

Article

Study on the Migration and Release of Sulfur during the Oxidizing Roasting of High-Sulfur Iron Ore

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Abstract: In China, most of the high-sulfur iron ores have not been fully developed and utilized due to the lack of breakthrough progress in the research on the sulfur migration and the desulfurization mechanism during the roasting process. This study will focus on revealing the release and fixation mechanisms of sulfur during the roasting process to achieve the transformation of desulfurization from terminal treatment to process control. Experimental results show that as the roasting temperature increases, the release rate of SO₂ also increases, reaching the maximum release rate at 900 °C. Simultaneously, it is found that at the same roasting temperature, the release rate and amount of SO₂ under the O₂/N₂ atmosphere is significantly greater than that under the pure N₂ and air atmospheres. Meanwhile, X-ray diffraction (XRD) is utilized to explore the phase composition of the roasted product and the sulfur release mechanism. In addition, the adsorption energy, stability and electron transfer of SO₂ on the CaO surface are calculated through density functional theory (DFT), and the optimal adsorption active site perpendicular to the O atom (O-top) is also determined. Finally, the sulfur fixing agent CaO is used to study the SO₂ fixation mechanism. When the concentration reaches 10%, the sulfur fixation efficiency reaches more than 80%. Therefore, this work will present basic knowledge and systematic guidance for the sulfur migration and release of high-sulfur iron ore under the oxidizing roasting process.

Keywords: sulfur migration and release; SO₂ release; high-sulfur iron ore; sulfur fixation reaction; oxidizing roasting



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1. Introduction

There are various types of iron ore in China, among which high-sulfur iron ore resources are abundant and widely distributed. This type of ore is mainly composed of hematite (Fe₂O₃), magnetite (Fe₃O₄), pyrite (FeS₂), quartz and other non-metallic minerals, in which the sulfur element mainly exists in the form of pyrite and sulfate. Pyrite is a naturally occurring material found in its concentrated form in nature and as an impurity in coal and many other minerals (shale, copper, limestone, uranium) [1,2]. The migration and transformation of sulfur in pyrite involves metallurgy, sulfuric acid preparation, coal burning, oil shale utilization and other industrial applications [3–5]. Most iron ore in China is rich in sulfur, and a series of physical and chemical transformations occur during the roasting process [6,7], which often leads to the high sulfur content of the iron concentrate produced and an excessive concentration of SO₂ in flue gas dispersed into the environment [8,9]. Oxidizing roasting is an alternative method for the treatment of sulfur in pyrite, the principle and purpose of which is to oxidize the pyrite at high temperatures to release sulfur to reduce its content in the iron concentrate [10], thus reducing the cost of subsequent blast furnace ironmaking. Then, a sulfur fixing agent is used to fix and remove SO₂ released from the discharged flue gas to meet the ultra-low emission standards (including SO₂-35 mg/m³) stipulated in China's environmental protection regulations [11,12].

Therefore, ascertaining the migration and release rules of the sulfur element during the roasting process of high-sulfur iron ore has important practical significance for the process control of sulfur emissions and efficient sulfur fixation. Many domestic and foreign scholars have carried out a lot of work on the migration direction of sulfur [13–17], but there are few studies on the migration and release of sulfur of high-sulfur iron ore during the roasting process. Wang et al. [18,19] investigates the effects of the roasting temperature, roasting time and dosage of reducing agent on sulfur migration in the process of direct reduction roasting of iron alum slag. The results show that $\text{Fe}_2(\text{SO}_4)_3$ is decomposed at 400 °C and produces SO_2 at 500 °C, and the sulfur element migrates from a solid phase to gas phase. Fe_2O_3 , Fe_3O_4 and SO_2 are confirmed to be the main final oxidation roasting products and dependent on experimental factors, such as the reaction temperature and reaction time [20]. In order to reduce the content of harmful sulfur in the separation concentrate and exhaust gas, related scholars tried to add a reinforcement sulfur agent to achieve this purpose and achieved some research results with scientific significance and application value, which has a good reference significance for research on sulfur fixation technology in the roasting process of high-sulfur iron ore. The common sulfur fixation agents in production are calcium sulfur fixation agents (CaO , MgO , CaCO_3 , etc.) [21–23], sodium sulfur fixation agents (NaOH , KOH , Na_2CO_3 , etc.) [24] and other sulfur fixation agents [25]. However, due to the current research work mainly focused on the selection of sulfur fixation agents and the optimization parameters, the key scientific issues, such as the migration and release trend of sulfur and the sulfur fixation mechanism, have not been systematic and targeted research work. So, it is difficult to achieve breakthrough progress on the control of sulfur, resulting in the excessive investment of the sulfur fixation agent, unstable operation results and high cost. In recent years, theoretical calculations such as density functional theory (DFT) have been widely applied to deeply understand the reaction mechanism [26]. For instance, some researchers have used DFT calculation to accurately predict adsorption energy, electron transfer and stability, among other features [27,28]. Shen et al. evaluated the O-top position as the best adsorption site for CO_2 on the surface of CaO (100) by using DFT calculation [29]. Therefore, theoretical calculation is a good auxiliary means to explore the mechanism of sulfur fixation.

This article is dedicated to revealing the removal rules of sulfur of high-sulfur iron ore through systematic exploration of the removal rules and oxidation mechanism at each stage under the roasting process. The restriction of the desulfurization reaction is determined to provide the necessary theoretical basis for improving the desulfurization efficiency, to optimize the oxidizing roasting process indicators and reduce consumption. Firstly, the distribution of sulfur elements in the solid phase and gas phase are studied to determine the migration trend of sulfur elements. Secondly, we obtain the release rate and release rule of sulfur in high-sulfur iron ore under different roasting parameters (sulfur content, roasting time, roasting temperature, oxygen concentration). Then, the migration mechanism of sulfur in the solid–gas phase and the fixed removal rule of SO_2 are studied. Finally, we use DFT calculation to estimate the optimal active site of SO_2 on the surface of CaO , adsorption energy, electron transfer and stability to further explore the mechanism of sulfur fixation. In summary, the mechanism of sulfur release and fixation in oxidizing roasting are studied in this paper, and the transition from end treatment to process control is realized.

2. Materials and Methods

The sulfur in the high-sulfur iron ore mainly exists in the form of pyrite and sulfate. The whole roasting process is carried out in an oxidizing atmosphere. Elemental sulfur and sulfur in sulfides are easily removed, but the decomposition of sulfate requires a higher temperature. Although the maximum roasting temperature in this study is set at 900 °C, this is less than the temperature at which the sulfate is decomposed. So, SO_2 in the flue gas is mainly produced from FeS_2 in the iron ore sample. Therefore, pyrite and hematite are used to prepare the sulfur-bearing iron ores in order to ensure the sample

purity and reduce interference components, and the mechanism of sulfur release, migration and transformation during roasting is mainly discussed in this study.

