First-principles study of calcium-based sulfur fixers and their products

Guoyan Chen*a; Jianing Chen*a; Anchao Zhang*a; Haoxin Deng*a; Yanyang Mei*a; Xiaoping Wen*a; Fahui Wang*a; Wei Sheng*a; Zheng Shen*a; Shuangshuang Zuo*a

a. School of Mechanical and Power Engineering, Henan Polytechnic University, Jiaozuo 454003, China

Corresponding Email: 254568182@qq.com; anchaozhang@126.com (A.Zhang)

Calcium-based sulfur-fixing agent, as the main sulfur-fixing product, is widely used in power plant boiler systems. In order to further study the thermodynamic properties and reaction characteristics of calcium-based sulfur fixing agent and its products, the method of combining power plant experiment with theory was used. The electronic structure, thermodynamic properties and density of states of quicklime, limestone, calcium sulfate and calcium sulfoaluminate have been calculated based on the first-principles ultra-soft pseudopotential plane wave method of density functional theory. The generalized gradient approximation algorithm is used to optimize the structure of various minerals to achieve the most stable state. The results show that the enthalpy, entropy, specific heat capacity at constant pressure and Gibbs free energy of calcium sulfonate vary greatly from 25K to 1000K, while the change of calcium oxide is small, and that of calcium carbonate and calcium sulfate are between them. It shows that calcium sulfoaluminate has strong stability and more energy is needed to destroy the molecular structure of calcium sulfoaluminate. Calcium oxide is the most unstable and requires less energy to react; Calcium carbonate and calcium sulfate are in between. The variation range of calcium sulfate is greater than that of calcium carbonate, indicating that the stability of calcium sulfate is higher than that of calcium carbonate. The experimental results show that the desulfurization efficiency of generating calcium sulfoaluminate is much higher than that of only generating calcium sulfate, indicating that calcium sulfoaluminate is very stable, which is consistent with the calculated results.

Keywords: First principles; Calcium-based sulfur-fixing agents; Desulfurization; Density functional theory

1. Introduction

In response to the increasingly stringent requirements for environmental protection, both coal-fired boilers and coal-fired kilns are basically equipped with in-furnace sulfur fixation facilities or flue gas desulfurization devices. Circulating fluidized bed boiler is a typical furnace for sulfur fixation, mainly by injecting quicklime or limestone of suitable particle size into the furnace as a sulfur fixation agent, which reacts with sulfur oxides in the furnace to generate sulfur fixation products such as calcium sulfate[1-4]. The investment and operating costs of this method are both low, and it has been widely used. However, the limestone furnace decomposition and sulfur fixation technology have their own
shortcomings[5-10]: (1) The decomposition time of limestone in the furnace is longer, and the organic sulfur volatilized in the coal is shorter, resulting in the decomposition of calcium oxide and the decomposed sulfur. Oxides cannot match the reaction well, which affect the efficiency of sulfur fixation in the furnace, resulting in a large concentration of sulfur oxides in the flue gas. (2) During the operation of the boiler, in order to increase the power generation, the load fluctuations will inevitably occur, causing the temperature in the furnace to rise more than 900 ℃, resulting in the instability of the solid sulfide calcium sulfite and calcium sulfate, which are decomposed into sulfur dioxide and sulfur trioxide enter the flue gas, reducing the desulfurization efficiency of the entire system. In addition, the local high temperature may cause the high temperature sintering the sulfur fixer and its common products, blocking the surface micropores of the desulfurizer, leading to the decrease of the specific surface area of the desulfurizer particles, affecting its reaction with sulfur oxides, and reducing the desulfurization efficiency[11-15].

