

Article

Polymeric Structure Evolution Behavior Analysis of Aluminosilicate-Based Smelting Slag

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Abstract: The physical and chemical properties of the CaO–SiO₂–Al₂O₃–MgO slag system depend on structure evolution caused by the synergistic mechanism among the components at high temperature, especially the structural complexity of the anion group. In this study, Si–O, Al–O, and Al–Si–O anion groups were found in the high-temperature slag systems at 1773 K. The [Si₂O₅]^{2−} (Q₃) structural unit of the silicate polymer changed to [Si₂O₆]^{4−} (Q₂), [Si₂O₇]^{6−} (Q₁), and [SiO₄]^{4−} (Q₀) as the binary basicity (*R*₂) and $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ increased, while there was a trend toward a simplified structure. That is, the stability of each structural unit weakened, and the relative content of non-bridging oxygen increased. As a result, the degree of polymerization of slag decreased, and the experimental results of the relative content of non-bridge oxygen can be fitted well with the calculations from the reference documents. At the same time, the number of Si–O–Al structural units gradually decreased. The ²⁷Al–MAS–NMR spectroscopy results showed that the structure of aluminate changed from [AlO₄]^{5−} tetrahedral structure to [AlO₅]^{7−} pentahedral and [AlO₆]^{9−} octahedral structure, and the degree of polymerization of the slag decreased. Comprehensive analysis showed that basicity controlled within 1.2 with the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio; less than 0.55 allows for suitable fluidity and energy-saving ability, which is beneficial for the stable and smooth production of the blast furnace.

Keywords: anion group; structural unit; *R*₂; $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$; degree of polymerization



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1. Introduction

Metallurgical smelting slags are multi-component substances whose microstructural information plays an important role in mastering the physical and chemical properties, optimized slag forming route, and slag-forming practices of blast furnace (BF) [1–5]. Moreover, the macro properties are affected by the anionic groups contained therein. Zhang et al. [6] studied the influence of the Al₂O₃/SiO₂ ratio on the viscosity of the CaO–Al₂O₃–SiO₂ melt and found that a maximum viscosity can result from the opposite variation tendencies of the mean bond strength and the degree of polymerization of the melt with the Al₂O₃/SiO₂ ratio. The mean bond strength decreased when SiO₂ was substituted with Al₂O₃ due to the lower bond strength of the Al–O bond compared to the Si–O bond, decreasing the viscosity, while the degree of polymerization (DOP) was enhanced by the charge compensation effect of the Al³⁺ ion, which increased the viscosity. Through infrared and Raman spectroscopy, Liao et al. [7] found that the DOP of the [SiO₄]^{4−} tetrahedral structure decreased with the increase of the $\omega(\text{Al}_2\text{O}_3)/\omega(\text{SiO}_2)$ ratio but increased sharply when the ratio was greater than 0.56. Park et al. [8] used NBO/T or Q to respectively represent the number of non-bridging oxygen or bridging oxygen carried by Si atoms and analyzed the structure information of the slag through infrared spectroscopy. They found that Al₂O₃ acted as a network former that could increase the DOP. Kim et al. [9] found that the infrared spectral intensity decreased when the [SiO₄]^{4−} tetrahedron had the lower NBO/Si, while

the infrared spectral band increased with the Al_2O_3 content. McMillan et al. [10] found that increasing CaO content, which may reflect a decrease polymerization of the aluminate units, and the coordination Al is detected by ^{27}Al -MAS-NMR, there are $[\text{AlO}_4]^{5-}$ and $[\text{AlO}_6]^{9-}$ structure in the glasses. Sunahara et al. [11] found that in the process of blast furnace (BF) smelting, with the increase of high quality Al_2O_3 , problems such as dripping zone, poor fluidity of slag, excessive slag accumulation, and increased pressure can happen, but it can be solved by reducing R_2 and increasing MgO content. Moreover, many studies combined different raw material conditions, then analyzed the changes in slag structure and metallurgical properties, and many optimization methods have been put forward, which are the basis for the selection of BF raw materials, as well as ensuring the reasonable flow slag can be provided [12–14]. In addition, other scholars have studied these polymers at the corresponding high temperatures in glass and silicate, and used the spectral data for detection and analysis [15–18]. These results can be used as a reference for the study of non-iron elements in the field of metallurgy. However, with the demand for more reasonable slag-making systems in China, research on the microstructural evolution of anionic agglomeration in BF slag with different R_2 and $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratios is currently not detailed enough.

In the paper, the samples of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ slag are quenched at 1773 K, then the X-ray diffraction (XRD), Fourier transform infrared (FTIR), and the ^{27}Al -SS-MAS-NMR spectroscopy are used for detection. Then, the existence form of the polymer and microstructure anionic group evolution behavior are explored with different R_2 ($R_2 = \omega(\text{CaO})/\omega(\text{SiO}_2)$), $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$, and NBO/T is the ratio of the non-bridging oxygen and the Si atom number, which is used to express the degree of polymerization (DOP), and the Q is the structural unit of silicates. Moreover, contrastive analysis is carried out between experiment and reference calculation results. In this way, the mutual synergy mechanism of the component is analyzed, from which basic reference data for the study of microstructure of non-iron elements in the smelting process, especially BF slag, are provided.