2.1. Material

The samples used in this study are powders composed of pyrite and hematite from southern China's Jiangxi Province in a certain proportion. A vertical ball mill is used to prepare high-sulfur iron ore sample powder by comminution and sieving, and the sample is dried and preserved in a vacuum anaerobic before the experiment. The prepared micro-nano-grade sample has a large specific surface area and heat transfer efficiency, and has a high fluidity in the suspension fluidized state in the vertical furnace. X-ray diffraction analysis shows that the pyrite sample is a pure mineral, as in Figure 1 (JCPDs # 65-3321). In addition, the X-ray fluorescence characterization test shows that the pyrite contains a large amount of sulfur and iron, of which the content of sulfur is 53.6% and the content of iron is 44.42% (Table 1). Moreover, calcium oxide used for sulfur fixation and sodium hydroxide for the exhaust gas absorber were purchased from Beijing Bailingwei Technology Co., Ltd. (Beijing, China). All chemicals used are the analytical reagents received, and the solution is prepared using deionized water (18.25 MΩ cm) from an ultrapure water system. Furthermore, the simulated flue gas is composed of N₂ (purity: 99.99%), O₂ (purity: 99.99%) and air in this experiment, with the flow range for 0–600 mL/min.

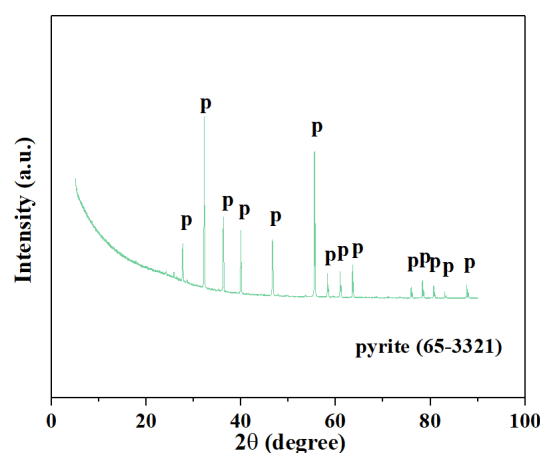


Figure 1. X-ray diffraction analysis spectrum of pyrite.

Table 1. Chemical composition analysis of the pyrite samples (wt%).

Composition	S	Fe	SiO ₂	MgO
Content	53.60	44.42	1.00	0.68

2.2. Experimental System

As can be seen in Figure 2, the experimental device is mainly composed of the flue gas preparation system, oxidizing roasting reaction system and measurement system. The simulated mixed flue gas used in this experiment is prepared by the O₂ and N₂ cylinders, and the purity of the gas is above 99.99%. The simulated gas is configured into different proportions of O₂ and N₂ by using a proton gas mixing proportioner according to the experimental requirements. The key part of the oxidizing roasting device is the vertical fluidized bed furnace, which is constructed by placing a transparent quartz tube with a diameter of 30 mm in the center. Firstly, the oxidizing roasting experiments of high-sulfur iron ore are carried out in a fluidized bed furnace to explore the optimal parameters of the sulfur release reaction. The configured high-sulfur iron ore is positioned on the fixed asbestos in a quartz tube for the roasting experiment in the temperature range of 400–900 °C, with the roasting time 30 min. Before the experiment, the furnace is first heated to the set

temperature of the experiment, and the reaction gas is passed into the furnace for 5 min to ensure a stable and uniform atmosphere in the furnace. In the sulfur fixation experiment, high-sulfur iron ore is mixed with the sulfur fixation agent placed in the pipe. The SO_2 (after drying) release concentration is on-line measured by the infrared gas analyzer, and the measuring result is recorded. Finally, the exhaust gas can be further processed through the exhaust gas absorber loaded with lye. For the collection of solid samples after roasting, because the sample is still in the quartz tube, it is necessary to continue to pass high-purity N_2 to isolate the sample from the outside air, so that the sample can be prevented from continuing to react, and the quartz tube and solid sample can be quickly cooled. When the solid sample is cooled to room temperature in the N_2 atmosphere, the solid product is removed and collected for subsequent testing. Subsequently, the different sulfur content, volume fraction ratio of O_2/N_2 , roasting atmosphere, roasting temperature and roasting time are studied to reveal the release law, transfer path and release mechanism of sulfur in the sulfur-bearing iron ores.

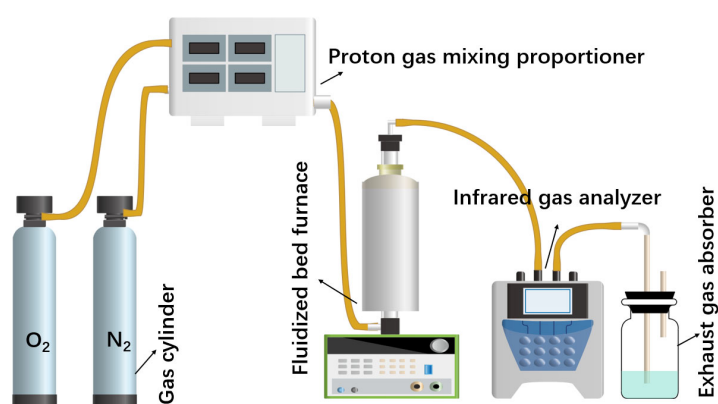


Figure 2. Schematic diagram of roasting experimental setup.

The phases of the raw samples and oxidation roasted products at various stages are detected using a Rigaku D/max-2500HB XRD analyzer using $\text{Cu K}\alpha$ radiation in the $\theta/2\theta$ coupled mode with a 0.02° step size. The concentration of SO_2 released from the flue gas is measured by the on-line infrared gas analyzer (Gasboard-3000plus).

2.3. DFT Computation

DFT calculations are performed using the DMol3 module of the Materials studio (MS) within the generalized gradient approximation (GGA) to simulate the SO_2 adsorption on the pristine CaO (100) surface. The adsorption energy (E_{ads}) is calculated following Equation (1) [30].

$$E_{\text{ads}} = E_{\text{adsorbate-substrate}} - E_{\text{adsorbate}} - E_{\text{substrate}} \quad (1)$$

where $E_{\text{adsorbate-substrate}}$, $E_{\text{adsorbate}}$, and $E_{\text{substrate}}$ symbolize the energy of the adsorbate—substrate, adsorbate and substrate in the adsorbate—substrate system.

