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EXPERIMENTAL INVESTIGATION OF SO_2 AND NO_x EMISSIONS FROM HUADIAN OIL SHALE DURING CIRCULATING FLUIDIZED-BED COMBUSTION

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The paper describes the effect of various operating parameters on formation and destruction of gaseous pollutants (SO_2 and NO_x) during combustion of oil shale in a circulating fluidized-bed pilot setup and gives some helpful recommendations for designing circulating fluidized-bed boiler. Experiments of NO_x and SO_2 release were carried out with oil shale test sample obtained from Huadian, China.

Introduction

Combustion of fossil fuels produces significant amounts of SO_2 and NO_x, well-known pollutants causing acid rain and photochemical smog. Fluidized-bed combustion is a promising technology for clean and efficient utilization of such fuels yielding low harmful emissions due to the relatively low combustion temperature. In Huadian (China), three 65-t/h circulating fluidized-bed (CFB) boilers have successfully operated for about seven years.

There are many publications on SO_2 and NO_x emissions at fluidized-bed combustion of coal, but few data on those of oil shale. The objective of the present work was to study how seven operating parameters influence the formation of gaseous pollutants at combustion of Huadian oil shale in an experimental circulating fluidized-bed setup, and to give some recommendations to reduce their amount.

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Experimental

The oil shale samples used in this work were obtained from Huadian, China. The analytical data characterizing oil shale and its ash are as follows: proximate analysis: M_{ad} 2.90%, V_{ad} 41.89%, A_{ad} 51.61%, FC_{ad} 3.60%, $Q_{ar.net}$ 8374 kJ/kg; ultimate analysis, %: C_{ad} 31.63, H_{ad} 4.370, O_{ad} 7.764, N_{ad} 0.726, S_{ad} 1.000; ash composition, %: SiO_2 52.9, Al_2O_3 17.74, Fe_2O_3 6.56, CaO 14.78, MgO 2.99, TiO_2 0.55, Na_2O 0.89, K_2O 1.27. The samples were ground and sieved to four size ranges (the Table) and dried in a desiccator.

The block diagram of the CFB pilot setup used for experimental study is shown in Fig. 1.

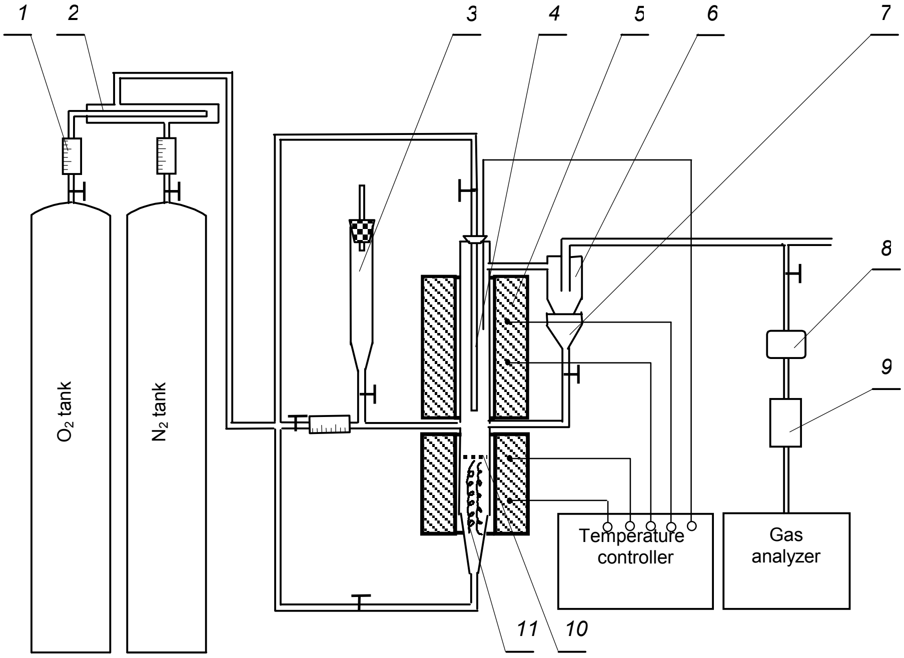

Fig. 1. Block diagram of a circulating fluidized bed: *1* – flowmeter, *2* – gas mixer, *3* – hopper, *4* – quartz tube, *5* – electric heater, *6* – cyclone, *7* – ash bucket, *8* – ash filter, *9* – desiccator, *10* – distributor plate, *11* – wire

