

Article

Effect of MgO/Al₂O₃ on Viscosity and Thermodynamic Properties of High-Titanium Slag Containing Chlorine

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Abstract: In order to study the effect of the change of MgO/Al₂O₃ on the viscosity and thermodynamic properties of the chlorinated blast-furnace slag, the CaO-SiO₂-MgO-Al₂O₃-TiO₂-CaCl₂ slag system was taken as the research object, and the viscosity change rule of the chlorinated high-titanium slag was studied by using the rotating cylinder method. The thermal stability of the chlorinated high-titanium slag was quantitatively analyzed by calculating the extreme heat release rate (EHRS) of the chlorinated high-titanium slag. At the same time, the qualitative and quantitative analysis of the high-titanium slag containing chlorine was carried out by combining FTIR and Raman spectroscopy, and the mechanism of the influence of MgO/Al₂O₃ on the viscous flow characteristics of the high-titanium slag containing chlorine was revealed. The results show that when the alkalinity (R₂) of the fixed slag is 1.15, when MgO/Al₂O₃ is in the range of 0.40–0.66, the viscosity of the high-titanium slag containing chlorine presents a significant decreasing trend with the gradual increase of MgO/Al₂O₃, and the viscous flow activation energy of the slag decreases from 98.75 kJ · mol⁻¹ to 95.21 kJ · mol⁻¹. The heat capacity and enthalpy change of slag decrease with the increase of MgO/Al₂O₃, but the change rule of slag extreme heat release is opposite to that of heat capacity and enthalpy change. When MgO/Al₂O₃ increases, the slag extreme heat release increases from 13.413 kJ to 15.172 kJ. The content of simple structural units Q⁰ and Q¹ of silicate tetrahedron in the slag gradually increases, the content of complex structural units Q² and Q³ gradually decreases, and the average amount of non-bridging oxygen decreases from 1.94 to 1.79, indicating that Al₂O₃ acts as a network maker in the internal network structure of the slag. The increase of MgO/Al₂O₃ destroys the complex silicate tetrahedron structure in the slag, reducing the degree of polymerization of the slag silicate network. In addition, the transmissivity of [SiO₄]⁴⁻ tetrahedron, [AlO₄]⁴⁻ tetrahedron and T-O-T bond bending vibration band in the slag shows a decreasing trend. Within the scope of the experiment, the increase of MgO/Al₂O₃ can effectively improve the fluidity of the chlorine-containing blast-furnace slag and improve the thermal stability of the chlorine-containing blast-furnace slag.

Keywords: chlorine-containing blast-furnace slag; viscosity; extreme heat release of slag; activation energy; slag structure



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1. Introduction

Vanadium-titanium magnetite (VTM) resources containing iron, vanadium, and titanium, as well as other available elements are abundant and mainly distributed in the Panzhihua region of China [1]. Until now, the main method to utilize VTM has been the blast-furnace (BF) ironmaking process. As the main raw materials, a lot of slag is produced with TiO₂ content of about 22 to 23 pct because the titanium component cannot be reduced and then enters the slag phase. Meanwhile, with the development of iron and steel industry, the structure of the enterprise and the raw and fuel conditions have a certain change. More and more chlorine elements enter the ore and fuel of the blast furnace, and chlorine will be absorbed by the blast-furnace slag, thus affecting its performance [2,3]. At present, in order to reduce the low temperature reduction pulverization rate of sinter added as raw material,

various iron and steel enterprises generally apply the technology of spraying calcium chloride on the surface of sinter, which leads to a sharp increase in the chlorine content of sinter and changes the composition of blast-furnace slag [4]. The typical amphoteric oxide Al_2O_3 in the blast-furnace slag components has the functions of high slag viscosity, slow flow rate, increased temperature drop and easy adhesion at high temperatures. Therefore, controlling the amount of Al_2O_3 and finding a suitable magnesia-alumina ratio of blast-furnace slag have become one of the research hotspots in the ironmaking industry [5].

A lot of research has been carried out domestically and internationally on the role of $\text{MgO}/\text{Al}_2\text{O}_3$ in different slag systems. Jiao Kexin et al. [6] analyzed the viscosity, heat capacity and enthalpy change of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ slag system. The heat capacity of slag increases with the increase of Al_2O_3 , $\text{MgO}/\text{Al}_2\text{O}_3$ and alkalinity. With the increase of Al_2O_3 content and $\text{MgO}/\text{Al}_2\text{O}_3$ content, the enthalpy change shows an upward trend. On the contrary, the enthalpy change decreases with the increase of alkalinity. When the slag heat is constant, the addition of Al_2O_3 will lead to a decrease in slag temperature and increase in slag viscosity. Seok et al. [7] studied the viscosity of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-FeO}$ slag system. When alkalinity and MgO content are constant, Al_2O_3 content and viscosity increase. Feng Cong et al. [8] studied the influence of $\text{MgO}/\text{Al}_2\text{O}_3$ on the viscosity behavior of $\text{MgO-Al}_2\text{O}_3\text{-TiO}_2\text{-CaO-SiO}_2$ slag system by using the rotating cylinder method, focusing on the structural characteristics of the slag. When $\text{MgO}/\text{Al}_2\text{O}_3$ increases from 0.82 to 1.36, the viscosity and activation energy (TiO_2 content of 43% and CaO/SiO_2 of 0.50) of the five component slag system decrease, and the melting temperature first decreases, and then increases. Moreover, when $\text{MgO}/\text{Al}_2\text{O}_3$ increases, O-Ti-O structure changes in the complex silicate network, $[\text{AlO}_4]^-$ tetrahedron structure depolymerizes into simple structural units, the polymerization degree of titanium-containing slag decreases, and the fluidity of slag is improved. Up to now, there are few basic studies on $\text{MgO}/\text{Al}_2\text{O}_3$ on chlorine-containing BF titanium slag, and the influence mechanism of $\text{MgO}/\text{Al}_2\text{O}_3$ on chlorine-containing BF titanium slag is not clear. At the same time, the change of slag composition causes the change of heat capacity. Under the condition of stable heat supply of the blast furnace, studying the relationship between $\text{MgO}/\text{Al}_2\text{O}_3$ and the heat release, as well as thermal stability of slag, is of great significance for a smooth and stable operation of the BF.

