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Molecular Dynamics Simulation on Microstructure and Physicochemical Properties of $\text{Fe}_x\text{O-SiO}_2\text{-CaO-MgO-“NiO”}$ Slag in Nickel Matte Smelting under Modulating CaO Content

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Received: 6 January 2020; Accepted: 7 February 2020; Published: 10 February 2020

Abstract: To improve the conditions of extracting iron from nickel smelting residues, the composition modulating from $\text{Fe}_x\text{O-SiO}_2\text{-CaO-MgO-“NiO”}$ slag source for matte smelting using high MgO nickel sulfide concentrate was carried out. Based on the molecular dynamics simulation and experimental characterization, the effect of CaO content in nickel slags on the physicochemical properties, the microstructure evolution, and the feasibility of subsequent iron extraction were analyzed. The results showed that, for nickel smelting slag with 9 wt.% MgO, 13–15 wt.% CaO and Fe/SiO₂ ratio of 1.2, the melting temperature of nickel slag was lower than 1200 °C, and the viscosity was lower than 0.22 Pa·s at 1350 °C. The electric conductivity was similar to that of the industrial slag, and the interfacial tension between slag and matte was relatively large, which ensured a good separating characteristic. It not only met the requirements for the slag performances in the existing flash smelting process but also improved conditions for the subsequent iron extraction. Additionally, it could be adapted to the current situation where an increasing MgO content exists in the nickel sulfide concentrate.

Keywords: nickel slag containing high MgO; molecular dynamics simulation; microstructure evolution; slag performance

1. Introduction

The emissions from Jinchuan Group Co. (Jinchang, China) are more than 1.6 million tons per year, with a cumulative stock of up to 40 million tons [1]. The basic composition of pyrometallurgical residues from nickel sulfide matte smelting belongs to the $\text{Fe}_x\text{O-SiO}_2\text{-CaO-MgO}$ slag system, which contains a considerable amount of valuable metals such as Ni, Co, Cu, and Fe components, and the iron content is as high as 25 wt.% to 45 wt.% [2]. At present, the most common methods to use iron resources in such waste slags include metal extraction, molten slag reduction, and magnetic separation after direct reduction; adding CaO to adjust the existing form of Fe to facilitate direct reduction magnetic separation is the most studied method [3–6]. Iron in nickel matte smelting residues mainly exists in the form of hortonolite and fayalite, with poor activity and recovery efficiency in molten reduction [1,4,7]. The addition of an appropriate amount of CaO can destroy the network structure of fayalite crystal phase in nickel smelting slags, which is beneficial to the reduction of 2FeO-SiO_2 in slags [1]. The

research results from the literatures [8,9] also show that the liquids temperature and viscosity of liquid phase can be reduced with an appropriate addition of CaO, a low amount of MgO and the reduction of oxygen potential in the system. Jian PAN et al. [6,10] used reduction-magnetic separation to recover valuable metals in nickel slags. It is shown that an increasing CaO content contributes to the enrichment of valuable metals and improves the recovery rate of Ni, Cu, Fe, and other metals. However, when CaO is added to extract Fe from waste slag, a lot of heat is consumed and a lot of waste slag is generated. Therefore, the direct addition of an appropriate amount of CaO and a reduction in SiO₂ in the smelting process is considered to regulate the nickel slag performance to meet the smelting requirements and obtain final slag, which is beneficial to the subsequent extraction of valuable metals. In this way, the proper regulation of the composition of the existing matte smelting slags from the source of solid waste is proposed to replace the past terminal treatment mode in the present study.

In the production practice, MgO content in nickel concentrate is required to be less than 6.5 wt.% in the nickel flash furnace smelting system, while the MgO content is generally as high as 10 wt.% in the nickel concentrate produced by Jinchuan company (Jinchang, China). Most of the MgO in the nickel concentrate is transferred into the slags, so that the MgO content reaches 8 wt.% to 13 wt.% in the slags when using Jinchuan self-mined concentrates. It is inevitable that MgO content at the current level in slag leads to higher melting temperature, lower fluidity, and worse separation characteristics between slag-matte than before. How to solve the above problems caused by high-MgO-containing slag? Increasing smelting temperature is bound to cause safety hazards of flash furnace with an irreversible deteriorated result. Is it still effective for that composition to regulate in high-MgO slag to maintain smooth production?

