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GREY RELATIONAL ANALYSIS OF N_2O EMISSION FROM OIL SHALE-FIRED CIRCULATING FLUIDIZED BED

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This study aims to identify key operating variables affecting N_2O emission from oil shale-fired circulating fluidized bed (CFB). These operating variables include bed temperature, excess air factor, particle size, secondary air ratio, Ca/S ratio, circulation rate and bed material height. Using an oil shale-fired CFB pilot setup composed of a quartz tube and heated by an electric heater, the experiments of N_2O emission were carried out with oil shale test samples obtained from Huadian, China. Grey relational method was used to treat the experimental data. Calculation results indicate that bed temperature is a variable most closely related to changes in N_2O emission; the effects of secondary air ratio and circulation rate are negligible. The operating variables sequenced in order of decreasing effect are bed temperature, excess air factor, Ca/S ratio, particle size, bed material height, secondary air ratio, circulation rate. The experimental results and grey relational analysis can provide reference data for design of oil shale-fired CFB furnaces.

Introduction

Because of very low NO_X emissions and high desulfurization efficiency, circulating fluidized bed (CFB) combustion has been widely accepted as one of the most advanced, environmentally benign technologies of coal combustion. However, the recognition of nitrous oxide (N_2O) as an extremely long-life and strong radiative forcing greenhouse gas and a stratospheric ozone destroyer has imposed concerns of the possible adverse impact on the environment of a wider application of coal-fired circulating fluidized-bed combustors that emit high levels of N_2O (potentially 200 ppmv or higher) [1, 2]. So far there have been many publications on the studies of N_2O

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emission from coal-fired fluidized bed. Fuel-bound nitrogen of fuel volatile matter is usually the main source for both NO_X and N_2O emissions from coal-fired CFB combustors [3-8]. Formation and decomposition reactions of NO_X and N_2O in CFB combustors are catalytically affected more or less by some materials, such as char, $CaCO_3$/CaO, calcium sulphates, ash [9, 10].

It has been proven that burning of oil shale in a CFB furnace is the most effective and economical among all the modes of oil shale combustion [11, 12]. However, there is few data reported on N_2O emissions of oil shale-fired CFB furnaces. In order to find out how operating factors influence changes in N_2O emission at combustion of oil shale in a circulating fluidized-bed furnace, the results of experimental investigations of N_2O emission made in an experimental CFB pilot setup are presented in this paper.

Grey relational analysis provides a useful approach to deal with the problems of limited and superficial ruleless data processing, so as to search for primary relationships among the factors and determine important factors that significantly influence some defined objectives [13]. So, grey relational analysis was applied to evaluate the effect of operating variables on N_2O emission and to find out key factors.

Experimental

The oil shale samples used in this work were obtained from Huadian, China. The analytical data characterizing oil shale and its ash have been given in [10]. The samples were ground and sieved to four size ranges (shown in Table 1) and dried in a desiccator.

The block diagram of the CFB pilot setup used for this experimental study is shown in Fig. 1. The detailed instruction has also been given in [10]. The pilot setup was equipped with a Maester gas analyzer enabling continuous measuring of conventional flue gas components, such as NO, CO_2, O_2. Chromatograph, mass spectrometer and Fourier-infrared analyzer can all be used to record N_2O concentration. By comparison, Fourier-infrared analyzer was the most convenient among these measuring sets and eventually adopted.

Seven operating factors under investigations included bed temperature, excess air factor, particle size, secondary air ratio, Ca/S ratio, circulation rate,

Table 1. **Operating conditions**

Parameter	Variable range
Bed temperature, °C	750, 850, 950, 1050
Particle size, μm	0–300; 300–600; 600–900; 900–1200
Ca/S molar ratio	4.36; 5; 6; 8
Excess air factor	1.14, 1.24, 1.68, 2.1
Circulation rate	0, 2, 4, 6, 12
Bed material height, cm	1, 2, 3, 4, 5, 7
Secondary air ratio, %	0, 20, 30, 40, 50