In this study, the $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-TiO}_2\text{-CaCl}_2$ slag system viscosity is measured by the rotating cylinder method. Qualitative and quantitative analyses of structural changes in slag are carried out using Fourier infrared spectroscopy and Raman spectroscopy to clarify the effect mechanism of $\text{MgO}/\text{Al}_2\text{O}_3$ on the viscous behavior of chlorine-containing BF titanium slag. The effective heat release of slag (EHRS) is put forward to quantitatively express the change in the thermal stability and provide theoretical guidance for optimizing the fluidity and thermal stability of high-titanium-melting slag containing chlorine.

2. Experiment

2.1. Preparation of Slag Sample

Based on the composition of blast-furnace slag in a domestic iron and steel enterprise (as shown in Table 1), the experimental scheme is designed to study the influence of the variation of slag composition on the performance of chlorine-containing high-titanium slag. The experiment is prepared with analytical pure reagents SiO_2 , CaO , MgO , Al_2O_3 , TiO_2 and CaCl_2 . SiO_2 , CaO , MgO , Al_2O_3 and TiO_2 are kept at $1000\text{ }^\circ\text{C}$ for 5 h in a muffle furnace to remove water, and CaCl_2 is dried at $105\text{ }^\circ\text{C}$ for 5 h. According to the proportion set in Table 2, when the alkalinity (R2) of fixed slag is 1.15, w (Al_2O_3) is 11%–18%, w (MgO) is 7.26% and $\text{MgO}/\text{Al}_2\text{O}_3$ is 0.40–0.66. A 250 g slag sample is weighed and placed into a molybdenum crucible, which is then placed into a high-temperature box resistance furnace, and heated at $1500\text{ }^\circ\text{C}$ under the protection of argon gas and is held for 3 h to ensure a more uniform slag composition. Water quenching is carried out immediately after heat preservation to maintain the state under high temperature, and then the obtained slag is dried and ground. The sample is ground to less than 200 mesh. After drying and grinding, the sample is divided into three parts. In the first part, the components of the

chlorine-containing high-titanium slag are analyzed by X-ray fluorescence spectrum, as shown in Table 3, and the measured values are close to the experimental design values. In the second part, the XRD results of samples cooled down rapidly with the change of $\text{MgO}/\text{Al}_2\text{O}_3$, as shown in Figure 1. There is no fine spectral peak structure, and only a large envelope peak exists, indicating that all the slag samples are of amorphous glass state at high temperature. The last part is used to measure the viscosity of molten slag.

Table 1. Chemical composition of site slag in steel works (%).

CaO	SiO ₂	MgO	Al ₂ O ₃	TiO ₂	Cl
28.86	25.14	7.17	13.87	21.75	0.16

Table 2. Composition ratio of chlorine-containing high-titanium slag.

Group Number	Initial Composition/%						C/S	MgO/Al ₂ O ₃
	CaO	SiO ₂	MgO	Al ₂ O ₃	TiO ₂	CaCl ₂		
1	27.12	23.60	7.26	18.00	22.02	2.00	1.15	0.40
2	27.66	24.06	7.26	17.00	22.02	2.00	1.15	0.42
3	28.19	24.53	7.26	16.00	22.02	2.00	1.15	0.45
4	28.73	24.99	7.26	15.00	22.02	2.00	1.15	0.48
5	29.80	25.92	7.26	13.00	22.02	2.00	1.15	0.56
6	30.33	26.39	7.26	12.00	22.02	2.00	1.15	0.61
7	30.87	26.85	7.26	11.00	22.02	2.00	1.15	0.66

Table 3. Composition ratio of chlorine-containing high-titanium slag after pre-melting.

Group Number	Actual Composition/%					
	CaO	SiO ₂	MgO	Al ₂ O ₃	TiO ₂	CaCl ₂
1	27.13	23.80	7.29	17.90	22.23	1.92
2	27.35	23.78	7.18	17.07	21.96	1.97
3	28.53	24.98	7.23	16.23	21.84	1.98
4	29.06	25.49	7.31	14.83	21.78	1.99
5	30.53	26.32	7.33	12.95	21.97	1.95
6	30.71	26.70	7.25	11.90	22.14	1.89
7	31.35	27.03	7.30	11.13	22.31	1.95

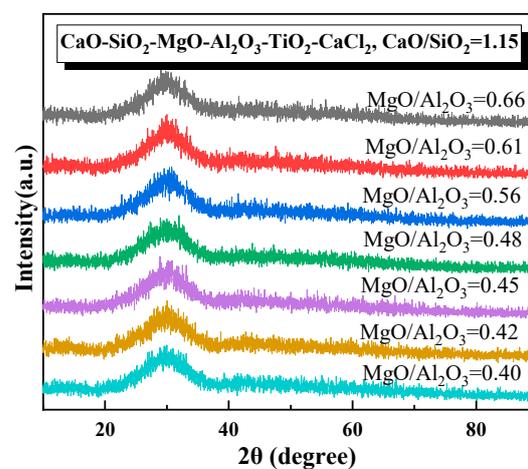


Figure 1. XRD curves of the quenched samples.

2.2. Thermodynamic Calculation

The good fluidity of slag is one of the preconditions to maintain the normal operation of blast-furnace smelting. The slag will inevitably be accompanied by heat loss in the flow

process, which will lead to the increase of slag viscosity. In order to ensure the normal production of the blast furnace, the slag viscosity should be controlled below 2.0 Pa·s [9] during smelting. On the premise of ensuring the free flow of slag, the maximum heat release it can bear reflects the thermal stability of slag. Therefore, the slag thermal stability is quantified by slag extreme heat release [10]. Figure 2 shows the schematic diagram of slag extreme heat release. The temperature corresponding to the slag viscosity value of 2.0 Pa·s is T_s , and EHRS is expressed as the heat loss during the period when the slag tapping temperature (T_b) decreases to the minimum temperature (T_s). The larger the EHRS, the more heat loss the slag can bear, and the better the thermal stability of the slag.