The quartz tube riser used is 20 mm i.d. and about 450 mm in height. Fuel was fed into the primary line by the hopper, and then transported into bed by primary air. Quartz tube and quartz sand bed material on the distributor plate in the tube were heated to the designated temperature by electric heater, whose temperature was kept constant by the controller before the sample was plunged into the bed. The air used for combustion was mixed from O_2 and N_2 (21-percent oxygen content controlled by flowmeter), and directed into the quartz tube. Near its top, flue gas entered the cyclone to recover entrained particles, which were sent into the bed or gathered in the ash bucket. Fluidizing air was heated by the wire under distributor plate. The pilot setup was equipped with Maester gas analyzer (produced by Nanjing Alpha Electronics PLC Company of China) enabling continuous measuring of exhaust gas composition.

Seven operating parameters under investigation included bed temperature, particle size, Ca/S ratio, excess air, circulating ratio, bed material height and secondary air ratio. To find out their effect on the quantity of gaseous pollutants, each parameter was changed keeping the others constant (see the Table). The concentration of gaseous pollutants in exhaust gas was recorded for each value of operating parameter changed. The optimum value of each variable yielding the lowest concentration of gaseous pollutants was elucidated.

Operating Conditions

Parameter	Variable range
Bed temperature, °C	650, 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	1.1, 1.2, 1.3, 1.4, 1.5, 1.68, 1.77
Circulating ratio	1, 2, 4, 6
Fixed bed height, mm	10, 20, 30, 40, 50
Secondary air ratio, %	20, 30, 40, 50

Results and Discussion

Bed Temperature

The concentration of all the gaseous pollutants (SO_2, NO and NO_2) changes with bed temperature (Fig. 2,*a*). SO_2 concentration increases at first reaching its maximum value at 750 °C and above it decreases with increasing bed temperature. Usually, oil shale contains two kinds of sulphur: 60% in organic and 40% in inorganic compounds, organic sulphur being pyrolyzed into SO_2 below 550 °C [1].

At low bed temperature the amount of SO_2 increases because calcination and sulphation reactions do not occur yet. At high temperature (750–950 °C) carbonates of oil shale and bed material calcine to CaO and other metal oxides such as MgO, Fe_2O_3, etc., and CaO reacts with SO_2 producing $CaSO_4$ with Fe_2O_3 as catalyzer. Instead of leaving the boiler as a gaseous pollutant sulphur is discharged as $CaSO_4$, a solid residue, and thus the amount of SO_2 measured decreases with increasing bed temperature.

