

SO₂ emission characteristics from co-firing of petroleum coke and coal in circulating fluidized bed

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Abstract: Combustion and sulfur retention experiments of mixed fuel of petroleum coke and coal were conducted on a pilot-scale circulating fluidized bed (CFB) combustor with the thermal input of 0.6 MW. The effects of several parameters, such as the primary air percentage, excess air coefficient, bed temperature, Ca/S molar ratio and mass ratio of petroleum coke to coal on SO₂ emission were verified. Experimental results show that when the ratio of petroleum coke to coal in the mixed fuel increases, the SO₂ emission increases. The maximum SO₂ emission appears when pure coke burns. The SO₂ concentration in flue gas reduces with the increase in the primary air percentage, excess air coefficient and Ca/S molar ratio for all kinds of fuel mixtures. The range between 830 °C and 850 °C is the optimal temperature for sulfur retention during co-firing of petroleum coke and coal with the mass ratio R of 1 and 3 in CFB.

Key words: circulating fluidized bed; petroleum coke; coal; co-firing; desulfurization

Petroleum cokes including delayed coke, fluid coke, needle coke, shot coke and flexicoke are by-products of solid residuals from the crude refining process. With the capability development of crude refining, more and more petroleum coke is produced. It has become an urgent issue for most countries to dispose a great deal of industrial waste. It is possible to use high sulfur petroleum coke as an alternative fuel owing to its high fixed carbon and low ash content. But petroleum cokes are rather difficult to ignite due to their low volatile content. Their substantial concentrations of vanadium, nickel, nitrogen and sulfur can be sources of emission and fireside fouling or corrosion problems if not properly handled. Co-firing petroleum coke with coal in circulating fluidized bed (CFB) is beneficial in keeping the bed inventory and circulating materials rate complementary with coal ash. Good slag performance and self-scouring of fly ash from mixture fuel can eliminate agglomeration in the cyclone, the dip leg and the loop seal and fouling and deposits on the heating surface in back convection pass. A large number of coal-fired CFB boiler units and a few pure petroleum coke-fired CFB boiler units have been installed and are in operation so far. Some problems such as ash agglomeration in hot cyclone were encountered in some 50 to 100 MW electrical output pure petroleum coke-fired CFB boiler units in

the United States and China^[1–3]. Many researches on desulfurization in coal-fired CFB combustors have been conducted. But few are available for desulfurization characteristics in CFB combustors simultaneously firing coal and petroleum coke with high sulfur content. There is an urgent need to investigate the combustion and pollutants' emission performance of co-firing petroleum coke and coal in CFB systematically.

SO₂ emission from burning mixtures of petroleum coke and coal was investigated in this paper. Experiments were carried out on a 0.6 MW CFB pilot-scale facility. The fuels with different mixing ratios of petroleum coke to coal were tested. The SO₂ concentration as well as CO₂, CO, O₂, NO and N₂O in flue gas were measured on line. The effects of the primary air percentage, excess air coefficient, bed temperature, Ca/S ratio and ratio of petroleum coke to coal on the emission of SO₂ were verified and analyzed. The results provide a database for optimal design and operation of CFB boilers firing mixed fuel of petroleum coke and coal.