2. Experiment Schemes

The slag samples used in the experimental research were all prepared with pure chemical analysis reagents, which were obtained from Tianjin Zhiyuan Chemical Reagent Co., Ltd. China. The purity was 99% and the chemical composition including R_2 and $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ slag system is shown in Table 1. Before the experiment, the raw materials were fully dried for 10 h at 1773 K in an electrothermal constant-temperature dry oven, Tianjin Taisite intelligent instrument Co., Ltd. China, type 202-0AB. The water was removed, each group of slag samples was 50 g, and the samples were mixed evenly in the agate mortar, then placed in a $\phi 45 \times 30$ mm graphite pot and heated to 1773 K to melt fully in the muffle furnace (Luoyang Tairui intelligent electric furnace Co., Ltd. China, type TRL-18LB). The high-temperature samples were removed and poured into water for rapid cooling to ensure that the structure of the water-quenched slag was consistent with high-temperature melt slag. After drying for 10 h at 1773 K, the slag was ground in an agate mortar to a particle size of 74 μm . Finally, 300 mg of the sample was weighed for XRD, FTIR, and ^{27}Al -SS-MAS-NMR analyses, and the structure of the molten slag at high temperatures was determined.

Table 1. Chemical composition of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ slag system.

No.	CaO (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	MgO (%)	R ₂	$\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$
1	38.1	42.4	13.0	6.5	0.9	0.50
2	40.2	40.3	13.0	6.5	1.0	0.50
3	42.1	38.4	13.0	6.5	1.1	0.50
4	43.9	36.6	13.0	6.5	1.2	0.50

Table 1. Cont.

No.	CaO (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	MgO (%)	R ₂	$\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$
5	45.0	35.5	13.0	6.5	1.3	0.50
6	43.2	39.2	13.0	4.6	1.1	0.35
7	42.9	38.9	13.0	5.2	1.1	0.40
8	42.5	38.6	13.0	5.9	1.1	0.45
9	41.8	38.0	13.0	7.2	1.1	0.55
10	41.5	37.7	13.0	7.8	1.1	0.60

3. Results and discussion

3.1. Phase Analysis

According to XRD detection, it was found that when the temperature was increased to 1773 K, the curves of the slag with different R_2 and $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratios showed large peaks (Figure 1). It is clear that the prepared CaO–SiO₂–Al₂O₃–MgO slag systems had completely melted at this temperature. Thus, the structure of the samples tested is consistent with that of the melt slag at high temperatures.

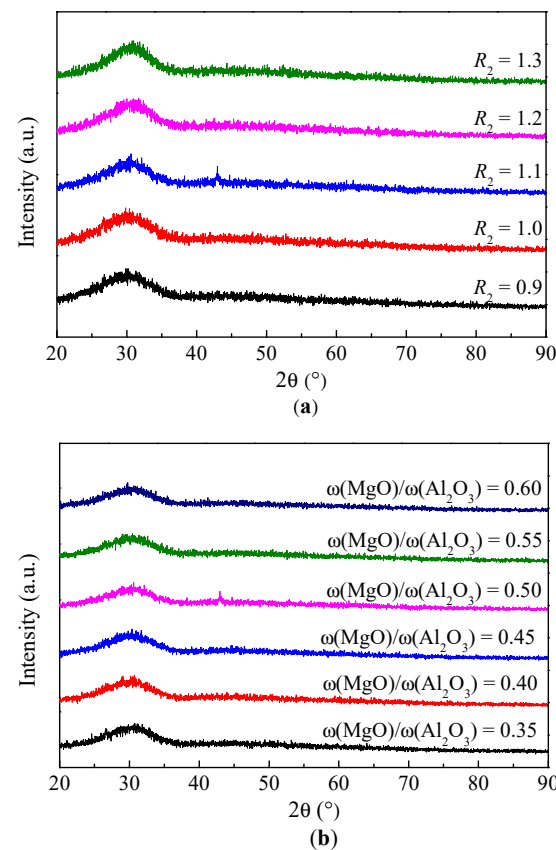


Figure 1. XRD results with the various R_2 (a) and $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratios (b).

3.2. Anion Group Structure Evolution Analysis

Spectral analysis is an effective method used to detect the DOP of slag. The influence of R_2 and the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio on the structural units in the slag was first analyzed by FTIR spectroscopy. Table 2 shows the corresponding characteristic vibration spectrum segments of different silicate and aluminate structural units by the references and analysis [12,19].

Table 2. Infrared active vibrational spectrum of the silicate and aluminate structural units.

Structural Units	Connecting Format	Q_n	Wave Number (cm^{-1})	Vibrations
$[\text{Si}_2\text{O}_5]^{2-}$	Facet	Q_3	1100–1050	Symmetric stretching
$[\text{Si}_2\text{O}_6]^{4-}$	Chain and cyclic annular	Q_2	980–950	Symmetric stretching
$[\text{Si}_2\text{O}_7]^{6-}$	Double polymers	Q_1	920–900	Symmetric stretching
$[\text{SiO}_4]^{4-}$	Single polymer	Q_0	880–850	Symmetric stretching
$[\text{AlO}_4]^{5-}$	-	-	720–630	Anti-symmetric bend
$[\text{AlO}_6]^{9-}$	-	-	570–520	Anti-symmetric bend
Si-O-Al	-	-	500	Symmetric bend

Figure 2 shows the FTIR detection results of water-quenching BF slag with different R_2 when the temperature is 1773 K, ($\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3) = 0.50$). It can be seen that with the increase of R_2 , the $[\text{AlO}_4]^{5-}$ antisymmetrical bending vibration intensity at 720–630 cm^{-1} decreased gradually; this indicates that the number of $[\text{AlO}_4]^{5-}$ tetrahedral structural units in the form of tetra-coordination aluminum is reduced. In addition, the symmetrical bending vibration strength of Si–O–Al at about 500 cm^{-1} decreased with increasing R_2 . At the same time, the number of Si–O–Al structural units decreased. The symmetrical stretching vibration of the silicate structural unit Q_n ($n = 0, 1, 2, 3$) at 1200–800 cm^{-1} did not change significantly as R_2 increased. Thus, it is necessary to fit the peak divisions at 1200–800 cm^{-1} into four peaks corresponding to the Q_0, Q_1, Q_2 , and Q_3 structural units. The content of each unit can then be characterized by calculating the relative contents of each peak area.