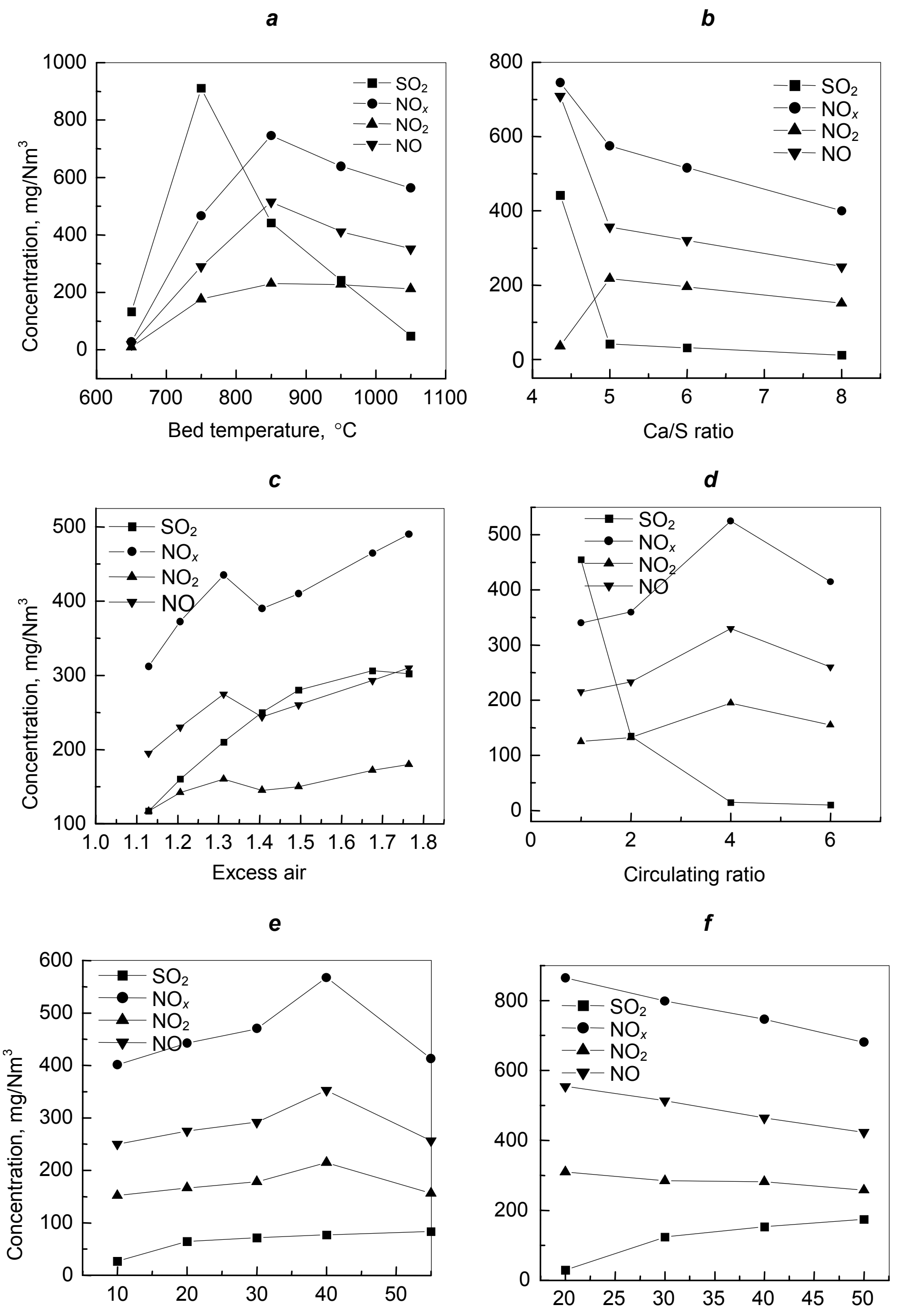

Fig. 2. Emission of gaseous pollutants at various bed temperatures (*a*), Ca/S ratios (*b*), excess air values (*c*), circulating ratios (*d*), different fixed bed heights (*e*), and secondary air ratios (*f*)

The above calcination and calcium sulphate formation occur according to the reactions

$$CaCO_3 = CaO + CO_2 \qquad (1)$$

and

$$CaO + SO_2 + \frac{1}{2}O_2 = CaSO_4 \qquad (2)$$

NO_x concentration also increases with bed temperature increase at first (see Fig. 2,*a*) reaching the maximum at 850 °C and above it decreases with increasing bed temperature. CO concentration is much higher at low bed temperature due to oil shale incomplete burning. In this oxygen-deficient zone NO_x deoxidizes to N_2. Oil shale burns more completely with increasing bed temperature, and CO concentration in furnace decreases so that the release amount of NO_x increases before 850 °C. Above it, CO concentration in the furnace remains constant and NO_x concentration decreases quickly due to its decomposition.

Considering the efficiency of CFB boiler, the cost of heat-resistant equipment, and the emission quantity of gaseous pollutants, 800–950 °C would be the optimum temperature range for operating oil-shale-fired circulating fluidized-bed unit.

Particle Size

Under the same feed fuel rate, the resistance of big particles to SO_2 diffusion usually exceeds that of small particles, and specific surface area of big particles is less than that of small ones. In big particles SO_2 cannot completely react with inner CaO, and self-desulphuration ability of oil shale worsens with increasing particle size (Fig. 3).