According to the above literature, adding CaO changes the composition of nickel slag, leading to the change of silicate structure of slag, and affects the performance of nickel slag. At the same time, the loss of valuable metals in slag is mainly mechanical entrainment and chemical dissolution. Adding CaO affects the separation characteristics of slag matte and the recovery of valuable metals and Fe₃O₄/FeO ratio in slag. Therefore, this study develops a further understanding of the effect of slag CaO content regulation on microstructure evolution, physicochemical properties, Fe₃O₄/FeO ratio, and loss of valuable metals in flash smelting with Jinchuan high MgO nickel sulfide concentrate. Molecular dynamics simulations [11–14] are used to obtain part of the short-range ordered structure of the molten slag, atomic scale shows even more microscopic structure information of how the scale and the kinetic characteristics are directly reflected in the high temperature, and the simulation results are characterized and verified by X-ray diffraction and Raman spectrum. In addition, the slag composition is closely related to the physicochemical properties from the microscopic point of view to provide theoretical guidance.

2. Materials and Methods

2.1. Materials

Slag with 0.26 wt.% NiO, 8–13wt.% MgO, 3–17 wt.% CaO, Fe/SiO₂ = 1.2–1.4 was selected as the research object. NiO, SiO₂, CaO, and MgO are analytically pure reagents. The FeO was prepared by decomposition reaction of ferrous oxalate in MXG1200-80 vacuum tube furnace (Shanghai Weixing Furnace Co., Ltd., Suzhou, China) at high temperature. Ferrous oxalate was held for 30 min in a reaction tube heated at a rate of 10 °C/min to 950 °C. High purity argon 99.99% was used as protective gas with a flow rate of 100 mL/min. After isothermal treatment, it was cooled naturally.

2.2. Experimental Method

2.2.1. Molecular Dynamics Simulation

The amorphous cell module of Material Studio 2017 software (BIOVIA, San Diego, CA, USA) was used to build an amorphous model. The atoms in Table 1 were added to one frame by choosing

packing task, then processed by molecular dynamics simulation. Considering the processing ability of a computer and the number of particles that could represent the microstructure of high temperature melt, the number of particles per component in the simulation was kept at about 3700. According to the preliminary research, some Fe^{2+} is converted into Fe^{3+} in the smelting process. Therefore, considering the actual situation, the particle composition of the slag system used in the molecular dynamics simulation was obtained by combining the composition ratio. The density was calculated according to the actual situation, and the composition is shown in Table 1.

Table 1. Particle composition of molecular dynamics simulation of nickel slag.

CaO/wt. %	Number of Ions							Density/ (g/cm ³)	$\text{Fe}^{2+}/\text{Fe}^{3+}$
	Ni^{2+}	Fe^{2+}	Fe^{3+}	Si^{4+}	Ca^{2+}	Mg^{2+}	O^{2-}		
11	3	625	48	516	196	223	2154	3.50	12.93
13	3	607	50	504	232	223	2147	3.50	12.09
15	3	578	62	491	267	223	2146	3.49	9.30
17	3	554	69	478	303	223	2142	3.49	8.02

Then, the smart algorithm was used to obtain the low energy structure. To eliminate the influence of initial ion distribution inequality on the simulation, the system was relaxed at 6000 °C for 30 ps, then cooled to 2000 °C in 30 ps; at 2000 °C, it was relaxed for 30 ps and then cooled to 1150 °C in 30 ps. Finally, the equilibrium conformation information was obtained after relaxation at 1150 °C for 30 ps. The relaxation process used the micro-canonical ensemble (NVE) to ensure the energy stability of the system; the cooling process used the canonical ensemble (NVT). The force field comes from the calculation of the potential energy of the ion pair by using the Doml3 module in the Material Studio 2017 software, and then it was fitted by the Born–Mayer–Huggins (BMH) [15,16] potential function. The formula (1) shows the two body BMH potential function, and Table 2 shows the fitted BMH potential parameters of $\text{NiO-Fe}_x\text{O-SiO}_2\text{-CaO-MgO}$ nickel slag.

$$E_{ij} = \frac{q_i q_j}{4\pi\epsilon r_{ij}} + A_{ij} \exp(-\beta_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

where E_{ij} is the potential function between ion i and ion j, q_i and q_j are the charge of ion i and ion j, respectively, r_{ij} is the distance between ion i and ion j, ϵ is the dielectric constant, and A_{ij} , β_{ij} and C_{ij} are the energy parameters of ion.

Table 2. Fitted Born–Mayer–Huggins (BMH) potential parameters of $\text{NiO-Fe}_x\text{O-SiO}_2\text{-CaO-MgO}$ nickel slag system.

Ion i	Ion j	A_{ij} , eV	β_{ij} , 1/Å	C_{ij} , eV Å ⁶	R ²
O^{2-}	O^{2-}	117,584.04	7.31	0.00	0.996
O^{2-}	Ni^{2+}	367,217.18	6.64	0.00	0.997
O^{2-}	Fe^{2+}	274,205.07	6.08	0.00	0.992
O^{2-}	Ca^{2+}	152,301.61	4.93	0.00	0.997
O^{2-}	Si^{4+}	198,320.86	5.77	0.00	0.988
O^{2-}	Mg^{2+}	105,782.04	4.95	0.00	0.992
Ni^{2+}	Ni^{2+}	761,382.64	6.49	0.00	0.999
Ni^{2+}	Fe^{2+}	671,045.87	6.31	0.00	0.999
Ni^{2+}	Ca^{2+}	487,920.85	5.88	0.00	0.999
Ni^{2+}	Si^{4+}	622,188.81	6.73	60.51	0.997
Ni^{2+}	Mg^{2+}	282,774.68	5.71	0.00	0.999

Table 2. Cont.

