

EFFECT OF TEMPERATURE ON THE OXIDATION BEHAVIOR AND OCCURRENCE OF SULFUR IN KR SLAG

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Abstract

The main component (CaO) in KR (Kambara reaction) desulfurization slag is a high value slag raw material for converter smelting, and attempts to utilize KR desulfurization slag in converter smelting are conducive to reducing the buildup of KR desulfurization slag and improving the economic efficiency of converter smelting. However, the removal of sulfur in the slag is a key issue. The influence of temperature on the sulfur oxidation behavior in KR slag in the form of synthetic slag was investigated. SEM-EDS, XRD, and an infrared carbon and sulfur analyzer were used to analyze and detect the oxidized slag samples at different temperatures. The results show that the desulfurization rate increases gradually with the increase in temperature at a flow rate of Ar-50%O₂ of 2 L/min. Under the condition of low temperature ($T \leq 1220$ °C), the desulfurization rate of slag is less affected by temperature. When $T > 1220$ °C, the desulfurization rate of slag is greatly affected by temperature. When the reaction temperature reaches 1420 °C, the desulfurization rate reaches 93.5%. Furthermore, the types of sulfur-containing phases in the oxidized slag samples gradually decrease with the increase of temperature, and the sulfur in the oxidized slag samples is mainly present in the silicate phase when the temperature is less than or equal to 1220 °C.

Keywords: KR slag; Temperature; Sulfur; Oxidation behavior

1. Introduction

Mechanical stirring technique was used in steel production to desulfurize hot metal. There are a number of hot metal desulfurization techniques using mechanical stirring, such as the Demag-Ostberg (DORA) process and the Rheinstahl method, both of which were developed in the 1960s. The KR desulfurization process was the first to be used in Japan for the desulfurization of hot metal. KR desulfurization slag is the tail slag produced in the KR desulfurization process. KR (CaO as based flux) desulfurization process is currently the best process for hot-metal pretreatment desulfurization[1,2].

KR desulfurization slag buildup poses a risk of environmental pollution [3]. Therefore, many scholars have studied different utilization methods for KR desulfurization slag. For example, the treatment of KR desulfurization slag in China is mainly carried out by graded magnetic separation to recover the Fe in the slag [4]. In addition, KR desulphurization slag was used to prepare the sintered feedstock by Kazuya et al.

[5]. In addition, Nakai et al. [6] proposed a method for direct reuse of hot KR desulphurization slag for hot-metal pretreatment desulphurization. Kuo et al. [7] also used KR desulfurization slag for soil modification. Besides, KR desulphurization slag was used by Shiha et al. [8] to replace natural fine aggregates in ready-mixed soil components. In addition, KR desulfurization slag was mainly used for soil backfilling and cement clinker production. However, the added value for KR from these applications is low, and the overall utilization rate is low.

The main components of KR desulfurization slag are CaF₂, CaS, f-CaO, 2CaO·SiO₂, 3CaO·SiO₂, and a small amount of CaSO₄ [9,10]. With the exception of CaS and CaSO₄, all components of the slag can be reused in steel smelting. The 2CaO·SiO₂ in the slag can form a 2CaO·SiO₂-3CaO·P₂O₅ solid solution with 3CaO·P₂O₅ in the converter smelting process to enhance the stability of the phosphorus in the slag [11,12]. It can be seen that the efficiency of phosphorus removal in converter smelting can be

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improved by using the KR desulfurization slag as the pre-melt slag instead of quicklime for converter smelting. If the sulfur in the KR desulfurization slag can be properly eliminated, it will be possible to apply the slag to the converter slagging, effectively decreasing the workload associated with treating KR desulfurization slag. However, previous studies mainly focused on the analysis of the oxidation behavior of pure CaS, CaS in coking coal and sulfur in refining slag [13,14].

Almost no scholars have studied the oxidation behavior of KR desulfurization slag. However, the sulfur oxidation behavior in KR desulfurization slag has not yet been sufficiently investigated. Therefore, the effect of temperature on the sulfur oxidation behavior in KR slag in the form of synthetic slag is investigated in this study. In order to use the KR desulfurization slag after oxidative desulphurization as slagging material for converter smelting, and thus achieve a high utilization rate of the KR desulphurization slag.

2. Experimental

2.1. Slag Preparation

According to KR desulfurization slag composition, the synthetic slag basicity (CaO/SiO_2) was set at 3.5 [15]. The content of sulfur, Al_2O_3 , and MgO in the slag was 1.5%, 6.00%, and 3.00%, respectively. The CaO and CaF_2 composition was added in the mass ratio of 9:1, the slag sulfur was added in the form of CaS, and the synthetic slag composition is shown in Table 1. The CaS added to the slag was prepared in the laboratory. CaSO_4 (purity >99.95%) and carbon powder (purity >99.85%) were used i.e. $n(\text{CaSO}_4) : n(\text{carbon powder}) = 2:1$ (n - the amount of substance) The reaction temperature of the experiment was 1100 °C for 2 hours, and the furnace was under an atmosphere of high purity N_2 with a flow rate of 10 L/min. CaO, SiO_2 , MgO, Al_2O_3 , and CaF_2 were analytically pure chemical reagents, except for CaS in the slag, which was prepared by the laboratory. The mass of the

Table 1. Composition of synthetic slag / wt.%

Basicity	CaO	SiO_2	Al_2O_3	MgO	CaS	CaF_2
3.5	62.73	17.92	6.00	3.00	3.38	6.97

prepared slag sample was 100g. According to the composition of the slag in Table 1, the mixed slag sample was weighed with the standard 35 mesh and 200 mesh sieve, and placed in the constant temperature zone of high-temperature carbon tube furnace. Then the temperature was set at 1600 °C, and the heating rate was 15 °C/min. In addition, the furnace protective atmosphere was high-purity N_2 and

the flow rate was 2 L / min. Finally, the slag sample was pulled out through a glass tube with an inner diameter of 4 mm after the temperature was maintained at 1600 °C for 15 min. The oxidation experiments required slag samples and were then made up.