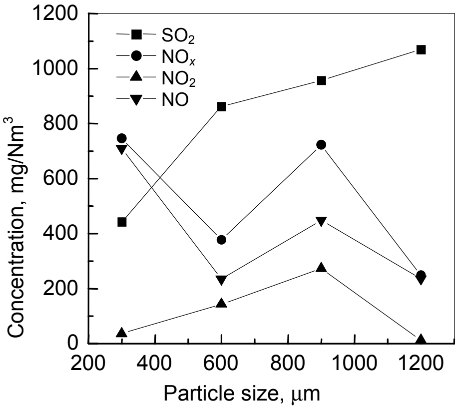

Fig. 3. Emission of gaseous pollutants *vs*. oil shale particle size

The changes in the released amounts of NO and NO_x have a complex nature when particle diameter is below 900 μm. Oil shale combustion improves, i.e. its reaction rate increases with decreasing particle size. During combustion, the partial pressure of O_2 near the surface of oil shale particle is reduced and CO forms relatively easily when small particles are burnt. It results in plenty of CO being able to react with NO_x.

Also CO will oxidize to CO_2 and NO_x deoxidize to N_2 in this oxygen-deficient zone. Among reactions between CO and nitrogen compounds, the reaction $CO + NO \leftrightarrow CO_2 + N$ is the most important one for NO_x to be reduced. Conversely, because rate increases with decreasing particle size, nitrogen will easily oxidize into NO_x and NO increasing their concentrations.

When particle size exceeds 900 μm, the amounts of NO_x and NO decrease (see Fig. 3). It is possible that devolatilization is confined, and the amounts of NH_3 and HCN usually oxidized to NO_x are reduced when greater particles are combusted. At the same time, because combustion and emission of combustion products occur on the solid–gas interface, they will gradually be influenced by mass transfer, and burnout of oil shale worsens with increasing particle size, that results in nitrogen partial release from the CFB furnace as nitride rather than NO_x. These above factors reduce NO_2 and NO emissions.

In general, the particle diameter below 10 mm is the best for CFB boiler practical operating. As for gaseous pollutant emissions, the particle size should be in the range of 0.3–0.6 mm.

Ca/S Ratio

NO_x concentration decreases during fuel combustion after CaO mixes with oil shale (Fig. 2,*b*). Usually, in the oxygen-deficient zone containing CaO and CO, CaO is a good catalyzer for CO to deoxidize NO to N_2, and so the quantity of NO emission is reduced. Haosheng [2] also proved catalytic action of CaO; Beijing and Weibiao [3] proved that metal oxides of coal ash show a strong catalytic effect on heterogeneous deoxidization of NO. So, metal oxides influence NO deoxidization in both homogeneous and heterogeneous reactions. Although CaO promotes NO_2 emission, overall concentration of NO_x emission still decreases.

With increasing Ca/S ratio, the probability of SO_2 reacting with CaO (Eq. (2)) increases. Much sulphur is discharged as $CaSO_4$ and the emission of SO_2 diminishes (see Fig. 4). Emission of SO_2 decreases sharply at Ca/S ratio between 4 and 5. In experiments almost all the SO_2 had already reacted with desulphuration agent after Ca/S value reached 5.

Excess Air

Sulphide and nitride easily oxidize to SO_2 and NO_x in the oxygen-rich zone (Fig. 2,*c*).

Circulating Ratio

SO_2 concentration decreases drastically and that of NO_x increases with increasing circulating ratio (Fig. 2,*d*). When it equals 4, SO_2 will be almost completely removed and at its higher values the curve SO_2 *vs*. circulating ratio becomes smooth. Oil shale contains plenty of metal oxides including 14.78% CaO. This high amount cannot be completely sulphated at once. For complete use of CaO present in ash, it is necessary to elevate circulating ratio, i.e. to lengthen the contact of SO_2 with desulphurizer, and so to promote the utilization rate of metal oxide in the ash. Circulating ratio 4 is sufficient for complete removal of SO_2.