In order to avoid the occurrence of the above situation, a composite mineralized sulfur-fixing agent with quicklime and aluminum oxide as the main components is selected for the desulfurization reaction. Adding appropriate amount of alkali metals (ferric oxide, calcium fluoride) to the compound mineralized sulfur fixation agent, calcium fluoride and ferric oxide and calcium based sulfur fixation agent at high temperature can form a low melting point of solid-liquid phase eutectic, reduce the reaction temperature of the product, promote the formation of the reaction at a lower temperature[16]. In addition, the solid-liquid eutectic can promote the reformation of the calcium-based lattice structure, with more voids, larger pore size and more uniform distribution. In order to further study the change of microstructure, the thermodynamic properties of calcium-based sulfur fixing agent and its products were analyzed by the first principles method[17-19]. The first principles method does not rely on empirical data, and takes the polyatomic system as a multiparticle system composed of electrons and nucleus. Starting from the basic laws of quantum mechanics, we can reasonably predict the properties of the microscopic system. In recent years, there have been many reports on the calculation of the electronic structure and thermodynamic properties of solids based on the first principles. It is the first time to study the structure model of inorganic minerals in sulfur-fixing agents. In this study, the structural optimization and thermodynamic properties calculation of calcium carbonate, calcium oxide, calcium sulfate, and calcium sulfoaluminate are used to study the principle of sulfur fixation of calcium-based sulfur fixation agents, and provide theoretical guidance for the application of sulfur fixation in the process of coal combustion[20-27].

2. Experiment and simulation calculation

2.1. Experiment introduction

A circulating fluidized bed boiler in a certain power plant was selected for the experiment, with a rated load of 465 t/h, and model HG-465/13.7-LWM17. The test equipment selected is Qingdao Laoying 3102H automatic flue gas tester. Table 1 is the coal sample and the received basic industrial analysis data after mixing the coal sample and the composite mineralized sulfur-fixing agent according to a certain mass ratio.

<table>
<thead>
<tr>
<th>sample</th>
<th>Total</th>
<th>Flee</th>
<th>Internal</th>
<th>ash</th>
<th>Volatile</th>
<th>Fixed</th>
<th>Calorific</th>
</tr>
</thead>
</table>

Tab. 1 Proximate analysis of coal and fixing sulfur agent
It is the preparation method of composite mineralization sulfur fixation agent. After mixing certain raw materials according to the proportion in Table 2, grind them into small particles of about 0.5mm with a mill. The composition of the composite mineralization sulfur stabilizer is rich in nature. The materials can choose slag, bauxite, etc. Under the action of high temperature and accelerator, the calcium and aluminum groups can react with sulfur to form the compound calcium sulfoaluminate which is very stable under high temperature conditions. Fe_2O_3 and CaF_2 as accelerators can improve the chemical activity of the reaction, reduce the activation energy of the reaction, and improve the sulfur fixation efficiency of the composite mineralized sulfur fixation agent.

Tab. 2 Main component of fixing sulfur agent

<table>
<thead>
<tr>
<th>Mass percent /%</th>
<th>CaO</th>
<th>Al_2O_3</th>
<th>Fe_2O_3</th>
<th>CaF_2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50</td>
<td>40</td>
<td>7</td>
<td>3</td>
</tr>
</tbody>
</table>

(1) The formation reaction of calcium sulfate.

The SO_2 precipitated in the coal reacts with CaO to form sulfate, namely:

\[
2\text{CaO}+2\text{SO}_2+\text{O}_2 \rightarrow 2\text{CaSO}_4
\]

(2) Formation reaction of calcium sulfoaluminate.

Calcium sulfate is an important part of sulfur fixation products, and its stability is also very important. Under high temperature conditions, especially in the presence of calcium fluoride, calcium sulfate is easy to decompose to form sulfur oxides and calcium-based compounds, reducing the desulfurization efficiency. In order to prevent it from decomposing, it is necessary to perform a resolidification reaction on the generated calcium sulfate to generate calcium sulfoaluminate that is stable under high temperature conditions and ensure the desulfurization efficiency in the furnace.

\[
\text{CaO}+\text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot \text{Al}_2\text{O}_3
\]

\[
3(\text{CaO} \cdot \text{Al}_2\text{O}_3)+\text{CaSO}_4 \rightarrow 3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4
\]

\[
3\text{CaO}+3\text{Al}_2\text{O}_3+\text{CaSO}_4 \rightarrow 3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4
\]

In the reaction, the sulfur-fixing agents are CaO, Al_2O_3, and the accelerators are Fe_2O_3, CaF_2, which promote the formation of calcium sulfoaluminate.