3. Results

3.1. Release Characteristics of Sulfur under Different Roasting Conditions

Figure 3 illustrates the release rule of sulfur of high-sulfur iron ore in the oxidizing roasting process with different S-content.

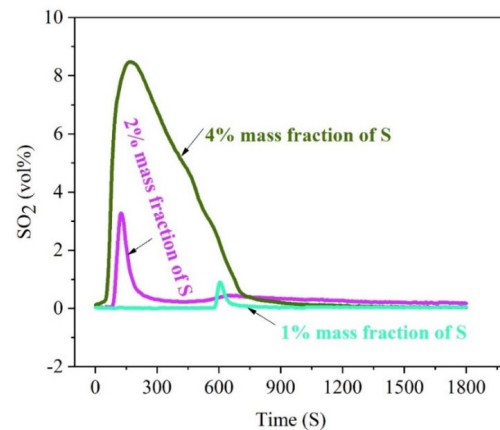


Figure 3. The concentration-time curve of SO_2 release from high-sulfur iron ore at different mass fractions of sulfur element (N_2 —470 mL/min, O_2 —130 mL/min, temperature—500 °C, roasting time—30 min).

The processing of pyrite in the high-sulfur iron ore decomposition is an endothermic process, which can be considered as a heat control process. Therefore, the influence of the roasting temperature on the S-release rate is investigated under the same roasting time for 30 min, as shown in Figure 4. However, this study also investigates the migration and release of sulfur in a pure nitrogen without-oxygen atmosphere at different roasting temperatures, as shown Figure 5.

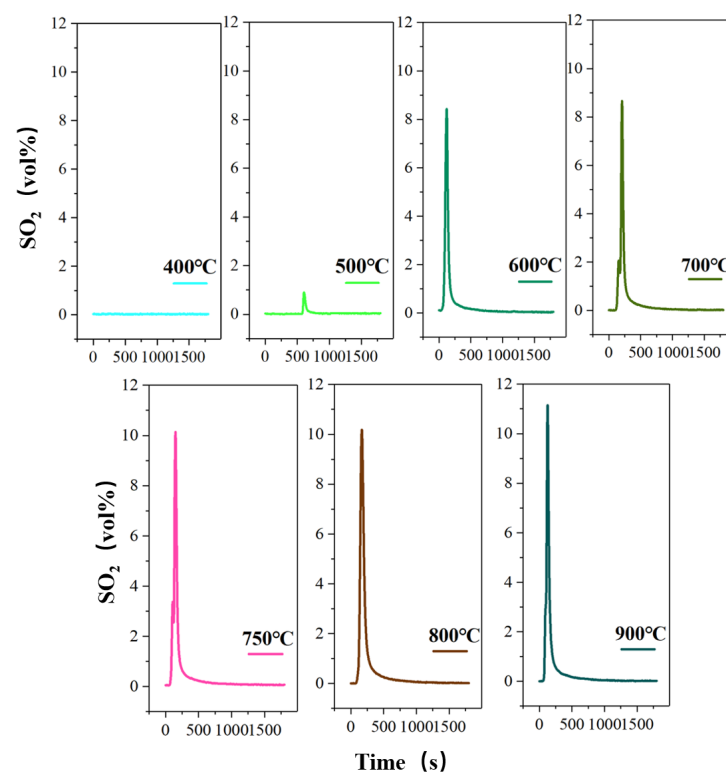


Figure 4. The concentration-time curve of SO_2 release from high-sulfur iron ore at different roasting temperatures in the presence of oxygen (N_2 —470 mL/min, O_2 —130 mL/min, S—1wt%, roasting time—30 min).

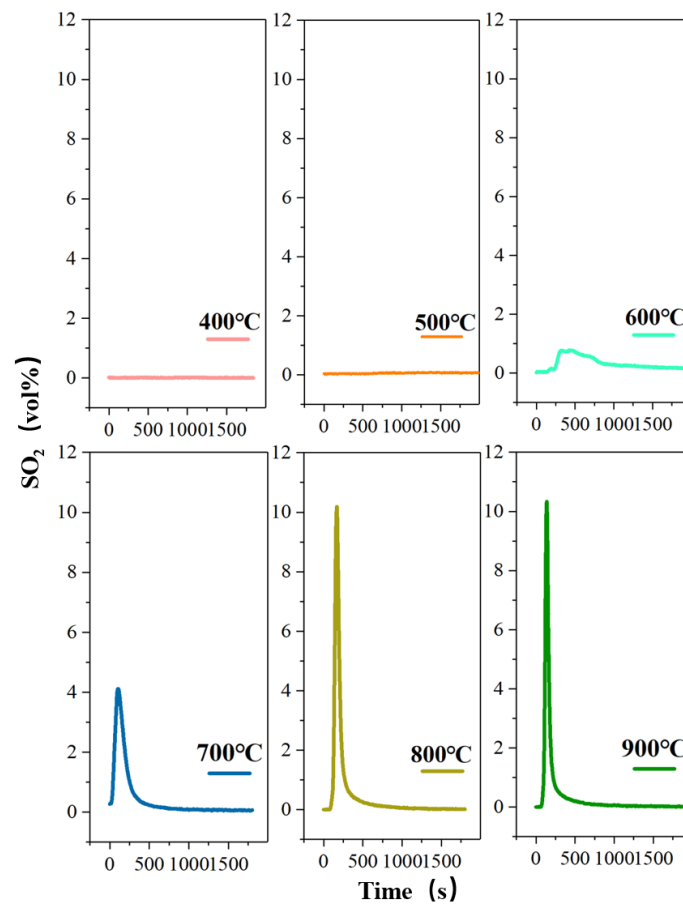


Figure 5. The concentration-time curve of SO_2 release from high-sulfur iron ore at different roasting temperatures in the absence of oxygen (N_2 —500 mL/min, O_2 —0 mL/min, S—1 wt%, roasting time—30 min).

Oxygen plays an important role in the migration and release of the sulfur element under the roasting process, so Figure 6 investigates the effect of oxygen concentration on the release of sulfur during roasting.