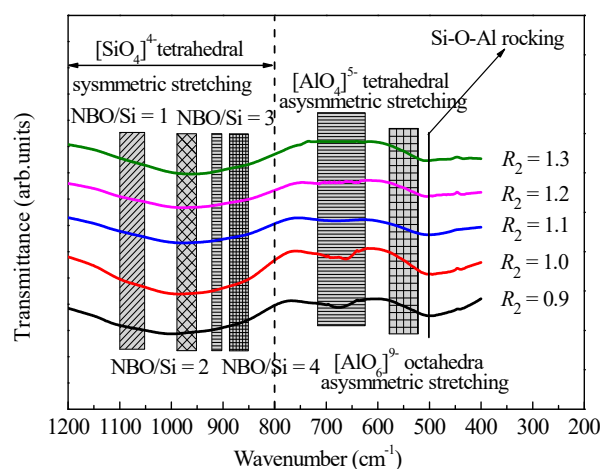
**Figure 2.** FTIR spectra of smelting slag with the varied basicity.

Figure 3 shows the peak division results of the FTIR spectra of BF slag in the wavenumber range of 1200–800 cm^{-1} under different R_2 conditions. It can be seen that with the increase of R_2 , the corresponding peak center positions of the Q_0, Q_1, Q_2 , and Q_3 structures gradually moved to a low wavenumber region, respectively decreasing from 844.3 to 828.1 cm^{-1} , 904.7 to 892.3 cm^{-1} , 982.5 to 976.9 cm^{-1} , and 1056.6 to 1038.0 cm^{-1} . This shows that the stability of the tetrahedral elements in the slag structure decreased with the increase of R_2 and tended to simplify in structure.

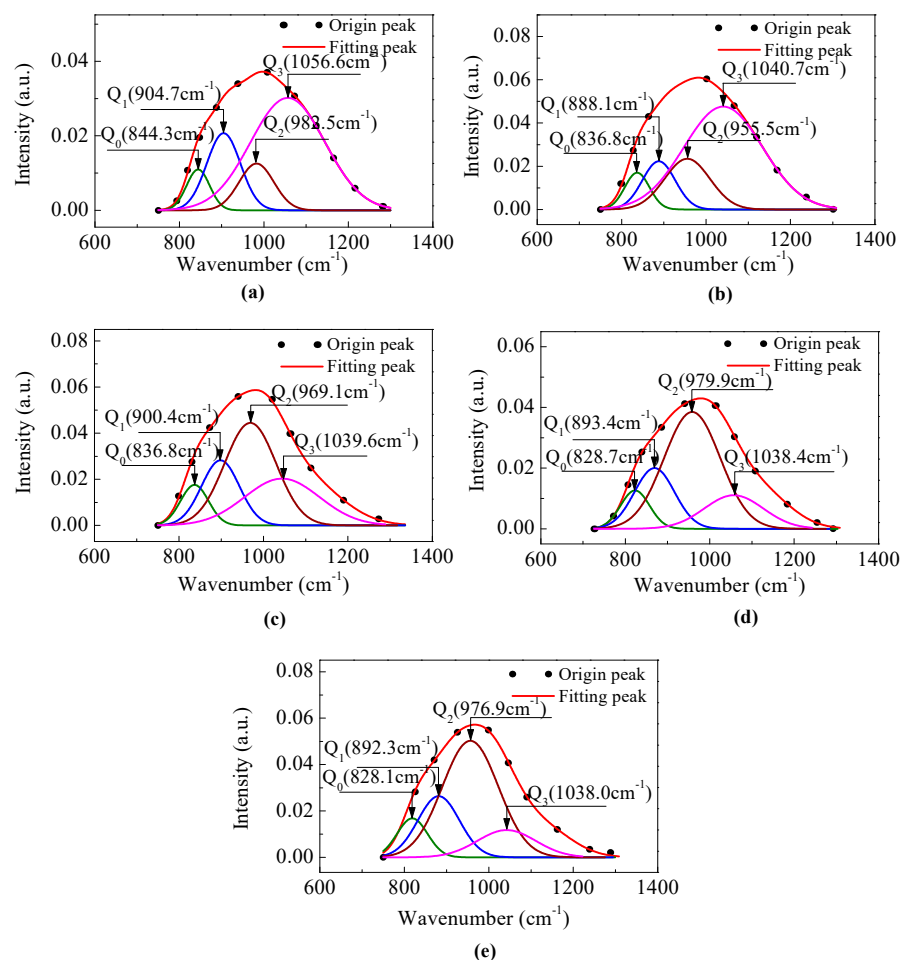


Figure 3. Deconvolution results of the FTIR curves with the various R_2 , and (a) the R_2 is 0.9, (b) the R_2 is 1.0, (c) the R_2 is 1.1, (d) the R_2 is 1.2, (e) the R_2 is 1.3.