Ioni	Ionj	A_{ij} , eV	β_{ij} , 1/Å	C_{ij} , eV Å ⁶	R ²
Fe ²⁺	Fe ²⁺	848,529.41	6.89	0.00	0.999
Fe ²⁺	Ca ²⁺	387,583.35	5.53	0.00	0.999
Fe ²⁺	Si ⁴⁺	579,168.00	6.64	65.58	0.996
Fe ²⁺	Mg ²⁺	251,819.69	5.59	0.00	0.999
Ca ²⁺	Ca ²⁺	255,057.57	4.68	0.00	0.999
Ca ²⁺	Si ⁴⁺	243,110.79	5.52	7.65	0.998
Ca ²⁺	Mg ²⁺	181,673.62	5.08	0.00	0.999
Si ⁴⁺	Si ⁴⁺	832,193.36	8.77	27.51	0.999
Si ⁴⁺	Mg ²⁺	585,831.01	7.64	46.54	0.999
Mg ²⁺	Mg ²⁺	416,041.84	6.75	69.12	0.999
O ²⁻	Fe ³⁺	315,438.74	6.27	0.00	0.999
Ni ²⁺	Fe ³⁺	740,398.65	6.56	0.00	0.999
Fe ²⁺	Fe ³⁺	1,040,710.00	7.23	26.53	0.999
Fe ³⁺	Ca ²⁺	419,396.09	5.68	0.00	0.999
Fe ³⁺	Si ⁴⁺	575,165.97	6.75	64.99	0.999
Fe ³⁺	Mg ²⁺	336,931.32	6.20	0.00	0.999
Fe ³⁺	Fe ³⁺	1,143,420.00	7.59	0.00	0.999

2.2.2. Phase and Microstructure Characterization of Slag

FactSage for the analysis of chemical thermodynamics was successfully used in the prediction of high-temperature processes with complex multi-component phase equilibria [17]. The phase diagrams of nickel slag containing 0.26 wt.% NiO, 5 wt.%, 9 wt.%, 13 wt.%, and 17 wt.% CaO individually under 10^{-7} atm partial pressure were calculated by “Equilib” module of FactSage 7.0 (Thermfact, Montreal, QC, Canada; GTT-Technologies, Ahern, Germany) with the databases “FactPS” and “FToxid”.

The prepared samples were placed into a corundum crucible in the ZPT90/16A vertical tubular resistance furnace (Luoyang Zhipu furnace industry Co., Ltd., Luoyang, China). During the experiment, CO and CO₂ gases were continuously introduced to ensure partial pressure of oxygen. The temperature was raised to 1400 °C at a heating rate of 5 °C/min and then kept for 1 h to ensure slag completely melting. Then, it was cooled to 1150 °C at a rate of 5 °C/min and held for another 1 h to ensure that the nickel slag phase reached equilibrium. Finally, the sample was quenched to water and ground into powders.

The slag structure was analyzed by micro Raman spectrometer (Renishaw Invia, London, UK, with resolution of 1 cm⁻¹, spectral range of 300–1200 cm⁻¹, and wavelength of 532 nm).

The XRD phase analysis was carried out by X-ray powder diffractometer (D/MAX-2400, Rigaku, Tokyo, Japan). The major measurement parameters are: Cu-Kα radiation $\lambda = 1.54050$, 42 kV, 100 mA, and step size 0.026°.

2.2.3. Determination of Physicochemical Properties

The melting temperature of slag was measured by the CQKJ-II slag melting temperature tester (Chongqing university of science and technology, Chongqing, China). Slag viscosity was measured by the RTW-10 type melt physical and chemical properties comprehensive analyzer (RTW-10, Northeastern University, Shenyang, China). Each sample had 200 g weight to control the molten slag liquid level height to 40 mm to determine viscosity, electric conductivity, and surface tension parameters of the nickel slag.

3. Results and Discussions

3.1. Effect of CaO on Liquidus Temperature of Slag

To analyze the effect of adding CaO on the metallurgical properties of slag in nickel matte smelting, the “Phase” module in FactSage software Version 7.0 was used to calculate the phase diagram and the phase equilibrium of the $\text{Fe}_x\text{O-SiO}_2\text{-CaO-MgO-“NiO”}$ slag system. Figure 1 shows the partial calculation results of slag with 0.26 wt.% NiO, 5 wt.%, 9 wt.%, 13 wt.%, and 17 wt.% CaO individually under 10^{-7} atm partial pressure.