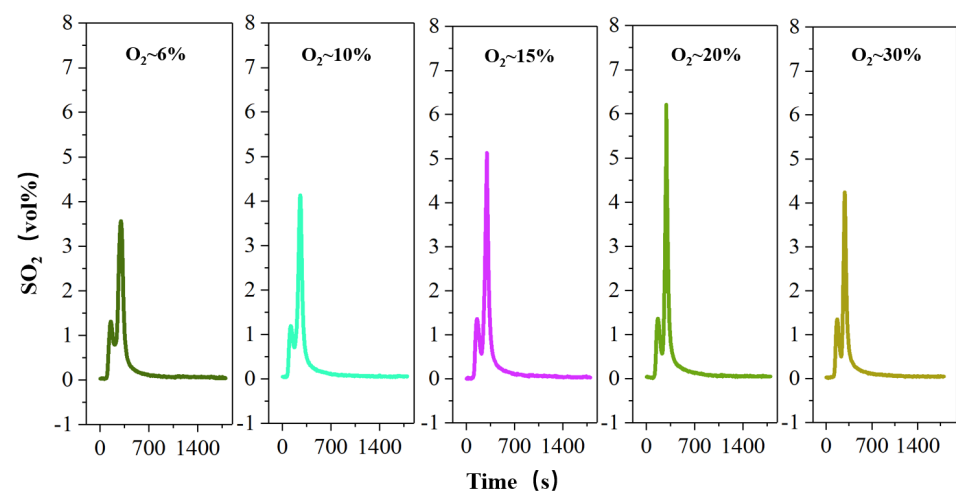


Figure 6. The concentration-time curve of SO_2 release from high-sulfur iron ore at different concentrations of oxygen (S—1 wt%, temperature—600 °C, roasting time—30 min).

By comparing the release concentration and release rate of SO_2 under a traditional air atmosphere and O_2/N_2 (O_2 —21%) atmosphere, it is obviously found that the release

amount and release rate of SO_2 under an O_2/N_2 atmosphere is significantly stronger than that under an air atmosphere, as shown in Figure 7.

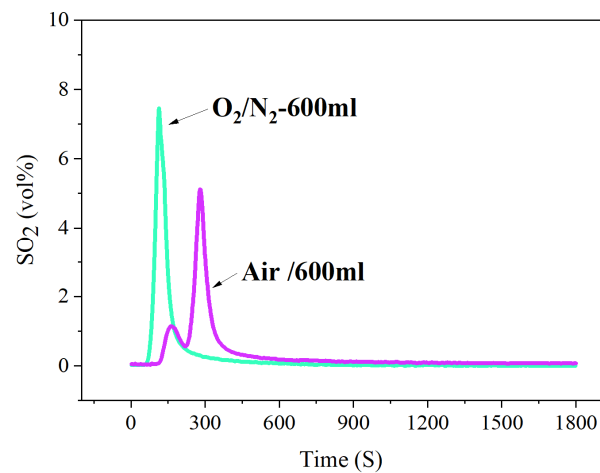


Figure 7. The concentration-time curve of SO_2 release from high-sulfur iron ore under different combustion atmosphere (S—1 wt%, temperature—600 °C, time—30 min, O_2 —21%, N_2 —79%).

3.2. Mechanism of Sulfur Element Release

In order to improve the release rate of sulfur to prepare for the subsequent sulfur fixation process, the decomposition and oxidation mechanism analysis during the roasting process is very important and needs to be studied. The X-ray diffraction analysis spectrum of the oxidizing roasting product of high-sulfur iron ore is shown in Figure 8. The mechanism model of the desulfurization, decomposition and oxidation of pyrite particles in oxidizing roasting is shown in Figure 9.

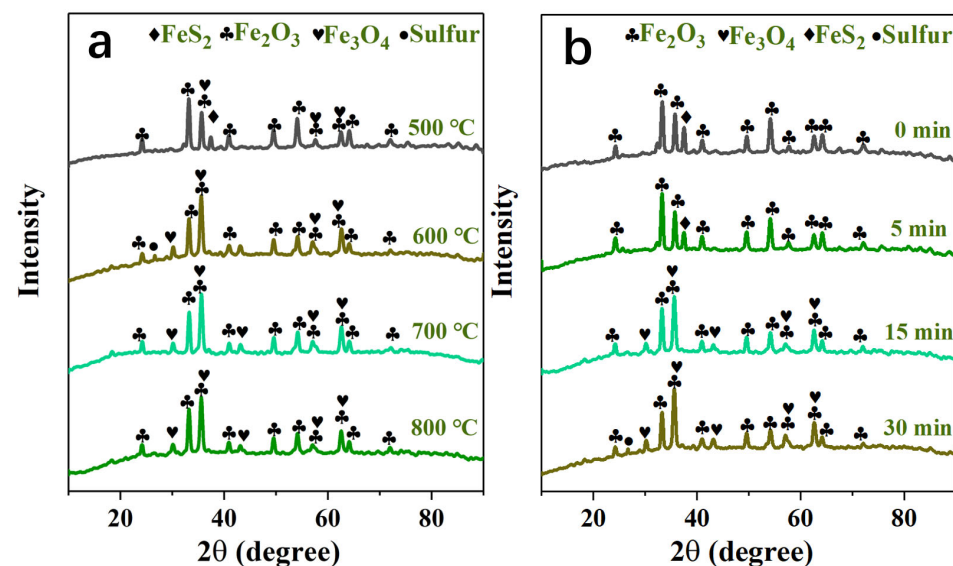


Figure 8. (a) XRD patterns of products at different oxygen-roasting temperatures; (b) XRD patterns of products at different oxygen-roasting times under roasting temperature 600 °C.

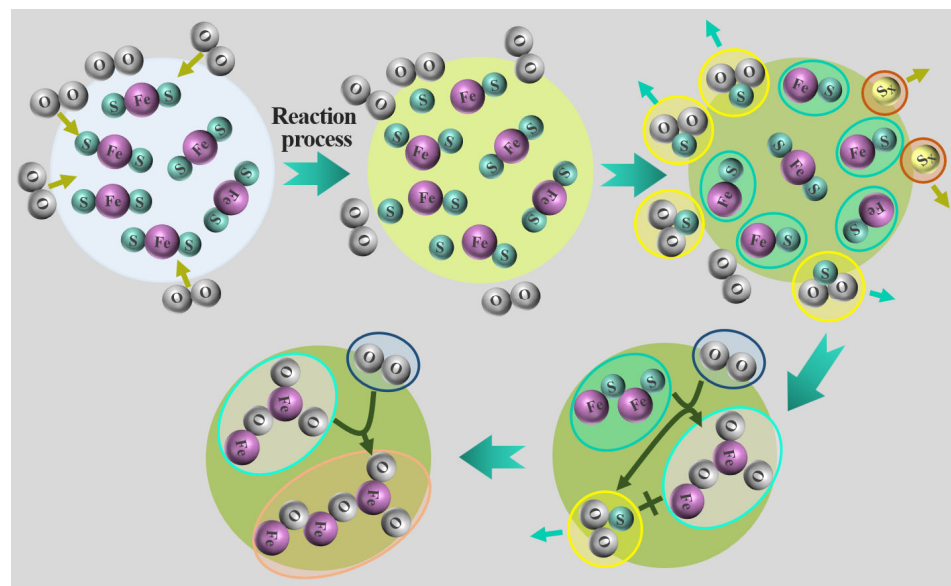


Figure 9. Mechanism model of desulfurization, decomposition and oxidation of pyrite particles in oxidizing roasting.