The relative area of each peak corresponding to each structural unit Q_n ($n = 0, 1, 2, 3$) was calculated according to the peak division results. Then, the curve of the relative content of each structural unit was obtained with increasing R_2 (Figure 4). It can be seen that as R_2 increased from 0.9 to 1.3, the relative content of Q_0 and Q_1 gradually increased but the range of change was not large, from 7.0% to 10.0% and from 19.2% to 21.4%, respectively, while the relative content of Q_3 decreased significantly from 61.8% to 13.4% and the relative content of Q_2 increased significantly from 12.0% to 55.1%. As R_2 increased, Ca^{2+} and free oxygen ions (O^{2-}) were elevated, which interacted with bridge oxygen. As a result, the complex Q_3 structural unit changed into more simple Q_0 , Q_1 , and Q_2 structural units, thereby eventually reducing the viscosity of the slag. The DOP of the slag can be more intuitively represented by the relative content of non-bridging oxygen (NBO/T) in the slag structure. Based on previous research [12,20,21], the theoretical calculation of NBO/T can be written as:

$$NBO/T = 2(\sum X_{MgO} + \sum X_{CaO} - X_{Al_2O_3}) / (X_{SiO_2} + 2X_{Al_2O_3}) \quad (1)$$

where X is the mole fraction of oxide, mol%.

Compared with the theoretical value, the relative content of Q_n obtained based on spectral detection can reflect the actual slag polymerization more accurately. The relationship between NBO/T and the relative content of Q_n is shown in Equation (2):

$$NBO/T = 4Q_0 + 3Q_1 + 2Q_2 + Q_3 \quad (2)$$

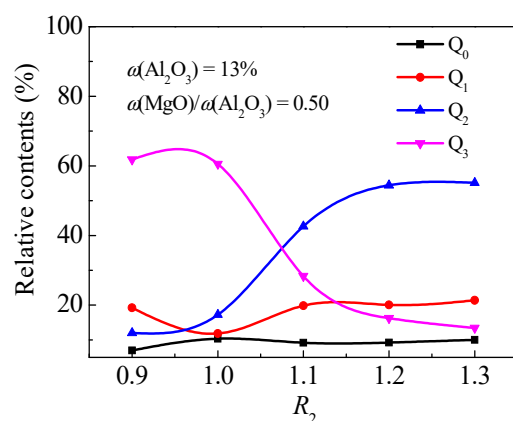


Figure 4. Relative content curves of Q_n with the various R_2 .

According to Equations (1) and (2), the theoretical and detected values of the relative content of non-bridging oxygen were calculated for different R_2 . As shown in Figure 5, a good correlation between the theoretical and detected values was observed. Therefore, Equation (2) can be used for the calculation of NBO/T. At the same time, the relative content of non-bridging oxygen gradually increased with R_2 , indicating that Ca^{2+} and free oxygen ions (O^{2-}) are network modifiers in the slag structure, and the increase of R_2 led to the decrease of the DOP.

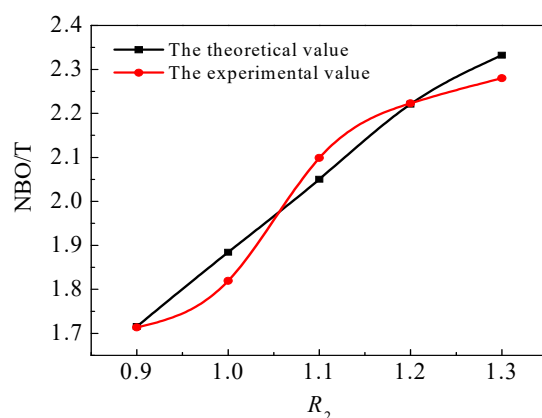


Figure 5. Theoretical and measured values of the relative content of non-bridging oxygen with different R_2 .

The water-quenching furnace slag FTIR spectra for different $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratios are shown in Figure 6 (temperature 1773 K; $R = 1.1$). With the increase of the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio, both the $[\text{AlO}_4]^{5-}$ antisymmetric bending vibration strength at $720\text{--}630\text{ cm}^{-1}$ and the Si–O–Al symmetric bending vibration strength at about 500 cm^{-1} weakened. This indicates that the number of $[\text{AlO}_4]^{5-}$ tetrahedral structural units and Si–O–Al structural units in the form of tetra-coordinated aluminum decreased gradually in the slag structure. The symmetrical stretching vibration of the silicate structural unit Q_n ($n = 0, 1, 2, 3$) at $1200\text{--}800\text{ cm}^{-1}$ did not change significantly. Thus, it is necessary to fit the peak divisions at $1200\text{--}800\text{ cm}^{-1}$ into four peaks corresponding to the Q_0 , Q_1 , Q_2 , and Q_3 structural units, respectively. The relative content of each unit can then be characterized by calculating the relative contents of each peak area.

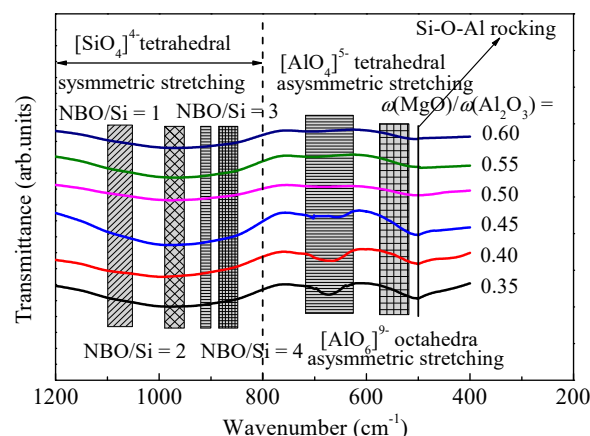


Figure 6. FTIR spectra of smelting slag with the various $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratios.