In the experiment when oil shale feed rate was 40 g/h, practical rate of the sample (with ash) feed into the furnace was 80 g/h when circulating ratio equaled 1, and 280 g/h when it equaled 6. High circulating ratio decreases the combustible content in the furnace.

For comparing experimental data excess air was kept constant under different circulating ratios. Excess air coefficient was determined in the experiment with the highest circulation ratio in order to guarantee fuel entry into the furnace and its complete burning.

At high excess air coefficient, concentration of CO is very low and that of oxygen relatively high. At circulating ratio less than 4, the fact that circulating ash will gradually strengthen its catalytic effect on the reaction between CO and NO with increasing circulating ratio, cannot not offset the fact that NH_3 and HCN will be oxidized to NO and NO_2 in this oxygen-rich zone.

At the same time, combustible matter of coke in circulating ash also produces some NO and NO_2. Thus, the emission of NO and NO_2 increases under low circulating ratio. Because of constant excess air, the catalytic effect of metal oxides on the reaction of CO and NO_x grows gradually to reach finally the dominating role in NO and NO_2 removal with increasing circulating ratio among the factors which influence NO_x concentration. So, the emission of NO and NO_2 will decrease under high circulating ratio.

Circulating ratio is a crucial parameter at designing a CFB boiler. Considering attrition of CFB boiler heating surface, occupational safety, emission quantity of gaseous pollutants and other correlative factors, circulating ratio 6 would be optimum for oil shale-fired circulating fluidized-bed boiler.

Bed Material Height

The emission concentration of gaseous pollutants somewhat increased with increasing bed material height (Fig. 2,*e*). Usually, most of SO_2 and NO_x is formed in the dense zone and decomposed in the dilute one. Desroches-Ducarne *et al.* [4] noticed the occurrence of insignificant formation of NO from ammonia in the bottom part of the fluidized bed, and NO destruction just above the feeding zone. So, with increasing bed material height, the space of dense zone increases and that of dilute one decreases, which increase the concentration of gaseous pollutants. On the whole, their amounts were not evidently affected by the bed material height.

Because the latter has a small effect on the concentration of gaseous pollutant emissions, it should be determined only for steady combustion in the furnace. If the bed material height is comparatively low, combustion becomes unsteady, and the efficiency of the CFB boiler diminishes due to bad thermal storage of bed materials. Basing on operating experience of CFB boiler and theoretical analysis, it may be advised that the bed material height should be 5% of the total furnace height.

Secondary Air Ratio

The emission of NO and NO_2 decreases with increasing secondary air ratio (Fig. 2,*f*). Usually, a great part of NO_x is formed in the dense zone and decomposed and deoxidized to N_2 in the dilute one. With increasing secondary air ratio, the concentration of oxygen ions in the dense zone decreases, that, in turn, diminishes the probability of the reaction between N and O. Much more likely dissociative nitrogen ions combine to form N_2 in the dense zone. Although the concentration of oxygen in the dilute zone is high, N_2 formed there could not be oxidized to NO_x. So, the emission of NO_x decreased.

SO_2 comes mainly from oil shale coke, and some from volatiles. After secondary air entering the furnace, coke entrained into the dilute zone could burn completely, and sulphide oxidize to SO_2, whose concentration increases smoothly.

Conclusions

This paper discusses the effect of different operating parameters on formation and destruction of gaseous pollutants (SO_2, NO, and NO_2) during combustion of oil shale in a circulating fluidized-bed pilot setup. Some helpful recommendations for oil-shale-fired circulating fluidized-bed boiler design are:

1. Considering efficiency of CFB boiler, cost of heat-resistant equipment and emission quantity of gaseous pollutants 800–950 °C would be the optimum bed temperature range for operation.
2. Considering only the emission amount of gaseous pollutants, the suitable particle size should be in the range of 0.3–0.6 mm.
3. The optimum value of circulating ratio for oil shale-fired circulating fluidized-bed boiler is 6.
4. Based on operating experience of CFB boiler and theoretical analysis, it can be advised that the bed material height should be 5% of total furnace height.

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