3.3. Effect of Sulfur Fixative CaO on the Release of Sulfate and Mechanism Analysis

Calcium oxide (CaO) was selected as the fixative for SO_2 because of its advantages of a wide source of raw materials, low cost and environmental friendliness. The law of sulfur release and the efficiency of sulfur fixation are investigated, as shown in Figure 10.

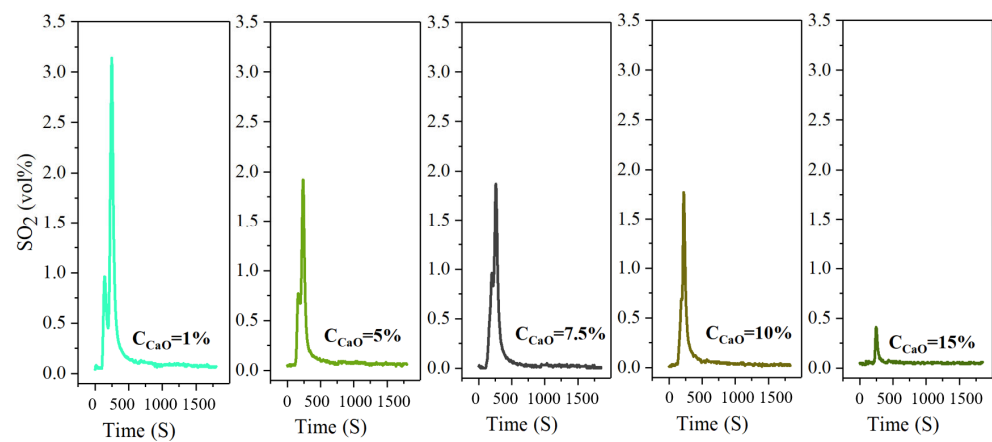


Figure 10. The concentration-time curve of SO_2 release from high-sulfur iron ore at different concentrations of sulfur fixer CaO (S—1 wt%, temperature—600 °C, time—30 min, O_2 —21%, N_2 —79%).

The above DFT calculation is applied to analyze the adsorption energy and stability of SO_2 on the surface of CaO during sulfur fixation of calcium. Figure 11a–d show the adsorption stable configuration of Ca-top, O-top, hollow and bridge adsorption sites of SO_2 on the surface of CaO (100), respectively. Figure 11e–h show the stability.

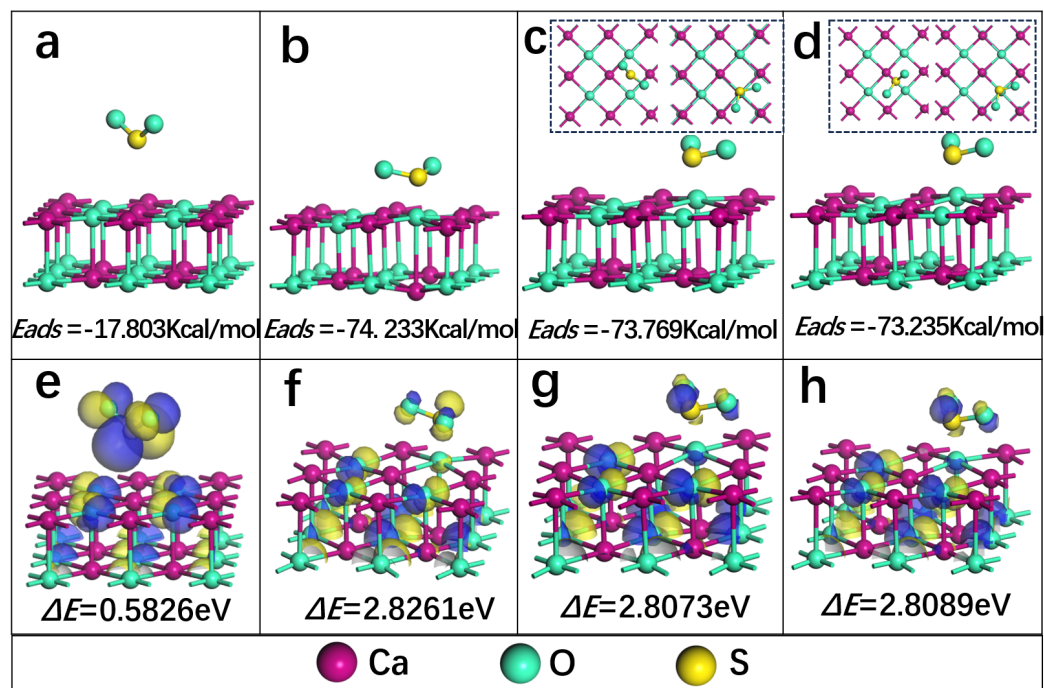


Figure 11. (a–d) The adsorption stable configuration of Ca-top, O-top, hollow and bridge adsorption sites of SO_2 on the surface of CaO (100), respectively (the illustrations in (c,d) represent top views of the position changes of before and after adsorption of SO_2 on the CaO (100) surface); (e–h) The stability of the adsorption configuration at different adsorption sites depends on HOMO and LUMO. Note: For (e–h), the blue and yellow colors represent the positive and negative phases of the molecular orbitals of the compounds, respectively.

4. Discussion

4.1. Release Characteristics of Sulfur under Different Roasting Conditions

4.1.1. Effect of the SO_2 Release on the Mass Concentration of Sulfur Element

Figure 3 illustrates that the release rule of sulfur of high-sulfur iron ore in the oxidizing roasting process with different S-content is consistent with a single peak, that is, the volume percentage of SO_2 released increases with the advance of the roasting reaction and decreases rapidly after reaching the maximum value. However, there are obvious distinctions in the characteristics of peaks and the time when the maximum peak value appears, showing that the peak shape of 1% and 2% sulfur mass concentration is sharper, and the peak of 1% sulfur mass concentration appears latter. Under the same conditions of oxygen roasting (roasting temperature 500°C and roasting time 30 min), the volume percentage of S-release increases with the increase in sulfur content in high-sulfur iron ore. When the mass fraction of sulfur is 1% and 2%, the maximum volume percentage of SO_2 released is 3.28% and 0.9%, respectively. Moreover, when the mass fraction of sulfur in the ore is as high as 4%, the maximum volume percentage of SO_2 release is close to 8.47%, and the time of the SO_2 high-value release lasted up to 12 min, which is much higher than the other two. This indicates that the higher the sulfur content is, the earlier the release peak appears and the larger the maximum peak is. The lower the sulfur content is, the sharper the release peak shape is.