1 Experimental Apparatus

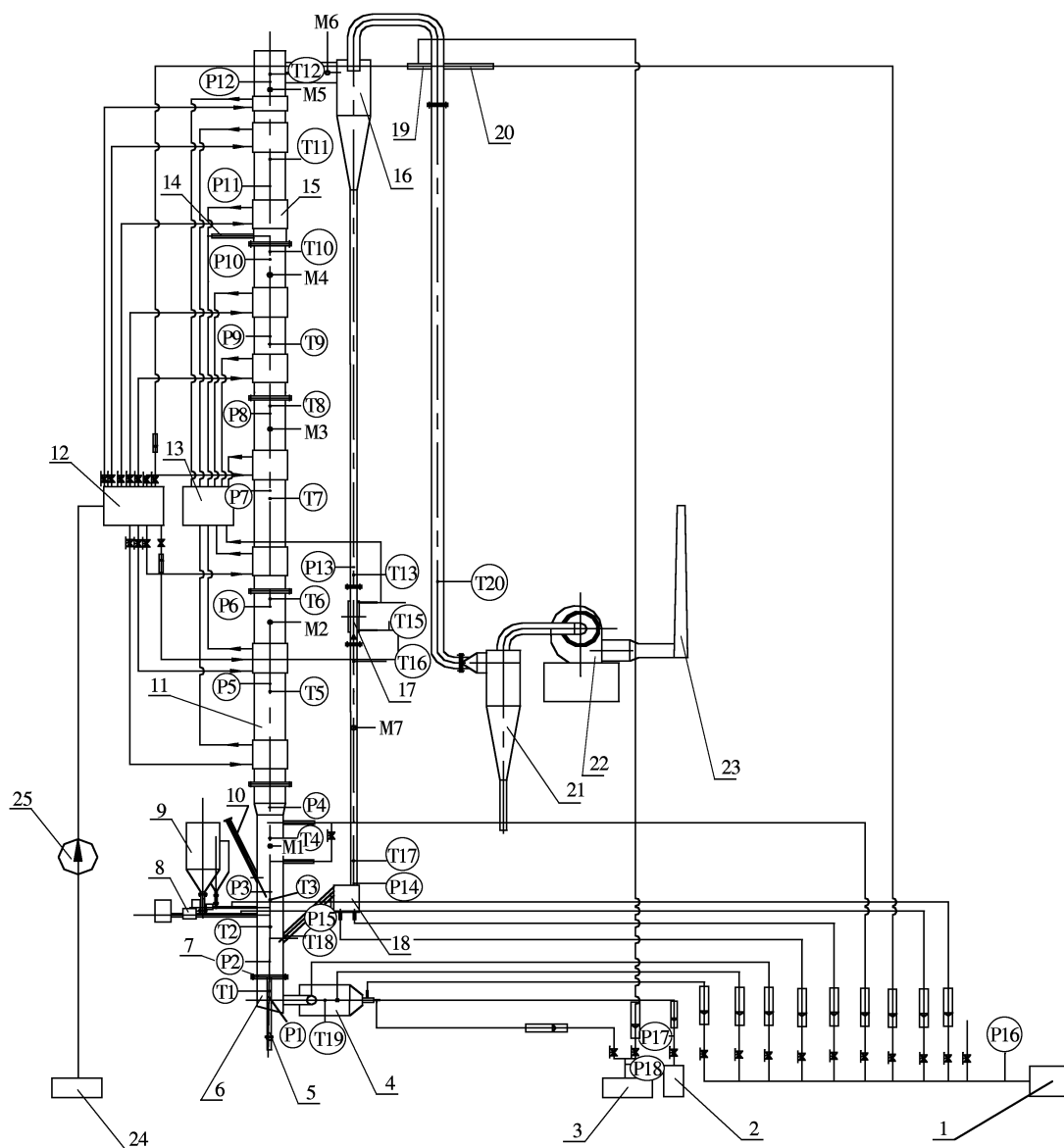
Combustion and gas emission tests were conducted on a 0.6 MW hot CFB test facility as shown in Fig. 1. The facility consists of the Roots blower, the start-up burner, the wind box, the air distributor, the combustor, the re-burning system, the cyclone, the loop seal, the water cooling system, the cyclone dust collector, the induced fan, the fuel hopper and the screw feeder, etc. The combustor consists of a dense

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phase zone of 300 mm in diameter and a dilute phase zone of 400 mm in diameter. The total net height of the combustor from the air distributor to its exit is 12 m. The residence time of gas and particles in the combustor can be kept to at least 2 s for normal fluidizing velocity in CFB. The whole combustor is made of stainless steel 2520 with an outer refractory layer and an insulation layer. A castable refractory layer of 50 mm thick is covered on the inner surface of the dense bed section. There are two water jackets on each of the four dilute phase sections. The cooling surface area can be adjusted based on test requirements. Premixed

fuel added with limestone corresponding to definite Ca/S molar ratio is fed into the combustor at 800 mm above the distributor via the screw feeder with variable speed drive. Two secondary air injection ports are located at 1.5 m and 2 m respectively above the distributor. The measuring system including temperature, pressure and flow rate is arranged for the rig. Solid particle and gas sampling can be made at several pre-arranged locations. The concentrations of six kinds of gas components were measured simultaneously on line with the NGA2000 gas analyzer from Rosemount Co.^[4].