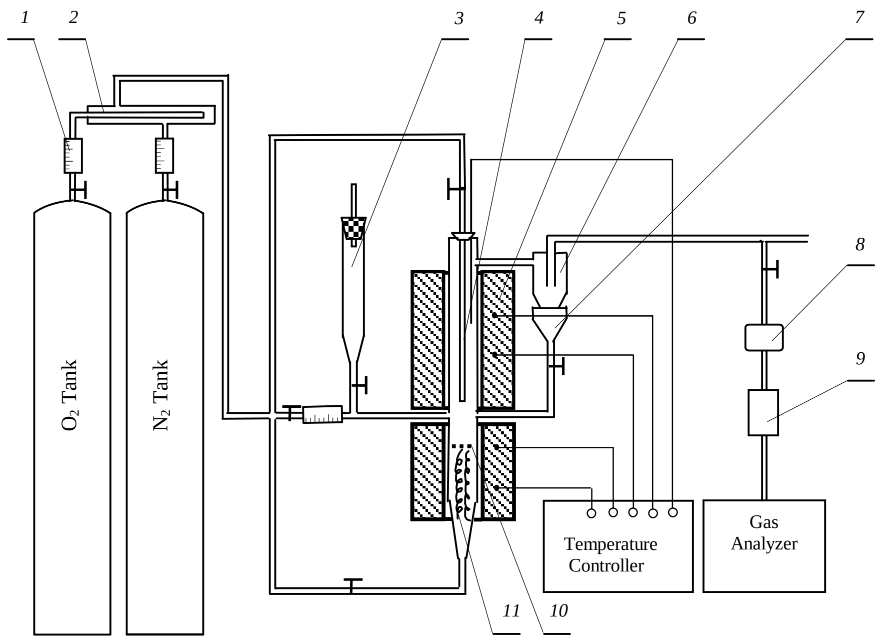

Fig. 1. Block diagram of the circulating fluidized-bed pilot setup: *1* – flowmeter, *2* – gas mixer, *3* – hopper, *4* – quartz tube, *5* – electric heater, *6* – cyclone, *7* – ash bucket, *8* – ash filter, *9* – desiccator, *10* – distributor plate, *11* – wire

and bed material height. To find out their effect on N_2O emission, each factor was changed keeping the others constant. N_2O mol concentration in flue gas was recorded for each value of operating variables changed when O_2 mol concentration in flue gas was equal to 6%.

Results and Discussion

Bed temperature

Kilpinen and Hupa [14] studied the effect of bed temperature on conversion of HCN and NH_3 into N_2O. They showed that the concentration of O, OH and H increased with increasing bed temperature, which would make most of NCOs react with these free radicals to form NO rather than N_2O. The reaction paths into NO are as follows:

$$\mathrm{NCO + H \rightarrow NH + CO} \quad (1)$$

$$\mathrm{H + NH \rightarrow H_2 + N} \quad (2)$$

$$\mathrm{N + OH \rightarrow NO + H} \quad \text{and} \quad \mathrm{N + O_2 \rightarrow NO + O} \quad (3)$$

Because most of NCOs have been transformed into NO, the following predominant homogeneous reactions forming N_2O weaken:

$$NCO + NO \rightarrow N_2O + CO \quad (4)$$

$$NH + NO \rightarrow N_2O + H \quad (5)$$

Furthermore, increasing bed temperature can accelerate the following elementary reactions that usually play an important role in decomposing N_2O

$$N_2O + H \rightarrow N_2 + OH \quad (6)$$

$$N_2O + OH \rightarrow N_2 + HO_2 \quad (7)$$

In Fig. 2a, homogeneous formation and decomposition reactions of N_2O weaken and intensify, respectively, with increasing bed temperature, which makes N_2O emission first increase below 850 °C, and then diminish above 850 °C. A possible cause that the first point in Fig. 2a is lower is ascribed to incomplete combustion of oil shale particles.