4.1.2. Effect of the S-Release on the Different Roasting Temperatures

The processing of pyrite in the high-sulfur iron ore decomposition is an endothermic process, which can be considered as a heat control process. Wang et al. verified the phase transformation is strongly dependent on the reaction temperature during the oxidation of pyrite [31]. Therefore, the influence of the roasting temperature on the S-release rate is investigated under the same roasting time of 30 min, as shown in Figure 4. The peak

mainly appears at about 200 s, and the peak shape is sharp. After about 800 s, the curve tends to be straight, and the release of SO_2 is close to zero. However, when the roasting temperature is 500 °C, the peak is delayed due to the slow decomposition of sulfur caused by the low temperature. The results show that the oxygen roasting temperature has a significant effect on the volume percentage of SO_2 released, that is, the maximum volume percentage gradually increases with the increase in roasting temperature. It can be found that at 400 °C, the concentration-time curve of SO_2 release tends to be straight, and no obvious peak shape is produced. The measured volume percentage of SO_2 approaches 0.03%, indicating that the pyrite begins to decompose and release the sulfur component at 400 °C, but only a small amount of SO_2 is produced. This also shows that pyrite is stable and not decomposed below 400 °C. Then, as the temperature rises to 500 °C, there is a small spike in the release of SO_2 , with the maximum volume fraction of 0.9%. When the roasting temperature continues to rise to 600 °C, the release of SO_2 shows an explosive increase, with the maximum volume fraction reaching 8.42%, which is due to the rapid fracture of the Fe-S bond in pyrite caused by the temperature rise realizing the quick release of sulfur [32,33]. The results also indicate that the extensive decomposition of pyrite occurs at 600 °C. Subsequently, the roasting temperature increases from 700 °C to 800 °C, and the maximum volume percentage increases from 8.66% to 10.18%. In this case, the volume percentage and the total release amount of SO_2 do not change significantly, which indicates that the temperature rise has little effect on the decomposition of pyrite to SO_2 when the temperature is higher than 700 °C. Finally, the highest SO_2 release rate is obtained when the temperature is raised to 900 °C, accompanied by the maximum volume percentage of 11.15%. However, 600 °C should be the best oxygen roasting temperature from the perspective of energy saving.

In order to better understand the behavior of the sulfur element during the oxidizing roasting, this study also investigates the migration and release of sulfur in a pure-nitrogen-without-oxygen atmosphere at different roasting temperatures (Figure 5). At the roasting temperature 400 °C, there is no obvious change in the ore sample and almost no SO_2 discharge. When the temperature rises to 500 °C, trace amounts of SO_2 are detected with an infrared gas analyzer. Furthermore, it can be seen that the desulfurization reaction rate increases with the increase in roasting temperature. According to a previous study [34], the sulfur element in SO_2 derives from the desulfurization reaction of FeS_2 , and pyrrhotite (FeS_x) is the product of the desulfurization reaction. Also, the oxygen element in SO_2 should come from Fe_2O_3 , which causes Fe_2O_3 to generate Fe_3O_4 . Compared to Figures 3 and 4, the desulfurization effect under the O_2/N_2 roasting atmosphere is obviously stronger than that of under the nitrogen atmosphere at various roasting temperatures. Therefore, it can be concluded that the presence of oxygen in the roasting process promotes the formation and release of SO_2 , reducing the content of sulfur in the high-sulfur iron ore sample, which is conducive to the subsequent blast furnace ironmaking. Fe_2O_3 is deprived of oxygen, leading to formation of Fe_3O_4 , which is conducive to the subsequent magnetic separation of iron ore. Therefore, for iron ore with low sulfur content, the nitrogen atmosphere can be tried. Compared with iron ore with higher sulfur content, better desulfurization efficiency is obtained by oxidizing roasting. In addition, yellow condensed sulfur is also found at the tail flue gas outlet, which indicates that the sulfur in the FeS_2 is released in the form of elemental sulfur (S_x) in the N_2 atmosphere.

4.1.3. Effect of the SO_2 Release on the Concentration of Oxygen

Oxygen plays an important role in the migration and release of the sulfur element under the roasting process, so it is imperative to discuss the parameter of oxygen concentration (Figure 6). The results show that with the increase in oxygen concentration by 6% to 21%, the maximum volume fraction of SO_2 produced gradually increases from 3.56% to 5.04%. With the increase in O_2 concentration, the decomposition trend of FeS_2 increases significantly. The main reason is that the reaction boundary radius of O_2 and sulfur decrease with the increase in O_2 concentration [35], so the heat absorbed by particles

increases, which is conducive to the further decomposition of FeS_2 . Surprisingly, however, when the oxygen concentration increases to 30%, the release of SO_2 does not continue to increase but shows a slight decrease to 4.24%. This is because the main solid roasting products of FeS_2 roasting are FeS and Fe_3O_4 under the combustion condition of low O_2 concentration, and the Fe_3O_4 increase in the product leads to the decrease in the slagging tendency of the solid product [36,37], which is conducive to sulfur migration and release. Nevertheless, under the combustion condition of high O_2 concentration (O_2 -30%), the products of FeS_2 roasting are Fe_3O_4 and Fe_2O_3 , and the proportion of Fe_2O_3 in the product increases relative to the high oxygen concentration. Since the increase in Fe_2O_3 has no obvious improvement effect on the slagging tendency of the FeS_2 roasting product [38], the product slagging prevents the diffusion of sulfur-internal particles to the surface and the diffusion of O_2 to the interior. And because the S-release is controlled by the diffusion process, the release of SO_2 is slightly reduced.

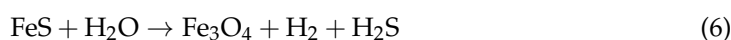
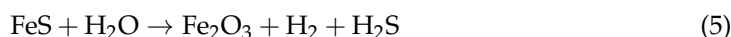
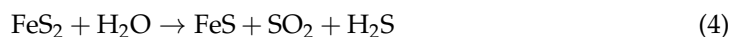
Furthermore, FeS_2 undergoes the following chemical reaction under oxidizing roasting (Equation (2)) [39]. After the sulfur element in FeS_2 is converted to SO_2 gas, part of SO_2 continues to react with O_2 (Equation (3)) [39]. This shows that the higher the oxygen concentration, the more SO_2 is converted to SO_3 . Therefore, as the oxygen concentration continues to increase to 30%, the release of SO_2 decreases.