1—Roots fan; 2—Oil pump; 3—Air compressor; 4—Start-up burner; 5—Bottom ash removal; 6—Wind box; 7—Air distributor; 8—Screw feeder; 9—Hopper; 10—Feeding pipe; 11—Furnace; 12—Inlet water header; 13—Outlet water header; 14—Re-burning system; 15—Water cooling surface; 16—Cyclone; 17—Measuring instrument of circulating material; 18—Nonmechanical loop seal; 19—Water cooling system; 20—Air cooling system; 21—Cyclone dust collector; 22—Induced fan; 23—Stack; 24—Pond; 25—Water pump

Fig. 1 Schematic diagram of hot circulating fluidized bed combustor

Fuel and Sorbent Characteristics

The petroleum coke and coal used for tests are from Jinling Petroleum and Chemical Company where two 220T/H CFB utility boilers firing petroleum coke and coal mixture are installed. The proximate and ultimate analysis data of the petroleum coke and the coal are listed in Tabs. 1 and 2. It can be seen that petroleum coke has very high carbon content (87.01%), very low ash content (0.63%) and higher heating value. Compared with coal, sulfur and nitrogen contents in petroleum coke are higher. The coal size range is between 0 and 8 mm with the mean particle size of 2.508 mm. Petroleum coke size range is from 0 to 6 mm with the smaller mean particle size of 1.413 mm. Local limestone is used as sorbent in tests. Its particle size distribution is shown in Tab. 3, the mean size is 0.687 mm.

Tab. 1 Fuel proximate analysis (as received basis)

Fuel	$w(M_t)/\%$	$w(A_{ar})/\%$	$w(V_{ar})/\%$	$w(C_{fx})/\%$	$Q_{net}^w/(MJ \cdot kg^{-1})$
Coke	6.10	21.02	23.61	49.27	22.42
Coal	2.40	0.63	13.53	83.44	33.85

Tab. 2 Fuel ultimate analysis (as received) %

Fuel	$w(C_{ar})$	$w(H_{ar})$	$w(O_{ar})$	$w(N_{ar})$	$w(S_{ar})$
Coke	58.98	2.90	9.39	0.86	0.76
Coal	87.01	3.68	2.22	2.18	1.88

Tab. 3 Limestone size distribution

Size range/mm	Mass fraction/%
<0.160	1.03
0.160 to 0.315	2.69
0.315 to 0.630	42.95
0.630 to 1.250	51.60
1.250 to 2.500	1.49
2.500 to 5.000	0.24

Results and Discussion

In all the test runs the Ca/S molar ratio was kept 1.5, the gaseous component concentrations were based on the oxygen concentration of 6% in volume in flue gas. R , the ratio of coke to coal, was adjusted according to the test arrangement.

3.1 Effect of excess air coefficient

The curves in Fig. 2 show the effect of the excess air coefficient on SO_2 emissions for two kinds of mixed fuels. It is rather clear that for the fuels tested SO_2 concentration decreases with the increase in excess air coefficient α . It can be seen from the two curves that the higher the sulfur content in fuel, the higher the SO_2 emission.

It is well known that in oxidizing atmosphere

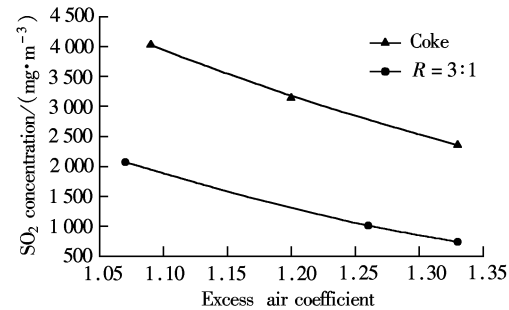
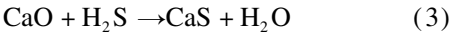
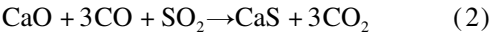
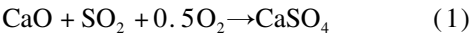
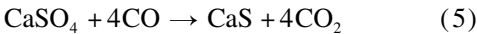
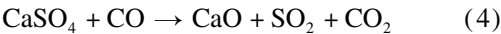