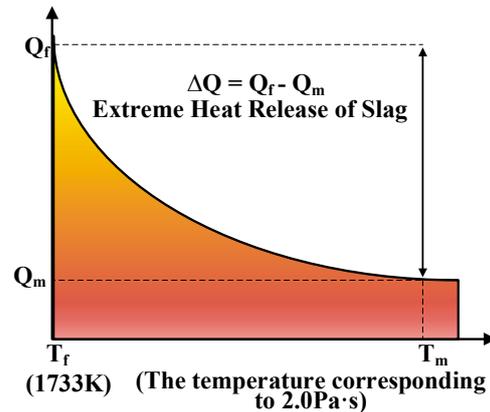


Figure 2. The calculation process of the extreme heat release of slag.

In the thermodynamic calculation, the sample mass is set at 100 g, and the initial conditions are 101.325 KPa and 298 K. According to the first law of thermodynamics, when the pressure is constant, the enthalpy change of slag at a certain temperature is approximately equal to the heat absorbed by the slag. The heat capacity (C_p), enthalpy change (ΔH) and EHRS (ΔQ) of slag at 1823 K, 1793 K, 1763 K and 1733 K are calculated according to formulas (1)~(11) [11].

$$C_{pCaO} = 1.048 - 2.046 \times 10^4 T^{-2} - 2.388 T^{-1/2} + 1.836 \times 10^6 T^{-3} \quad (298-2845 \text{ K}) \quad (1)$$

$$C_{pSiO_2} = 1.332 - 5.903 \times 10^4 T^{-2} - 3.999 T^{-1/2} + 8.181 \times 10^6 T^{-3} \quad (298-1996 \text{ K}) \quad (2)$$

$$C_{pMgO} = 1.516 - 1.541 \times 10^4 T^{-2} - 7.349 T^{-1/2} + 1.45 \times 10^4 T^{-3} \quad (298-3098 \text{ K}) \quad (3)$$

$$C_{pAl_2O_3} = -0.154 + 2.973 \times 10^{-4} T + 4.899 \times 10^4 T^{-2} - 1.099 \times 10^3 T^{-1} + 69.33 T^{-1/2} \quad (298-1200 \text{ K}) \quad (4)$$

$$C_{pAl_2O_3} = -7.724 + 6.461 \times 10^{-4} T + 2.587 \times 10^6 T^{-2} - 1.496 T \times 10^4 T^{-1} + 6.56 \times 10^2 T^{-1/2} \quad (1200-2327 \text{ K}) \quad (5)$$

$$C_{pTiO_2} = 0.975 - 4.217 \times 10^4 T^{-2} + 5.045 \times 10^6 T^{-3} \quad (298-2130 \text{ K}) \quad (6)$$

$$C_{pCaCl_2} = -3.053 + 9.844 \times 10^{-4} T + 7.173 \times 10^4 T^{-2} - 1.617 \times 10^3 T^{-1} + 1.387 \times 10^2 T^{-1/2} \quad (298-1045 \text{ K}) \quad (7)$$

$$C_{pCaCl_2} = 0.507 + 2.646 \times 10^{-4} T + 1.253 \times 10^3 T^{-2} \quad (1045-2000 \text{ K}) \quad (8)$$

$$C_p = \sum m_i C_{pi} \quad (1045-2000 \text{ K}) \quad (9)$$

$$\Delta H = \int_{298}^{T_{tr}} C_{pi} dT + \Delta_{tr} H_i + \int_{T_{tr}}^{T_M} C'_{Pi(s)} dT + \Delta_s^1 H_i + \int_{T_M}^T C'_{Pi(l)} dT \quad (10)$$

$$\Delta H_T = \sum m_i \Delta H_i \quad (11)$$

where C_{pi} is the heat capacity of component i , J/g·K; i is CaO, MgO, SiO₂, Al₂O₃, TiO₂, CaCl₂ and other slag components, J/g·K; C_p is the heat capacity of slag at a certain temperature, J/g·K; M_i is the mass of slag composition, g; ΔH is enthalpy change of slag at specific temperature, J/g; $\Delta_{tr} H_i$ is the enthalpy of the crystal phase transition of component i at a specific temperature, J/g; $\Delta_s^1 H_i$ is the melting enthalpy of component i at a specific temperature, J/g; ΔH_T is the enthalpy change of slag at a specific temperature, kJ; T_{tr} and T_M are crystal phase transition temperature and melting temperature, K, respectively; N is the mass fraction of precipitated solid phase, %; and C_{ps} is the heat capacity of solid phase, J/g·K.

2.3. Viscosity Measurement

RTW-type melt physical property tester is used to measure the slag viscosity, as shown in Figure 3. The experimental equipment is mainly composed of high temperature heating

furnace, torque sensor, control cabinet and software system. In this study, the heating element is U-shaped MoSi_2 , and the lower part of the furnace is equipped with a refractory base. Pt-6% Rh and Pt-30% Rh thermocouples are used to control the temperature in the furnace, and the measurement error is less than ± 2 K. The suspension rod and molybdenum probe are suspended below the torque sensor, the motor drives the probe to rotate and output signals, calculate and record the viscosity value.

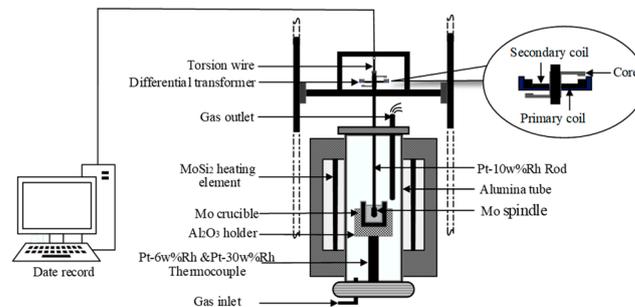


Figure 3. Viscosity measuring device.

