The effect of additives on NO reduction using sewage sludge as a denitration agent for cement kiln flue gas

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Abstract: Experimental study on the effects of additives on the NO reduction efficiency by sludge combustion was carried out on a simulated cement precalciner, and the feasibility of sludge as a denitration agent for cement kiln flue gas was evaluated. The NO reduction efficiency by sludge combustion with and without cement raw meal are 53.75% and 59.03%, respectively. It indicates that cement raw meal(CRM) inhibit the NO reduction by sludge combustion, while its inhibitory effect is not obvious. Besides, the inhibitory effect of CRM on NO reduction can be further reduced by controlling the addition amount of Al₂O₃ and Fe₂O₃ in CRM. Meanwhile, when urea is added to the sludge, the NO reduction efficiency can reach 74.21% by sludge combustion, indicating that urea significantly promotes the NO reduction, which is attributed to the decomposition of urea to form NH₃. Therefore, it is feasible to add sludge as a denitration agent in the cement precalciner to reduce NO in cement kiln flue gas.

1. Introduction

Nitrogen oxides(NOₓ) are considered as harmful air pollutants, while a large amount of NOₓ are emitted from cement production. The combustion temperature range in the cement precalciner is 900-1200°C, and the flue gas residence time is relatively long. Therefore, selective non-catalytic reduction(SNCR) is a suitable denitration technology for cement kiln flue gas. Meanwhile, almost all cement industry have installed SNCR denitration device in China, while the deNOx efficiency of SNCR technology is around 50%[1,2].

Sludge is a by-product of municipal sewage treatment. Considering the complexity of its components and the technical difficulties of treatment, co-processing of sewage sludge in cement kiln has attracted widespread attention in recent years. Co-processing of sewage sludge in cement kiln can not only achieve sludge disposal, but also the reducing gases produced by sludge combustion can reduce NO from cement kiln flue gas[3,4]. For example, Fang et al.⁴ reported the monitoring findings that NOₓ removal efficiency can reached more than 70% by sludge combustion, which is superior to SNCR technology (approximately 50%) in cement kiln. It’s worth noting that there is a large amount of cement raw meal(CRM) in the cement precalciner, while the effect of CRM on NO reduction by sludge combustion is lack of relevant research.
In this study, the feasibility of sludge as a denitrification agent for cement kiln flue gas was studied on a gas-solid suspension reactor. Under the condition of simulated atmosphere in cement precalciner, the additives variety (CRM and its composition, urea, coal ash, calcium acetate) affecting the NO reduction by sludge combustion were systematically investigated. Based on the experimental results and literature, the influencing mechanism of additives on the NO reduction by sludge combustion was also discussed. The present work research can provide a theoretical basis for improving the sludge denitrification technology of practical engineering.

2. Experimental setup

2.1. Materials

The sewage sludge containing 78%-80% moisture was sampled from a municipal wastewater treatment plant located in the Guangzhou city, China. After 5-8 days of natural drying, it reaches constant weight to obtain air-dry sludge. Then the sewage sludge was ground and sieved to a size range of 0.18-0.25mm. The proximate analysis, ultimate analysis, and net calorific value of sewage sludge are referred to our previous articles\cite{5}.

The cement raw meal (CRM) used in this experiment was prepared according to the saturation ratio, the silicic acid ratio and the aluminum oxygen ratio. The main components of CRM were shown in table 1.

| Composition (w/g) | CaCO$_3$ | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | MgO | K$_2$CO$_3$ | Na$_2$SO$_4$ |
|------------------|----------|--------|-------------|------------|-----|-------------|-------------|
| 77.46            | 13.47    | 3.01   | 1.98        | 2.48       | 0.264 | 0.186       |

2.2. Experimental methods

Figure 1 display the schematic drawing of gas-solid suspension reactor to simulate the suspension state of cement precalciner. A gas-solid suspension quartz tube was composed of three parts, the conical zone (40 mm height), the upper of conical zone (20 mm ID) and the lower of conical zone (4 mm ID). The furnace temperature was designed to be 900°C.

Figure 1. Schematic drawing of gas-solid suspension reactor.
1-Quartz reactor; 2-Vertical tube electric furnace; 3-Thermocouple; 4-Temperature controller; 5-Hopper; 6-Holder; 7-Gasmet; 8-Computer; 9,10,11-Gas cylinder; 12,13,14-Mass flow controller; 15-Buffer bottle; 16-Filter
The initial concentrations of CO$_2$, O$_2$, NO and SO$_2$ in the simulated flue gas were 25 vol.%, 3 vol.%, 600mg/m$^3$ and 200mg/m$^3$, respectively. N$_2$ provided the balance, and the flue gas flow was maintained at 500 mL/min. The added amounts of sludge were 0.1 g. According to the actual operating conditions, the addition amount of CRM and its composition were 10 times that of sludge, the addition dosage of urea, coal ash and calcium acetate were 1/10 of the sludge. The NO concentration were analyzed by Gasmet analyzer, the interval time of Gasmet online sampling was set as 5 s.