Excess air factor

In Fig. 2b, N_2O emission increases with an increase in excess air factor, which corresponds to the results of previous experiments made on coals. Formation of HCO through HCN-mechanism requires O, and formation of NO, (–N), (–CNO) also involves O. If there is oxygen deficit, the amount of these intermediate products forming N_2O will decrease and N_2O concentration will reduce.

Particle size

Boavida with coworkers [15] showed that a decrease in devolatilization rate with increasing particle size made N_2O emission decrease. Furthermore, Feng with coworkers [16] found that particle size had only a little effect on the amount of N_2O emission after bed temperature exceeded 850 °C, because volatiles could quickly be released under higher bed temperature.

In this experiment, N_2O concentration gradually decreased with increasing particle size under the bed temperature of 850 °C, just as shown in Fig. 2c.

Secondary air ratio

Figure 2d shows the effect of secondary air ratio on N_2O emission. With increasing secondary air ratio, N_2O emission quickly diminishes when the ratio is below 0.2 and increases subsequently.

Although previous experimental results showed that the effect of stepwise combustion on N_2O emission was widely divergent, the change in the temperature of the dilute phase was all emphasized. Lan with coworkers [17] found that stepwise combustion would make N_2O and NO_X emissions diminish at temperatures ranging from 800 °C to 950 °C. Concentration of coke and CO increased, and deoxidation medium became intense in the