Determination of slag viscosity [12–14]: The molybdenum crucible-containing slag samples was placed in the constant temperature zone at the upper part of the reaction chamber base of the resistance furnace, and heated to 1773 K at the speed of $5 \text{ K} \cdot \text{min}^{-1}$ under the protection of argon gas. It has been proven that the molybdenum crucible does not react with the slag system, so it has no effect on the experimental results [15]. The furnace temperature is kept stable for 30 min to make the slag composition uniform. The molybdenum ingot is then slowly dipped into the slag with its tip about 7 mm from the bottom of the crucible and rotated at a constant speed of 100 rpm. Due to the volatilization of chlorine during the viscosity test, the viscosity test is performed at a fixed temperature (the temperature difference of each test is 10 K, the cooling rate is $3 \text{ K} \cdot \text{min}^{-1}$ and the holding time is 10 min). Before each measurement, castor oil is calibrated to ensure the accuracy of viscosity. The actual viscosity is the average viscosity at a fixed temperature (measured twice at each fixed temperature, 200 s each time, 40 data points, the average value taken). After each viscosity measurement, the sample is water quenched, dried and fully ground before being sent for further testing.

2.4. Fourier Transform Infrared (FTIR) and Raman Spectroscopy

The slag structure is qualitatively analyzed by Fourier infrared spectroscopy. An amount of 2.0 mg of quenching slag sample is mixed with 300 mg of potassium bromide (KBr) and pressed into a film. The wave number range of the quenching slag sample is recorded in the range of $400\text{--}4000 \text{ cm}^{-1}$, the scanning time is set to 32 s, and the resolution is set to 4 cm^{-1} . The qualitative analysis of quenching slag sample structure is determined by Raman spectrometer. At room temperature, a semiconductor laser source with excitation wavelength of 532 nm is used to collect the Raman spectra of quenched samples in the frequency range of $200\text{--}1600 \text{ cm}^{-1}$. Gaussian function is used to deconvolute the Raman spectrum, and the bridge oxygen number is calculated according to the relative area fraction of the fitting curve.

3. Results and Discussion

3.1. Effect of $\text{MgO}/\text{Al}_2\text{O}_3$ on Viscosity of Chlorinated Blast-Furnace Slag

When the alkalinity is constant at 1.15, the MgO mass fraction is 7.26%, TiO_2 mass fraction is 22.02%, and Al_2O_3 mass fraction is 11%–18%. The viscosity of chlorine-containing high-titanium slag ($\text{CaO}\text{--}\text{SiO}_2\text{--}\text{MgO}\text{--}\text{Al}_2\text{O}_3\text{--}\text{CaCl}_2\text{--}\text{TiO}_2$) changes from 0.40 to 0.66 with the ratio of $\text{MgO}/\text{Al}_2\text{O}_3$, as shown in Figure 4. At the same temperature, the increase of $\text{MgO}/\text{Al}_2\text{O}_3$ reduces the slag viscosity. There may be three reasons for this. First of all, the higher the proportion of Al_2O_3 , the easier it is to generate high melting point compounds,

such as magnesium aluminum spinel ($\text{MgO}\cdot\text{Al}_2\text{O}_3$) and calcium aluminate ($\text{CaO}\cdot\text{Al}_2\text{O}_3$). These high melting point compounds have strong crystallization ability, and a large number of heterogeneous phases are generated. After crystallization, they will exist in the slag in a solid state, which makes the internal structure of the slag more complex and worsens the slag fluidity. Secondly, from a microscopic perspective, Al_2O_3 is an acid oxide that can absorb free oxygen ions to form a four-coordinated aluminum oxide tetrahedron structure, which supports the silicate network structure, enhances the complexity of the melt structure, and increases the slag viscosity. In addition, with the increase of temperature, the influence of $\text{MgO}/\text{Al}_2\text{O}_3$ ratio on slag viscosity gradually weakens. When the temperature is 1733 K, the $\text{MgO}/\text{Al}_2\text{O}_3$ ratio increases from 0.40 to 0.66, and the slag viscosity decreases by about 0.05 Pa · s. When the temperature is 1823 K, the $\text{MgO}/\text{Al}_2\text{O}_3$ ratio increases from 0.40 to 0.66, and the slag viscosity decreases by about 0.03 Pa · s. The increase of slag viscosity means the deterioration of slag fluidity, which will also affect the stability and smooth running of the blast furnace to a certain extent. Therefore, in order to better improve the fluidity of the slag and maintain the smooth operation of the blast furnace, the proportion of $\text{MgO}/\text{Al}_2\text{O}_3$ in the slag must be controlled to avoid excessive Al_2O_3 composition.

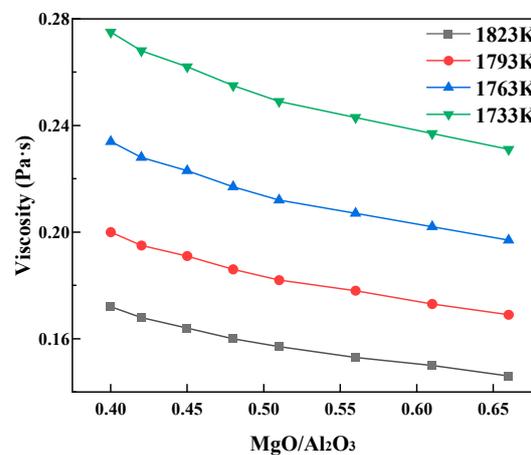


Figure 4. Viscosity curves of high-titanium slag with different $\text{MgO}/\text{Al}_2\text{O}_3$.