Fig. 2 Effect of excess air coefficient on SO_2 emission

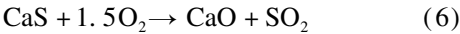
CaO decomposed from limestone fed into the combustor reacts with SO_2 , which is released from sulfur in coal burning, and the final product is $CaSO_4$. But in a strong reducing atmosphere in the dense phase the situation is different; sulfur in coal releases H_2S or COS instead of SO_2 and the following reactions occur:



In addition, in a strong reducing atmosphere with smaller α sulfuration, product $CaSO_4$ becomes unstable. The reaction between $CaSO_4$ and CO releases SO_2 or leads to CaS formation. The chemical reactions are as follows^[5]:



After getting into the dilute phase, the CaS and COS are oxidized, and SO_2 is reformed.



When excess air coefficient α increases, CO concentration drops, reduction reaction of $CaSO_4$ becomes weaker, which is beneficial in decreasing SO_2 emission.

3.2 Effect of temperature

SO_2 emission variation with combustor temperature is shown in Fig. 3. When the temperature in the dense phase zone or the dilute phase zone increases, SO_2 concentration drops first and then goes up after reaching the minimum value.

There is an optimum temperature at which corresponding SO_2 emission is the lowest. For the mixed fuel with R of 3:1 which has higher sulfur content, sulfur retention performance is more sensitive to temperature and the optimum temperature is about 830 °C. For the mixed fuel with R of 1:1, the optimum dense bed temperature is 850 °C.

Sulfation reaction shown in (1) is a first-order reaction. Its reaction rate constant k can be expressed as^[6]

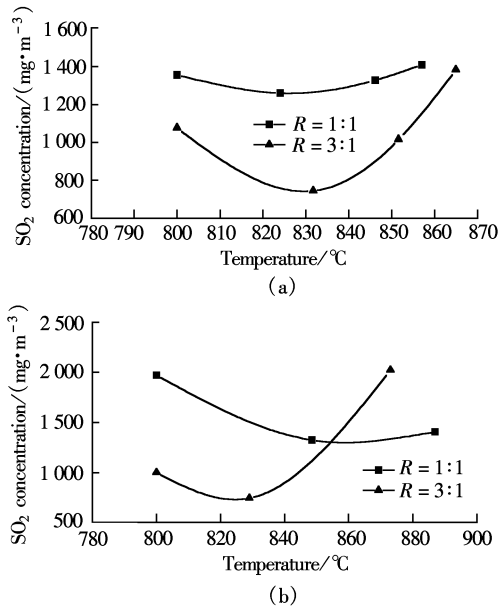


Fig. 3 Effect of temperature on SO₂ emission. (a) Dilute phase zone; (b) Dense phase zone

$$\frac{1}{k} = \frac{1}{k_s} + \frac{1}{k_m} + \frac{\lambda}{D_e} \quad (7)$$

where k_s is an intrinsic reaction rate constant, k_m is the gas film mass transfer coefficient on outer surface of particle, D_e is the effective diffusion coefficient inside inner pores, and λ is a distance between reaction surface and particle surface.

In CFB the mass transfer resistance against gas film can be neglected because of excellent outer mass transfer condition for sorbent particles. Diffusion resistance inside inner pores increases rapidly with reaction time. When the temperature is lower, for instance, less than 800 °C, smaller k_s limits the reaction rate constant k , finally the poor desulfurization performance is induced. When the temperature gets too high, although intrinsic reaction rate constant k_s is quite great, the desulfurization performance is also poor because of too early blocking of pores on the particle surface, which causes augmented diffusion resistance. At very high temperature, typically over 1000 °C, CaSO₄ formed in sulfation reaction decomposes into CaO and releases SO₂. In addition, at the temperature over 900 °C, pore agglomeration inside CaO reduces reaction rate between CaO and SO₂. Therefore, there is an optimum desulfurization temperature, as shown in Fig. 3.