Figure 1. Phase diagram of $\text{Fe}_x\text{O-SiO}_2\text{-CaO-MgO-“NiO”}$ system, at $P_{\text{O}_2} = 10^{-7}$ atm, 0.26 wt.% NiO (a) 5 wt.% CaO; (b) 9 wt.% CaO; (c) 13 wt.% CaO; (d) 17 wt.% CaO.

According to the phase equilibrium at different temperatures and Figure 1, spinel (mainly Fe_3O_4), olivine [mainly Mg_2SiO_4 , Fe_2SiO_4 , $(\text{Fe, Mg})\text{SiO}_4$, $(\text{Ca, Fe})\text{SiO}_4$], pyroxene [mainly $(\text{Ca, Mg})\text{Si}_2\text{O}_6$, $(\text{Ca, Fe})\text{Si}_2\text{O}_6$, $\text{Fe}_2\text{Si}_2\text{O}_6$, $\text{Mg}_2\text{Si}_2\text{O}_6$, $(\text{Fe, Mg})\text{Si}_2\text{O}_6$], and single oxide were mainly formed in the slag. With the increase of CaO content in nickel slag, the proportions of the spinel phase and the single oxide phase increased gradually, while the proportions of the olivine phase decreased gradually, and the pyroxene phase decreased first and then increased. This was mainly attributed to CaO promoting the complex anion SiO_4^{4-} disintegration in nickel slag. Some of Fe^{2+} was dissociated from the olivine and the pyroxene phases and oxidized to Fe_3O_4 . Therefore, the amounts of the olivine and the pyroxene phases became lower, while the spinel phase increased gradually. When CaO content was higher than 15 wt.%, the melting temperature increased due to the high amount of single oxide and spinel phases. Thus, the diffusion in the slag structure became difficult, which led to the aggregation of silica ions and the increase of pyroxene phase. To observe the effect of CaO on the liquidus region more

clearly, the liquid phase regions with different CaO contents at 1200 °C, 1250 °C, and 1300 °C were superimposed to obtain Figure 2.

Figure 2. Superposition diagram of liquidus region of $\text{Fe}_x\text{O-SiO}_2\text{-CaO-MgO-‘NiO’}$ (a) 1200 °C; (b) 1250 °C; (c) 1300 °C.

Figure 2 shows that, with the increase of CaO content in nickel matte slag, the low melting temperature area lower than 1200 °C in the phase diagram increased first and then decreased, while the low melting temperature area lower than 1250 °C and 1300 °C was enlarged continuously. Therefore, under the condition of smelting temperature, the adjustable range of the nickel matte smelting slag composition was also enlarged correspondingly and moved in the direction where Fe/SiO₂ decreased. The melting characteristics of synthesized nickel slag were consistent with the work conducted by previous research [1] and by Nikolic Stanko [18–21] et al. in which the liquid phase temperature of copper concentrate smelting “Cu₂O”-FeO-Fe₂O₃-CaO-SiO₂ slag was studied. When the CaO content in slag increased to 15 wt.%, the maximum content of MgO in nickel slag could reach 12 wt.% at the melting temperature below 1300 °C, which catered for the characteristics of the raw materials with a high MgO content in nickel sulfide concentrate produced by flash smelting in Jinchuan. With the CaO content increase in slag, the adjustable range of Fe/SiO₂ in nickel slag gradually increased, but the maximum value of Fe/SiO₂ gradually decreased, i.e., more quartz sand was needed to adjust basicity after increasing CaO content in slag, which was verified by the subsequent measurement of the melting temperature of nickel slag. Therefore, the CaO content could be increased appropriately in the smelting process until 15 wt.%, and the composition of nickel slag could be adjusted in a wider range.

3.2. Influence of CaO on Melting Temperature and Conductivity

The molten slag is required to have good fluidity in the nickel matte smelting process, and the electrodes need to be heated in the dilution zone to improve the recovery rate of valuable metals. Therefore, the melting temperature and the electric conductivity of the slag are very important for the nickel matte smelting. To analyze the effect of CaO on the physicochemical characteristic of $\text{Fe}_x\text{O-SiO}_2\text{-CaO-MgO-‘NiO’}$ slag, the hemispherical temperature, the flow temperature, and the conductivity of 0.26 wt.% NiO, 9 wt.% MgO, Fe/SiO₂ = 1.2, 5–17 wt.% CaO of nickel slags were determined by melting temperature tester and physicochemical performance analyzer and are shown in Figure 3.

Figure 3. Effect of CaO in nickel slag of $Fe_xO-SiO_2-CaO-MgO-NiO$ (a) melting characteristic; (b) electric conductivity.