3.2. Effect of $\text{MgO}/\text{Al}_2\text{O}_3$ on Viscous Flow Activation Energy of Chlorinated Blast-Furnace Slag

The resistance of slag in the viscous flow process is closely related to the slag structure [16–18]. Each particle in the slag is in a certain range of potential barrier, which must be overcome by a certain amount of energy to activate the particles. The activation energy is necessary for particle movement. The six-component slag system of high-titanium slag containing chlorine is a typical silicate slag system, in which the silicon oxygen complex ion is the main viscous flow unit in the slag. The change of slag composition is bound to affect the existing form of silicon oxygen complex ion, thus causing the change of slag viscosity.

The temperature dependence of viscosity is often expressed by the Arrhenius equation, as shown in Equation (12):

$$\eta = A \exp\left(\frac{E_\eta}{RT}\right) \quad (12)$$

The logarithm of Equation (1) is written as Equation (2), as shown in Equation (13):

$$\ln \eta = \ln A + E_\eta \left(\frac{1}{RT}\right) \quad (13)$$

among which η is slag viscosity; A is the pre exponential factor; R is the gas constant (8.314 J/mol · K); T is the thermodynamic temperature; and E_η is viscous flow activation energy. The activation energy of viscous flow is an important viscous characteristic of slag melt. Viscous flow activation energy represents viscous flow barrier, and its change

can reflect the change of slag structure or flow unit. This has been revealed in previous studies [19].

Figure 5 shows $\ln \eta$ when $\text{MgO}/\text{Al}_2\text{O}_3$ changes η and $1/T$. As can be seen from the figure, $\ln \eta$ is linear with $1/T$. Calculate the viscous flow activation energy of slag with the fitting line ($R^2 > 0.99$), where $\ln A$ and E_η/T are the intercept and slope of the fitting line, respectively. The calculation results of viscous flow activation energy change with $\text{MgO}/\text{Al}_2\text{O}_3$ are shown in Table 4. As $\text{MgO}/\text{Al}_2\text{O}_3$ increases from 0.40 to 0.66, the corresponding viscous flow activation energy decreases from 98.75 kJ/mol to 95.21 kJ/mol. With the increase of the proportion of Al_2O_3 , Al^{3+} combines with free oxygen ions to form complex aluminum oxide tetrahedral structural units. In order to maintain charge balance, Ca^{2+} is consumed for charge compensation, forming more complex structural units. The friction resistance of slag becomes larger when flowing, which worsens the fluidity of slag.

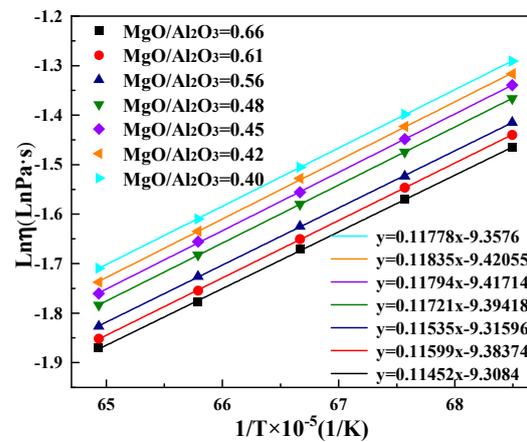


Figure 5. Variation of $\ln \eta$ and $1/T$ with $\text{MgO}/\text{Al}_2\text{O}_3$ ratio.

Table 4. The calculated apparent activation energy of different slags.

$\text{MgO}/\text{Al}_2\text{O}_3$	Regression Equation	E_a (kJ·mol ⁻¹)
0.40	$y = 0.11878x - 9.3576$	98.75
0.42	$y = 0.11834x - 9.42055$	98.39
0.45	$y = 0.11794x - 9.41714$	98.06
0.48	$y = 0.11721x - 9.39418$	97.45
0.56	$y = 0.11635x - 9.31596$	96.73
0.61	$y = 0.11599x - 9.38374$	96.43
0.66	$y = 0.11452x - 9.3084$	95.21

3.3. Effect of $\text{MgO}/\text{Al}_2\text{O}_3$ on Heat Capacity, Enthalpy Change and EHRS of Chloro-Containing Blast-Furnace Slag

As shown in Figure 6, the slag heat capacity decreases linearly with the increase of $\text{MgO}/\text{Al}_2\text{O}_3$ at a fixed temperature. This is consistent with the change in heat capacity. This shows that the increase of $\text{MgO}/\text{Al}_2\text{O}_3$ in the slag, that is, the decrease of Al_2O_3 mass fraction, weakens the thermal stability of the slag. The heat absorbed by the slag will increase when the temperature rises by 1 K. Therefore, in order to keep the slag temperature stable, when using iron ore with low $\text{MgO}/\text{Al}_2\text{O}_3$, the heat supply of the blast furnace should be appropriately increased to maintain the smooth running of the blast furnace.

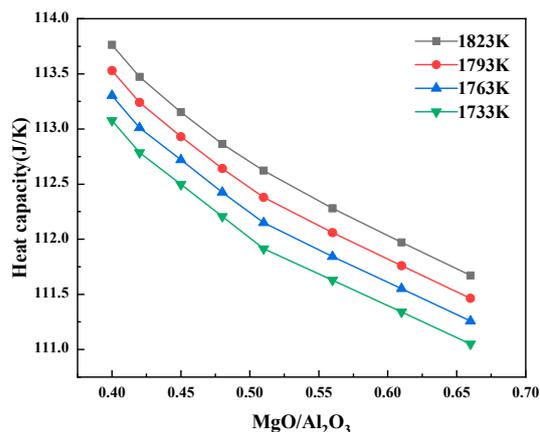


Figure 6. The heat capacity of slag with varying MgO/Al₂O₃.

It can be seen from Figure 7 that when the temperature is constant, the enthalpy change of blast-furnace slag decreases linearly with the increase of MgO/Al₂O₃. When MgO/Al₂O₃ is constant, the enthalpy change of slag is obviously increased with the increase of temperature. This shows that increasing MgO/Al₂O₃ reduces blast-furnace energy consumption, especially when the increase of blast-furnace coal injection and the use of low-grade ore lead to the decrease of MgO/Al₂O₃ in slag, it is necessary to increase the supply of blast-furnace fuel.