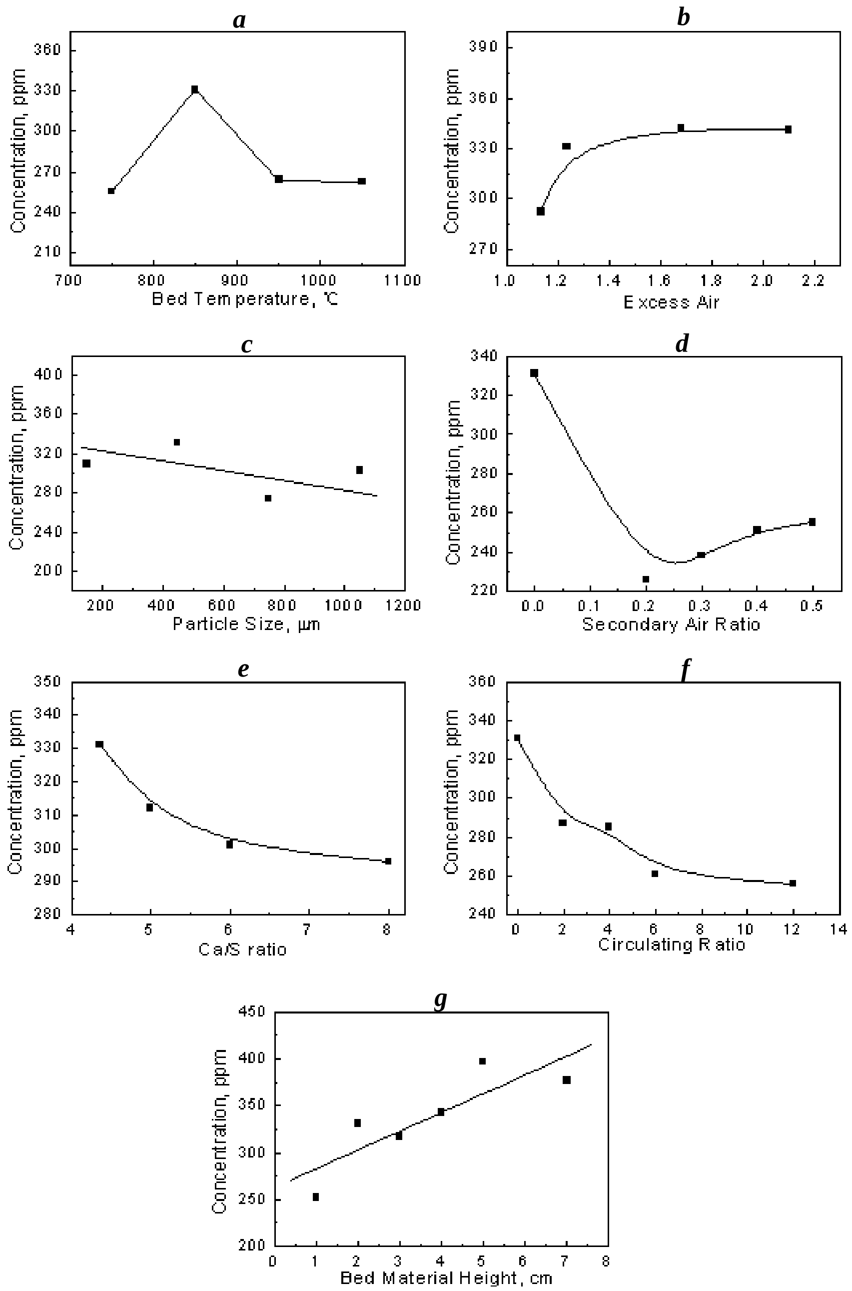

Fig. 2. Emission of N_2O at various values of bed temperature (*a*), excess air factor (*b*), particle size (*c*), secondary air ratio (*d*), Ca/S ratio (*e*), circulation rate (*f*), and bed material height (*g*)

dense phase at stepwise combustion, which could greatly reduce NO_X and make the decomposition product of fuel-bound nitrogen easy to compound to N_2; and a decrease in N_2O emission was mainly ascribed to an increase of 70–80 °C in temperature of the dilute phase. However, Lu with coworkers [18] showed that N_2O concentration was slightly (by about 20 ppm) increased with increasing secondary air ratio. One possible reason was that excessively high secondary air ratio decreased temperature of the dilute phase.

Ca/S ratio

Figure 2e demonstrates that N_2O emission gradually decreases after addition of CaO into the pilot setup proving that CaO exerts an effect on N_2O decomposition, like shown by Lan and coworkers [17]. Catalytic action of CaO on N_2O may be described as follows:

$$2N_2O \xrightarrow{CaO} 2N_2 + O_2 \quad (8)$$

$$N_2O + CO \xrightarrow{CaO} N_2 + CO_2 \quad (9)$$

CaO may also react with HCN and NH_3 through the following equations:

$$CaO + HCN \rightarrow Ca + NO + CH \quad (10)$$

$$2CaO + HCN \rightarrow 2Ca + NO + CO + \frac{1}{2}H_2 \quad (11)$$

$$2CaO + NH_3 \rightarrow Ca + NO + H_2 + CaOH \quad (12)$$

Moreover, $CaSO_4$ and CaS formed in the furnace have also a certain catalytic action on N_2O decomposition, even directly on reduction of N_2O

$$3N_2O + CaS \rightarrow 3N_2 + SO_2 + CaO \quad (13)$$

The reactions above consume HCN and NH_3 and change the pathway of N_2O formation through homogeneous reaction. So N_2O concentration of flue gas decreases.

Circulation rate

Just as said above, N_2O is mainly derived from fuel volatile matter at combustion. When the amount of the fuel in the furnace remains constant, ash concentration in the furnace will increase with increasing circulation rate. According to the analytical data on composition of oil shale and its ash, we know that oil shale is a kind of low-rank fuel with high ash content and plenty of metal oxides which have a certain catalytic effect on the reduction reaction of N_2O and NO_X [17, 19]. However, the experimental results of this paper are opposite to that of Lan et al. [17]. The authors ascribed the difference to fuel species. Nitrogen content of oil shale volatile matter is more than that of shale ash. After oil shale was put into the furnace, volatiles would sharply be pyrolyzed, and only a small amount remains in ash. Although N in the circulating ash may form N_2O during combustion in the furnace, this amount is so small that it cannot offset the catalytic effect of metal oxides within circulating ash on N_2O decomposition. Just as shown in Fig. 2f, N_2O emission will decrease with increasing circulation rate.

