

Effect of conditioner Fe₂O₃ on N-containing gaseous products distribution during sewage sludge thermal decomposition

Zijun Tang^{1,2,a}, Ping Fang^{1,2,b*}, Jianhang Huang^{1,2,c} and Peiyi Zhong^{1,2,d}

¹ South China Institute of Environmental Sciences, Ministry of Environmental Protection, Guangzhou 510655, PR China

² Guangzhou Huake Environmental Engineering CO., Ltd, Guangzhou 510655, PR China

^a tangzijun@scies.org, ^b fangping@scies.org, ^c 674097794@qq.com, ^d zhongpeiyi@scies.org

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Abstract. Thermal disposal of sewage sludge is likely to cause serious nitrogen related environmental problem, since it contains considerable amount of nitrogen. Considering that iron oxide (Fe₂O₃) is widely applied chemical condition for sewage sludge treatment, this study was focus on investigating the role of Fe₂O₃ in N-containing gaseous products distribution during sewage sludge thermal decomposition in a tube/fixed-bed furnace at 900°C with or without oxygen, respectively. According to the result, conditioner Fe₂O₃ had little influence on N-containing component transformation when using raw sludge sample, while NO rose roughly with the increasing amount of Fe₂O₃ as de-mineralized sludge was used. Oxygen content promoted the formation of nitrogen oxidative products while inhibited the reductive ones. In practical application, adjusting oxygen content can make N-containing components to convert into reductive products, which reduced the NO_x emission ultimately.

Introduction

Sewage sludge is unavoidable by-product of the waste water purification. In recent years, pyrolysis and combustion have aroused increasing attention for sewage sludge disposal and treatment, and begun to be used as a renewable energy^[1-2]. However, sludge contains considerable amount of nitrogen(2.4-9.0wt.%), which is much higher than that of coal(<1.0wt.%)^[3-5]. Although thermal disposal methods have many significant advantages, they are not widely used since oxides of nitrogen in the flue gas will cause severe environmental pollution, and the recovered heat energy is low beyond thermal energy utilization. The generation of NO_x during pyrolysis/combustion mainly depends on the types and concentration of NO_x precursors, such as HCN, NH₃. As one of chemical conditioners, iron oxide (Fe₂O₃) is widely used in sludge dewatering process. In this study, the distribution of N-containing gaseous products under different experimental conditions will be investigated, NO_x precursor types and concentration will be discussed.

Materials and methods

Preparation and property of raw sludge sample. Sewage sludge used in this study was dewatered sludge which came from a municipal sewage treatment plant in Guangzhou, China. After natural drying in open area for 3-5 days, the sludge was milled into 3-5mm particles, and then put into constant temperature and constant humidity box (T: 20°C, H: 60%) for 3 days before use. The

compositions of the raw sludge sample are shown in Table 1.

Table 1 Proximate, ultimate analysis and chemical compositions of sludge sample

| Proximate analysis(wt.%) | | | | | Ultimate analysis(wt.%, dry base) | | | | |
|---------------------------------------|------------------|------------------|------------------|-------------------|-----------------------------------|-------------|-------------|-------------|-------------|
| $\omega(M_t)$ | $\omega(M_{ad})$ | $\omega(A_{ad})$ | $\omega(V_{ad})$ | $\omega(FC_{ad})$ | $\omega(C)$ | $\omega(H)$ | $\omega(N)$ | $\omega(S)$ | $\omega(O)$ |
| 76.34 | 3.81 | 68.51 | 24.54 | 3.14 | 27.33 | 5.24 | 4.12 | 0.98 | 19.32 |
| Chemical compositions(wt.%, dry base) | | | | | | | | | |
| Al_2O_3 | CaO | Fe_2O_3 | K_2O | MgO | NiO | P_2O_5 | SO_3 | SiO_2 | ZnO |
| 14.637 | 8.679 | 15.617 | 5.749 | 3.693 | 0.046 | 8.343 | 2.418 | 35.375 | 0.592 |