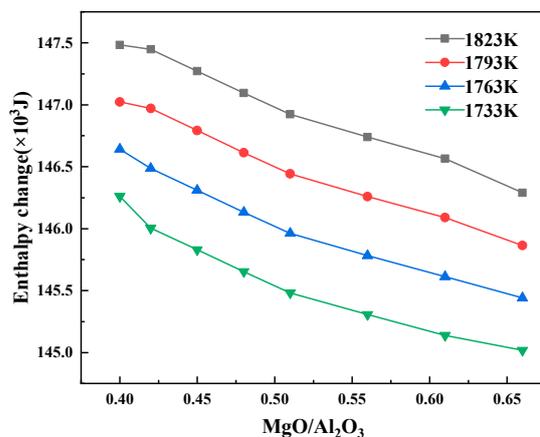


Figure 7. The enthalpy change of slag with varying MgO/Al₂O₃.

Figure 8 shows the effect of MgO/Al₂O₃ on EHRS of high-titanium slag containing chlorine. The increase of MgO/Al₂O₃ obviously increases the slag EHRS value. MgO/Al₂O₃ increased from 0.40 to 0.66, and EHRS increased from 14.83 kJ to 20.51 kJ. The higher the EHRS value, the smaller the viscosity fluctuation caused by the change of slag composition or temperature. Therefore, when using high alumina ore for blast-furnace smelting, in order to maintain the stability of slag temperature and promote the stable operation of the blast furnace, it is necessary to appropriately increase the coke ratio or fuel ratio to maintain the smooth operation of the blast furnace.

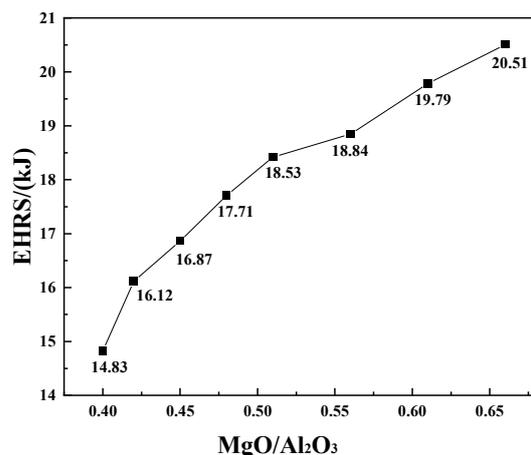


Figure 8. Effect of MgO/Al₂O₃ on the value of EHRS.

3.4. Infrared Spectral Analysis

The viscosity of melt is closely related to its structure. The influence of slag structure on viscosity can be confirmed by FTIR spectrum analysis. As shown in Figure 9, MgO/Al₂O₃ decreases, and the center of [SiO₄]^{4−} tetrahedron vibration band shifts from 972 cm^{−1} to 998 cm^{−1}, which indicates that the slag structure tends to be complicated. As the mass fraction of MgO remains unchanged, the higher the content of Al₂O₃, the easier the Si-O network structure is to polymerize. Al₂O₃ is an amphoteric oxide. In this experiment, Al₂O₃ is an acid oxide. When Al₂O₃ is added in the initial stage, the viscosity increases because it can absorb free oxygen ions to form a composite anion group as an acid oxide, which increases the complexity of the slag structure. In addition, [AlO₄]^{5−} tetrahedron vibration band gradually increases. This is because aluminum ions can replace tetrahedral coordinated silicon ions to form [AlO₄]^{5−} tetrahedron. The valence state of aluminum ion is different from that of silicon ion. In order to maintain the charge balance, metal cations are required for charge compensation, thus increasing the complexity of slag structure. With the further increase of Al₂O₃ content, aluminum no longer exists in tetrahedron instead of silicon ion, but exists in [AlO₆]^{9−} octahedron as a network modifier. The change of 600–800 cm^{−1} band in FTIR spectrum also confirms this point. The results show that Al₂O₃ is a network-forming agent, that is, MgO/Al₂O₃ decreases and slag viscosity increases. This is consistent with the experimental results of MgO/Al₂O₃ on slag viscosity in this paper. In addition, the T-O-T bond vibration band strengthens with the decrease of MgO/Al₂O₃. The formed [AlO₄]^{5−} tetrahedron and [SiO₄]^{4−} tetrahedron or [TiO₂]^{4−} tetrahedron are connected with each other through T-O-T bond to form a more complex structure, further increasing the complexity of the structure.

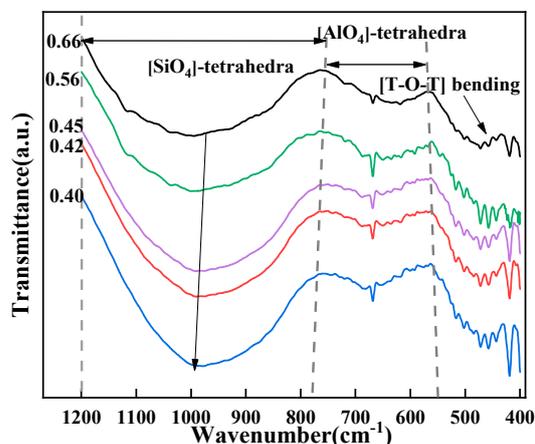


Figure 9. Effect of different MgO/Al₂O₃ ratios on slag structure.