3.3 Effect of primary air fraction

Fig. 4 shows the effect of primary air fraction on SO₂ emission. Generally, when the primary air fraction goes up i.e. staged combustion effect becomes weaker, SO₂ concentration declines. The relationship

between SO₂ and the primary air fraction for pure coke firing is much stronger than two fuels with lower mixing ratios. Under the condition of higher primary air fraction i.e. weaker reducing atmosphere, higher oxygen partial pressure is favorable for sulfation reaction. In addition, higher primary air fraction makes temperature distribution in the combustor more even.

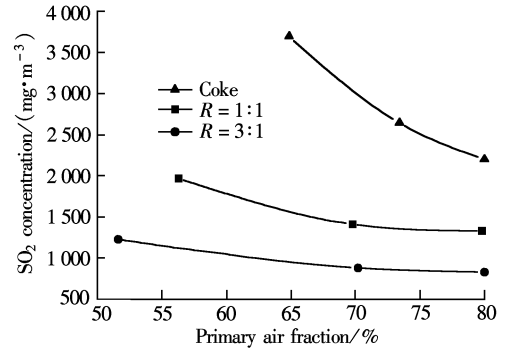


Fig. 4 Effect of primary air fraction on SO₂ emission

3.4 Effect of Ca/S ratio

Ca/S molar ratio is an important factor to the desulfurization efficiency in CFB, which has been verified by the curve of SO₂ vs. Ca/S for fuel with the mixing ratio $R = 1:1$ in Fig. 5. SO₂ emission declines with the increase in Ca/S molar ratio. When the Ca/S molar ratio further increases over 2.5, SO₂ concentration declines slightly. Too high Ca/S leads to a lower calcium utilization rate and high operation cost. Those trends are different from those for firing coal in CFB because of special combustion and pollutants formation mechanism during co-firing of petroleum coke and coal^[6]. There is an optimum Ca/S molar ratio for integrated gaseous pollutants emission reduction consideration. Based on the experimental data obtained, the optimum Ca/S molar ratio is 2 for the mixed fuel of petroleum coke and coal.

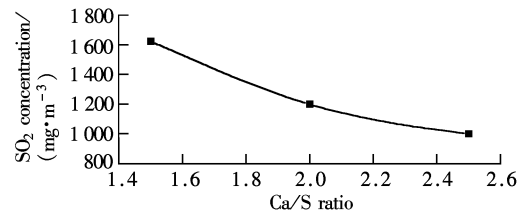


Fig. 5 Effect of Ca/S ratio on SO₂ emission ($R = 1:1$)

4 Conclusions

Some findings about gaseous pollutants from co-firing of petroleum coke and coal in CFB can be drawn from experimental results:

- 1) When the ratio of petroleum coke to coal in

the mixed fuel increases, the SO_2 emission increases. The maximum SO_2 emission appears when pure coke burns because of its highest sulfur content.

2) SO_2 concentration in flue gas decreases with the increase in primary air ratio, excess air coefficient and Ca/S ratio for all fuel mixtures.

3) There is an optimum combustor temperature for sulfur retention for co-firing of petroleum coke and coal in CFB. For the fuels with the mixing ratio R of 1 and 3, the optimum combustor temperatures are $850\text{ }^\circ\text{C}$ and $830\text{ }^\circ\text{C}$, respectively.

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石油焦与煤在循环流化床中混合燃烧时 SO_2 排放试验研究

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摘要: 在一热输入为 0.6 MW 的循环流化床燃烧中试装置上进行了石油焦与煤混合燃烧和脱硫试验研究, 得到燃料中石油焦与煤质量混合比、过量空气系数、床层温度、一次风率和钙硫摩尔比等参数对 SO_2 排放的影响规律. 结果表明, 混合燃料中掺焦比例越大, 混合燃料的硫含量越高, SO_2 排放浓度越高; 纯烧石油焦时 SO_2 排放浓度最高. 对不同配比的混合燃料, 随过量空气系数、一次风率和 Ca/S 摩尔比增大, SO_2 排放浓度降低. $830\sim 850\text{ }^\circ\text{C}$ 的床温对脱硫最为有利, 在燃用石油焦与煤质量混合比 R 为 1 和 3 的混合燃料时可获得最低 SO_2 排放.

关键词: 循环流化床; 石油焦; 煤; 混合燃烧; 脱硫

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