Figure 3a shows the hemispheric temperature of nickel slag decreased first and then increased as CaO content increased from 5 wt.% to 17 wt.%. When the CaO content was 13–15 wt.%, the hemispheric temperature reached the lowest value, 1181 °C, and then increased rapidly after 15 wt.%. This was in accordance with the trend of the influence of CaO content on the liquid phase zone of the $Fe_xO-SiO_2-CaO-MgO-NiO$ slag system in Figure 2. Phase analysis of slag samples after melting property measurement showed that, with the increase of CaO content in nickel slag from 5 to 17 wt.%, the high melting temperature olivine phase in nickel slag decreased gradually. When CaO content exceeded 15 wt.%, the melilite phase in nickel slag increased suddenly, resulting in the increase of hemispheric temperature of nickel slag.

From Figure 3b, it can be seen that the electric conductivity of nickel slag was affected by CaO content. Because the conductivity of nickel slag was mainly subject to the migration of anions and cations, when the temperature was low, the anions in nickel slag mainly existed in the form of $Si_xO_y^{z-}$ complex, and the movement of ions in nickel slag was hindered greatly. Due to the valence change of Fe, many free electrons or electronic holes were formed, which made the oxide exhibit high electronic conductivity.

With the CaO content increase in nickel slag, the increased Ca^{2+} could promote the dissociation of complex $Si_xO_y^{z-}$ anions into simple anions with smaller radius, which reduced the hindrance of cations in slag and increased the amount of conductive ions in the system. Therefore, the electric conductivity of slag increased with the increase of CaO content. When the CaO amount increased continuously, the effect of CaO on conductivity decreased until the complex $Si_xO_y^{z-}$ anion dissociation was complete in nickel slag. In a word, the conductivity of nickel slag with high CaO content was higher than that of nickel slag with low CaO content at high temperature.

In the process of nickel pyrometallurgy, slag melting temperature is generally required to be 80 °C lower than smelting temperature. At present, the temperature control in Jinchuan nickel flash smelting is between 1360 °C to 1400 °C. The conductivity of slag is basically at the same level as the slag that is currently used, thus the property of melting temperature conductivity of this series of slag can meet the requirements of nickel matte smelting process.

3.3. Effect of CaO on Phase Composition and Microstructure of Nickel Slag

3.3.1. Molecular Dynamics Simulation on Phase Composition and Microstructure

To study the influence of the microstructure of nickel slag on its macroscopic properties, the change mechanism of nickel slag structure was comprehensively analyzed by molecular dynamics simulation and experimental characterization. Figure 4 shows the radial distribution function of ion pairs of the nickel slags with 11 wt.% CaO at 1150 °C. The radial distribution function (RDF) refers to the probability of another particle appearing in the unit volume of the certain space position, which reflects

the degree of particle aggregation in the irregular network structure [22], where r is the distance between pairs of particles, and $g(r)$ is the number of pairs of particles with r . It can be seen from the graph that the overall shape of the radial distribution functions between ion pairs was similar. The main difference was that the position and the intensity of the peaks changed slightly. There were sharp peaks between anions and cations, and the first coordination distance of the same ions was larger the others, which indicates that the strong electrostatic repulsion existed between the congener ions, which led to a longer distance between ions, while the electrostatic attraction existed between the anions and the cations. There were two peaks between Si^{4+} - Si^{4+} , indicating that there were two relatively stable short-range coordination distances between Si^{4+} - Si^{4+} , while the first peak was relatively low, and the half-height and the width were relatively large, indicating that there was a strong repulsion between the congener ions.

Figure 4. Radial distribution function of different ion pairs in nickel slag with 11 wt.% CaO at 1150 °C.

Figure 5 shows the coordination number function $N(r)$ between Si^{4+} - O^{2-} and Si^{4+} - Si^{4+} . With the CaO content increase from 11 wt.% to 17 wt.%, the coordination numbers of Si^{4+} - O^{2-} and Si^{4+} - Si^{4+} decreased first and then increased. The coordination number of Si^{4+} - Si^{4+} reflected the degree of polymerization of silicate melt. With the CaO content increase in the slags, the complex silica ions began to dissociate into simple silica ions. Therefore, the coordination number of Si^{4+} - Si^{4+} showed a decreasing trend, which indicates a decrease of the degree of polymerization of the melts. It is noteworthy that, when the CaO content increased from 11 wt.% to 15 wt.%, the coordination number of Si^{4+} - Si^{4+} decreased notably, while a further increase of CaO content to 17 wt.% increased the coordination number of Si^{4+} - Si^{4+} . The melting point of the system gradually increased with the addition of CaO, and the complex silicon oxide ions were more difficult to be dissociated. Therefore, the coordination number of Si^{4+} - Si^{4+} tended to increase.