2.2. Experimental Equipment

Figure 1 shows the structure of the high-temperature quenching furnace equipment in the laboratory. The high-temperature quenching furnace consisted of a gas supply system, a control panel, and a furnace body. The gas supply system consisted of high-purity oxygen, high-purity argon, two pressure-reducing valves, two flow meters, and a mixing chamber. Two pressure-reducing valves were used to control the pressure of high-purity argon and high-purity oxygen respectively, and two flow meters were used to control the flow of high-purity oxygen and high-purity argon respectively. The quenching furnace control panel consisted of a quenching furnace power supply and program control plate, the control plate was used to set the temperature rise program and monitor the temperature in the furnace, and a clamp was used to place the slag sample in the quenching furnace thermostat area, from the air inlet to the furnace sprayed into the gas mixture containing oxygen, and the synthetic slag oxidation experiments can be carried out.

2.3. Oxidation Experiments

Firstly, the Ar-50% O_2 flow rate was determined to be 2L/min. Then, 15 g of the prepared samples were weighed and placed in a quenching furnace at 1020 °C, 1120 °C, 1220 °C, 1320 °C, and 1420 °C with an oxygen partial pressure of 0.50 atm for 2 hours to investigate the effect of temperature on the oxidation behavior of sulfur in the slag. The slag samples were oxidized under different temperature conditions and numbered A1, A2, A3, A4, and A5, respectively.

An infrared carbon and sulfur analyzer was used to examine the sulfur content in the laboratory-prepared synthetic slag and the oxidized slag samples, and to calculate the reaction desulfurization rate. The relationship between the sulfur oxidation behavior in KR desulfurization slag and the variation of reaction temperature was investigated by conducting oxidation experiments on laboratory-prepared synthetic slag at different temperatures, and the equation of the slag desulfurization rate is shown in equation (1).

$$\eta = \frac{S_0 - S_t}{S_0} \quad (1)$$

where, S_0 is the sulfur content of the original slag, and S_t is sulfur content of the slag after the reaction.



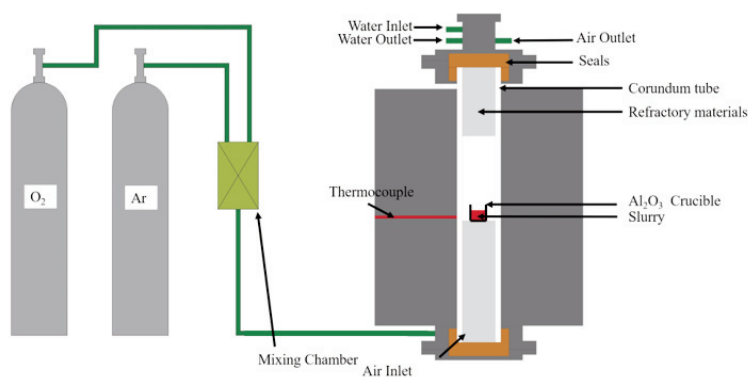


Figure 1. Equipment structure of quenching furnace

2.4. Analysis Method

To quantify the sulfur content in the raw slag samples and the oxidized slag samples, infrared carbon, and the sulfur analyzer were used to test the sulfur content in the raw slag samples, and the oxidized slag samples and to calculate the oxidized desulfurization rate of the slag. An X-ray diffraction analyzer (XRD, Rigaku/Smart Lab SE, Japan) was used to analyze the sulfur-containing mineral composition in different oxidized slag samples and the effect of reaction temperature on the sulfur-containing mineral composition in the oxidized slag samples was clarified. Scanning electron microscopy (SEM-EDS, ThermoFisher /Apreo S HiVac, USA) was used to analyze the distribution of sulfur-bearing phases in the oxidized slag samples to clarify the mechanism of temperature influence on the sulfur-bearing phase assignment in the oxidized slag samples.

3. Experiment Results

3.1. Removal Rate of Sulfur in Oxidized Samples

Figure 2 shows the relationship between the removal rate of sulfur from KR slag and the temperature. When the oxidation temperature was 1020°C, the removal rate of sulfur in oxidized samples was only 2.74%. When the oxidation temperature was 1220 °C and 1320 °C, the removal rates of sulfur were 13.92% and 58.1%, respectively. However, when the oxidation temperature was 1420 °C, the removal rate of sulfur was high at 93.5%, and the residual sulfur in the slag was only 0.1%. The desulfurization rate of the slag was less affected by temperatures between 1020 °C and 1220 °C, and the removal rate of sulfur in the slag was more affected by oxidation temperatures between 1220 °C and 1420 °C. It can be seen that with the increase of reaction temperature slag oxidation removal rate of sulfur

gradually increased, and the increase in the removal rate of sulfur under high-temperature conditions was greater than under low-temperature conditions. With the increase in temperature, the residual sulfur content in the slag gradually decreased, and the amount of desulfurization gradually increased as the slag desulfurization rate increased.

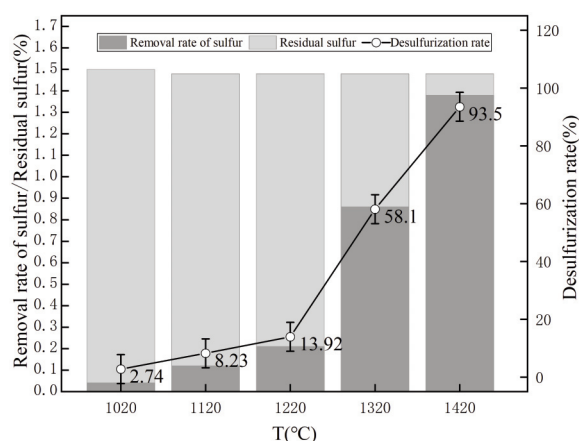


Figure 2. Effect of temperature on Desulfurization Rate of synthetic slag

3.2. Evolution of Sulfur-Containing Mineral Phases in Oxidized Samples

The main mineral phases in the original slag samples and the oxidized slag samples are shown in Figure 3. The slag sample A0 corresponded to the structure of the original slag sample before oxidation. The slag samples A1, A2, A3, A4, and A5 were the structure of the oxidized slag sample made by using the slag sample with a basicity of 3.5 and a sulfur content of 1.5% after oxidized at different temperatures for 2 hours. According to Figure 3, the main phase in the original slag sample is the C3S(3CaO·SiO₂) phase, while the silicate phase in the oxidized slag sample is the C2S(2CaO·SiO₂) phase.