Preparation of de-mineralized sludge sample. 27(v/v)% HCl + 9(v/v)% HF mixed acid solution was prepared and used as 10(ml):1(g) with raw sludge sample, after be put into a constant temperature water bath at 80°C for 6 hours, the sample was cooled to room temperature; de-ion water was used to wash the sample for several times until Cl⁻ can't be detected in filtrate; after that the sample was dried, milled into 3-5mm particles and put into the constant temperature and constant humidity box (T: 20°C, H: 60%) for 3 days before use.

Sludge pyrolysis/combustion procedure and sample analysis method. Sludge pyrolysis/combustion experiments were carried out in an electric tube furnace (600mm long with 120mm internal diameter), as shown in Fig.1. The concentrations of N-containing gaseous products were determined by Fourier infrared analyzer after removing particles by a quartz filter. The tail gas was absorbed by activated carbon before emission.

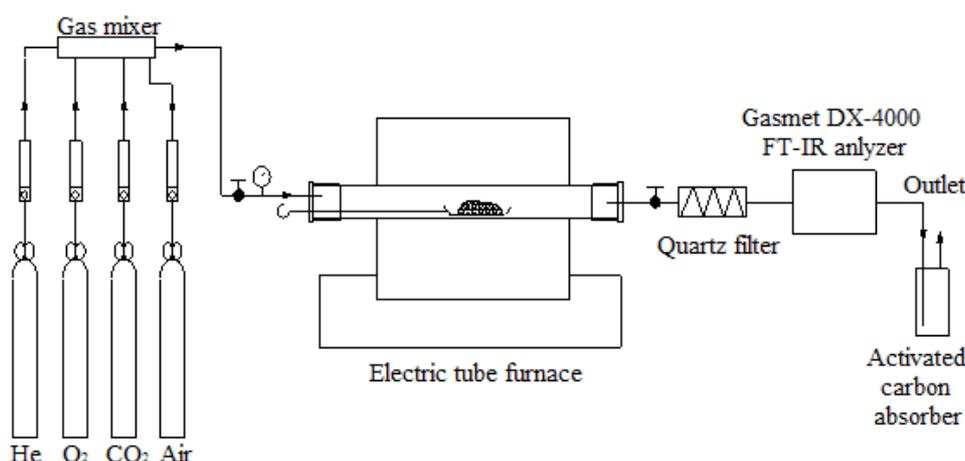


Fig.1 Schematic diagram of experimental device

Results and Discussions

The reactive gas was made of Ar and O₂, the total reactive gas flow was 5L/min, the reaction time was 20min, and the mass of sludge sample was 5g. The results of N-containing products distribution with different addition amount of Fe₂O₃ with or without oxygen were shown in Fig.2.

In oxygen-free atmosphere, the main N-containing products was NO, NH₃ and HCN. With the increasing mass ratio of Fe₂O₃, the proportion of NO-N in gaseous phase increased first and then decreased slightly, which accounted for 26.38% - 42.00% of total N content. The reduced products NH₃ and HCN didn't change much with the addition of Fe₂O₃; when the mass ratio of Fe₂O₃ was 0%, the proportion of NH₃-N was the dominated component which occupied 53.86%. As the oxygen content increased to 5%, NO, N₂O and HCN were the major species of N-containing

gaseous products comparing with oxygen-free atmosphere; with the rising amount of conditioner Fe_2O_3 , above mentioned three gas components didn't change obviously. So it can be concluded that the sewage sludge regulator Fe_2O_3 had little effect on the distribution of N-containing products during pyrolysis or combustion, while the existence of oxygen had a significant influence on the species and its distribution of gaseous components in the flue gas. The differences between two reactive atmosphere indicated that the existence of oxygen promoted the generation oxidative gaseous products, such as NO and NO_2 , while the reductive product especially NH_3 was inhibited.

