Study on speciation distribution and chemical reaction mechanism of sulfur during coal combustion

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Abstract. The combustion and pyrolysis of coal is a very complex process including pyrolysis, volatile combustion and coke burnout. There are many homogeneous and heterogeneous chemical reactions in this process. In this paper, the thermodynamic equilibrium calculation model is used to predict the possible speciation distribution and chemical reaction mechanism of mercury and sulfur in coal combustion and pyrolysis. This will provide a theoretical basis for the removal of mercury and sulfur by mild thermal upgrading of coal before combustion and the control of mercury and sulfur emissions during coal combustion.

1. Introduction

The combustion and pyrolysis process of coal is considered to be controlled by chemical kinetics[1-2]. However, due to the extremely low concentration of trace elements in coal, as well as the limitations of experiments and instruments, there are few experimental data on the distribution of physical and chemical forms of trace elements in the process of coal combustion and pyrolysis, and there is a lack of reference kinetic parameters. Therefore, at present, it is the main theoretical analysis method to simulate the distribution of trace elements in the combustion and pyrolysis process by chemical thermodynamic equilibrium analysis[3-4]. The thermodynamic equilibrium calculation method can analyze the most stable chemical and physical forms of trace elements such as mercury and major elements such as sulfur under the determined temperature, pressure and total composition [5], so as to predict the migration, transformation and evolution behavior of these elements in coal combustion and pyrolysis flue gas[6].

In this paper, the influence of various factors on the speciation distribution of sulfur in LZ coal sample from Guizhou Province is studied by means of chemical thermodynamic equilibrium simulation using Factsage thermodynamic calculation software.

2. Calculation principle of thermodynamic equilibrium

In practical calculation, Gibbs free energy minimization (GEA) is the most widely used thermodynamic method, which can solve chemical equilibrium and phase equilibrium simultaneously[7].

Gibbs free energy G is a function of temperature, pressure and the number of moles of each component, and a broad criterion. Under the condition of constant temperature and pressure, the necessary and sufficient condition for the system to reach equilibrium is that the total free energy $G_T$ of the system is the minimum, or the small change of $G_T$ must be greater than or equal to zero [80],
which is shown as

\[(\delta G)_{T,P} \geq 0\] (1)

The standard molar Gibbs free energy is calculated as

\[G_m^\Theta = H_m^\Theta - TS_m^\Theta = [H_m^\Theta_{(298)} + \int_{298.15}^{T} C_p dT] - T[S_m^\Theta_{(298)}] + \int_{298.15}^{T} \frac{C_p}{T} dT\] (2)

According to the condition of Gibbs free energy minimum:

\[\frac{\partial G_m}{\partial x_i} = 0 \quad (i = 1, 2, \ldots, n)\] (3)

By solving the simultaneous equations meeting the extreme conditions, the components of each phase corresponding to the minimum total Gibbs free energy of the system can be obtained, that is, the components of the system in equilibrium [7].

3. Simulation on the influence of sulfur element in coal

In order to investigate the influence of sulfur element in coal on the distribution of mercury in flue gas after heat saving, in the coal-mercury-sulfur system, when the content of other components is unchanged, the content of sulfur element is changed only, and the effect of sulfur element on the distribution of mercury is observed. In the reducing atmosphere, after adding sulfur element, the elemental mercury is still the stable form of mercury. Under reducing atmosphere, sulfur has no effect on the distribution of mercury.

Under the oxidizing atmosphere, the content of sulfur in coal has an obvious effect on the distribution of mercury in flue gas. As shown in Figure 1, there is an area where divalent mercury and elemental mercury compete with each other to become the main component at about 300°C. Among them, mercury sulfate and elemental mercury are the main components, and mercury oxide is the secondary component. And with the increase of temperature, when the temperature of mercuric oxide is higher than 280°C, it increases first and then decreases, and reaches the peak at about 320°C. With the increase of temperature, elemental mercury becomes a stable form of mercury.
Figure 1. Speciation distribution of mercury in oxidable atmosphere of coal-mercury-sulfur system

Figure 2. Effect of different sulfur content on mercury distribution in coal mercury sulfur system in oxidizing atmosphere

In order to investigate the effect of different sulfur content on the distribution of main products of mercury under oxidizing conditions, this simulation ignores the generation of mercury oxide and only considers the change of equilibrium components of mercury and mercury sulfate under different sulfur content. The shape distribution of mercury under different sulfur content is shown in Figure 2. As shown in the figure, when the sulfur content is 0.5mol, 2mol, 8mol and 12mol respectively, the
temperature range of competition between elemental mercury and mercuric sulfate is around 315℃, 325℃, 335℃ and 305℃, respectively. With the increase of sulfur content, the temperature of the competition zone between mercuric sulfate and elemental mercury first increases and then decreases. Therefore, it is inferred that there is a sulfur content value between 8-12mol, that is, the sulfur content is between 25.6-38.4%, which makes the temperature of the competition zone between mercury sulfate and mercury reach the highest. However, in general coal types, especially in China, the sulfur content will not exceed 10%, so it can be said that with the increase of sulfur content, the temperature of the competition zone between mercuric sulfate and elemental mercury will increase, the temperature range of mercuric sulfate as a stable phase will expand, and the temperature range of elemental mercury as a stable phase will narrow.

In the case of different sulfur content, the distribution pattern of mercury has the same rule, that is, in the temperature range below 300℃, mercury sulfate is the stable form of mercury, in the only range above 350℃, elemental mercury becomes the stable form of mercury. Therefore, in the combustion process, when the sulfur content of coal is relatively large, with the decrease of flue gas temperature, more mercury will appear in the form of mercuric sulfate. Therefore, the proportion of mercury in the form of mercury sulfate in the low temperature range is directly proportional to the sulfur content of coal. On the other hand, when Mercury is removed from the raw coal by mild thermal upgrading of coal before combustion, if the pyrolysis temperature is lower than 300 ℃, the mercury in the coal is likely to exist in the form of solid mercury sulfate in the coal, thus reducing the proportion of mercury released. When the pyrolysis temperature is higher than 300 ℃, the mercury in the coal will first be released into the flue gas in the form of gaseous elemental mercury, along with the smoke. With the decrease of gas temperature, some elemental mercury is oxidized into mercuric sulfate in flue gas.

Frandsen [8] and others proposed the oxidation model of sulfur and chlorine elements in coal to mercury in flue gas, which pointed out that SO₂ in flue gas can participate in the oxidation of elemental mercury through the following reactions. When the temperature is lower than 590k, HgSO₄ is the main divalent mercury in flue gas. This is similar to the simulation results in this paper.

\[
2\text{HgO(g)} + 2\text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{HgSO}_4(s)
\]

4. Conclusion
The effects of atmosphere, sulfur content and chlorine content on the distribution of mercury speciation were investigated by chemical thermodynamic equilibrium calculation. The simulation results show that the main product of mercury is mercuric sulfate instead of mercuric oxide in the presence of sulfur.

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