1 Introduction

As a byproduct of municipal sewage treatment, the rapid growth of sewage sludge production causes severe environmental problems.\(^1\)\(^-\)\(^3\) It is worth noting that the caloric value of sewage sludge exceeds the minimum requirement for alternative fuels in the cement industry (>6250 J g\(^-1\)). Meanwhile, sewage sludge contains inorganics (CaO, SiO\(_2\), Al\(_2\)O\(_3\), FeO\(_3\), MgO) and other components of cement.\(^4\)\(^-\)\(^6\) Therefore, considering the technical difficulties of sewage sludge treatment and the soaring price of fossil fuels and cement raw meal, the co-processing of sewage sludge in cement kilns has gained extensive attention in recent years;\(^7\)\(^-\)\(^10\) and has been considered a cost-effective and environment-friendly route for energy recovery and sludge disposal.\(^10\)\(^-\)\(^12\)

The production of cement consumes large quantity of original materials (clay, limestone, and fuel), which produces lots of air pollutants such as particles, SO\(_2\) and NO\(_X\). The cement industry has become the third largest industrial NO\(_X\) emission source in China.\(^13\) Several NO\(_X\) emission control technologies, such as low-NO\(_X\) burners, staged combustion (air and fuel staged) and selective non-catalytic reduction (SNCR), have been developed. Among them, low-NO\(_X\) burners and staged combustion technologies have been widely applied to control NO\(_X\) emission due to the advantages of relatively low investment and operation costs. However, their removal efficiency is only roughly 30%. SNCR is also regarded as a proper technology in considering the temperature range of cement precalciner (850–1200 °C).\(^14\)\(^-\)\(^15\) Its NO\(_X\) removal efficiency is approximately 40%. Nevertheless, the SNCR technology will consume a large amount of ammonia and cause the ammonia escape. Therefore, more efforts should be put into the development of more efficient and cost-effective NO\(_X\) removal technology for cement industry in view of energy conservation and environmental protection.

With the gradual increase of sludge treatment in cement kiln, some researchers have found that co-processing sludge in cement kiln contributes to the decrease of NO\(_X\) emission.\(^16\) For instance, Fang \textit{et al.}\(^14\) discovered that combustion temperature, O\(_2\) concentration, sludge dosage and feed point influenced the NO reduction substantially. Lv \textit{et al.}\(^17\) found that co-processing of sludge in cement kiln was beneficial to NO reduction, and the yield of NH\(_3\) released from sludge affected NO reduction remarkably. During sludge reburning under hypoxic conditions, various reducing species, such as short-chain hydrocarbon (mainly CH\(_4\)), CO, HCN and NH\(_3\), are generated. These reducing species can effectively reduce NO to N\(_2\) by producing a large number of C-containing (CH\(_4\)) and nitrogenous (NH\(_3\)) radicals.\(^15\)\(^-\)\(^16\) It is worth noting that CH\(_4\) is firstly decomposed into CH\(_4\) radicals, which react with NO to form HCN, and then HCN can reduce NO again by forming NH\(_3\) radicals. Of course, due to the limitation of residence time, HCN may also be a precursor to generate NO.\(^14\)\(^-\)\(^19\) Although it has been reported...
that co-processing of sludge in cement kiln has synergistic denitrification effect, the reaction mechanism between reducing gases released and NO reduction has not been well studied. In particular, the working conditions of the cement precalciner are relatively complicated, especially the CO₂ concentration can be higher than 30 vol%. Besides, there existing coupling effects between the decomposition of cement raw meal and the combustion of sludge. Therefore, in order to elucidate the influence of CO₂ concentration on NO reduction and its mechanism during sludge reburning in cement kiln in the presence of cement raw meal, the characteristics of reducing gases (HCN, NH₃, CO, CH₄) released and the properties of NO reduction should be researched in detail.

In this study, the types and sources of reducing gases released during sludge combustion were analyzed, and the influences of CO₂ concentration on the release of reducing gases were systematically investigated. Meanwhile, the influences of CO₂ concentration on the dynamic variation process of NO reduction by sludge reburning were researched. Furthermore, the relationship between homogeneous and heterogeneous NO reduction was also explored. On the basis of the above discussions, the results are expected to disclose the mechanism of NO reduction by sludge reburning in a pilot scale cement precalciner, which can provide theoretical references for improving the technology of industrial application and realizing the efficient disposal of sludge.