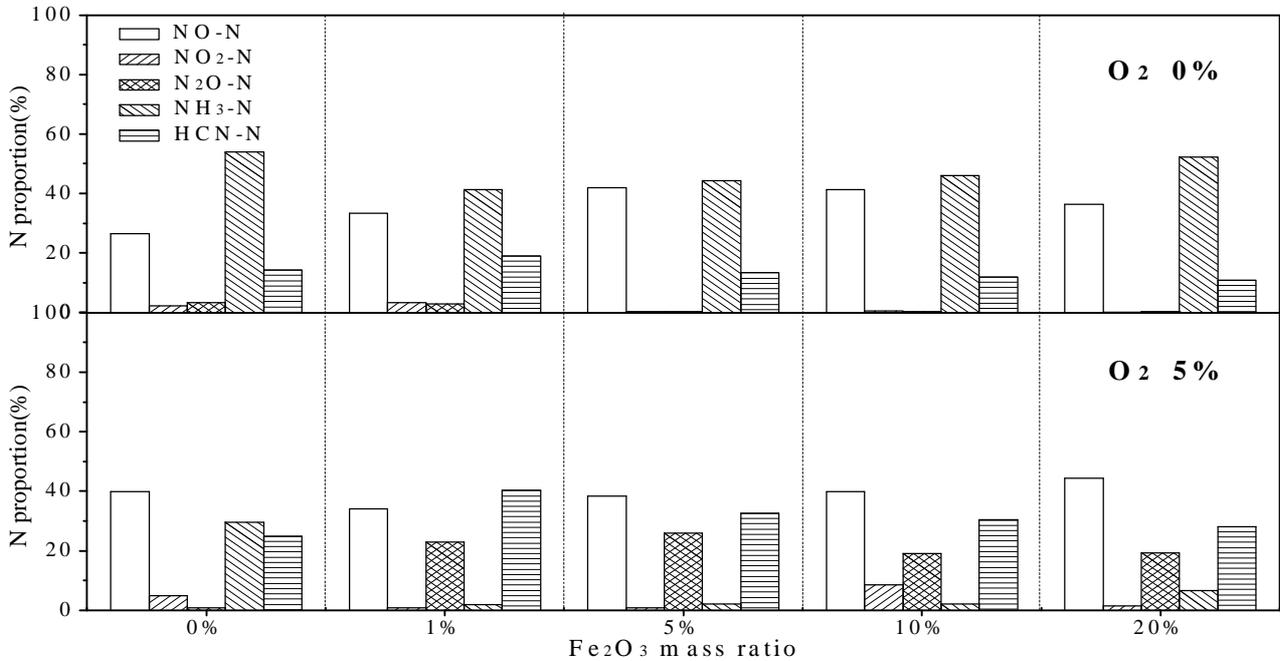


Fig.2 Effect of conditioner Fe_2O_3 on nitrogen transformation of raw sludge

Under the same experimental condition, de-mineralized sludge was used to replace raw sludge sample to study the effect of conditioner Fe_2O_3 on nitrogen transformation ruling out the effect of sludge metal salts components, results were shown in Fig.3.