2.2. Calculation principle

2.2.1. Calculation method and theory [28-30]

In this paper, the CASTEP module of Materials Studio platform is used to optimize and simulate the structure of calcium carbonate, calcium oxide, calcium sulfate, and calcium sulfoaluminate. The
research is based on density functional theory, super soft pseudopotential plane wave method, and pseudopotential instead of ion potential, using the plane wave basis set to expand the wave function of the orbit for optimization. The most important step of this research is to solve the Kohn-Sham equation simplified by density functional theory.

\[
h_{ks} \phi_i(r) = \left[ -\frac{\nabla}{2} - \sum \frac{Z_q}{|r-R_q|} + \int \frac{\rho(r)}{|r-r'|} dr' + V_{XC} \right] \phi_i(r)
\]

(1)

\[
\rho(r) = \sum \big| \phi_i(r) \big|^2
\]

(2)

\[
E_x^{GGA} = E_x^{LDA} - \int F(x_\sigma) \rho_\sigma^{4/3} (r) dr
\]

(3)

\[
E_x^{LDA} [\rho] = E_x^{LDA} [\rho] + E_x^{LDA} [\rho] = \int \epsilon_x [\rho] \rho(r) dr + \int \epsilon_c [\rho] \rho(r) dr
\]

(4)

In equation (1): \( h_{ks} \) represents the Hamiltonian in the K-S equation, \(-\frac{\nabla}{2}\) means electronic kinetic energy, \(- \sum \frac{Z_q}{|r-R_q|}\) represents the positional potential energy of the electron and each nucleus, \( \int \frac{\rho(r)}{|r-r'|} dr' \) represents the interaction term of the potential energy between the electrons, which is the Hartree potential energy phase, \( V_{XC} \) represents the functional derivative of the exchange correlation energy, \( \phi_i(r) \) represents the wave function of a single electron.

In equation (2): \( \rho(r) \) represents the electron density; \( n_i \) represents the occupancy number; \( \phi_i(r) \) represents the wave function of a single electron.

In equation (3), \( E_x^{GGA} \) is expressed as the generalized gradient approximation, \( E_x^{LDA} \) is the local density approximation (LDA), \( F(x_\sigma) \rho_\sigma^{4/3} \) is the gradient.

In equation (4): \( E_x^{LDA} [\rho] \) is expressed as the exchange correlation energy of electrons; \( \epsilon_x [\rho] \) and \( \epsilon_c [\rho] \) are respectively expressed as exchange energy density function and correlation energy density function.

According to the above equations, the spatial structure of these four minerals are geometrically optimized to obtain the most stable structure of each mineral. In the geometric optimization calculation, in order to ensure that the geometric optimization is close to the real structure, some specific parameters need to be set. In order to select a finite plane wave number, the cutoff energy was set to 350 eV, the single atom convergence standard of the system was set to \( 1.0 \times 10^{-5} \) eV. In order to ensure that the calculation is carried out under periodic boundary conditions, the crystal unit cells of 4 minerals are selected, and the k points of the Brillouin zone are selected as shown in Table 3.

The ground state charge density and phonon frequency distribution can be obtained by self-consistent iterative calculation. According to the state density of phonons, the thermodynamic properties of these four minerals are obtained.

The influence of lattice resonance (temperature) on crystal free energy G:

\[
G(T) = E_{tot} + \frac{1}{2} \int F(\omega) h \omega d\omega + kT \int F(\omega) \ln \left[ 1 - \exp \left( \frac{h\omega}{kT} \right) \right] d\omega
\]

(5)

The effect of temperature on entropy:

\[
S(T) = k \left\{ \int \frac{h\omega}{\exp \left( \frac{h\omega}{kT} \right)} F(\omega) d\omega - \int F(\omega) \ln \left[ 1 - \exp \left( \frac{h\omega}{kT} \right) \right] d\omega \right\}
\]

(6)