2 Materials and methods

2.1 Materials

Preparation of sludge. Sewage sludge used in this study was dewatered sewage sludge which came from a municipal wastewater treatment plant located in Guangzhou, China. After natural drying for 3–5 days, the dry sludge was milled and sieved to a particle size of ASTM 60–80 mesh.

Preparation of sludge char. Sludge char was prepared by pyrolyzing the sewage sludge (1.1 g) in N₂ atmosphere at 900 °C for 5 minutes. Then the char was taken out from the lower end of the reaction tube. Similarly, the char was milled and sieved to a particle size of ASTM 60–80 mesh. The results of proximate and ultimate analyses of sludge and sludge char were shown in Table 1.

2.2 Experimental methods

The experimental platform (Fig. 1) was a high temperature gas-solid suspension system which was established to simulate the suspension state of cement precalciner. A gas-solid suspension quartz tube was adopted to simulate the suspension and spurt effects. The quartz tube was composed of three parts, namely, the conical zone (40 mm height), the upper of conical zone (20 mm ID) and the lower of conical zone (4 mm ID). The quartz tube was placed in a vertical electric furnace to simulate the reburning zone of the cement precalciner. The electric furnace can provide a relatively constant temperature with a length of about 60 mm. The flow rate of the flue gas was maintained at 500 mL min⁻¹. The residence time of flue gas through the conical zone of quartz tube was approximately 1 s, and 1.5 s for the constant temperature area of the electric furnace.

In order to maintain the constant temperature in the reaction tube and reduce the metrical deviation of gaseous products concentration, the added amounts of sludge/char and cement raw meal were 0.1 g and 1 g, respectively. Each experiment was repeated to ensure the reliability of the experimental data. The data deviation of repeated experiments was not more than 5% and the variation trend was consistent. In addition, the cement raw meal used in this experiment was prepared according to the saturation ratio, the silicic acid ratio and the aluminum oxygen ratio. The main components of cement raw meal were shown in Table 2.

The O₂ concentration was 3 vol%, the CO₂ concentration was set as 0, 10, 25, 30 and 35 vol%, respectively, and N₂ provided the balance. When the experiment of NO reduction was conducted, the initial concentrations of NO and SO₂ at reactor inlet were designed as 600 and 200 mg m⁻³ respectively based on the

| Sample       | Mad  | Vad  | Aad  | FCad | C    | H    | N    | S    |
|--------------|------|------|------|------|------|------|------|------|
| Sludge       | 6.71 | 30.42| 58.82| 4.05 | 2.71 | 3.13 | 3.62 | 0.76 |
| Sludge char  | 1.24 | 1.85 | 92.57| 4.34 | 2.58 | 0.18 | 0.21 | 0.43 |

![Fig. 1 Schematic drawing of experimental apparatus.](image)
atmospheric composition in cement precalciner. Other atmospheric conditions were consistent with the experiment condition of reducing gases released. Meanwhile, the reaction temperature of the conical zone was controlled as 900 °C.

2.3 Characterization method

Elemental compositions of the samples were determined by elemental analyzer equipped with a TCD detector (EuroVector-EA3000, Italy). The weight loss of the samples with temperature during the conventional combustion was characterized by thermogravimetric analysis (TGA: Netzsch-STA449F3, Germany). The gaseous products released from the thermochemical process were detected on Fourier transform infrared spectroscopy (FTIR: Thermo Fisher Scientific, America). The surface atomic states of the samples were analyzed by X-ray photoelectron spectroscopy (XPS: Thermo Escalab 250Xi, America). The morphology of the samples were characterized by transmission electron microscopy (TEM: JEM-2010, Japan). The surface area of the samples were calculated by the Brunauer–Emmett–Teller (BET: ASAP 2020, USA) method, with the samples degassed at 100 °C for 12 h prior to measurements. The concentrations of the main gaseous products during NO reduction by sludge reburning were analyzed by Gasmet analyzer (Gasmet technologies-DX4000, Finland). The interval time of Gasmet online sampling was set as 5 s.