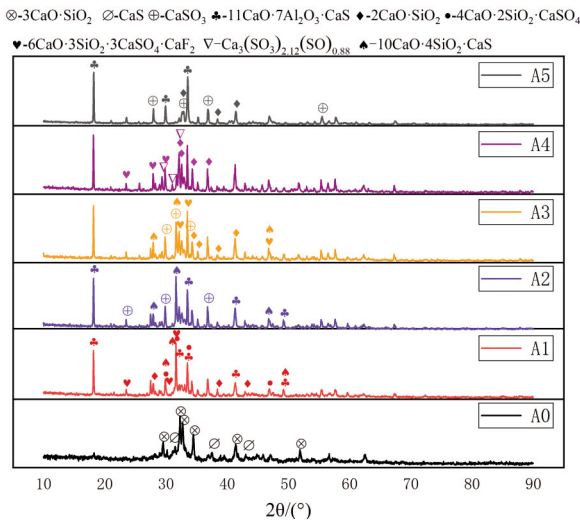


Figure 3. XRD patterns of synthetic slag before and after oxidation

The sulfur-containing phase in the original sample was mainly in the CaS phase, and the residual sulfur in the oxidized slag sample was mainly in the silicate solid solution containing sulfur.

Firstly, when the reaction temperature was 1020 °C, the residual sulfur in the slag was mainly present in the solid solution phases of $11\text{CaO}\cdot 7\text{Al}_2\text{O}_3\cdot \text{CaS}$, $4\text{CaO}\cdot 2\text{SiO}_2\cdot \text{CaSO}_4$, $6\text{CaO}\cdot 3\text{SiO}_2\cdot 3\text{CaSO}_4\cdot \text{CaF}_2$ and $10\text{CaO}\cdot 4\text{SiO}_2\cdot \text{CaS}$. Secondly, when the reaction temperature was 1120 °C, the residual sulfur in the slag was mainly present in the solid solution phases of $4\text{CaO}\cdot 2\text{SiO}_2\cdot \text{CaSO}_4$, $6\text{CaO}\cdot 3\text{SiO}_2\cdot 3\text{CaSO}_4\cdot \text{CaF}_2$, and $10\text{CaO}\cdot 4\text{SiO}_2\cdot \text{CaS}$. When the reaction temperature was 1220 °C, the residual sulfur in the slag was mainly in the solid solution phase of $6\text{CaO}\cdot 3\text{SiO}_2\cdot 3\text{CaSO}_4\cdot \text{CaF}_2$ and $10\text{CaO}\cdot 4\text{SiO}_2\cdot \text{CaS}$. When the reaction temperature was 1320 °C, the sulfur was mainly endowed as $6\text{CaO}\cdot 3\text{SiO}_2\cdot 3\text{CaSO}_4\cdot \text{CaF}_2$ and $\text{Ca}_3(\text{SO}_3)_{2.12}(\text{SO}_4)_{0.88}$ solid solution phases. At last, when the oxidation temperature is 1420 °C, the oxidized slag sample contained only a small amount of $11\text{CaO}\cdot 7\text{Al}_2\text{O}_3\cdot \text{CaS}$ and CaSO_3 sulfur-containing phases. The characteristic peaks of the sulfate phase solid solution of the oxidized slag samples at different temperatures were compared. It can be seen that the characteristic peaks of the sulfate phase formed by the residual sulfur in the oxidized slag samples at low temperatures were more intense than those of the sulfate phase in the oxidized slag samples at high temperatures. This indicates that the residual sulfur in the slag was higher at low temperatures than at high temperatures, which is consistent with the results of the detection of the residual sulfur in the oxidized slag sample using the infrared carbon and sulfur analyzer in Figure 2.

3.3. Microstructure Properties of Slag Samples after Oxidized

Figure 4 shows the reaction of the synthetic slag mineral microstructure with oxidation temperature. As can be seen from Figure 4, the original slag sample contained mainly three kinds of phases. Phases a, b, and c were the silicate-based (C3S) phase, the matrix phase of the slag, and the CaS phase, respectively. The slag sample contained mainly two kinds of phases, phase d was the silicate-based (C2S) phase, and phase e was the matrix phase of the oxidized slag. When the reaction temperature was 1020 °C, the silicate phase was low in the slag grain area. Moreover, the silicate phase and the matrix phase in the slag mosaic were distributed in the slag, and the slag contained a small number of pores. When the reaction temperature was 1120 °C and 1220 °C, the silicate phase in the slag area was larger than in the A1 slag sample. When the reaction temperature was 1320 °C, the oxidized slag sample showed larger pores. In summary, the area of the silicate phase in the slag gradually increased at temperatures above or equal to 1020 °C and below 1320 °C. At the reaction temperature of 1320 °C, the microscopic morphology of slag differed significantly from that of slag samples after oxidation at 1020 °C to 1220 °C. In addition, the oxidized slag sample contained a large number of pores at 1320 °C, and the oxidized slag sample had a dense structure and a small amount of round cake silicate phase appeared in the slag at 1420 °C.

Based on the above analysis of the evolution of the mineral structure of the oxidized slag samples with temperatures, EDS was used to analyze the mineral elements in different slag samples. As can be seen from Table 2, the silicate phase contains 2.8% sulfur at 1020 °C, 3.5% sulfur at 1120 °C, and 3.0% sulfur at 1220 °C. When the reaction temperature was less than or equal to 1220 °C, the slag contained elemental sulfur, and sulfur was mainly in the silicate phase of the slag. However, when the reaction temperature was 1320 °C and 1420 °C, no elemental sulfur was found in the oxidized slag samples, and no sulfur was found in the matrix phase of the oxidized slag samples at different temperature conditions. In summary, the residual sulfur in the oxidized slag samples under Ar-50% O₂ conditions was mainly present in the silicate phase, and it was mainly in the form of the solid solution phase.