Tab. 3 The parameters of different mineral
<table>
<thead>
<tr>
<th>Mineralization</th>
<th>Space group</th>
<th>Crystal face angle /°</th>
<th>Lattice constant /Å</th>
<th>Single atom convergence criterion</th>
<th>Truncation energy</th>
<th>k-point</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSO₄</td>
<td>BMMB</td>
<td>α 90 β 90 γ 90</td>
<td>a 6.991 b 6.999 c 6.240</td>
<td>1.0×10⁻⁵</td>
<td>350</td>
<td>6×5×2</td>
</tr>
<tr>
<td>CaO</td>
<td>FM-3M</td>
<td>α 90 β 90 γ 90</td>
<td>a 4.999 b 4.991 c 4.990</td>
<td>1.0×10⁻⁵</td>
<td>350</td>
<td>2×3×1</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>R-3C</td>
<td>α 90 β 90 γ 120</td>
<td>a 4.993 b 4.993 c 16.917</td>
<td>1.0×10⁻⁵</td>
<td>350</td>
<td>6×5×2</td>
</tr>
<tr>
<td>3CaO·3Al₂O₃·CaSO₄</td>
<td>I23</td>
<td>α 90 β 90 γ 90</td>
<td>a 9.190 b 9.190 c 9.190</td>
<td>1.0×10⁻⁵</td>
<td>350</td>
<td>6×6×4</td>
</tr>
</tbody>
</table>

The influence of temperature versus heat capacity:

\[
C_v(T) = k \int \left( \frac{\hbar \omega}{kT} \right)^2 \frac{\exp \left( \frac{\hbar \omega}{kT} \right)}{\left[ \exp \left( \frac{\hbar \omega}{kT} \right) - 1 \right]^2} F(\omega) d\omega
\]  

(7)

\[
C_p = C_v + \alpha^2 B V T
\]

(8)

\[
H = G + TS
\]

(9)

In the above equation, \( F \) represents free energy, \( E_{\text{tot}} \) represents lattice equilibrium energy, \( \hbar \) represents Planck’s constant, \( \omega \) represents lattice wave frequency, \( k \) represents Boltzmann’s constant, \( T \) represents temperature, \( \alpha \) represents linear thermal expansion coefficient, \( B \) represents volume Modulus of elasticity.

### 2.2.2. Model construction and optimization

Calcium carbonate belongs to the trigonal crystal system, its space group is R-3C, the crystal face angle is \( \alpha = \beta = 90^\circ, \gamma = 120^\circ \), \( a = b = 4.993 \text{ Å}, c = 16.917 \text{ Å} \). Calcium oxide belongs to the cubic crystal system, its space group is FM-3M, the crystal face angle is \( \alpha = \beta = \gamma = 90^\circ \), \( a = b = c = 4.99 \text{ Å} \). Calcium sulfate belongs to the orthorhombic crystal system, and its space group is CMCM, \( \alpha = \beta = \gamma = 90^\circ \), \( a = 6.991 \text{ Å}, b = 6.999 \text{ Å}, c = 6.24 \text{ Å} \). Calcium sulphoaluminate belongs to cubic crystal system, its space group is I23, and its crystal face angle is \( \alpha = \beta = \gamma = 90^\circ \), \( a = b = c = 9.19 \text{ Å} \). The single atom convergence standard, truncation energy and k-point of minerals are shown in Table 3. After the model was built, the three-dimensional structure of the unit cell was optimized, Figure 1 shows the crystal structure of calcium carbonate, Figure 2 shows the crystal structure of calcium oxide, Figure 3 shows the crystal structure of calcium sulfate, and Figure 4 shows the crystal structure of calcium sulphoaluminate.
3. Results and discussion