4.1.4. Effect of the SO_2 Release under Air Atmosphere

By comparing the release concentration and release rate of SO_2 under a traditional air atmosphere and O_2/N_2 (O_2 -21%) atmosphere, it is obviously found that the release amount and release rate of SO_2 under an O_2/N_2 atmosphere is significantly stronger than that under an air atmosphere. It may be that the air contains water vapor, CO_2 and other impurities. Water vapor can convert SO_2 to sulfuric acid, and CO_2 can make SO_2 convert to carbon thiooxide (COS), both of which reduce the emission concentration of SO_2 , causing the results shown in Figure 7.

In addition, the presence of water vapor in the air causes FeS_2 to react with H_2O to form H_2S and H_2 (Equations (4)–(7)) [40–42]. Therefore, part of the sulfur released is converted to H_2S in the atmosphere in the presence of H_2O molecules, thereby reducing SO_2 emissions.



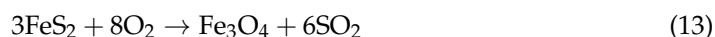
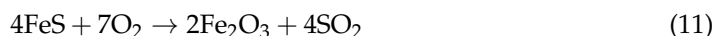
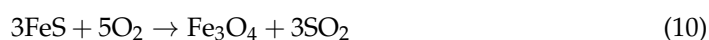
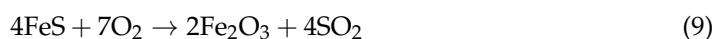
It should be noted that the curve of SO_2 -release in the air atmosphere contains two peaks, with a small peak shape appearing at the initial stage of the reaction, while the SO_2 -release curve in the O_2/N_2 atmosphere has only one sharp peak in Figure 6. This is because the SO_2 formed in the roasting process will go through the process of release, absorption and secondary release, showing the characteristics of SO_2 emission in iron ore. Due to the air atmosphere containing water vapor, the released SO_2 is absorbed to form sulfuric acid, which in turn forms sulfates and sulfites. The presence of water vapor provides good conditions for the absorption of SO_2 . However, with the process of the roasting reaction, the absorption capacity of SO_2 is gradually weakened, and the SO_2 is re-released into the flue gas. The above processes form the phenomena of SO_2 release, absorption and secondary release during the sintering process, and also cause two peaks in the curve of SO_2 release under the air atmosphere.

4.2. Mechanism of Sulfur Element Release

The mechanisms of the decomposition and oxidation of the high-sulfur iron ore sample roasting process under an O_2/N_2 atmosphere are studied. The X-ray diffraction analysis spectrum of the oxidizing roasting product of high-sulfur iron ore is shown in Figure 8. As can be seen in Figure 8a: when the oxidizing roasting temperature increases from 500 °C to 600 °C, the diffraction peak of FeS_2 gradually weakens until it disappears, which is caused by the thermal decomposition of FeS_2 . Meanwhile, the diffraction peak of elemental sulfur is detected (Equation (8)), and an obvious diffraction peak of Fe_3O_4 appears. The appearance of the diffraction peak of Fe_3O_4 is due to the reaction of FeS_2 and O_2 producing FeO , and the generated intermediate-phase FeO is unstable at 200–550 °C, and then will be thermally decomposed into Fe_3O_4 [43]. When the oxidizing roasting temperature increases to 800 °C, solid-phase diffusion and crystallization need to occur at a higher temperature during the oxidation process due to the poor oxidation activity of Fe_2O_3 , so the peak value of Fe_2O_3 detected has no significant changes. On the contrary, the diffraction peak of Fe_3O_4 gradually weakens, which may be caused by the reaction of Fe_3O_4 with O_2 to produce Fe_2O_3 . The above conclusion is consistent with those of Thauan Gomes et al., that is, the main products are Fe_3O_4 and Fe_2O_3 [20].

In addition, XRD is used to detect the phase changes of high-sulfur iron ore samples under different roasting times at the roasting temperature 600 °C, as shown in Figure 8b. The diffraction peaks of FeS_2 and Fe_2O_3 are detected in the primary sample. The FeS_2 content decreased at the reaction time 5 min, and with the advance of the reaction process, the diffraction peak of FeS_2 vanishes, and no other sulfur-containing minerals are detected, indicating that most of the pyrite contained in the sample has undergone a desulfurization reaction. The sulfur element is mainly released in the form of SO_2 gas, without a sulfur fixation reaction with other minerals. And the diffraction peak intensity of elemental sulfur increases with the progress of the reaction. In addition, the diffraction peak of Fe_3O_4 is detected at 15 min, which is due to the oxidative decomposition of FeS_2 to produce Fe_3O_4 . Notably, no $FeSO_4$ is detected because the $FeSO_4$ stability zone shrank as the temperature increased, hindering sulfate formation. Therefore, higher concentrations of oxygen and SO_2 are required at high temperatures to produce sulfates and sulfites. Due to the low concentration of SO_2 and oxygen involved in this study, the formation of $FeSO_4$ is avoided.

Previous studies have pointed out that during the decomposition process of pyrite particles, part of the sulfur element is first lost on the surface, and the release of sulfur forms a porous structure on the surface of the particles, and the inside of the particles is still dense pyrite. Therefore, the FeS_2 in high-sulfur iron ore particles first is decomposed into FeS and sulfur vapor S_x . And the sulfur vapor S_x reacts with oxygen entering the pore in the process of outward diffusion to produce SO_2 in a secondary reaction (Equation (9)), which will expand the pore structure of the particles and accelerate the oxidation rate. FeS is then oxidized by O_2 to Fe_3O_4 and Fe_2O_3 (Equations (10) and (11)). Part of the Fe_3O_4 then reacts with oxygen to form Fe_2O_3 . No sulfate formation is detected during the reaction; in addition to the low oxidizing roasting temperature, it may also be that the SO_2 produced in this reaction is low concentration and is easily carried out of the reactor by the incoming O_2/N_2 gaseous mixture. In addition, the FeS_2 in high-sulfur iron ore particles is more likely to react directly with oxygen to form Fe_3O_4 and Fe_2O_3 rather than sulfate (Equations (12) and (13)) (Figure 9).