4. Discussion

4.1. Relationship between Temperature and Removal Rate of sulfur from Slags

Figure 5 is the predominance area diagram of Ca-O-S range 1020 °C - 1420 °C using the phase diagram module of the thermodynamic database Factsage 8.1.

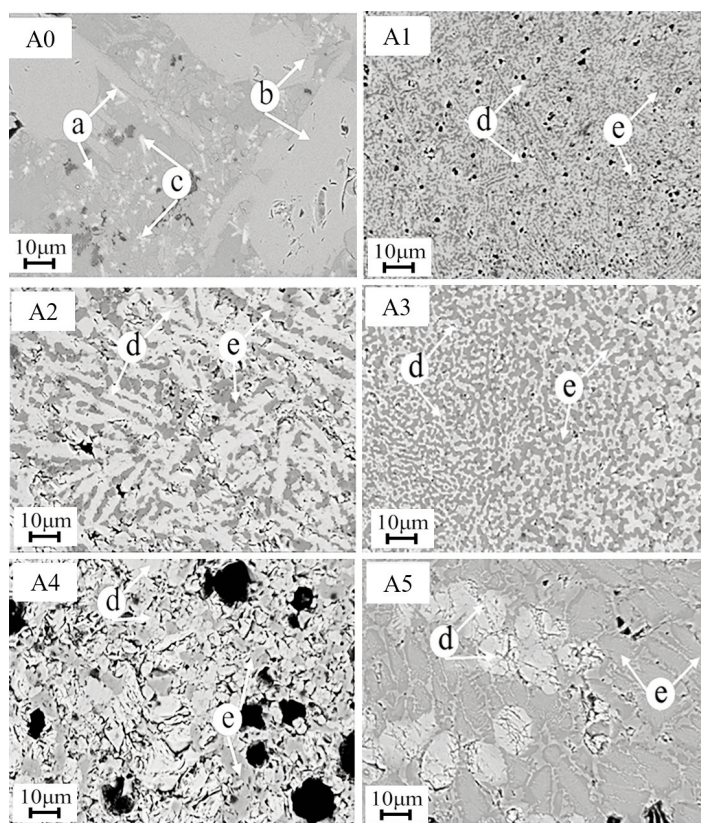


Figure 4. Microstructure of oxidized slag samples at different temperatures; a- Silicate phase (C3S), b- Matrixphase, c- CaS phase, d- Silicate phase (C2S), e- Solid solution phase; (A0- original slag sample, A1-1020 °C, A2- 1120 °C, A3- 1220 °C, A4- 1320 °C, A5- 1420°C)

Table 2. EDS analysis of slag mineral element on differential oxidation temperature

Slag sample	Phase	Ca mass%	Si mass%	Al mass%	F mass%	Mg mass%	O mass%	S mass%	Oxidation temperature
A0	a	50.2	11.3	—	—	—	38.5	—	1600°C
	b	42.9	3.5	13.6	8.6	1.7	29.8	—	
	c	59.1	—	—	—	—	—	40.9	
A1	d	50.7	11.7	3.2	—	—	31.6	2.8	1020°C
	e	40.7	4.2	16.3	3.5	1.3	33.9	—	
A2	d	50.8	11.6	1.5	—	1.6	31.1	3.5	1120°C
	e	35.7	0.9	24.5	3.6	1.7	33.5	—	
A3	d	50.2	13	1.3	—	1.2	31.4	3	1220°C
	e	38.9	1.8	25.1	—	1	33.3	—	
A4	d	48.6	15.7	0.8	—	—	35	—	1320°C
	e	34.5	1.9	39.7	—	1.5	—	—	
A5	d	49.3	16.8	—	—	—	33.9	—	1420°C
	e	40.8	10.2	11.6	—	2.9	34.5	—	

Under the experimental conditions, the atmosphere of the reaction system is distributed in the labeled region (triangular region) of the predominance area diagram

of Ca-O-S. As can be seen from Figure 5, with the increase in temperature, the CaO stability zone gradually moved to the right and the CaSO₄ stability

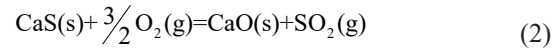


zone gradually decreased. In conclusion, sulfur in KR desulfurization slag can be effectively oxidized to SO_2 and CaO by adjusting the temperature of the reaction system.

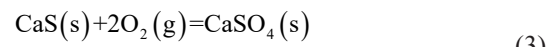
Under the Ar-50% O_2 conditions, when the temperature is less than or equal to 1220 °C, the slag desulfurization rate does not vary much with temperature and the slag mineral structure was tight. This is mainly related to the thermodynamic and kinetic behavior of the sulfur oxidation processes in the slag at different temperatures. The thermodynamic behavior of the slag during sulfur oxidation process is analyzed based on thermodynamic data, as shown in Figure 5. When the temperature is 1020 °C to 1420 °C, both Eq. (2) and Eq. (3) can proceed spontaneously. While the ΔG^θ of CaS oxidation to form CaSO_4 in Eq. (3) is more negative than Eq. (2) under the same temperature conditions, it can accordingly be thermodynamically determined that the oxidation of sulfur in slag under the same conditions is more likely to proceed with Eq. (3) than with Eq. (2). It can be seen from the thermodynamic analysis when the temperature is lower than 1220 °C, the slag desulfurization rate varies less with temperature, which is due to the sulfur in the slag mainly to form CaSO_4 , then only a small amount of sulfur directly oxidized during the reaction to form CaO and SO_2 . Xiao, H. et al. [16] conducted a thermogravimetric experimental study on the characteristics of CaS oxidation reaction. It was found that the decomposition of CaSO_4 formed by CaS oxidation started when the temperature of the reaction system was 1175 °C, and the SO_2 precipitation reached 96.91% when the temperature reached 1400 °C. Li et al. [17] studied the decomposition behavior of CaS and indicated that CaSO_4 could decompose to form CaO and SO_2 at 1300 °C. When the temperature was greater than or equal to 1320 °C, there were larger

pores in the slag, and the desulfurization rate of the slag reached 58.1%. Therefore, it can be considered that the removal rate of sulfur is greatly improved due to CaSO_4 formed in the slag reaction process starting to decompose to generate SO_2 .