3.1. Analysis of results

It can be seen from Figure 5 that after adding two desulfurizers, the mass concentration of SO\(_2\) in the flue gas gradually decreases with the increase of the Ca/S ratio. As the Ca/S ratio increases, the initial desulfurization efficiency differs greatly, and then the gap gradually narrows, mainly because when the Ca/S ratio increases to a certain level, the desulfurization efficiency of calcium-based sulfur fixer increases little. Adding limestone as a desulfurizer, with the increase of Ca/S, and finally increase to Ca/S=3.0, it cannot meet the ultra-low emission requirements, and the minimum SO\(_2\) mass concentration in the flue gas can reach about 80mg/Nm\(^3\). Adding a composite mineralized sulfur-fixing agent as a desulfurizing agent, when Ca/S=2.5 (3.0), the mass concentration of SO\(_2\) in the flue gas is below 30mg/Nm\(^3\), which can meet the ultra-low emission requirements. Because of the existence of Fe\(_2\)O\(_3\), CaF\(_2\) and other accelerants, the intermediate products Ca\(_4\)Al\(_2\)Fe\(_2\)O\(_{10}\), Ca\(_2\)Al\(_2\)SiO\(_7\), Ca\(_2\)SiO\(_4\) in the formation process of calcium sulfoaluminate encapsulate the generated CaSO\(_4\) and inhibit the high temperature decomposition of CaSO\(_4\). In addition, on the basis of one-time sulfur fixation to generate CaSO\(_4\), it continues to react with aluminum bases to form calcium sulfoaluminate that is difficult to decompose at high temperatures, which not only prevents the decomposition of CaSO\(_4\), but also forms a
new calcium sulfoaluminate phase, ensuring sulfur fixation effect.

It can be seen from Figure 6 that when an appropriate amount of limestone powder (Ca/S=2.5) is sprayed into the circulating fluidized bed furnace, the mass concentration of SO$_2$ in the flue gas is unstable in the first 5 hours, mainly because the limestone is sprayed into the furnace. Decomposition in the furnace requires time and has a certain lag. With the passage of time, the SO$_2$ concentration is basically stable, and the maximum is basically not more than 100 mg/Nm$^3$. After the coal (Ca/S=2.5) added with the composite mineralized sulfur-fixing agent is burned, the SO$_2$ mass concentration is unstable in the first 4 hours, and then basically maintained at a low position (<30 mg/Nm$^3$). The wave amplitude is very small, mainly because the composite mineralization sulfur fixer and coal are uniformly mixed and enter the furnace at the same time. At the same calcium-sulfur ratio (Ca/S=2.5), the SO$_2$ concentration of limestone added is about three times that of composite mineralized sulfur-fixing agent.

![Graph](image1)

**Fig.5. Concentration of SO$_2$ changes along with Ca/S**

![Graph](image2)

**Fig.6. Concentration of SO$_2$ changes along with time**

### 3.2. Thermodynamic analysis

According to the first principles, calcium carbonate, calcium oxide, calcium sulfate and calcium sulfoaluminate are optimized. After the stable structures are obtained by geometric optimization, the ground state charge density is calculated, and then the phonon frequency distribution and phonon state density are obtained by self-consistent iteration. The thermodynamic properties of these four minerals can be obtained. The calculation of the thermodynamic properties of these four minerals were carried out under one atmosphere, with the thermodynamic temperatures ranging from 25 to 1000K, and a set of data was recorded every 25K. According to the calculation results, find out the enthalpy H, entropy TS, heat capacity C$_p$, and Gibbs free energy G of the four minerals as a function of temperature (see Figures 7-10). In the entire temperature range (25~1000K), the entropy TS, constant pressure heat capacity C$_p$, and enthalpy H of the four minerals all increase with the increase of temperature, while the Gibbs free energy G decreases with the increase of temperature. It conforms to the laws of thermodynamics.

Figures 7 and 8 show that the enthalpy and entropy of the four minerals show an upward trend with temperature. Before 150K, the enthalpy and entropy of the four minerals have little difference. As the temperature rises, the enthalpy and entropy of the four minerals have little difference. The enthalpy and
entropy increase rapidly, and the difference between enthalpy and entropy is larger, indicating that more energy is needed to decompose calcium sulfoaluminate, and calcium sulfoaluminate is more stable.

The enthalpy and entropy of calcium carbonate increase very slowly, and the difference in enthalpy and entropy is small, indicating that it takes very little energy to decompose calcium oxide, and calcium oxide is more likely to participate in the reaction. The increasing trend of enthalpy and entropy of calcium carbonate and calcium sulfate is between them, and their stability is between them. The enthalpy and entropy values of calcium carbonate are slightly higher than those of calcium carbonate, indicating that calcium sulfate is more stable than calcium carbonate. The generation of calcium sulfate requires the decomposition of calcium carbonate, so it takes more time than the reaction of calcium oxide.