Bed material height

The effect of bed material height on N_2O emission was seldom reported. In fact, bed material height is an important operating variable in regulating furnace temperature, fuel combustion and emission of gaseous pollutants. The amount of bed material elutriated into the dilute phase will increase with increasing height of bed material, which favors reduction of the temperature of the dilute phase keeping temperature in the furnace uniform. So, Fig. 2g shows that N_2O concentration increases with an increase in bed material height other operating variables being kept constant because the decrease in temperature of the dilute phase will make N_2O emission increase.

Grey relational analysis of the factors influencing N_2O emission

Principles of grey relational analysis

In a system that is complex and multivariate, the relationship between various factors such as those described above is unclear. Such systems are often “grey” implying poor, incomplete, and uncertain information. Their analysis by classical statistical procedures may not be acceptable without large data sets and data satisfying certain mathematical criteria. The grey theory, on the contrary, makes use of relatively small data sets and does not demand strict compliance to certain statistical laws, simple or linear relationships among the observables. So it is suitable to apply grey system theory to identification of causative factors of N_2O emission.

Grey system theory believes that a random process is a grey quantity variable in an area of a certain amplitude and time zone. Grey process describes the course of looking for the regularity of variable by dealing with raw data. Grey relational analysis is defined as quantity analysis to developing trend in various systems, and the more similar are developing trends, the greater is the relational extent. The way to compare the relational extent among factors is called relational coefficient or relational grade method [20].

Procedure of grey relational analysis

Affirming comparison sequence and reference sequence

Grey relational analysis is substantially suitable to compare geometrical similarities between objects. On the average, the closer geometrical similarities are, the closer changeable tendency is, and the bigger relational grade is. So, before grey relational analysis is carried out, reference sequence must firstly be constructed, then trend degree between other sequences and reference sequence can be compared, lastly other sequences can be compared with each other.

Now, reference sequence can be expressed as follows:

$$X_0 = \left\{ X_0(k) \big|_{k=1,2,3,...,n} \right\} \tag{14}$$

Comparison sequence is

$$X_1 = \left\{ X_1(k) \big|_{k=1,2,3,...,m} \right\} \tag{15}$$

where, n represents the number of factors that have a certain relational effect on reference factor; and m is the number of dynamic observed value of comparison sequence.

Initializing the original data

In relational analysis, the dimensions of all sorts of factors are usually different, and the difference in magnitude order is large. Initializing the original data is making magnitude order of the original data close, unit dimensionless, relational analysis reasonable and error small. Initialization method usually marks out data (0, 1).

$$X_i(k) = \frac{X_i(k)}{X_{i\max}} \quad (k = 1, 2, 3, \cdots, n, \quad i = 1, 2, 3, \cdots, m) \tag{16}$$

where: $X_{i\max} = \max\left\{ X_i(1), X_i(2), X_i(3), \cdots, X_i(n) \right\} \quad (i = 1, 2, 3, \cdots, m)$

Absolute dispersion between comparison sequence and reference sequence

$$\Delta_i(k) = \left\| X_0(k) - X_i(k) \right\| \quad (i = 1, 2, 3, \cdots, m) \tag{17}$$

where: $\Delta_i(k)$ is called absolute dispersion between X_0 and X_i at moment k.

Two-stage maximum and minimum difference value

The minimum distance between the points of X_i curve and the relevant points of X_0 curve is called one-level minimum difference $\min\Delta_i(k)$:

$$\min \Delta_i(k) = \min\left\{ \Delta_i(1), \Delta_i(2), \Delta_i(3), \cdots, \Delta_i(n) \right\} \tag{18}$$

The two-staged minimum difference $\min\min\Delta_i(k)$ is written as:

$$\min\min \Delta_i(k) = \min\left\{ \min \Delta_i(1), \min \Delta_i(2), \min \Delta_i(3), \cdots, \min \Delta_i(n) \right\} \tag{19}$$