3 Results and discussion

3.1 Characteristics of sewage sludge

The combustion process of sludge under air atmosphere was depicted by thermogravimetry (TG) and differential thermogravimetry (DTG) curves, as shown in Fig. 2. Three individual peaks can be detached from DTG curve, indicating that the combustion of sludge can be grouped into three different stages, corresponding to the release of moisture, the release and combustion of light organic volatile and the combustion of heavy molecular weight components and fixed carbon. The maximum weight loss rates are reached at 80, 290, 520 °C, respectively.\(^ {22,23}\)

![Fig. 2 TG and DTG results of sewage sludge with a heating rate of 20 K min\(^{-1}\) under air atmosphere.](image)

FTIR spectrometer coupled with TGA can provide useful online observation of gaseous products released from the combustion process of sewage sludge. The three-dimensional FTIR absorbance spectra of gaseous products released from the combustion of the sewage sludge is shown in Fig. 3(a). Regions of strong IR absorbance can be identified, which is the absorption peak generated by CO\(_2\) anti-symmetric stretching vibration (2400–2240 cm\(^{-1}\)). Fig. 3(b) shows FTIR absorbance stack spectra of gaseous products at 80, 290 and 520 °C, which are respectively screened from the maximum loss rates of three stages from DTG. At 80 °C, the broad band at 4000–3400 cm\(^{-1}\) corresponding to the vibration (O–H) of H\(_2\)O. The decomposition of C=O bonds at around 1780–1600 cm\(^{-1}\) led to the yield of CO. With the temperature rising to 290 °C, it is evident that there exist more gaseous products in addition to H\(_2\)O and CO. The C–H bonds at around 3200–2700 cm\(^{-1}\) revealed that the compounds of alkyl and aliphatic hydrocarbons exist. The decomposition of C–H bonds led to the yields of CH\(_4\), C\(_2\)H\(_6\), C\(_3\)H\(_8\), and other light hydrocarbons. The C–N bonds at around 1340–1020 cm\(^{-1}\) attribute to the presence of amides, which can be decomposed to generate NH\(_3\). Furthermore, a strong HCN absorption peak appears at 748 cm\(^{-1}\).\(^ {22,24}\) When the temperature is 520 °C, the gaseous products contain H\(_2\)O, CO\(_2\), CO, HCN and hydrocarbons. The above results further indicate that the reducing gas of NH\(_3\) is mainly derived from low-volatility components and can be completely released at the initial stage of combustion, while CO, HCN and hydrocarbons are slowly converted from thermally unstable and stable functional groups.\(^ {25}\)

XPS measurement is carried out to investigate the chemical state of sewage sludge. As shown in Fig. 4(a), the C 1s spectra can be fitted with four characteristic peaks corresponding to COOH (288.3 eV), C=O (287.2 eV), C=O (285.9 eV) and C–C/C–H (284.8 eV). The C/C–H is the major carbon functional group of sewage sludge, which accounts for about 60% of total carbon in sewage sludge. The contents of other functional groups (C–O, COOH, and C=O) are 20%, 11%, and 9%. Fig. 4(b) shows that the nitrogen functionalities in sewage sludge are mainly presented as protein-N (53.73%), amine-N (33.65%), inorganic-N (11.54%), and pyrrole-N (1.08%), the corresponding electron binding energies of which are 400, 399.1, 401.7, and 400.6 eV, respectively.\(^ {26}\) It is worth noting that the relative surface content of protein-N is much higher than that of other nitrogen functionalities.