3.5. Raman Spectral Analysis

Raman spectroscopy is used to quantitatively analyze the structural units of slag [20]. The Raman spectra of the slag are mainly concentrated in the high frequency region (1200–800 cm^{-1}) and low frequency region (800–600 cm^{-1}). The origin software is used to subtract the Raman spectral background, and the Gaussian function is used to deconvolute the original Raman spectral curve and fit the minimum correction coefficient $R^2 > 0.99$ to obtain the characteristic peak. In previous studies, according to the number of bridge oxygen, the high frequency region of Raman spectrum can be deconvoluted into four typical peaks: Q^0 ($[\text{SiO}_4]^{4-}$, $\sim 850 \text{ cm}^{-1}$), Q^1 ($[\text{Si}_2\text{O}_7]^{6-}$, 910–930 cm^{-1}), Q^2 ($[\text{SiO}_3]^{2-}$ chain, $\sim 980 \text{ cm}^{-1}$) and Q^3 ($[\text{Si}_3\text{O}_9]^{6-}$ ring, $\sim 1050 \text{ cm}^{-1}$). Q^n represents the degree of polymerization of the slag, and n is the amount of bridging oxygen in the silicate tetrahedron structure. In addition, according to Mysen et al. [21], bands located at 600–650 cm^{-1} , $\sim 720 \text{ cm}^{-1}$, and 820–850 cm^{-1} are assigned to Ti-O and O-Ti-O and Ti-O-(Ti or Si).

As shown in Figure 10, with the increase of $\text{MgO}/\text{Al}_2\text{O}_3$, the peak position in the Raman spectrum gradually moves to a lower wave number. Q^0 and Q^1 structural units are relatively reduced, Q^2 structural units are relatively increased, Ti-O-(Ti or Si) structural units are increased, and Al-O-Al bonds are reduced. This shows that the slag structure is simplified. Al_2O_3 is an amphoteric oxide, which can play a role as a network builder when the slag is acidic, forming complex anion groups with free oxygen ions, thus making the slag structure more complex. When the slag is alkaline, it can play the role of network modifier to destroy the Si-O network structure and reduce the slag viscosity. Obviously, in this slag system, Al_2O_3 is an acid oxide, and Al^{3+} is dissociated to participate in the formation of $[\text{AlO}_4]^{5-}$ tetrahedron structure. Moreover, due to the charge compensation effect, metal cations such as Ca will compensate the missing charge of Al^{3+} in the formation of four coordinated aluminum oxide tetrahedron structure, so the increase of $\text{MgO}/\text{Al}_2\text{O}_3$ makes the structural unit of the melt simpler to some extent.

In order to semi quantitatively analyze the influence of $\text{MgO}/\text{Al}_2\text{O}_3$ on each structural unit of slag, the relative area fraction of the fitting curve of each structural unit is calculated, and Q_{Si}^n (relative mole fraction) is calculated according to the relative area fraction (A_i) of S_i structural unit and the corresponding amount of bridge oxygen. The results are shown in Figure 11 through Equation (14):

$$X_i = (A_i/S_i) / (\sum_{i=0}^3 A_i/S_i) \quad (14)$$

Here, X_i , A_i and S_i represent the relative mole fraction of Q_{Si}^n , the area of Gaussian function fitting curve and the Raman scattering coefficient of Q_{Si}^n , respectively.

It can be seen from Figure 11 that the relative mole fraction of Q^1 gradually increases, the relative mole fraction of Q^2 gradually decreases, and the relative mole fraction of Q^0 slightly increases. This shows that the number of simple structural units in silicate structure increases, and the melt is not easy to polymerize. At the same time, with the increase of $\text{MgO}/\text{Al}_2\text{O}_3$, the relative area fraction of Al-O-Al vibrational bands in the 500–550 cm^{-1} band decreased significantly. In the slag, the number of aluminum-oxygen composite anions connected by bridging oxygen and silica tetrahedron is reduced, the complex Si-O-Al composite anions are depolymerized, and the complexity of the internal structure of the slag is reduced.

It can be seen from Figure 12 that with the increase of $\text{MgO}/\text{Al}_2\text{O}_3$ from 0.40 to 0.66, the average number of BOs/Si decreases from 1.94 to 1.79. Therefore, Al_2O_3 plays a role in increasing the degree of polymerization in blast-furnace slag. Al_2O_3 acts as a network-forming agent in the network structure, connecting simple anion groups through bridging oxygen, which makes the slag structure more complex, improves the polymerization degree of the slag structure, and worsens the fluidity of the slag. Therefore, the increase of $\text{MgO}/\text{Al}_2\text{O}_3$ improves the fluidity of slag, which is consistent with the measured results of slag viscosity.