In the similar way, one-level maximum difference and two-staged maximum difference are described, respectively, as:

$$\max \Delta_i(k) = \max\left\{ \Delta_i(1), \Delta_i(2), \Delta_i(3), \cdots, \Delta_i(n) \right\} \tag{20}$$

$$\max\max \Delta_i(k) = \max\left\{ \max \Delta_i(1), \max \Delta_i(2), \max \Delta_i(3), \cdots, \max \Delta_i(n) \right\} \tag{21}$$

Grey relational coefficient

$$\xi_i(k) = \frac{\min\min\Delta_i(k) + p\max\max\Delta_i(k)}{\Delta_i(k) + p\max\max\Delta_i(k)} \quad (22)$$

where, $p \in (0,+\infty)$ is the index for distinguishability. The smaller p, the higher the distinguishability; usually $p \in (0,1)$; $p = 0.5$ under most situations.

Relational coefficient matrix constructed with equation (22) is described as follows:

$$[\xi] = \begin{bmatrix} \xi_1(1) & \xi_1(2) & \cdots & \xi_1(n) \\ \xi_2(1) & \xi_2(2) & \cdots & \xi_2(n) \\ \cdots & \cdots & \cdots & \cdots \\ \xi_m(1) & \xi_m(2) & \cdots & \xi_m(n) \end{bmatrix} \quad (23)$$

Grey relational grade

Relational coefficient of each individual comparison sequence at any moment can be presented by one value known as grey relational grade that is obtained with average-value processing:

$$y_i = \frac{1}{n}\sum_{k=1}^{n}\xi_i(k) \quad (i = 1,2,3,\cdots,m) \quad (24)$$

So, grey relational sequence $\{y_i\}$ is obtained:

$$\{y_i\} = \{y_1, y_2, y_3, \cdots, y_m\} \quad (25)$$

Ordering the grey relational grade and result analysis

By ordering $\{y_i\}$, the magnitude of the effect of comparison sequences on the reference sequence can be worked out.

Analysis of calculation results

After original experimental data of N_2O emission are input into equations (14)–(25), the relational order of operating variables and N_2O emission is

$$y_1 > y_4 > y_3 > y_2 > y_6 > y_7 > y_5$$

where: $y_1 = 0.824$ (bed temperature), $y_2 = 0.637$ (particle size), $y_3 = 0.750$ (Ca/S ratio), $y_4 = 0.801$ (excess air factor), $y_5 = 0.434$ (circulation rate), $y_6 = 0.565$ (bed material height), $y_7 = 0.456$ (secondary air ratio).

Generally, grey relational grade $y > 0.9$ indicates a marked influence, $y > 0.8$ a relatively marked influence, $y > 0.7$ a noticeable influence, and $y < 0.6$ a negligible influence [13]. On the basis of the above calculation results, bed temperature and excess air factor are variables relatively markedly influencing N_2O emission. The influence of secondary air ratio and circulation rate is negligible.

Controlling N_2O emission from oil shale-fired CFB

Current experimental studies of the technical measures of reducing the amount of N_2O emission were finished in a small-scale CFB furnace. N_2O emission is affected mainly by bed temperature, excess air factor, Ca/S ratio and particle size, and, to reduce the emission, reasonable values of these factors should be chosen. However, the optimal operating conditions of circulating fluidized bed combustion should be confirmed after comprehensive consideration of the above seven operating variables.

Conclusion

The effect of seven operating variables on N_2O emission during combustion of oil shale in a CFB pilot setup has been studied, and key operating variables affecting N_2O emission have been identified by treating experimental data using grey relational analysis. Bed temperature and excess air factor are variables relatively markedly influencing N_2O emission, the effect of secondary air ratio and circulation rate being negligible. The operating variables sequenced in order of decreasing effect on N_2O emission are: bed temperature, excess air factor, Ca/S ratio, particle size, bed material height, secondary air ratio, circulation rate. However, optimal operating conditions of circulating fluidized bed should be confirmed after comprehensive consideration of operating variables.

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