In combination with the FTIR observation (Fig. 3), it is inferred that the CH\(_4\) release is due to the secondary cleavage of long fatty chain (C–C/C–H) and fracture of aliphatic chain attached to oxygen atom (COOH, C=O, C–O). The thermal cracking of ether bond, hydroxyl group and oxygen-containing heterocycles is the main route for CO formation. NH\(_3\) is derived from the decomposition of inorganic-N and the deammoniation of amine-N which is produced by the protein pyrolysis. HCN is generated from the cracking of pyrrole-N, nitrile-N and heterocyclic-N, while the nitrile-N and heterocyclic-N are produced by the pyrolysis of protein.\(^ {27,28}\)
3.2 Effects of CO2 concentration on the release of reducing gases

Fig. 5 shows the releasing characteristic curves of HCN during sludge combustion under different CO2 concentrations. There is a negative correlation between CO2 concentration and HCN releasing rate. The effect of CO2 concentration on HCN released is attributed to the combined action of suppression and gasification. On the one hand, CO2 could be absorbed on the surface of sludge/char to directly react with HCN and form nitrogen oxides; on the other hand, the nitrogen-containing functional groups in char may also directly react with CO2 before the conversion to HCN by hydrogenation, which reduces the possibility of HCN release. Furthermore, the release of HCN decreased significantly when the CO2 concentration is higher than 25 vol%. Excessive CO2 (25–35 vol%) will reduce the local reaction temperature due to the strong radiation absorption of CO2, resulting in the weakness of gasification rate, which subsequently lowers the exfoliation of H-radical in char. Also, the reaction of –CN with H-radical to form HCN is limited greatly. It can been speculated that the dominant factor affecting the HCN release is the gasification instead of suppression at a relatively higher CO2 concentration (25–35 vol%).

It is well-known that CO can be generated by the gasification reaction between CO2 and char. It can be speculated that the gasification rate is the main factor affecting the CO release under different CO2 concentrations. The releasing characteristic curves of CO are depicted in Fig. 6. The gasification rate gradually increased because the increase of CO2 concentration (0–25 vol%). The promoting effect is stronger when the CO2 concentration is higher due to a larger peak value and more CO released. However, when the concentration of CO2 further increased (25–35 vol%), the CO yield decreased. In combination with the influence of relatively higher CO2 concentration (25–35 vol%) on HCN release in Fig. 5, the excessive CO2 can reduce the local reaction temperature, which decreases the gasification rate between CO2 and char. Therefore, the inhibition effect of local reaction temperature decreased is obviously greater than the promotion effect of reactant concentration increased, which leads to the gradual decline of CO released at a relatively higher CO2 concentration (25–35 vol%). The above results indicate that
an appropriate concentration of CO\textsubscript{2} plays a key role in enhancing the CO release during sludge combustion.

Fig. 7 illustrates the influence of CO\textsubscript{2} concentration on CH\textsubscript{4} release. The release of CH\textsubscript{4} gradually decreases with the concentration of CO\textsubscript{2} increasing from 0 to 25 vol\%. This may be attributed to the gasification effect, which results in the promotion of condensation polymerization reaction between semi-char and tar. Then, the methyl functional group is more likely to participate in the condensation polymerization reaction, preventing the release of CH\textsubscript{4} from sludge reburning. In addition, the increasing gasification rate probably increases the specific surface area of the activated char, enhancing the catalytic cracking reaction of CH\textsubscript{4}, which further reduces the release of CH\textsubscript{4}.\textsuperscript{27} However, the release of CH\textsubscript{4} increased when the concentration of CO\textsubscript{2} raised to 35 vol\%. This phenomenon may be attributed to the fact that excessive CO\textsubscript{2} may weaken the gasification rate, which decreases the surface area of the char. Thus, the effective contact area between CH\textsubscript{4} and activated char is fewer, which results in the weakening of the catalytic cracking reaction of CH\textsubscript{4}.\textsuperscript{29}

The releasing characteristic curves of NH\textsubscript{3} at different CO\textsubscript{2} concentrations are shown in Fig. 8. The releasing peak value and amount of NH\textsubscript{3} decrease with the increase of CO\textsubscript{2} concentration from 0 to 25 vol\%. This may be attributed to the suppression effect of CO\textsubscript{2} through the consumption of H-radical and nitrogen-containing functional groups.\textsuperscript{34} When the CO\textsubscript{2} concentration further increases to 35 vol\%, the amount of NH\textsubscript{3} released is relatively stable. Although a comparatively higher CO\textsubscript{2} concentration weakens the gasification rate and reduces the exfoliation of H radical of char. In combination with the previous analysis of sludge characteristic in Fig. 3, the release of NH\textsubscript{3} mainly occurred at the initial stage of combustion. NH\textsubscript{3} formation is not at the same stage as the gasification reaction. So, the weakening of gasification reaction does not affect the release of NH\textsubscript{3}. Moreover, a relatively higher concentration of CO\textsubscript{2} reduces the local reaction temperature, which may reduce the suppression effect that unstable nitrogen-containing functional groups are consumed by CO\textsubscript{2}. Thus, NH\textsubscript{3} release is relatively stable with a considerably higher CO\textsubscript{2} concentration (25–35 vol\%).