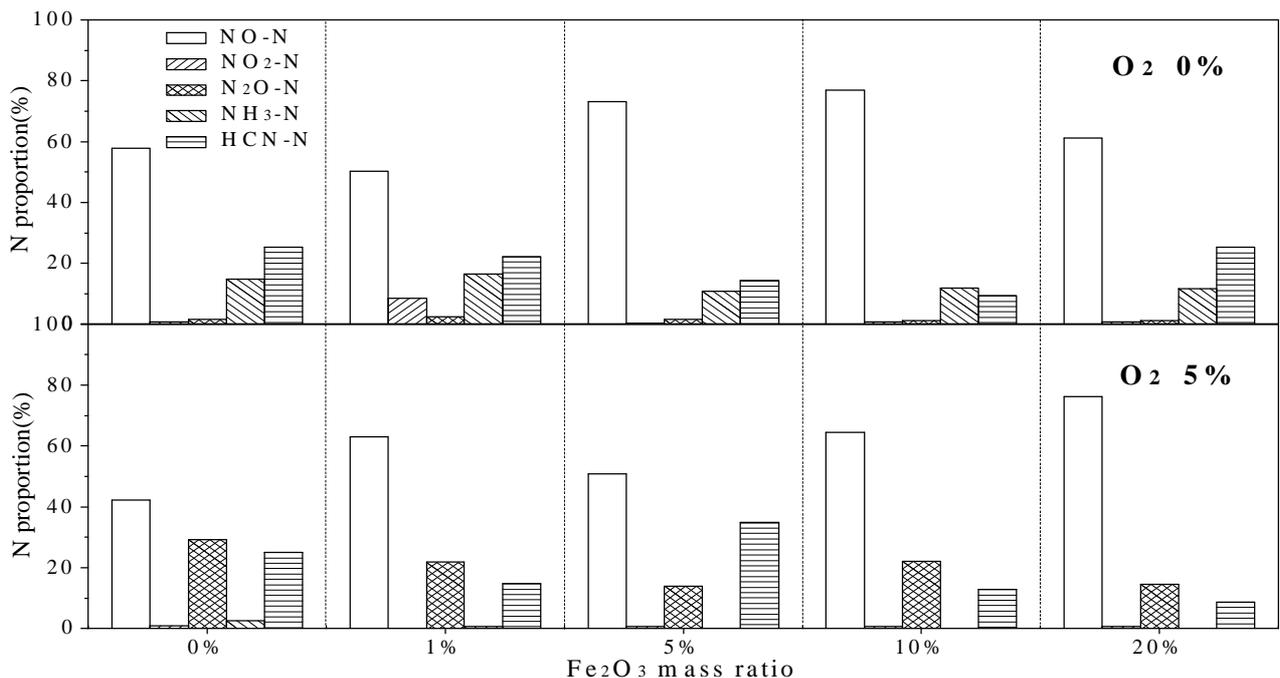


Fig.3 Effect of conditioner Fe_2O_3 on nitrogen transformation of de-mineralized sludge

It can be learned from Fig.3 that using the de-mineralized sludge sample, the ratio of NO

increased dramatically. Although the trends of all five gaseous components were not apparent, the tendency of NO proportion rose with the adding of Fe_2O_3 , while the NH_3 and HCN decreased was obviously. This provided a contrast with the N transformation between the raw sludge and the de-mineralized sludge during thermal decomposition. The reason can be explained as mineralizers in the sludge were essential agents, which played a significant role in nitrogen precursors converting into the final products. Oxidative gaseous components were prohibited to generate with the existing of mineralizers, while the addition of Fe_2O_3 promoted the formation of NO which transformed from N-containing components of the sludge sample.

Further research on the effect of oxygen content on nitrogen transformation was performed by using de-mineralized sludge with 10wt.% conditioner Fe_2O_3 , the result was shown in Fig.4.

