Study on the Effect of Additives on Na Migration of Zhundong Coal by Thermodynamic Calculation and Analysis

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Abstract. As a kind of low rank coal, ash of Zhundong coal contains relatively high content of alkali metals and alkaline earth metals, which leads to a strong slagging property. In this paper, the influence of kaolin and silica additive on the migration of alkali metal Na in Zhundong coal is studied by chemical thermodynamics calculation software, the results show that: The main form of sodium in the coal ash sample is Na₂SO₄. With the increase of temperature, the NaCl (g) in the ash sample begins to precipitate at 600 °C, and Na₂SO₄ changes to NaOH (g) and Na (g) at higher temperature. Both kaolin and silica can inhibit the release of sodium. After adding kaolin, NaAlSiO₄ is the main form of solid Na in the ash, and after adding SiO₂, Na₂SiO₃, Na₂O₂SiO₂ and Na₂O, 3SiO₂ exist in the solid Na₂SiO₃.

1. Introduction
Zhundong coal has the characteristics of strong coking and strong smearing, which is closely related to its ash phase composition[1-3]. In recent years, thermodynamic calculation software has been widely used to predict the transformation and precipitation of alkali metals, alkaline earth metals and trace substances in biomass, refuse fuels, coal and other fuels during combustion. Li Yong [4] used Aspen Plus process simulation software to simulate the deposit and transfer of alkali metals in coal combustion process under different influence factors, Yang.T[5] studied the migration of alkali metals in the process of mixing stalk with coal by means of experiment and software simulation.

At present, the release of alkali metals and alkaline earth metals before and after mixing silicon-aluminum series additives in Zhundong coal is relatively less calculated by using chemical heat balance software. In this paper, the inhibition effect of silicon-aluminum series additives on alkali metals and alkaline earth metals in ash is studied by using chemical heat balance analysis software.

2. Experimental part

2.1. Coal quality analysis
Proximate analysis and chemical compositions of ash samples for ZDC (selected as the research object) were shown in Table 1, high purity kaolin and SiO₂ are used as additives.
Tab. 1 Proximate analysis and chemical compositions of ash samples for ZDC

| Proximate analysis/% | chemical compositions of ash samples% |
|---------------------|---------------------------------------|
| M<sub>t</sub> | A<sub>ad</sub> | V<sub>ar</sub> | FC<sub>ad</sub> | Fe<sub>2</sub>O<sub>3</sub> | Al<sub>2</sub>O<sub>3</sub> | CaO | MgO | TiO<sub>2</sub> | SiO<sub>2</sub> | SO<sub>3</sub> | K<sub>2</sub>O | Na<sub>2</sub>O | ST/℃ |
|---------------------|---------------|--------------|----------------|----------------|----------------|-----|-----|----------------|-------------|-------------|-------------|-------------|-----------|-------|
| 29                  | 5.12          | 29.47        | 63.75          | 8.01           | 7.36           | 24.54 | 6.96 | 0.99           | 14.3         | 32.8        | 0.4         | 4.65       | 1360     |

2.2. Input condition of chemical heat balance calculation

The whole process is regarded as an ideal reaction system when calculating the chemical heat balance, and the mole number of each component is calculated when the total Gibbs free energy G of the whole system reaches the minimum, without considering the specific reactions occurring in the system, so that the concentration distribution of alkali metal compounds in the system can be obtained.

Input condition: the composition of ash is taken as the input condition, and the amount of each component is equal to the molar amount in ash after combustion of 1 kg dry-based coal, the molar weight of Cl input is calculated based on the analysis of raw coal elements. Assuming that the atmosphere composition after combustion is N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O (g), CO<sub>2</sub> and excess air coefficient is 1.2, the calculation step is 10 ℃, the calculation interval is 500 ~ 1400℃, and the calculation pressure is 1bar. The input conditions are shown in Table 2.

Tab. 2 Initial input condition/mol

| project | Fe<sub>2</sub>O<sub>3</sub> | Al<sub>2</sub>O<sub>3</sub> | CaO | MgO | TiO<sub>2</sub> | Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub> | SiO<sub>2</sub> | SO<sub>3</sub> | K<sub>2</sub>O | Na<sub>2</sub>O | H<sub>2</sub>O | O<sub>2</sub> | Cl |
|---------|----------------|----------------|-----|-----|---------------|----------------|-------------|-------------|-------------|-------------|-----------|---------|-----|
| Ash sample | 0.02 | 0.03 | 0.21 | 0.08 | 0.00 | 0 | 0.11 | 0.15 | 0.00 | 0.03 | 23.00 | 0 | 6.00 | 0.02 |
| 3% Si O<sub>2</sub> | 0.02 | 0.03 | 0.20 | 0.08 | 0.00 | 0 | 0.61 | 0.15 | 0.00 | 0.03 | 22.31 | 0 | 5.82 | 0.02 |
| 6% Si O<sub>2</sub> | 0.02 | 0.03 | 0.19 | 0.08 | 0.00 | 0 | 1.11 | 0.14 | 0.00 | 0.03 | 21.62 | 0 | 5.64 | 0.02 |
| 3% kaolin | 0.02 | 0.03 | 0.20 | 0.08 | 0.00 | 0.118 | 0.11 | 0.15 | 0.00 | 0.03 | 22.31 | 0 | 5.82 | 0.02 |
| 6% kaolin | 0.02 | 0.03 | 0.19 | 0.08 | 0.00 | 0.235 | 0.11 | 0.14 | 0.00 | 0.03 | 21.62 | 0 | 5.64 | 0.02 |

3. Results and discussion

3.1. Chemical heat balance calculation of sodium migration during the combustion of ZDC

Fig. 1 shows the equilibrium concentration of sodium in the gas phase of coal ash in the 500 ~ 1400℃. It can be seen that NaCl (g), NaOH (g), Na (g) and Na<sub>2</sub>SO<sub>4</sub> (g) are the main forms of sodium in the ash stage. NaCl (g) precipitates obviously after 700℃, while other forms release after 1100 ℃.
Fig. 1 Distribution map of equilibrium concentration of sodium in gas phase

Fig. 2 Distribution map of equilibrium concentration of sodium in solid phase

Fig. 2 shows the equilibrium concentration distribution of sodium in the solid phase. It can be seen from the graph that Na$_2$SO$_4$ is the main solid phase of sodium in the ash sample, and there are a small amount of NaCl, Na$_2$SiO$_2$ and Na$_2$O-Fe$_2$O$_3$ conjugates.