The ratio of the amount of the nitrogen-containing gases released to the nitrogen content in sludge is defined as the yield. The N\textsubscript{2} yield is calculated by eqn (1). The yields of the N-containing gaseous products are shown in Fig. 9.

\[
\eta(\text{N}_2) = \frac{n - n(\text{NH}_3) - n(\text{HCN}) - n(\text{NO}_x)}{n}
\]  

(1)

where \(n\) is the molar concentration of nitrogen-containing substance of the added sludge, 0.00027 mol.

With the increase of CO\textsubscript{2} concentration from 0 to 25 vol\%, the yield of N\textsubscript{2} increases significantly from 47% to 55%. When the CO\textsubscript{2} concentration further increases to 35 vol\%, the yield of N\textsubscript{2} is stable, while the release of NO\textsubscript{X} somewhat increases. When
combustion temperature and O₂ concentration do not change, NOₓ release is mainly affected by the reduction reaction of NO, which preliminarily indicates that a higher CO₂ concentration (25–35%) leads to the decline of the reduction of NO.

3.3 Effects of CO₂ concentration on NO reduction

NO reduction efficiency is calculated by eqn (2)

\[ \eta_{NO} = \frac{C_0 - C_1}{C_0} \times 100\% \]  

where \( C_0 \) is the NO concentration at reactor inlet; \( C_0 \) is 600 mg m\(^{-3}\) confirmed by Gasmet; \( C_1 \) is the NO concentration at reactor outlet at different reaction times.

Fig. 10(a) shows the variation of NO concentration during NO reduction by sludge reburning under different CO₂ concentrations. There are three stages in the reaction between sludge and NO with oxygen concentration of 3%. The first stage is that the NO concentration increase and exceeds 600 mg m\(^{-3}\). When sludge is added to the reaction tube at one time (completed in 2 s), volatiles and fixed carbon are burned to generate large amounts of NO under well-oxygenated conditions. The amount of NO generated exceeds the amount that of reduced by reducing gas and nascent char. Therefore, the initial stage is dominated by the NO oxidation. At the second stage, with the gradual release of reducing gases (HCN, CO, CH₄ and NH₃), O₂ in atmosphere is depleted quickly and is correspondingly insufficient surrounding the reducing species. Therefore, the amount of NO reduced by reducing gases and char is more than the amount of NO generated. This stage is dominated by the NO reduction, which decreases the NO concentration to less than 600 mg m\(^{-3}\) at the reactor outlet. At
the last stage, as the reaction continues, the residual volatiles and char gradually decreased. The rate of O2 consumption becomes correspondingly lower, and O2 is sufficient to oxidize the reducing gases and char. Thus, the rate of NO reduction by reducing gases and char is lower than that of NO formation. The NO concentration at the reactor outlet is more than 600 mg m$^{-3}$ again. This stage is dominated by NO oxidation.

NO reduction efficiency at the reduction stage (second stage) is displayed in Fig. 10(b). It is observed that CO2 concentration affects NO reduction. NO reduction efficiency follows a pattern of first increasing and then decreasing with the increase of CO2 concentration. When the CO2 concentration increased from 0 to 25 vol%, NO reduction efficiency showed a slightly increasing trend. As the CO2 concentration further increased (25–35 vol%), the NO reduction clearly decreased. The optimal NO reduction efficiency is 54% at a CO2 concentration of 25 vol% during sludge reburning. Results suggest that a comparatively higher NO reduction efficiency (more than 50%) could be acquired during sludge reburning with a CO2 concentration of 10–30 vol%.