Figure 7 shows the peak division results of the FTIR with different $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratios in the wavenumber range of 1200–800 cm^{-1} . The peak center position corresponding to each tetrahedral structure increased, and the wavenumber corresponding to the peak center positions of the Q_0 and Q_1 structures (834.7 and 886.8 cm^{-1} , respectively) did not change significantly. The peaks corresponding to the Q_2 and Q_3 structures gradually moved to the low wavenumber region, decreasing from 985.0 to 970.3 cm^{-1} and from 1047.2 to 1030.6 cm^{-1} , respectively. This shows that the stability of the Q_2 and Q_3 structural units in the slag structure decreased with the increase of the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio and tended to simplify in structure.

The relative area of each peak corresponding to each structural unit Q_n ($n = 0, 1, 2, 3$) was calculated according to the peak division results. The change curve of the relative content of each structural unit with the increase of the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio was then obtained (Figure 8). It can be seen that the relative content of Q_2 , Q_1 , and Q_0 gradually increased as the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio increased from 0.35 to 0.55. The number of Mg^{2+} ions in the slag structure had increased and interacted with the bridge oxygen, transforming the more complex Q_3 structural unit into simpler Q_0 , Q_1 , and Q_2 structural units. Thus, the overall DOP decreased and the macroscopic viscosity was reduced [22–24]. Moreover, the Q_2 and Q_1 curves were smooth and steady when the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio is above 0.55. The percent content of Q_2 and Q_1 was higher than that of the others, while continuously increasing the MgO content was detrimental to the energy-saving ability of the BF. Therefore, the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio should be controlled at less than 0.55. To better analyze the evolution behavior of the silicon–oxygen anion groups, the schematic diagram of its structural evolution is shown in Figure 9.

To better understand the structure of Al in the slag and the change of its structural form in relation to R_2 and the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio, ^{27}Al -SS-MAS-NMR analysis was employed. According to previous studies [25–27], images from the ^{27}Al -SS-MAS-NMR spectrum can be divided into three parts: –10–30 ppm, the $[\text{AlO}_6]^{9-}$ octahedral structure of six-coordinated Al; 30–60 ppm, the $[\text{AlO}_5]^{7-}$ pentahedral structure of five-coordinated Al; and 60–80 ppm, the $[\text{AlO}_4]^{5-}$ tetrahedral structure of four-coordinated Al. To better reflect the variation of the structural unit content of each coordinating Al with increasing R_2 and $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio, Gaussian peak partitioning was performed on the obtained NMR spectrum.

The ^{27}Al -SS-MAS-NMR peak results for different R_2 are shown in Figure 10. The peak points do not clearly show changes in the content of Al structural units for each ligand, so calculations of the relative contents of each peak area are needed in Figure 11. The relative content of the $[\text{AlO}_4]^{5-}$ tetrahedral structural units of tetra-coordinated Al gradually decreased from 66.1% to 20.0% as R_2 increased from 0.9 to 1.3. The relative content of the $[\text{AlO}_5]^{7-}$ pentahedral units and the $[\text{AlO}_6]^{9-}$ octahedral increased gradually from 26.7% to 52.8% and from 7.2% to 27.2%, respectively. The results show that Al

in slag changed from $[\text{AlO}_4]^{5-}$ tetrahedral structure to $[\text{AlO}_5]^{7-}$ pentahedral structure and $[\text{AlO}_6]^{9-}$ octahedral structure with increasing of R_2 , the $[\text{AlO}_4]^{5-}$ structural unit of tetrahedral Al is a network former in the slag structure, and the complexity of the slag structure increases with the Al content. In addition, the $[\text{AlO}_5]^{7-}$ unit of five-coordinated Al and the $[\text{AlO}_6]^{9-}$ unit of six-coordinated Al are network modifiers in the slag structure, simplifying the slag structure will increasing Al content. Therefore, the increase of R_2 leads to the transition from $[\text{AlO}_4]^{5-}$ to $[\text{AlO}_5]^{7-}$ and $[\text{AlO}_6]^{9-}$, reducing the DOP of the slag, while an R_2 above 1.2 is not conducive to the transition of $[\text{AlO}_6]^{9-}$.