When the temperature was greater than or equal to 1320 °C, the temperature required for the decomposition of CaSO_4 was satisfied, and the CaSO_4 formed during the oxidation of the slag was decomposed into CaO and SO_2 , so that the removal rate of sulfur in the slag was rapidly increased.



$$\Delta G^\theta = -454330 + 74.5T \text{ J/mol}$$



$$\Delta G^\theta = -907100 + 309.37T \text{ J/mol}$$

where ΔG^θ is Standard Gibbs free energy of the reaction (J/mol), T refers Reaction temperature (K).

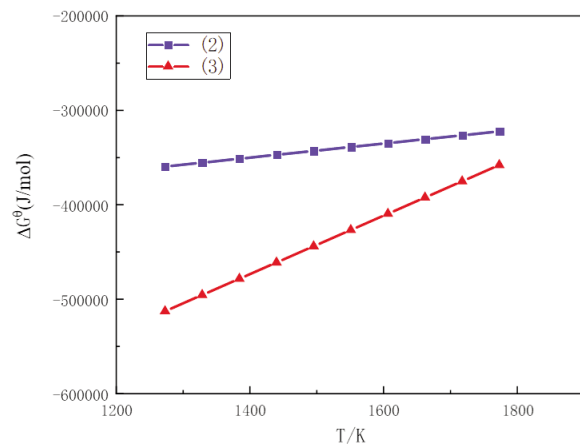


Figure 6. ΔG^θ - T diagram of Eq. (2) - (3)

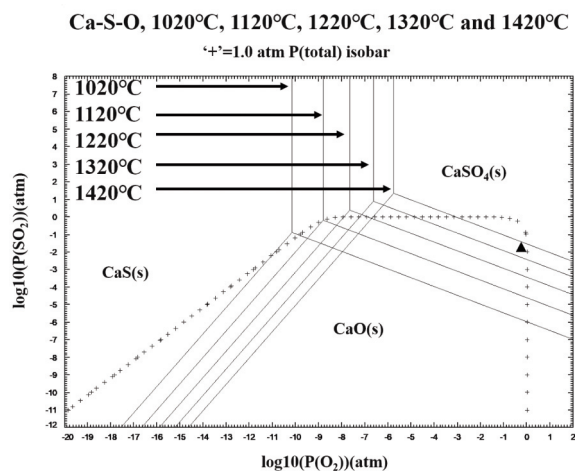


Figure 5. Predominance area diagram of Ca-S-O system at 1020 °C-1420 °C

The kinetic behavior of the sulfur oxidation process in the slag is related to the state of the slag during the reaction process. When the reaction temperature is below or equal to 1320 °C, the synthesized slag is a solid slag. However, when the temperature is equal to 1420 °C, the synthesized slag contains a significant amount of liquid phase. This was known from the experimental phenomena of the slag at different temperatures during the experiment. Therefore, the evolution of the kinetic behavior of the sulfur oxidation process in the slag with the reaction temperature can be analyzed by using the gas-solid unreacted nucleus model and the gas-liquid reaction model for the sulfur oxidation in the slag according to the slag state during the reaction process. When the temperature is less than or equal to 1320 °C, the kinetic behavior of the sulfur oxidation process in the

slag can be analyzed by the unreacted core model of the gas-solid reaction. Under solid-state conditions, the sulfur oxidation process in the slag is mainly controlled by the internal diffusion of Ar-50%O₂ due to the formation of CaSO₄ on the surface of CaS in slag, which obstructs the diffusion of oxygen. According to XRD analysis, CaSO₄ produced by slag oxidation at low temperatures will form a solid solution with CaS, CaSO₃, and the silicate phase in the slag during the holding process.

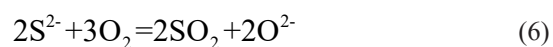
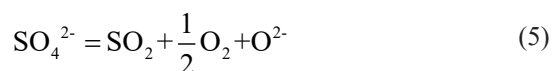
It can be seen that the slag desulfurization rate was low at low temperatures ($T \leq 1220$ °C), and the slag desulfurization rate do not change significantly with increasing temperature. This is due to the formation of CaSO₄ with CaS surface layer forming CaS-CaSO₄ and CaSO₃-CaSO₄ solid solution, which binds the sulfur in the slag and deteriorates the kinetic conditions for sulfur oxidation in the slag. In addition, because the slag is solid at low temperatures, the slag structure is tight, which is against the diffusion of SO₂ formed in the slag. Moreover, the CaSO₄ fails to decompose and forms in the slag at low temperature, then enriches in the CaS surface in the slag, then the further oxidation of CaS is hindered.

When the temperature is equal to 1320 °C, larger pores appear in the slag and the desulfurization rate rises to 58.1%. It is because the system temperature reaches 1320 °C to meet the condition of CaSO₄ decomposition in the slag. Therefore, the CaSO₄ forms on the surface of CaS during oxidation can be a quickly decomposed reaction. Then the kinetic conditions of Ar-50%O₂ diffusion to the surface of the CaS phase are improved and the oxidation reaction of sulfur in the slag is promoted to be fully carried out. When the temperature was equal to 1420 °C, the kinetic behavior of the sulfur oxidation process in the slag can be analyzed by the gas-liquid film model because a large amount of liquid phase appears in the slag. The oxidation reaction of sulfur in the slag of the reaction process is divided into four stages. To start with the gas reactant O₂ diffuses from the gas phase main body to the gas-liquid phase interface. Next, the gas reactant O₂ diffuses from the gas-liquid phase interface into the liquid phase and reacts within the liquid phase. In addition, the liquid reactant CaS diffuses from the liquid phase main body to the gas-liquid phase interface and reacts with the dissolved A during the diffusion process.