As presented in Fig. 11, variation of O2 and CO2 concentrations during sludge combustion also have some effects on NO reduction. When the sludge is added downward into the reaction tube, O2 in the atmosphere is consumed quickly, and a large amount of CO2 is generated during the combustion process. Compared with Fig. 10, there is a valley value for O2 consumption and a peak value for CO2 generation when the NO reduction efficiency reaches the maximum value. At the same time, the combustion reaction of sludge is the most severe, which is consistent with the variation of NO concentration.

3.4 Homogeneous and heterogeneous mechanisms of NO reduction

TEM investigations give information on the morphology and structural characteristics of sludge char. Fig. 12(a) and (b), show that sludge char has two-dimensional sheet-like nanostructure. The structure is compact with some clearly visible cracks. The crystal at different orientations can be observed (Fig. 12(c)), suggesting that the char nanosheets are composed of numerous crystalline subunits with various orientations. The nitrogen adsorption–desorption isotherms and corresponding pore size distribution curves of sludge char are shown in Fig. 12(d). The specific surface area of char is 70 m$^{2}$ g$^{-1}$, which offers lots of active sites and increases the adsorption of reactants. The isotherm of char is type V with an H3-type hysteresis loop within a relative pressure range of 0.4 to 1.0. A narrow distribution range of pore size from 1 to 10 nm can also been found, indicating a mesoporous feature (2–50 nm). The specific surface areas, pore volume, and pore size of char are provided in Table 3.

Dynamic properties of NO reduction by sludge char are shown in Fig. 13. The optimum NO reduction efficiency by char reburning is 11%. The reducing capacity of char may be associated with the specific surface area and the distribution of active sites. On the basis of the previous discussion, the reduction efficiency of NO by sludge reburning can reach 54% under the same conditions, which implies that the reducing gases have an important influence on the NO reduction efficiency. The results indicate that NO reduction is dominated by the gas–gas homogeneous reduction reactions during sludge reburning.
In order to characterize the gas–gas homogeneous reduction reactions, the dynamic processes of NO reduction by CO are investigated. CO exhibited negligible activity on the reduction of NO from the result of blank experiment. The addition of CO can improve NO reduction efficiency in the presence of char, which confirm that the NO reduction by CO requires the presence of catalysts. Compared with the case without CO, the NO reduction increased about 8.5% and 19% corresponding to the CO concentration of 600 and 2400 mg m$^{-3}$, respectively. The increase of NO reduction efficiency over sludge char is attributed to the enhancement of solid–gas reaction between NO and char and its surface-catalyzed reaction of NO with CO. The results indicate that the reactions between CO, NO and char play an important role in NO reduction, especially under a relatively higher concentration ratio of CO to NO. The highest reduction ratio of 30% is achieved when the concentration ratio of CO to NO is 4 : 1.

NO can react with NH$_3$ to produce the final product N$_2$, which involves three reactions presented as eqn (3)–(5).**

**Table 3** The specific surface areas, pore parameters and optimal NO reduction ratio of sludge char

| Sample      | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | Total volume (cm$^3$ g$^{-1}$) | Peak pore size (nm) | Optimal NO reduction ratio |
|-------------|----------------------------------|-------------------------------|--------------------|---------------------------|
| Sludge char | 70.12                            | 0.12                          | 6.63               | 11%                       |