Combining Fig. 1 and Fig. 2, we can get the change rule and release rule of sodium in ash: Na$_2$SO$_4$ and NaCl are the main forms of sodium in ZDC ash. NaCl begins to release in gas phase at 700℃, and Na$_2$SO$_4$ in solid phase begins to release in NaCl (g) and NaOH (g) after 1000℃, but not Na$_2$SO$_4$ (g) and Na$_2$SO$_4$ are all converted to other forms of sodium at 1300℃. After more than 1200℃, NaCl(g) is stable, but NaOH(g) begins to change to Na (g).

3.2. Thermodynamic equilibrium calculation of influence of additives on sodium migration in ash

Fig. 3 shows the equilibrium distribution of sodium in the gas phase after mixing silica in 500-1400℃.
Compared figs. 3 (a) with (b), it can be seen that the content of NaCl in the vapor phase decreases obviously after mixing SiO₂. In addition, the content of NaOH (g) which begins to precipitate at 1000°C is also greatly affected after mixing SiO₂, which indicates that the vapor phase sodium (Na (g), NaOH (g)) after mixing SiO₂ is inhibited. With the increase of the proportion of SiO₂, the inhibiting effect becomes more and more obvious.
Figs. 4 shows the equilibrium concentration distribution of sodium in solid phase after mixing different ratios of SiO₂. Compared Fig.4 (a) with (b), it can be seen that the temperature of final disappearance of solid Na₂SO₄ is obviously earlier, which indicates that the mixing of SiO₂ can significantly promote its transformation to other forms of solid Na, such as Na₂SiO₃, Na₂O·2SiO₂, Na₂O·3SiO₂ and so on, thus controlling the formation of vapor NaOH (g), Na (g) and inhibiting the release of sodium.

Compared figs. 4 (a) with (b), it can be found that the equilibrium concentration of Na₂SiO₃ decreases with the increase of SiO₂ blending ratio, while the equilibrium concentration of Na₂O·2SiO₂, Na₂O·3SiO₂ and other substances increases. Literature [6] considers that with the increase of SiO₂ blending ratio, sodium salt is more likely to react with SiO₂ to produce Na₂O·2SiO₂, Na₂O·3SiO₂.

Figs. 5 shows the concentration distribution of sodium in the gas phase after mixing different ratios of kaolin. Contrasting fig.1-2 and figs.5, it can be found that the release of NaCl (g), NaOH (g) and Na (g) at high temperature can also be greatly reduced by mixing kaolin. Contrasting figs.5(a) and (b), it can be found that the hindrance of kaolin to vapor phase sodium is more and more obvious with the increase of mixing ratio. Compared with the calculation results of SiO₂ and kaolin in the same
proportion, it can be found that the inhibition of SiO$_2$ on the release of vapor phase sodium is better than that of kaolin.

\[ \text{(a) Mixed 3\% kaolin} \]

\[ \text{(b) Mixed 6\% kaolin} \]

**Figs. 5** Concentration distribution of sodium in the gas phase after mixing kaolin.

Figs. 6 shows the concentration distribution of sodium in the solid phase after mixing different ratios of kaolin. Comparing figs. 4 and 6, it can be seen that Na$_2$SO$_4$ disappeared at 1200°C in solid phase after mixing kaolin, 100°C earlier than that without mixing kaolin. NaAlSiO$_4$ appears in the solid phase, which indicates that kaolin can effectively prevent the transformation of Na$_2$SO$_4$ to NaOH (g), Na (g) at high temperature, thus controlling the release of sodium during ZDC combustion.

Comparing fig. 6 (a) and (b), it can be found that the equilibrium concentration of sodium aluminosilicate in solid phase increases obviously with the increase of kaolin addition ratio, which indicates that more Na$_2$SO$_4$ can be converted into silicate aluminate by increasing kaolin mixing ratio, and the effect of controlling sodium precipitation is more significant.
4. Conclusion

Based on the above chemical thermodynamic equilibrium calculation, it can be concluded that Na$_2$SO$_4$ and NaCl are the main forms of sodium in ash of ZDC, and Na$_2$SO$_4$ is released mainly in the form of NaOH (g) and Na (g) at high temperature. After mixing SiO$_2$ and kaolin, Na$_2$SO$_4$ in ash can change to other solid substances in advance, thus reducing the release of NaOH (g) and Na (g) at high temperature. With the increase of SiO$_2$ and kaolin addition ratio, the release of sodium in ash decreases, the content of solid sodium in ash increases, and the effect of sodium fixation of SiO$_2$ is better than that of kaolin in the same proportion. The main forms of sodium fixation of SiO$_2$ are Na$_2$SiO$_3$, Na$_2$O-2SiO$_2$ and Na$_2$O-3SiO$_2$, while the reaction products of kaolin and sodium salt are mainly NaAlSiO$_4$, Na$_2$SiO$_3$, NaAlSi$_3$O$_8$. 

Figs.6 Concentration distribution of sodium in the solid phase after mixing kaolin
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