Finally, the reaction product SO₂ diffuses to the interface and enters the main body of the gas phase. Since the oxygen supply is sufficient during the reaction, the limiting link of sulfur oxidation in the slag is mainly controlled by S²⁻ diffusion in the slag phase. Pelton et al. [18] studied the kinetic behavior of the sulfur oxidation process in a liquid ternary slag system (CaO-SiO₂-Al₂O₃) in the temperature range of 1360-1460 °C and clarified that S²⁻ diffusion control

in the liquid phase under the condition of oxygen supply is the limiting link of the sulfur oxidation process in the slag.

In the case of slag containing a large amount of liquid phase, the mechanism of sulfur oxidation in the slag is shown in Eqs. (4) to (6). According to the low-temperature conditions of the slag in the sulfur phase, the slag can be determined at 1420 °C, and the system oxygen partial pressure can be determined at 0.50 atm. The reaction process of sulfur in the slag mainly reacts first to form CaSO₄ and then decomposes to form SO₂. When the temperature reached 1420 °C, the desulfurization rate is 93.5%, and the sulfur content in the slag is only 0.1%. Allertz et al. [19] studied the oxidation process of sulfur-containing steel slag from 1100 to 1400 °C and found that the desulfurization rate of the slag was less affected by temperature when the slag was solid or contained a small amount of liquid phase, and the desulfurization rate of the slag increased rapidly to 86% when the slag contained a large amount of liquid phase. This indicates that the presence of a large amount of liquid phase in the slag can improve the kinetic conditions of sulfur diffusion in the slag during oxidation so that the oxidation reaction of sulfur in the slag can be fully carried out.



The above analysis of the mechanism of temperature influencing the sulfur oxidation behavior in slag shows that the influence of the thermodynamic and kinetic behavior of the sulfur oxidation process in synthetic slag is closely related to the oxidation temperature.

When low temperatures ($T \leq 1220$ °C), the slag desulfurization rate does not change much with increasing temperature, which is because CaSO₄ produced by the oxidation of CaS surface in slag hinders the diffusion of Ar-50%O₂, resulting in a lower slag desulfurization rate. When the temperature is 1320 °C, the desulfurization rate of slag increases to 58.1%, which is due to the kinetic conditions of sulfur oxidation being improved by the full decomposition of CaSO₄ produced on the surface of the CaS phase in slag. When the temperature reached 1420 °C, the removal rate of sulfur in the slag reached 93.5%, and the residual sulfur of the slag sample is only 0.1%. It is because the slag produced a large amount of liquid phase at 1420 °C to improve the kinetic conditions for sulfur diffusion in the slag to fully promote the oxidation reaction of sulfur in the slag.



4.2. Effect of Temperature on Evolution Behavior of Mineral phases Containing Sulfur in Oxidized Samples

The silicate phase in the oxidized slag sample will undergo a phase change, and it is dominated by the C3S phase in the original slag sample. However, the silicate phase in the oxidized slag sample is dominated by the C2S phase. This is based on the analysis of the mineral composition and structure of the virgin slag sample and the oxidized slag sample. Since the original slag sample is prepared by holding at 1600 °C under an inert atmosphere for 15 min, the equilibrium phase diagram of the CaO-SiO₂-Al₂O₃ system at 1600 °C is calculated by using the phase diagram module of FactSage 8.1, as shown in Figure 7. As can be seen from Table 1, the contents of CaO, SiO₂, and Al₂O₃ in the original slag sample are 62.73%, 17.92%, and 6.00%, respectively, and the main mineral phase zone of the slag is located in the C3S-C2S-L two-phase zone at the marked position in Fig. 7 at 1600 °C.

Since the reaction temperature of the oxidized slag sample is 1020-1420 °C, only C2S can stably exist in the oxidized slag sample, and C3S cannot stably exist. Therefore, the main phase C3S of the original slag sample decomposed into C2S after holding by oxidation.

R.L. Zhu et al. [20] experimentally proved that the sulfur in the original slag sample is mainly in the CaS phase at the boundary of the silicate phase, and the state of sulfur in the original slag sample is shown in Figure 8. However, the residual sulfur in the oxidized slag is mainly present in the silicate phase as complex compounds formed by CaSO₄. The change in the structure of the silicate phase containing sulfur after oxidation is shown in Figure 9. It is consistent with the XRD detection results in Figure 3 and the microstructure in Figure 4. At low temperatures ($T \leq$

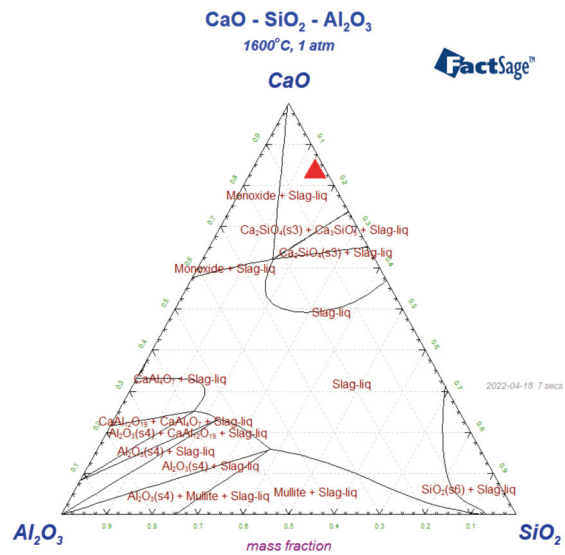


Figure 7. Ternary phase diagram of CaO-SiO₂-Al₂O₃ at 1600 °C

1220 °C), the residual sulfur in the KR desulfurization slag after oxidation consists mainly of CaSO₄ and C2S forming compounds, as shown in Figure 8. At high temperatures ($T > 1220$ °C), only a small amount of residual sulfur is present in the oxidized slag.