*Fig. 12* TEM (a–c) images, nitrogen adsorption–desorption isotherms and the corresponding size distribution curves (inset) of (d) sludge char.
When the moisture content of 0%, the gas–gas homogeneous phase reaction between NO and NH₃ does not occur without moisture. Thus, it is reasonable to deduce that \( \cdot \text{OH} \) and \( \cdot \text{O} \) radicals involved in these reactions initially come from the thermal decomposition of H₂O.\textsuperscript{14,15} To investigate the gas–gas homogeneous reduction reactions of NH₃ to NO, a certain amount of water vapor needs to be added. The influence of NH₃ concentration on NO reduction with an H₂O concentration of 3 vol% is shown in Fig. 14(a). The NO reduction efficiency (52.3%) under a NH₃ concentration of 1200 mg m\(^{-3}\) is much higher than that under a NH₃ concentration of 300 mg m\(^{-3}\) (29.6%). The significantly improved NO reduction can be ascribed to the increase of molecular weight of NH₃ in unit gas and the more sufficient reaction contact areas. When the concentration ratio of NH₃ to NO continually increases to 4 : 1, the NO reduction efficiency only increases to 56%. Besides, the influence of CH₄ concentration on NO reduction is presented in Fig. 14(b). When the concentration ratio of CH₄ to NO is 4 : 1, the NO reduction efficiency is only 6%, which shows that CH₄ exhibits negligible effect on NO reduction compared with CO and NH₃. CH₄ can be decomposed into CH\(_i\) radicals, which react with NO to form HCN.\textsuperscript{14,19} Theoretically, the reduction of NO by CH₄ will show high efficiency. However, the actual results are opposite. It is reasonable to deduce that when CH\(_i\) radicals react with NO to form HCN. The generated HCN will be oxidized to NO as a precursor under the condition of a certain residence time (approximately 1.5 s), reaching a balance between the reduction and oxidation of NO.

3.5 The mechanism of the effect of CO\(_2\) concentration on NO reduction

The mechanistic study on the effects of CO\(_2\) concentration on NO reduction by sludge reburning is carried out in a pilot scale cement precalciner. In combination with the above results, the mechanism of the effect of CO\(_2\) concentration on NO reduction is proposed, as shown in Fig. 15. The CO\(_2\) promotes the CO release significantly and inhibits the release of HCN, NH₃, and CH₄ when CO\(_2\) concentration increase from 0 to 25 vol%. The CO is confirmed to be one of the dominant reactive species during NO reduction.\textsuperscript{36} Hence, the increase of CO release counteracts the negative effect of the decrease of NH₃, HCN, and CH₄ release on the NO reduction, which leads to the significant increase of NO reduction efficiency from 44% to 54%. When CO\(_2\) concentration continuously increases to 35 vol%, the local reaction temperature decreases due to the strong radiation absorption of CO\(_2\), which results in the weakening of gasification rate.\textsuperscript{14,31} Thus, the releases of CO and HCN decrease slightly and obviously accordingly. NH₃ released is relatively stable. Besides, CH₄ released increases significantly, while CH₄ play a negligible role in the reduction of NO. As a result, there is an optimum CO\(_2\) concentration of 25 vol% for the NO reduction. Lower or higher than this concentration will result in the decrease of NO reduction efficiency.

![Fig. 13](image-url) Dynamic properties of NO reduction by CO in the presence of sludge char. Reaction conditions: 600 mg m\(^{-3}\) of NO, 25 vol% of CO\(_2\), 3 vol% of O\(_2\), and balanced N\(_2\), temperature = 900 °C.

![Fig. 14](image-url) (a) Efficiency of NO reduction by NH₃ (a) and CH₄ (b). Reaction conditions: 600 mg m\(^{-3}\) of NO, 3 vol% of O\(_2\), 25 vol% of CO\(_2\), 3 vol% of H₂O, and balanced N\(_2\), temperature = 900 °C.
4 Conclusion

The effects of CO₂ concentration on the release of reducing gases and NO reduction during sewage reburning are investigated. The main conclusions are summarized as follows:

(1) CO₂ concentration plays an important role on NO reduction during sludge reburning. The maximum NO reduction efficiency of 54% can be achieved with a CO₂ concentration of 25 vol%. It is feasible to use sludge as a reducing agent for NO reduction in the cement industry.

(2) The homogeneous and heterogeneous reduction reactions of NO occur simultaneously during sludge reburning. According to the reduction performance of NO by NH₃, CO, CH₄ and sludge char, CO and NH₃ make greater contributions to the NO reduction than sludge char. So NO reduction is dominated by homogeneous reduction reactions.

(3) The main types of reducing gases produced during sludge reburning are HCN, NH₃, CO and CH₄. Among them, NH₃ is mainly derived from low volatility components combustion, while HCN, CO and CH₄ are produced from thermally unstable and stable functional groups. Meanwhile, CO₂ concentration plays an important role in the release of HCN, CO and CH₄. The influence of CO₂ concentration on NO reduction is mainly attributed to the CO released.

Conflicts of interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

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