4.3. Effect of Sulfur Fixative CaO on the Release of Sulfate

Calcium oxide (CaO) has many advantages, such as a wide source of raw materials, low cost and environmental friendliness; it is especially easy for sulfation reaction. So, it is often used for high-temperature SO₂ capture. In the following study, the law of sulfur release and the efficiency of sulfur fixation are investigated when the sulfur reinforcing agent CaO is added to the reaction system under the oxidizing roasting temperature of 600 °C. Figure 10 reveals that the release law of SO₂ is consistent, and similar peak shapes are obtained at different concentrations of CaO added. During the whole roasting process, two sharp peaks of SO₂-release appear, and the highest peak appears around 250 s. The first peak gradually decreases with the increase in CaO concentration and completely disappears when the CaO concentration is 15%. The sulfur in the high-sulfur iron ore is basically fixed, and the release curve tends to be a straight line. Through the detection, when the concentration of CaO is 1%, the highest SO₂ emission volume percentage of 3.21% is significantly lower than 8.42% when no sulfur fixing agent is added, and the sulfur fixation efficiency is 35.93%. When the CaO concentration is increased to 5%, the maximum volume percentage of SO₂ emission further decreases to 1.91%, and the sulfur fixation efficiency also increases to 56.19%. The concentration of CaO increases to 7.5% and 10%, and the maximum emission volume percentage of SO₂ changes slightly to 1.87% and 1.77%, respectively, but the sulfur fixation efficiency enhances significantly to 64.44% and 70.02%, respectively. The concentration of CaO continues to increase to 15%, and the maximum emission volume percentage of SO₂ reaches 0.42%. At this time, SO₂ is almost completely fixed, and the maximum sulfur fixation efficiency is 82.48%. Figure 8 reveals that the SO₂ release peak shape is bimodal, and the reaction process can be clearly divided into two stages. The first stage is the intrinsic reaction kinetics control stage, in which the surface of absorbent particles is exposed to a large amount of unreacted CaO. And this time, the sulfation reaction is mainly controlled by the intrinsic chemical reaction rate.

In the sulfation reaction, CaSO₄ crystal nucleation islands are first formed on the surface of CaO, and the crystal nucleation gradually grows and fuses to form a product layer with the progress of the reaction. The product layer is not completely dense, but there are gaps through which SO₂ gas can contact CaO inside the product layer [44]. However, with the extension of the reaction time, since the molar volume of CaSO₄ (46 cm³/mol) is nearly three times that of CaO (16.9 cm³/mol), the CaSO₄ product layer will gradually cover the CaO surface. On the one hand, the resulting product layer can clog pores that are too small. On the other hand, blocking the mass transfer channel for SO₂ gas to diffuse into the small pores will increase the mass transfer resistance between SO₂ gas and fresh CaO in the product layer, resulting in a significant reduction in the macroscopic reaction rate, and the sulfation reaction will be from a fast intrinsic reaction. The kinetic control stage transitions to the product layer diffusion control stage [45].

In this work, the most stable adsorption structure of SO₂ on CaO (100) surface is studied with different adsorption sites. Figure 11a–d show the adsorption stable configuration perpendicular to the Ca atom (Ca-top), O-top, hollow and bridge adsorption sites of SO₂ on the surface of CaO (100), respectively. It can be observed that the distance of SO₂ to Ca-top on the CaO (100) adsorption surface increases after the optimization from 2.302 Å to 3.06 Å. Meanwhile, the adsorption energy obtained is −17.804 Kcal/mol (Equation (1)), which indicates weak chemisorption. In addition, the distance of SO₂ to O-top on the CaO (100) adsorption surface decreases from 2.302 Å to 1.741 Å, and the SO₂ on the hollow and bridge adsorption sites is shifted to the right above the O atom after adsorption. The adsorption energy obtained on O-top −74.233 Kcal/mol is much higher than the other two sites, −73.769 Kcal/mol and −73.235 Kcal/mol, indicating that the O-top position on the surface of CaO (100) requires less energy and is easier to reach a stable structure easier when SO₂ is adsorbed. Therefore, the above findings reveal that the O-top position is the best adsorption position for SO₂ on the CaO (100) surface. They also show that SO₂ is chemisorption at these three sites. The length of the S-O bond on the surface of CaO (100) with O-top as the adsorption site is shortened from 1.717 Å to 1.525 Å, which is consistent

with the simulation result 1.50 Å of Wang et al. [46]. Moreover, the bond angle augments from 92.109° to 112.366°. And the structure of SO₂ adsorbed on the surface of CaO (100) is similar to that of SO₃^{2−}, which indicates that SO₂ is adsorbed on the surface of CaO (100) in the form of sulfite by chemisorption.

Furthermore, the stability of the adsorption configuration at different adsorption sites is analyzed in terms of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) [28]. By comparing the ΔE data in Figure 11e–h, it is found that the stability is ranked in order from largest to smallest: O-top > bridge > hollow > Ca-top. The result further supports the view that the O-top position on the surface of CaO (100) is the optimal adsorption site, and the adsorption configuration obtained is the most suitable and stable. The electron transfer between S and O-top atoms enhances the chemical bond formation and reactivity of the surface. After calculation analysis, four sites obtain a similar electron transfer, according to population analysis: O-top 0.277 e, bridge 0.286 e, hollow 0.265 e and Ca-top 0.257 e. Spins exist and have been added, and the S atom obtains electrons. The above DFT calculation results presented the adsorption mechanism of SO₂ on the surface of CaO during the sulfur fixation of calcium.

5. Conclusions

In order to reduce the sulfur content in high-sulfur iron ore, improving the efficiency of subsequent blast furnace ironmaking, the release behavior and fixation of sulfur under the oxygen roasting process is investigated. The roasting temperature, roasting time and sulfur dosage have obvious effects on the sulfur migration and release of FeS₂. Experimental results reveal that as the roasting temperature increases, the release rate of SO₂ also increases, reaching the maximum release rate at 900 °C. However, the total amount of release does not continue to increase with rising roasting temperatures, reaching a maximum at 800 °C. Meanwhile, it is found that at the same roasting temperature, the release rate of SO₂ under the O₂/N₂ roasting atmosphere is significantly greater than that under the pure N₂ and air atmospheres. The maximum volume fraction of SO₂ increases with the increase in oxygen concentration, but an excessive oxygen concentration prevents the release of SO₂. And the mechanism of sulfur migration and release for the high-sulfur iron ore roasting system is determined using XRD. Fe₂O₃ and Fe₃O₄ are the main final oxidation products, and no sulfate is detected throughout the process. Finally, the sulfur fixation reaction is studied: when the CaO concentration reaches 10%, 80% sulfur fixation efficiency can be obtained. And O-top is determined as the best adsorption activity site of SO₂ on the CaO surface, according to the adsorption energy and stability calculated by the DFT theory. Moreover, the electron transfer is calculated as 0.277 e. This research will provide basic knowledge and guidance for the sulfur release of high-sulfur iron ore under the oxidizing roasting process, and enrich the theoretical system of sulfide roasting.

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