The variety of sulfur-containing phases under high temperature ($T > 1220$ °C) conditions This is mainly due to the compact structure of the slag at low temperatures which releases a large amount of energy during the reaction of the sulfur in the slag to form CaSO₄. Then the CaSO₄ is generated at the silicate interface accordingly, but the CaS phase generated at the interface is unstable When the temperature is low ($T \leq 1220$ °C). The solid-state diffusion of CaSO₄ is from the region of high chemical potential (silicate phase interface) to the region of low chemical potential (in the silicate phase) during the reaction.



Figure 8. Fugitive state of sulfur in the original slag sample (yellow-matrix phase, black-silicate phase (C3S), white - CaS)

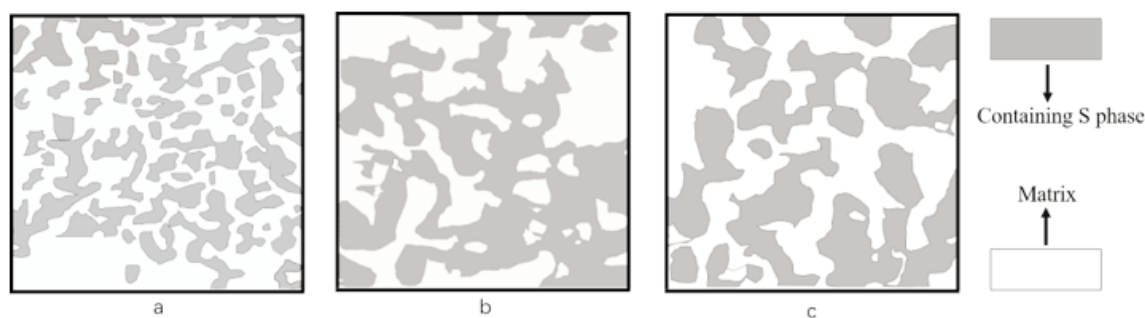


Figure 9. Structural change of sulfur-containing phase (silicate phase) of slag sample after oxidation: (a) 1020 °C, (b) 1120 °C, (c) 1220°C

Due to this, a composite structure silicate phase is formed containing the CaSO_4 , $2\text{CaO}\cdot\text{SiO}_2$, and $6\text{CaO}\cdot 3\text{SiO}_2\cdot\text{CaF}_2$. The sulfur content in the oxidized slag samples under low temperature ($T \leq 1220$ °C) conditions is relatively higher than under high temperature ($T > 1220$ °C) conditions, which is due to the rapid decomposition of CaSO_4 formed under high-temperature conditions. It can be seen that whether the sulfur-containing phase and the silicate phase in the oxidized slag sample can form new phases is closely related to whether the CaSO_4 formed by the oxidation of sulfur in the slag phase can be decomposed. If the CaSO_4 oxidized in the slag sample does not decompose quickly, it diffuses from the silicate phase interface to the silicate phase to form various CaSO_4 -containing silicate phases with the silicate phase in the slag during the holding process.

5. Conclusions

(1) Under the condition of 0.50 atm oxygen partial pressure, the desulfurization rate of sulfur oxidation in slag increases gradually with the increase of oxidation temperature. When the temperature is lower than 1220 °C, the slag desulfurization rate increases less with the temperature, and when the temperature is higher than 1220 °C, the slag desulfurization rate increases more with the temperature.

(2) The main phase of the original slag sample is C3S, and the main phase of the oxidized slag sample is decomposed from C3S to C2S by oxidation holding under the condition of oxygen partial pressure of 0.50 atm.

(3) When the oxygen partial pressure is 0.50 atm and the temperature is less than 1320 °C the slag contains more kinds of sulfur phases. Whereas the temperature is higher than 1320 °C, the oxidation slag sample contains a small amount of sulfur-containing phase. The residual sulfur in the slag after oxidation is mainly in the form of complex compounds in the silicate phase, and the separate CaS phase is not found in the slag samples.

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Author Contributions

J.-L. Li: Conceptualization, Funding acquisition, Investigation, Methodology, Validation, Visualization, Writing - original draft. J.-J. Jiang: Methodology, Software, Writing - original draft, Validation. C. Xiao: Validation, Writing - original draft. Y. Yu: Validation.

Data availability

The data cannot be made publicly available upon publication because they are not available in a format that is sufficiently accessible or reusable by other researchers. The data that support the findings of this study are available upon reasonable request from the authors.

Conflict of Interest

The authors declare that they have no conflict of interest.

References

- [1] Y. Nakai, I. Sumi, H. Matsuno, Effect of flux dispersion behavior on desulfurization of hot metal, *ISIJ International*, 50(3) (2010) 403-410. <https://doi.org/10.2355/isijinternational.50.403>
- [2] Y. Nakai, Y. Hino, I. Sumi, Effect of flux addition method on hot metal desulfurization by mechanical stirring process, *ISIJ International*, 55(7) (2015) 1398-1407. <https://doi.org/DOI:10.2355/isijinternational.55.1398>
- [3] H. Du, D. Xu, X. Li, Application of molten iron desulfurization slag to replace steel slag as an alkaline component in solid waste-based cementitious