As shown in Figure 9, the specific heat capacity at constant pressure of the four minerals all increased with the increase of temperature. The specific heat capacity at constant pressure of calcium sulfoaluminate is higher than that of the other three minerals in the whole temperature range. The specific heat capacity at constant pressure of calcium oxide is the lowest in hot melting, and the specific heat capacity of calcium carbonate and calcium sulfate is between them. Before 400K, the specific heat capacity of calcium sulfoaluminate changes drastically, and then gradually become flat, indicating that at low temperatures, calcium sulfoaluminate absorbs more heat. As the temperature rises, the heat absorption begins to decrease. Before 150K, the specific heat capacity of calcium carbonate at constant pressure is higher than that of calcium sulfate at constant pressure, indicating that calcium carbonate has more heat absorption, but the constant pressure hot melting of calcium sulfate and calcium carbonate have little change.

Fig. 10 shows that the Gibbs free energy of the four minerals decreases with increasing temperature. Before 150K, the Gibbs free energy of the four minerals is almost the same. After 150K, the change of Gibbs free energy of calcium oxide is very small, and the change of Gibbs free energy of calcium sulfoaluminate is very sharp. The Gibbs free energy of calcium carbonate and calcium sulfate is between them. Between 150K and 600K, the Gibbs free energy of calcium carbonate and calcium sulfate is almost the same. After 600K, the Gibbs free energy of calcium carbonate is always greater than that of calcium sulfate. It shows that before the temperature is lower than 600K, calcium carbonate decomposes very little, and the calcium sulfate is also very small, it is mainly calcium sulfoaluminate.
Using the simulated data based on the principle of quantum mechanics, the trend of each thermodynamic quantity with temperature change is compared by drawing, which provides a theoretical basis for the removal of sulfur from coal in industrial applications.

3.3. Energy band structure and density of states analysis

3.3.1. Energy band and density of states analysis of calcium oxide

It can be seen from Fig. 11 (a) that the valence band of calcium oxide is divided into four zones: a group of valence bands (1 # band) near -37.5eV, a group of valence bands (2 # band) near -19eV, a group of valence bands (3 # band) near -15eV, and a group of valence bands (4 # band) below -0eV. According to the comprehensive analysis of Fig. 11 (b) (c) (d), 1 # valence band mainly includes the 3s orbital contribution of Ca, 2 # valence band mainly includes the 3p orbital contribution of Ca and the 2s orbital contribution of a small amount of O, 3 # valence band mainly includes the 2s orbital contribution of O and the 3p orbital contribution of a small amount of Ca, 4 # valence band mainly includes the 2p orbital contribution of O and the 2p orbital contribution of a small amount of Ca. Therefore, the top of the valence band is mainly contributed by the 2p orbital of O, and the bottom of the conduction band is mainly contributed by the 3d orbital of Ca; the Ca ions involved in the reaction easily react with sulfur-containing substances to generate calcium sulfate or calcium sulfate.

3.3.2. Analysis of energy band and density of states of calcium carbonate

It can be seen from Figure 12 (a) that the valence band of calcium carbonate is divided into four zones: a group of valence bands (1 # band) near -38eV, a group of valence bands (2 # band) near -21eV, a group of valence bands (3 # band) near -19eV, a group of valence bands (4 # band) near -7eV, and a group of valence bands (5 # band) below 0eV. According to the comprehensive analysis of Fig. 11 (b) (c) (d), 1 # valence band mainly includes the 3s orbital contribution of Ca, 2 # valence band mainly includes the 2s orbital contribution of C and the 2s orbital contribution of O, 3 # valence band mainly includes the 3p orbital contribution of Ca and a small amount of 2p orbital contribution of C and 2s orbital contribution of O, 4 # valence band mainly includes the 2p orbital contribution of O and the 2p orbital contribution of C, 5 # valence band mainly includes the 2p orbital contribution of O and the 3d orbital contribution of a small amount of Ca. Therefore, the top of the valence band mainly has the 2p orbital.
contribution of O, and the bottom of the conduction band mainly has the 3d orbital contribution of Ca, the 2p orbital contribution of part of C, and the 2p orbital contribution of a small amount of O. The Ca ions involved in the reaction easily react with sulfur-containing substances. However, due to the C element on the conduction band, the C must be reacted before it can react with Ca. Therefore, the reaction speed is significantly slower than that of calcium oxide.