Figure 5. Coordination number of ion pairs in nickel slag with different contents of CaO at 1150 °C (a) Si^{4+} - O^{2-} coordination number; (b) Si^{4+} - Si^{4+} coordination number.

3.3.2. Experimental Characterization of Phase Composition and Microstructure

Raman spectra analysis results of nickel slag with different CaO contents quenched at 1150 °C are shown in Figure 6. There are five species of Si-O tetrahedral Q_i [23] (subscript i indicates that Q_i contains several bridging oxygen O_b , $i = 0, 1, 2, 3, 4$). Each Q_i contains one Si^{4+} and four O^{2-} . Each Si-O tetrahedral microstructure has its specific peak position.

Figure 6. Raman spectra of nickel slag with different CaO content quenched at 1150 °C.

The position of each peak is shown in Table 3. The ratio of each peak area to the total peak area is shown in Table 4. The Raman peak position of nickel slag in this system was mainly 811 cm^{-1} $Si-O_{nb}$ bending vibration and 846 cm^{-1} Q_0 symmetrical stretching vibration. The results show that the content of Q_0 [24] in the slag was higher, while the relative content of Q_1 and Q_2 were lower [25]. With the CaO content increase in the nickel slag system, the relative fractions of Q_0 increased first and then decreased, while Q_1 and Q_2 decreased first and then increased gradually. This was mainly due to the increase of CaO content and the decrease of silica ion content in the system, which led to the decrease of the degree of network polymerization. However, if the CaO content was higher than about 15%, the melting temperature of the system would rise. Therefore, the increase of CaO content would lead to the increase of viscosity in the system, which is not conducive to the diffusion and the dissociation of silicate ions, resulting in the transformation of Q_0 into Q_1 and Q_2 in nickel slag.

Table 3. Location of Raman characteristic peaks of nickel slag with different CaO content quenched at 1150 °C.

Raman Shift of Si-O	Composition of Nickel Slag				Vibration Mode
Mass Fraction of CaO	11%	13%	15%	17%	
Raman shift/ cm^{-1}	811	814	814	811	$Si-O_{nb}$ bending vibration
	843	846	846	844	$Si-O_b$ of Q_0 symmetrical stretching vibration
	890	894	894		$Si-O_b$ of Q_1 symmetrical stretching vibration
	940	940	936	933	$Si-O_b$ of Q_2 symmetrical stretching vibration

Table 4. Relative ratio of Raman characteristic peaks of nickel slag with different CaO content quenched at 1150 °C.

Area Ratio of Q_i	Composition of Nickel Slag				Vibration Mode
Mass Fraction of CaO	11%	13%	15%	17%	
Area ratio/%	79.68	82.13	81.83	79.68	$Si-O_b$ of Q_0 symmetrical stretching vibration
	10.59	10.08	8.61	10.59	$Si-O_b$ of Q_1 symmetrical stretching vibration
	9.74	7.79	9.56	9.74	$Si-O_b$ of Q_2 symmetrical stretching vibration

Figure 7 is the XRD phase analysis of the slags with different CaO content under $P_{O_2} = 10^{-7}$ atm quenched at 1150 °C, 1200 °C, and 1300 °C. It can be seen from Figure 7 that the phases of nickel slag present at 1150 °C–1300 °C were mainly $Ca_2Fe_2O_5$, $CaFe_2O_4$, pyroxene phase [$CaMgSi_2O_6Ca(Fe, Mg)Si_2O_6$, $CaFeSi_2O_6$], Fe_3O_4 , the melilite phase ($Ca_2MgSi_2O_7$), and a small amount of the olivine phase (Fe_2SiO_4). With the increase of temperature, the nickel slag began to melt, and the melilite phase gradually disappeared, forming a pyroxene phase, which was due to the gradual melting of the nickel slag with the increasing temperature, and $Si_2O_7^{2-}$ gradually transformed into SiO_6^{2-} . Figure 7 shows that, with the CaO content increase in the nickel slag, the proportions of the olivine phase and the pyroxene phase in the nickel slag gradually decreased and changed into $Ca_2Fe_2O_5$, $CaFe_2O_4$, Fe_3O_4 , $CaSiO_3$, and $Ca_2MgSi_2O_7$. This was consistent with the influence of CaO content on phase diagrams in the above Section 3.1. As the CaO content in nickel slag increased, the amounts of dissociated Ca^{2+} increased, which promoted the dissociation of Fe^{2+} ions in the iron-containing silicate phase, thus generating a large amount of Fe_3O_4 and further promoting the dissociation of complex silica anions and the generation of ferric ions. These results were consistent with the iron extraction experiment made by our group, in which iron reduction rate of synthetic slag was increased by about 20% by adding 15 wt.% CaO.

Figure 7. XRD diffraction patterns of water quenched nickel slag with different CaO contents (a) 1300 °C; (b) 1200 °C; (c) 1150 °C.