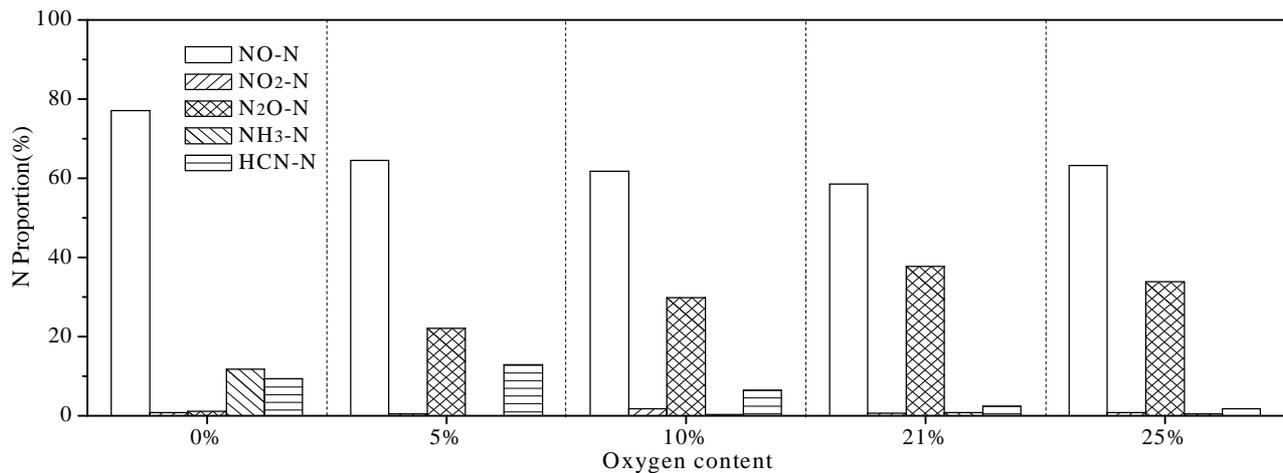


Fig.4 Effect of different oxygen content on nitrogen transformation with 10% Fe_2O_3

It can be seen in Fig.4 that with the rising content of oxygen, the total nitrogen containing oxides increased, NO concentration decreased slightly, NO_2 can't be detected and the content of N_2O grew; reductive components proportions declined, NH_3 can only be detected in oxygen-free atmosphere, and HCN decreased with the increasing oxygen content. It suggested that oxygen promoted N-containing components to transfer into oxidative products while inhibited the reductive ones, since NH_3 is widely used in denitration engineering applications, it indicated that controlling the oxygen content during sludge decomposition can make the nitrogen containing components to convert into NH_3 , which reacts with NO_x in other stage of pyrolysis/combustion, the total emission of NO_x will be reduced eventually.

Conclusion

1. Mineralizers in sludge played an important role in promoting nitrogen precursors to convert into reductive products. Conditioner Fe_2O_3 had little influence on N-containing component distribution when raw sludge was used; by using de-mineralized sludge, the ratio of NO rose roughly with the increasing amount of Fe_2O_3 .

2. With the rising content of oxygen, nitrogen oxidative products increased, reductive ones declined, NH_3 only formed in oxygen-free atmosphere.

3. In practical application, the addition of conditioner Fe_2O_3 had little influence on NO_x control, while regulating oxygen content can make N-containing components to convert into reductive products, which reduced NO_x emission.

Acknowledgements

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References

- [1] V.K. Tyagi and S.L. Lo: Sludge: A waste or renewable source for energy and resources recovery? [J]. *Renew. Sust. Energ. Rev.*, Vol. 25 (2013), p. 708-728.
- [2] H. Yao, I.S.N. Mkilaha and I Naruse: Screening of sorbents and capture of lead and cadmium compounds during sewage sludge combustion[J]. *Fuel*, Vol. 83 (2004), p. 1001-1007.
- [3] V.K. Tyagi and S.L. Lo: Microwave irradiation: a sustainable way for sludge treatment and resource recovery[J]. *Renew. Sust. Energ. Rev.*, Vol. 18 (2013), p. 288-305.
- [4] F.J. Tian, B.Q.Li and Y Chen: Formation of NO_x precursors during the pyrolysis of coal and biomass. Part V. Pyrolysis of a sewage sludge[J]. *Fuel*, Vol. 81 (2002), p. 2203-2208.
- [5] Y. Tian, J. zhang and W. Zuo: Nitrogen conversion in relation to NH₃ and HCN during microwave pyrolysis of sewage sludge[J]. *Environ. Sci. Technol.*, Vol. 47 (2013), p. 3498-3505.