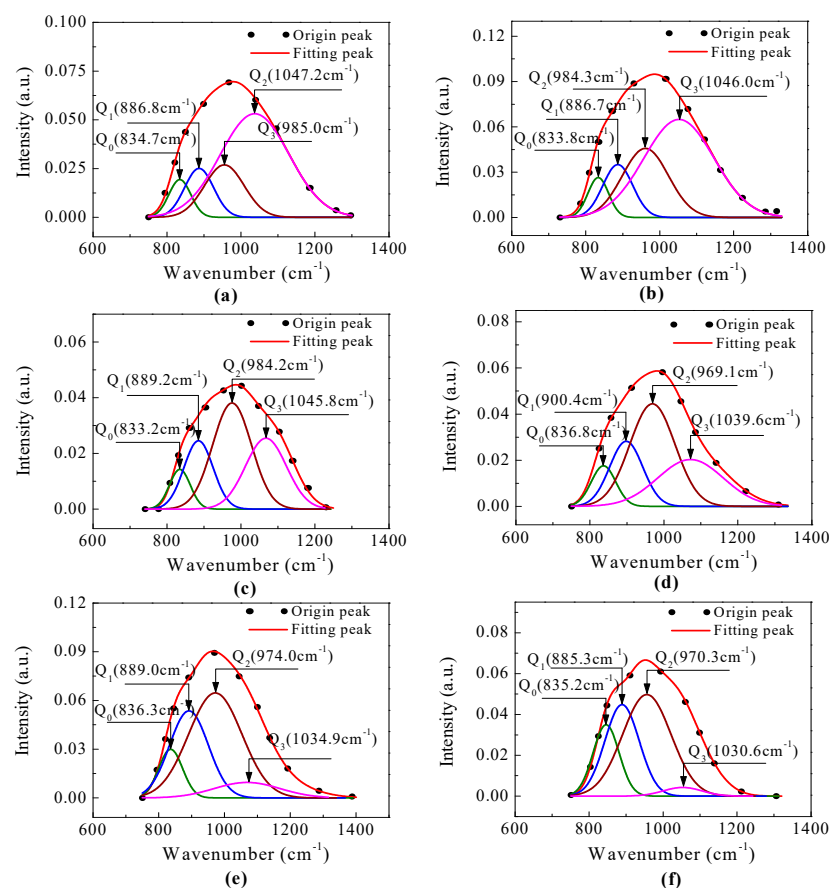


Figure 7. Deconvolution results of the FTIR curves with various $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratios, and (a) the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ is 0.35, (b) the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ is 0.40, (c) the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ is 0.45, (d) the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ is 0.50, (e) the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ is 0.55, (f) the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ is 0.60.

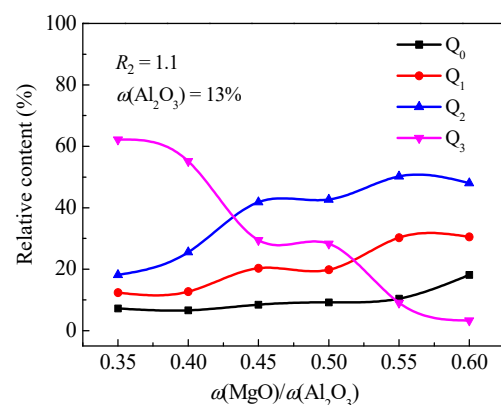


Figure 8. Relative content curves of Q_n with various $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratios.

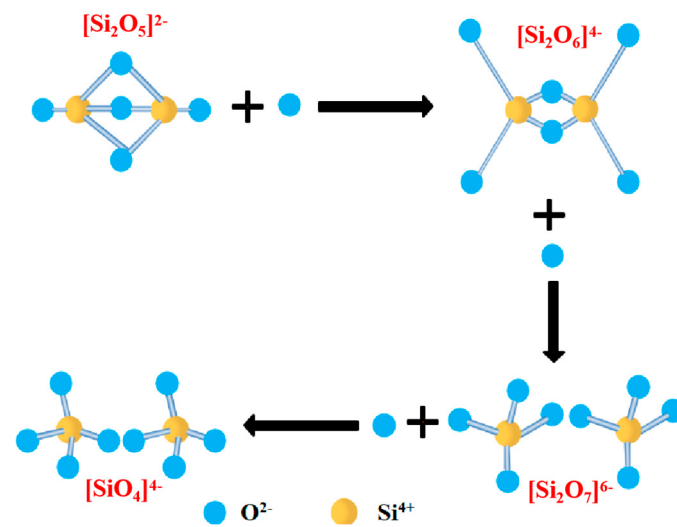


Figure 9. Silicon oxygen polymer microstructural evolution.