3. Results and Discussion

3.1. Effect of CRM and its composition

Figure 2a shows the variation of NO concentration during NO reduction by sludge combustion under the effect of CRM and its composition. There are three stages in the reaction between sludge and NO. The first stage is that the NO formed from sludge combustion is more than that reduced by volatiles, this stage is mainly dominated by homogeneous NO oxidation. At the second stage, with the gradual production of reducing gases, much of the NO can be reduced. This stage is dominated by the NO reduction. At the last stage, NO reduction by reducing gases and char is lower than that of NO formation. This stage is dominated by NO oxidation$^{[6]}$. The NO reduction efficiency at the reduction stage (second stage) is displayed in Figure 2b. It is observed that CRM and its composition inhibit the NO reduction, and the rule of its influence is MgO<CaCO$_3$<CRM<Al$_2$O$_3$<Fe$_2$O$_3$. For instance, the NO reduction efficiency by sludge combustion with and without CRM are 53.75% and 59.03%, respectively. Besides, because of Al$_2$O$_3$ and Fe$_2$O$_3$ obviously inhibit the NO reduction, so the ratio of Al$_2$O$_3$ and Fe$_2$O$_3$ can be appropriately reduced in the CRM, which is beneficial to decrease the inhibitory effect of CRM on NO reduction.

In our previous research, it has been proved that NH$_3$ and CO play a leading role in the NO reduction$^{[5]}$. While CRM and its composition absorb heat, resulting in a relatively low local operating temperature of precalciner, which is not conducive to the CO produced by sludge combustion$^{[6]}$. Meanwhile, CRM and its composition have catalytic effect, especially CaCO$_3$ may be the main catalytic material for catalyzing sludge combustion to produce large amounts of NH$_3$$^{[7]}$. Therefore, it is reasonable to deduce that the negative effect of the decrease of CO produced in inhibiting NO reduction is greater than the positive effect of the increase of NH$_3$ produced in promoting NO reduction, the combined effect leads to the decrease of NO reduction.

3.2. Effect of urea, calcium acetate and coal ash

The effects of urea, coal ash and calcium acetate on the performance of NO reduction by sludge combustion were studied, and the results are shown in Figure 3. It can be found that urea significantly promotes the NO reduction by sludge combustion, and the maximum reduction efficiency of NO is

![Figure 2](image-url)
74.21%. This result is because urea decomposes at high temperature to produce NH₃, which can effectively reduces NO⁵⁻⁸. Nevertheless, calcium acetate and coal ash inhibit the NO reduction, the NO reduction efficiency are 55.28% and 50.43%, respectively. The decomposition of calcium acetate produces CaO, which can catalyze the oxidation of CO, leading to a decrease in the amount of CO involved in NO reduction, which is not conducive to the NO reduction⁹. The inhibitory effect of coal ash on NO reduction is because coal ash contains some metals, such as Al₂O₃ and Fe₂O₃. Combined with the result in Figure 2, Al₂O₃ and Fe₂O₃ significantly inhibit the NO reduction. Therefore, the role of coal ash and CRM is consistent, and it cannot promote the NO reduction by sludge combustion. Comprehensive analysis shows that a certain amount of urea can be appropriately added to the sludge to further improve the efficiency of sludge as a flue gas denitration agent.

Figure 3. (a)Variation of NO concentration during NO reduction by sludge combustion in the presence of urea, coal and calcium acetate; (b) The NO reduction efficiency at the reduction stage of Figure 3a.

4. Conclusion
(1) Cement raw meal and its composition inhibit the NO reduction, and the rule of its influence is MgO<CaCO₃<CRM<Al₂O₃<Fe₂O₃. For instance, the NO reduction efficiency by sludge combustion with and without cement raw meal are 53.75% and 59.03%, respectively. The inhibition of NO reduction by cement raw meal is not obvious, and the inhibitory effect of cement raw meal can be further reduced by appropriately decreasing the addition of Al₂O₃ and Fe₂O₃ in cement raw meal.
(2) Urea can improve NO reduction by sludge combustion, the NO reduction efficiency can reach 74.21%. So a certain amount of urea can be appropriately added to the sludge to further improve the efficiency of sludge as a flue gas denitration agent. Therefore, adding sludge to the cement precalciner for the reduction of NO from cement kiln flue gas is feasible.

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