treatment technology status of the pollutants from ceramic furnace flue gas. Environmental Science & Technology, 37(12): 68-72.
[2] Department of Ecology and Environment of Guangdong Province, Guangdong Market Supervision and Administration Bureau. (2019) Emission standard of air pollutants for ceramic industry (DB 44/2160-2019).
[3] Department of Ecology and Environment of Shandong Province, Shandong Bureau of Quality and Technical Supervision, (2019) Emission standard of air pollutants for building material industry (DB 37/2373-2018, amending list).
[4] Huang L.H., Zeng L.K., Ren X.T., Yin H. (2000) NOx pollution from ceramic kiln and prevention and control techniques. China Ceramics, 36(06): 23-25.
[5] Fang H.X. (2005) Basic research on the formation mechanism of NOx in high temperature ceramic kiln. Guangzhou: South China University of Technology.
[6] Fang P., Cen C.P., Wang X.M., Tang Z.J., Tang Z.X., Chen D.S. (2013) Simultaneous removal of SO₂, NO and Hg⁰ by wet scrubbing using urea+KMnO₄ solution. Fuel Process. Technol., 106: 645-653.
[7] Fang P., Cen C.P., Tang Z.X., Zhong P.Y., Chen D.S., Chen Z.H. (2011) Simultaneous removal of SO₂ and NOx by wet scrubbing using urea solution. Chem. Eng. J., 168: 52-59.
[8] Cai C.J., Chen Z.C. (2013) SNCR denitrification technology for a 600t/d MSW incinerator. Thermal Power Generation, 42(02): 30-35.
[9] Chen Z.C., Yang W.J., Zhou J.H., He P., Wang Z.H., Cen K.F. (2010) The moving locus of urea solution atomizing particles in furnace of boiler. Thermal Power Generation, 39(02): 18-23.
[10] Zhao P.B., Sun T., Gao H.P., Yu W.G., An C., Liu D., Hui X.L. (2016) Common problems and countermeasures of CFB boiler SNCR denitrification technology. Clean Coal Technology, 22(01): 86-89.
[11] Ministry of Environmental Protection. (2010) Engineering technical specification of flue gas selective non-catalytic denitrification for thermal power plant (HJ 563-2010).