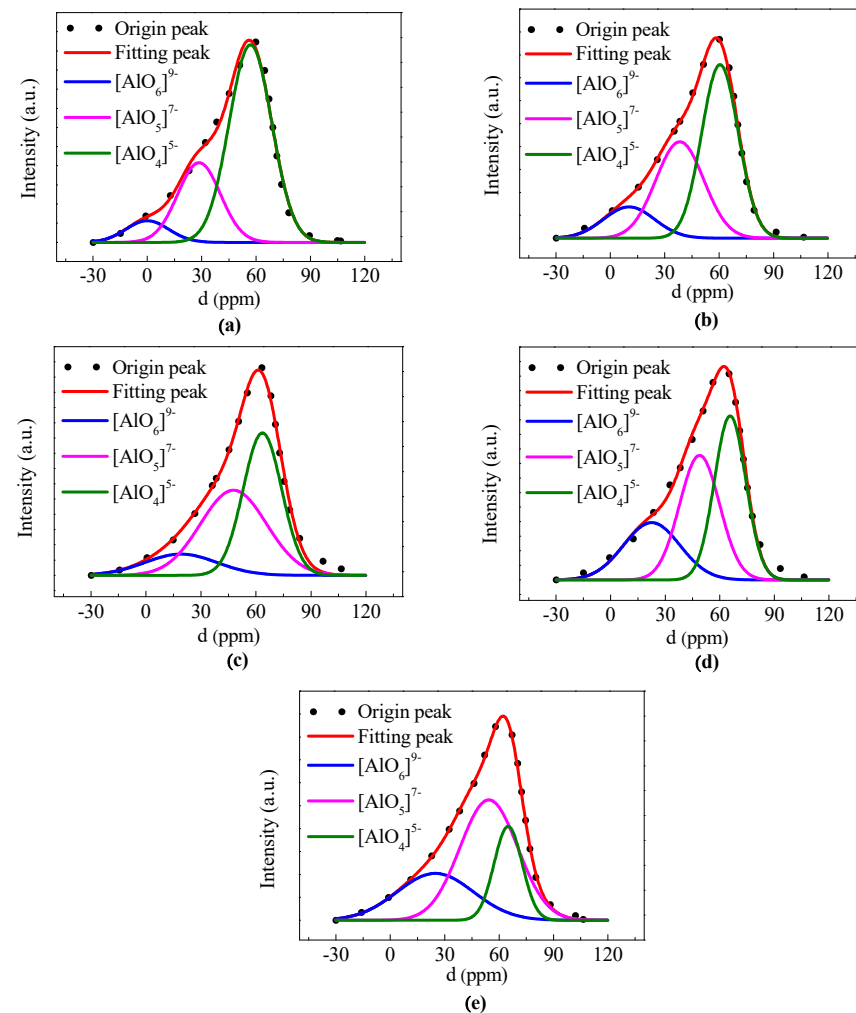


Figure 10. Deconvolution results of the ^{27}Al -SS-MAS-NMR curves with various R_2 , and (a) the R_2 is 0.9, (b) the R_2 is 1.0, (c) the R_2 is 1.1, (d) the R_2 is 1.2, (e) the R_2 is 1.3.

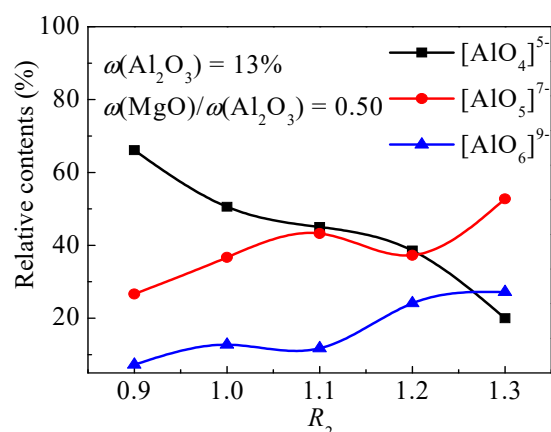


Figure 11. Relative content curves of $[\text{AlO}_4]^{5-}$, $[\text{AlO}_5]^{7-}$, and $[\text{AlO}_6]^{9-}$ with various R_2 .

Figures 12 and 13 show the ^{27}Al -SS-MAS-NMR peak separation results of the slag under different $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ conditions and the relative content of the Al structural unit of each coordination with the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ curve. As the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio increased from 0.35 to 0.60, the relative content of the $[\text{AlO}_4]^{5-}$ tetrahedral structural units of four-coordinated Al decreased gradually from 64.0% to 26.5%. The relative content of the $[\text{AlO}_5]^{7-}$ pentahedral units and $[\text{AlO}_6]^{9-}$ octahedral units increased from 29.6% to 44.8% and from 6.4% to 28.7%, respectively. As the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio increased, the structure of Al in the slag changed from $[\text{AlO}_4]^{5-}$ tetrahedral structure to $[\text{AlO}_5]^{7-}$ pentahedral structure and $[\text{AlO}_6]^{9-}$ octahedral structure (Figure 14). The content of $[\text{AlO}_5]^{7-}$ octahedral units was highest, but its relative content decreased when the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio was above 0.55. In regard to energy-saving ability in the production of BF, the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio should be controlled at less than 0.55.

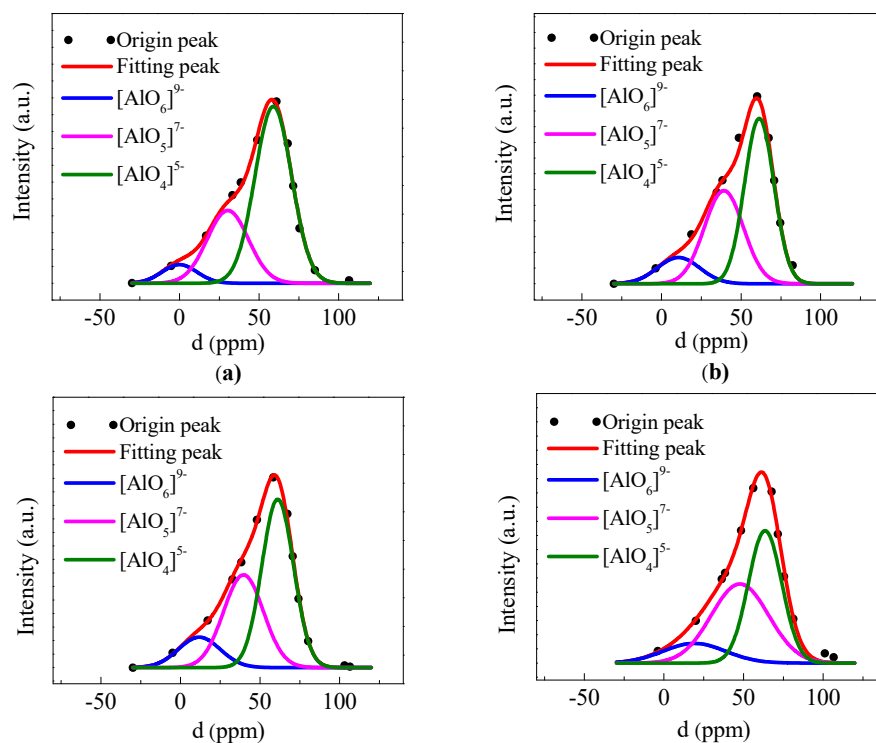


Figure 12. Cont.