3.4. Fluidity and Interface Separation of Nickel Slag with Varied CaO Content

3.4.1. Kinetic Properties of Molecular Dynamics Simulation

A molecular dynamics simulation on the kinetic properties of nickel slag was carried out. The mean square displacement of each ion in nickel slag with 11 wt.% CaO at 1150 °C was obtained from statistic of the ion trajectory in the molecular dynamics simulation.

Mean square displacement (MSD) refers to the square of the average displacement of particles in a certain period of time. In the molecular dynamics simulation system, the position and the direction

of the motion of particles keep changing, which reflects the active degree of particles in the irregular network structure. As shown in Figure 8, after initial diffusion for a period of time, the ions quickly reached the stable stage and then maintained a relatively stable diffusion level. The mean square displacement of ions in slag showed a good linear relationship against time. Figure 8 shows that the order of the average shift of ions in the nickel slag system was $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Fe}^{2+} > \text{O}^{2-} > \text{Fe}^{3+} > \text{Si}^{4+}$, which conformed to the diffusion rule of silicate system. It was also consistent with the results of Chunhe Jiang et al. [26,27].

Figure 8. Mean square displacement of ions in nickel slag with 11 wt.% CaO at 1150 °C.

Because Si^{4+} formed the main structure of silicon-oxygen tetrahedron in the system, the diffusion rate of Si^{4+} was the smallest, and the diffusion rates of O^{2-} and Si^{4+} were the same as that of tetrahedron. Therefore, the diffusion rate was much lower than that of other divalent ions. However, besides the coordination between Si^{4+} and O^{2-} , O^{2-} also coordinated with other cations. In this way, its diffusion rate was much higher than Si^{4+} . As Mg^{2+} , Ca^{2+} , Fe^{2+} and Fe^{3+} are tetrahedral network modifiers, their diffusion rates were much higher than Si^{4+} . It is noteworthy that the diffusion rate of Fe^{3+} was much lower than Fe^{2+} . This was because, when Fe^{2+} was converted to Fe^{3+} , the valence became higher, and the ability to combine with oxygen was stronger, thus it was more difficult to diffuse. This could also explain the rapid viscosity increase of nickel slag after the oxidation from Fe^{2+} to Fe^{3+} in nickel smelting, which resulted in the deterioration of smelting conditions. Therefore, the proportion of $\text{Fe}^{2+}/\text{Fe}^{3+}$ should be strictly controlled in the flash smelting of nickel. After exceeding the limit, smelting is difficult to continue.

The mean square displacement of ions in nickel slag with different CaO content is plotted in Figure 9. The chaos of each ion in the early stage was basically the same with little change. When the system was stabilized gradually, the difference gradually emerged. As the CaO content increased from 11 wt.% to 13 wt.%, the diffusion ability of each ion increased, because more and more complex silica ions were dissociated into simple forms. Additionally, the system was relatively loose, thus the diffusivities of various ions were enhanced. When CaO content continued to increase from 13 wt.% to 17 wt.%, the mean square displacement values of Si^{4+} , Fe^{2+} , Mg^{2+} , and Ca^{2+} decreased, while the diffusion coefficients of Fe^{3+} and O^{2-} decreased first and then increased. When the CaO content in the system increased gradually, the melting temperature and the viscosity of slag increased. Although more complex silica ions were dissociated, it could not resist the trend that the viscosity of the system increased because of the increase of the melting temperature. Therefore, the diffusion level of most ions decreased. When the CaO content increased from 13 wt.% to 15 wt.%, the Fe^{3+} was the most polar metal cation in the system, which was different from the main structure of Si^{4+} in the slag. When the polymeric degree of the slag system decreased, a small amount of Fe^{3+} was dissociated from the silicic acid ion system. It formed Fe_3O_4 with O^{2-} . Under the dual actions, the diffusion ability was also slightly improved, while other metal cations combined with more and more dissociated simple silica

ions, resulting in a decrease in the diffusion ability. Therefore, the mobility of components in nickel slag system was better when CaO content was 13 wt. %.

Figure 9. Effect of CaO content on the mean square displacement of ions in nickel slag (a) O^{2-} ; (b) Si^{4+} ; (c) Fe^{2+} ; (d) Fe^{3+} ; (e) Ca^{2+} ; (f) Mg^{2+} .

3.4.2. Experimental Characterization of Separation Characteristics of Slag Matte

Viscosity and surface tension affect the interface reaction, the heat and mass transfer, and other properties between slag and matte. Therefore, appropriate viscosity and surface tension of smelting slag should be provided to ensure good separation characteristics between slag and matte in smelting process.

The viscosity and the surface tension of $Fe_xO-SiO_2-CaO-MgO-NiO$ slag with different CaO content were measured and are shown in Figure 10.