It can be seen from Figure 13(a) that the valence band of calcium sulfate is divided into four zones. There is a set of valence bands near -38eV (1# valence band), and a set of valence bands near -23eV (2# valence band), and near -19eV. There is a set of price bands near -8eV (3# price band), and a set of price bands near -10eV (4# price band), and a set of price bands below 0eV (5# price band). According to the comprehensive analysis of Figure 13 (b) (c) (d) (e), 1 # valence band mainly includes the 3s orbital contribution of Ca, 2 # valence band mainly includes the 3s orbital contribution of S and the 2s orbital contribution of O, 3 # valence band mainly includes the 3p orbital contribution of Ca and a small amount of 3p orbital contribution of S and the 2s orbital contribution of O, 4 # valence band mainly includes the 2p orbital contribution of O and the 3s orbital contribution of S, 5 # valence band mainly includes the 3p orbital contribution of Ca and a small amount of 3p orbital contribution of S and the 2s orbital contribution of O. The 2p orbital contribution of S and the 3d orbital contribution of a small amount of Ca.

Fig. 11 CaO energy band structure and density of states diagram
Therefore, the top of the valence band is mainly contributed by the 2p orbital of O and a small amount of 3p orbital of S, while the bottom of the conduction band is mainly contributed by the 3d orbital of Ca, the 3p orbital of some S and a small amount of 2p orbital of O. The stable compounds were formed by the reaction of Ca with sulfur.

Fig. 12 CaCO$_3$ energy band structure and density of states diagram
It can be seen from Fig. 14 (a) that the calcium sulphoaluminate valence band is divided into four zones: there is a set of valence bands (1# valence band) around -38eV, a set of valence bands (2# valence band) around -22eV, a set of valence bands (3# valence band) around -20eV, a set of valence bands (4# valence band) around -17eV, and a set of valence bands (5# valence band) around -7eV. There is a group of valence bands below 0eV (valence band # 6). According to the comprehensive analysis of Figure 14 (b) (c) (d) (e) (f), 1 # valence band is mainly composed of 3s orbital contribution of Ca, 2 # valence band is mainly composed of 3s orbital contribution of S and 2s orbital contribution of O, 3 # valence band is mainly composed of 3p orbital contribution of Ca and a small amount of 3p orbital contribution of S and...
2s orbital contribution of O, 4 # valence band is mainly composed of 2s orbital contribution of O, 3p orbital contribution of S and 3s and 3p orbital contribution of Al, and 5 # valence band is mainly composed of O and 3p orbital contribution of O. The 2p orbital contribution of S and the 6 # valence band are mainly O 2p orbital contribution, Al 3p orbital contribution and a small amount of S 3p orbital contribution. Therefore, at the top of the valence band there are mainly 2p orbital contributions of O and a small amount of 3p orbital contributions of S and Al, while at the bottom of the guide band, there are mainly 3d orbital contributions of Ca, 3s and 3p orbital contributions of part of S, 3p orbital contributions of a small amount of Al and 2p orbital contributions of O. Elements Ca and S, Al, O form stable compounds.

Fig. 14 $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$ energy band structure and density of states
4. Conclusions
(1) The main components of the compound mineralization sulfur fixation agent are calcium oxide and aluminum oxide. When the ratio of calcium to sulfur reaches 2.5, the desulfurization efficiency is more than 95%.
(2) The thermodynamic values of calcium carbonate, calcium oxide, calcium sulfate, calcium sulfoaluminate and products are obtained by the first principles calculation method. Calcium sulfoaluminate has high stability, and calcium oxide is the easiest to react. Calcium carbonate is relatively stable at low temperature, and will decompose slowly after the temperature is higher than 600K. With the increase of temperature, it is conducive to the formation of calcium-based products.

Acknowledgements

The authors appreciate the support of the Innovative Research Team of Henan Polytechnic University (T2020-3) and the National Natural Science Foundation of China (Nos.51774115).

References


Submitted: 24.08.2021
Revised: 17.10.2021
Accepted: 30.10.2021