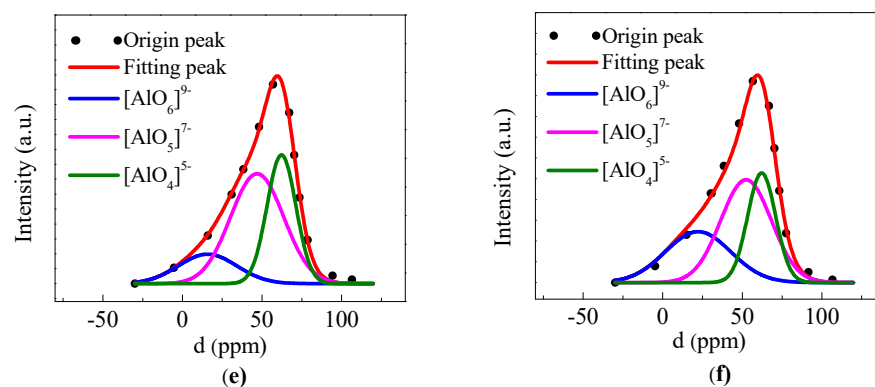


Figure 12. Deconvolution results of the ^{27}Al -SS-MAS-NMR curves with various $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratios, and (a) the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ is 0.35, (b) the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ is 0.40, (c) the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ is 0.45, (d) the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ is 0.50, (e) the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ is 0.55, (f) the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ is 0.60.

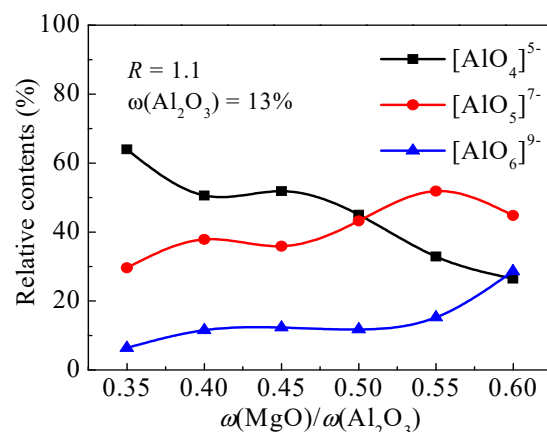


Figure 13. Relative content curves of $[\text{AlO}_4]^{5-}$, $[\text{AlO}_5]^{7-}$, and $[\text{AlO}_6]^{9-}$ with various $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratios.

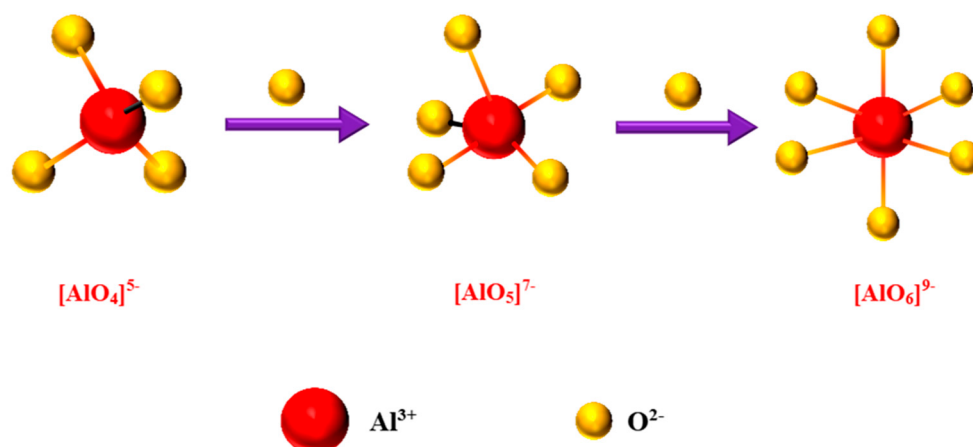


Figure 14. Aluminumoxygen polymer microstructural evolution of the BF smelting slag.

4. Conclusions

The influence of R_2 and $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ on the microstructural evolution of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ quaternary slag system was investigated by XRD, FTIR, and ^{27}Al -SS-MAS-NMR analyses, and the following conclusions can be drawn:

- (1) The CaO–SiO₂–Al₂O₃–MgO quaternary slag system entered the melting state when the temperature was increased to 1773 K, and the main structural units of the polymer were as follows: [Si₂O₅]^{2−}, [Si₂O₆]^{4−}, [Si₂O₇]^{6−}, [SiO₄]^{4−}, Si–O–Al, [AlO₄]^{5−}, [AlO₅]^{7−}, and [AlO₆]^{9−}.
- (2) With the increase of R_2 and $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$, the Q₃ structural unit of the silicate anion group changed to Q₀, Q₁, and Q₂, the DOP decreased, and the corresponding peak center position of each structural unit moved gradually to the lower wavenumber region. This indicates that the stability of each structural unit weakened and had a tendency to simplify in structure. The experimental data of the non-bridged oxygen content were compared with the formula in reference documents, and the fitting degree was found to be in agreement.
- (3) The ²⁷Al-SS-MAS-NMR results showed that R_2 can lead to the transformation of the Al in slag from [AlO₄]^{5−} tetrahedral structure to [AlO₅]^{7−} pentahedral structure and [AlO₆]^{9−} octahedral structure. Increasing the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio is more likely to cause the slag to eventually transform into [AlO₆]^{9−} octahedral structure, which functions as a network modifier in the slag structure. This would then reduce the DOP of the slag. In general, when the basicity is controlled within 1.2, especially when the $\omega(\text{MgO})/\omega(\text{Al}_2\text{O}_3)$ ratio is less than 0.55, the fluidity is suitable and energy can be saved in BF production.

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