Figure 10. Effect of CaO on the Fe_xO-SiO₂-CaO-MgO-“NiO” slag (a) viscosity; (b) surface tension.

Figure 10a shows that the viscosity of all tested nickel slag was lower than 0.3 Pa·s and decreased with the increase of temperature; it also increased first and then decreased with the CaO content increase. Phase analysis shows when the content of CaO in the nickel slag was low, SiO₂ in the system mainly existed in the form of Si₂O₆⁴⁻ and SiO₄⁴⁻ ions. Since calcium silicate is more stable than iron silicate, the dissociation of iron silicate in the slag was promoted by the increase of CaO content. A large amount of compound Fe₃O₄ with high melting point was generated, resulting in a gradual increase in the viscosity of the system. When the CaO content further increased, Fe₃O₄ in the slag was converted into iron-silicate Ca₂FeSi₂O₇ and other phases; thus, the viscosity of the system was rapidly reduced.

With the increase of temperature, the complex Si_xO_y^{z-} anions gradually disintegrated, increasing the fluidity of nickel slag and decreasing the viscosity. When CaO content was higher than 11 wt.% and the temperature was raised to 1350 °C, the effect of CaO on the viscosity of the nickel slag tended to be mild, but the viscosity gradually increased. This was because the complex Si_xO_y^{z-} anion was highly dissociated at this time, and it became a simple silicon-oxygen complex ion, which did not affect the anion, and the CaO content gradually increased. There was a large amount of free CaO in the system, thus the viscosity of the nickel residue increased with the increase of CaO content.

Figure 10b shows that the surface tension of nickel slag at different temperatures gradually increased with the CaO content increase. Due to the electrostatic attraction interaction among the cations, the surface ions were subjected to the tensile force of the internal system. Therefore, the slag always had a tendency to reduce the surface area. When the CaO content was low, the silicon-oxygen composite ions in the nickel slag had a higher degree of recombination, thus its ionic radius was large, and the interaction with other ions was small. In order to reduce the energy of the system, these silicon oxyanions were always pushed to the surface of the slag, thereby lowering the surface tension of the slag. With the CaO content increase in nickel slag, the dissociation of silicon-oxygen composite ions was more significant. Moreover, the ionic radius was gradually reduced, and the interaction between ions was relatively strong. Therefore, the surface tension of nickel slag was as high as 0.485 N/m at 1400 °C, thus the slag was relatively easy to separate, which meets the smelting requirements in actual production.

Under the condition of general nickel flash smelting slag temperature of 1300 °C to 1400 °C, the series of slag had low viscosity (less than 0.5 Pa·s) and good flow performance. The interfacial tension between slag and matte was large, and the separation characteristics were good. Therefore, it can meet the requirements of slag fluidity and slag-matte separation characteristics in actual production.

4. Conclusions

Molecular dynamics simulation and experimental characterization of the effect of CaO on the physicochemical properties and the microstructure of Fe_xO-SiO₂-CaO-MgO-“NiO” slag was analyzed. The following conclusions were obtained:

(1) Simulation results of molecular dynamics corresponded well with the characterization of the physicochemical properties experiment. The results indicate that the melting temperature of nickel slag was lower than 1200 °C in the current flash smelting slag maintaining 9 wt.% MgO, oxygen partial pressure of 10^{-7} atm, $\text{Fe/SiO}_2 = 1.2$; when CaO was about 13–15 wt.%, the viscosity of all samples was lower than 0.30 Pa·s at 1350 °C, ensuring good flow performance. The physicochemical properties of the tested slags were satisfied with the needs of high MgO nickel sulfide matte smelting.

(2) The molecular dynamics simulation combined with Raman spectroscopy and X-ray diffraction showed that silicon ions mainly existed in the form of $\text{Si}_2\text{O}_6^{4-}$ and SiO_4^{4-} , so that the degree of polymerization could be modified with the addition of CaO in nickel slag. The iron-containing phases, such as $\text{Ca}_2\text{Fe}_2\text{O}_5$, CaFe_2O_4 , and Fe_3O_4 , were greatly increased by adding of CaO, which would be beneficial to subsequent reduction and iron extraction.

Author Contributions: Writing—original draft, G.W.; writing—review & editing, Y.C.; formal analysis, X.L. (Xiaoming Li); software, S.Y.; methodology, J.Z.; data curation, H.T.; investigation, X.L. (Xuteng Li). All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Natural Science Foundation of China (No.51674186, 51674185, 51774224) and National Undergraduate Innovation and Entrepreneurship Training Program (No. 201910703014) for financial support.

Acknowledgments: The authors are grateful to Ji'an Yang for theoretical analysis and linguistic assistance during the preparation of this manuscript.

Conflicts of Interest: The authors declare no conflict of interest, and we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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