- materials, *Journal of Cleaner Production*, 377 (2022) 134353. <https://doi.org/10.1016/j.jclepro.2022.134353>
- [4] J. Guo, Y. Bao, M. Wang, Steel slag in China: Treatment, recycling, and management, *Waste management*, 78 (2018) 318-330. <https://doi.org/10.1016/j.wasman.2018.04.045>
- [5] F. Kazuya, O. Koichiro, M. Taichi, Effective utilization of KR slag in iron ore sintering process, *Tetsu-To-Hagané*, 103(6) (2017) 357-364. <https://doi.org/10.2355/tetsuohagane.tetsu-2016-098>
- [6] Y. Nakai, N. Kikuchi, M. Iwasa, Development of slag recycling process in hot metal desulfurization with mechanical stirring, *Steel Research International*, 80(10) (2009) 727-732. <https://doi.org/10.2374/SRI09SP082>
- [7] W.T. Kuo, T.C. Hou, Engineering properties of alkali-activated binders by use of desulfurization slag and GGBF, *Construction and Building Materials*, 66 (2014) 229-234. <https://doi.org/10.1016/j.conbuildmat.2014.05.05>
- [8] Y.F. Shiha, S.S. Tseng, H.Y. Wang, A study of the replacement of desulfurization slag for sand to ready-mixed soil materials (RMSM), *Computers and Concrete, An International Journal*, 17(3) (2016) 423-433. <https://doi.org/10.12989/cac.2016.17.3.423>
- [9] M.R. Bogala, M.M. Zhang, R.G. Reddy, *Characterization of Steelmaking Desulfurization Slag*, Hoboken, NJ, USA, 2015.
- [10] J. Peng, J. Wu, X.Y. Yang, Analysis on the existential state of sulfur of the molten iron desulfurization grinded slag in Wuhan Iron and Steel Corporation (WISCO), *Building Materials World*, 33(5) (2012) 4. <https://doi.org/10.3963/j.issn.1674-6066.2012.05.002>
- [11] J. Li, M. Zhang, M. Guo, Enrichment mechanism of phosphate in CaO-SiO₂-FeO-Fe₂O₃-P₂O₅ steelmaking slags, *Metallurgical and Materials Transactions B*, 45(5) (2014) 1666-1682. <https://doi.org/10.1007/s11663-014-0085-0>
- [12] S. Kitamura, S. Saito, K. Utagawa, Mass transfer of P₂O₅ between liquid slag and solid solution of 2CaO·SiO₂ and 3CaO·P₂O₅, *ISIJ International*, 49(12) (2009) 1838-1844. <https://doi.org/10.2355/isijinternational.49.1838>
- [13] K. Kobayashi, T. Hiraki, T. Nagasakaki, Oxidation of pure solid CaS with Ar-O₂ gas mixture, *High Temperature Materials and Processes*, 31(4-5) (2012) 66773. <https://doi.org/10.1515/htmp-2012-0104>
- [14] T. Hiraki, J. Kobayashi, S. Urushibata, Removal of Sulfur from CaF₂ containing desulfurization slag exhausted from secondary steelmaking process by oxidation, *Metallurgical and Materials Transactions B*, 43(4) (2012) 703-709. <https://doi.org/10.1007/s11663-012-9685-8>
- [15] R.L. Zhu, J.L. Li, J.J. Jiang, Effect of basicity on the sulfur precipitation and occurrence state in Kambara reactor desulfurization slag, *Minerals*, 11(9) (2021) 977. <https://doi.org/10.3390/min11090977>
- [16] H.P. Xiao, J.H. Zhou, J.Z. Liu, Thermogravimetric study of CaS oxidation reaction properties, *Journal of Zhejiang University*, 40(6) (2006) 982-985. (In Chinese) <https://doi.org/10.3785/j.issn.1008-973X.2006.06.013>
- [17] L. Li, L. Chun, G.Q. Zhang, Decomposition behavior of CaSO₄ during potassium extraction from a potash feldspar-CaSO₄ binary system by calcination, *Chinese Journal of Chemical Engineering*, 26(4) (2018) 172-178. <https://doi.org/10.1016/j.cjche.2017.10.001>
- [18] A.D. Pelton, J.B. See, J.F. Elliott, Kinetics of evolution of SO₂ from hot metallurgical slags, *Metallurgical Transactions*, 5(5) (1974) 1163-1171. <https://doi.org/10.1007/bf02644328>
- [19] C. Allertz, S.C. Du, Possibility of sulfur removal from ladle slag by oxidation in the temperature range 1373–1673 K, *Journal of Sustainable Metallurgy*, 1(3) (2015) 229-239. <https://doi.org/10.1007/s40831-015-0018-4>
- [20] R.L. Zhu, J.L. Li, Y. Yu, Influence of sulfur content on the state of sulfur fugacity in KR desulfurization slag, *Steel*, 57(2) (2022) 54-62. (In Chinese) <https://doi.org/10.13228/j.boyuan.issn0449-749x.20210405>



UTICAJ TEMPERATURE NA OKSIDACIONO PONAŠANJE I POJAVU SUMPORA U KR ŠLJACI

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Apstrakt

Glavna komponenta (CaO) u šljaci za odsumporavanje KR (Kambara reakcija) je visokokvalitetna sirovina za proizvodnju šljake za konvertorsko topljenje, a pokušaji da se KR desulfurizaciona šljaka iskoristi za konvertorsko topljenje doprinose smanjenju nakupljanja šljake za odsumporavanje KR i poboljšanju ekonomske efikasnosti konvertorskog topljenja. Međutim, uklanjanje sumpora iz šljake je ključno pitanje. Istražen je uticaj temperature na oksidaciono ponašanje sumpora u KR šljaci koja je u obliku sintetičke šljake. SEM-EDS, KSRD i infracrveni analizator ugljenika i sumpora korišćeni su za analizu i detekciju uzoraka oksidovane šljake na različitim temperaturama. Rezultati pokazuju da se brzina odsumporavanja postepeno povećava sa porastom temperature pri protoku Ar-50%O₂ od 2 L/min. U uslovima niske temperature ($T \leq 1220$ °C), temperatura manje utiče na brzinu odsumporavanja šljake. Kada je $T > 1220$ °C, na brzinu odsumporavanja šljake u velikoj meri utiče temperatura. Kada reakciona temperatura dostigne 1420 °C, brzina odsumporavanja dostiže 93,5%. Štaviše, tipovi faza koje sadrže sumpor u uzorcima oksidovane šljake postepeno se smanjuju sa povećanjem temperature, a sumpor u uzorcima oksidovane šljake je uglavnom prisutan u silikatnoj fazi kada je temperatura manja ili jednaka 1220 °C.

Ključne reči: KR šljaka; Temperatura; Sumpor; Oksidaciono ponašanje