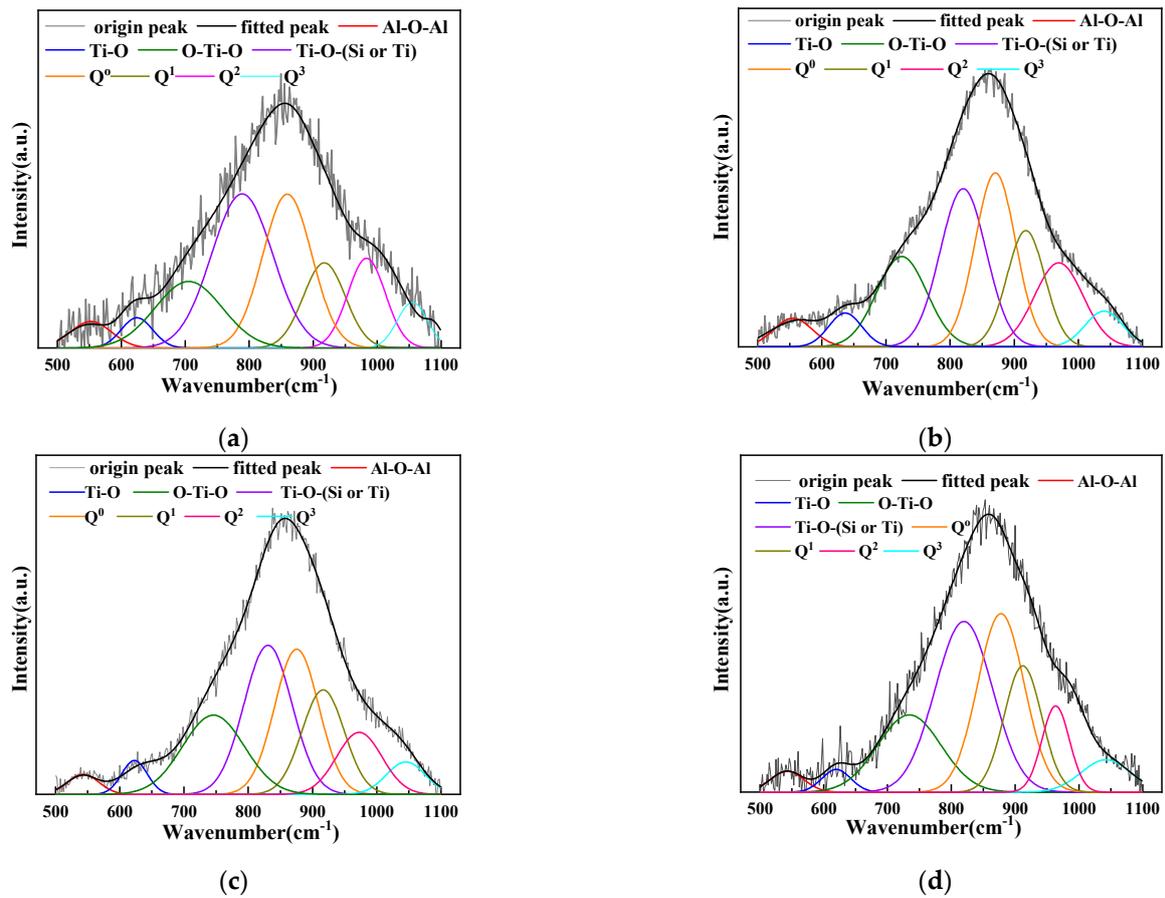


Figure 10. Raman spectra of slag with varying MgO/Al₂O₃: (a) MgO/Al₂O₃ = 0.40; (b) MgO/Al₂O₃ = 0.48; (c) MgO/Al₂O₃ = 0.56; (d) MgO/Al₂O₃ = 0.66.

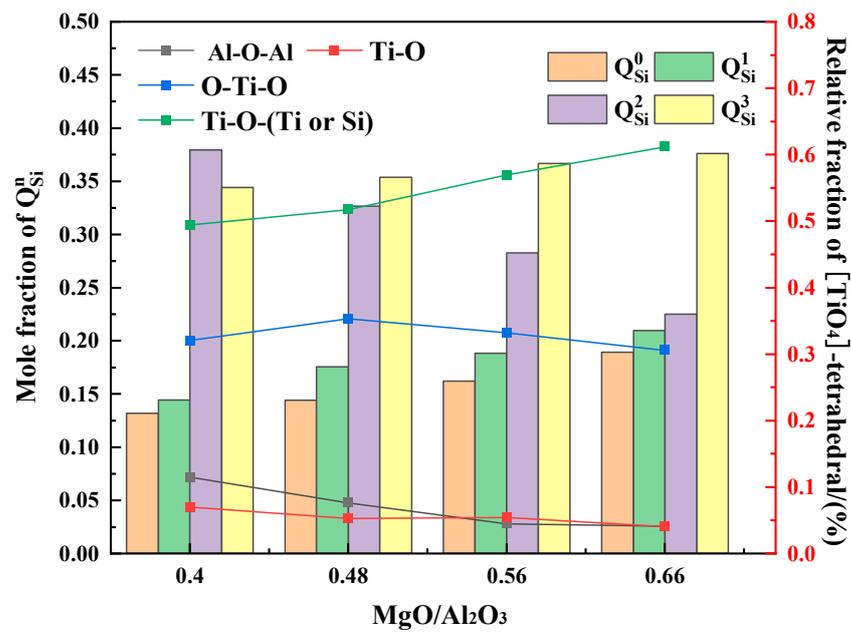


Figure 11. Relative area fractions of each band of chlorine-containing high-titanium slag.

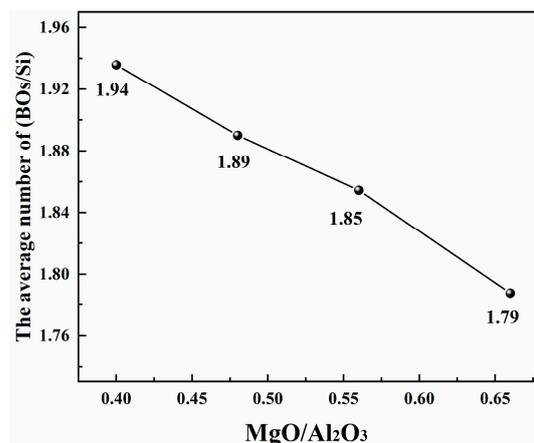


Figure 12. Influence of MgO/Al₂O₃ on average (BOS/Si).

4. Conclusions

(1) MgO/Al₂O₃ reduces slag viscosity, viscous flow activation energy and melting temperature [7]. With the increase of temperature, the effect of MgO/Al₂O₃ on slag viscosity gradually weakened. When the alkalinity is 1.15, the ratio of MgO/Al₂O₃ increases from 0.40 to 0.66, the viscosity of high-titanium slag containing chlorine decreases, and the activation energy of viscous flow decreases from 98.75 kJ·mol⁻¹ to 95.21 kJ·mol⁻¹. The reduction of slag viscosity optimizes the fluidity of slag.

(2) With the increase of MgO/Al₂O₃, the slag heat capacity and enthalpy change gradually decrease. When MgO/Al₂O₃ is fixed, the heat capacity and enthalpy of slag decrease significantly with increasing temperature. The slag EHRS gradually increases with the increase of MgO/Al₂O₃. The influence of heat fluctuation in the furnace on the slag temperature is weakened, and the influence on viscosity is also smaller, which improves the slag stability.

(3) The increase of MgO/Al₂O₃ makes the center of [SiO₄]⁴⁻ tetrahedral vibration zone shift from 998 cm⁻¹ to 972 cm⁻¹, and the slag structure tends to be simple. With the increase of MgO/Al₂O₃, the average number of BOs/Si decreased from 1.94 to 1.79. Al₂O₃ plays the role of network-forming agent in the network structure, and the increase of MgO/Al₂O₃ improves the fluidity of slag [8].

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