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### EFFECT OF FeO CONTENT ON MELTING CHARACTERISTICS AND STRUCTURE OF NICKEL SLAG

Y.-T. Ma <sup>a</sup>, P. Yang <sup>b</sup>, B.-G Lu <sup>a</sup>, Y.-L. Dou <sup>a</sup>, J.-K. Tian <sup>b</sup>, W.-B. Guo <sup>b</sup>, Z.-Q. Zhang <sup>b</sup>, Y.-Y. Shen <sup>b,\*</sup>

<sup>a</sup> Ltd., Jinchang, State Key Laboratory of Comprehensive Utilization of Nickel-Cobalt Resources, Jin chuan Group Co., China

<sup>b</sup> Lanzhou University of Technology, School of Materials & Science, State Key Laboratory of Advanced Processing and Recycling of Non-ferrous Metals, Lanzhou, China

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### *Abstrac*t

Nickel smelting produces a large amount of nickel slag which contains a lot of Fe in the form of FeO. The effect of FeO content on the melting properties and structure of nickel slag is investigated by thermodynamic calculations and experiments, using the nickel slag of water quenching furnace as raw material, which is simplified to CaO-SiO<sub>2</sub>-FeO-MgO slag system. The results are as follows: with increasing FeO content, the precipitated primary phase changes from melilite to olivine. The liquidus temperature, softening temperature, hemispherical temperature, flow temperature, viscosity, and critical viscosity temperature of the slag system tend to decrease gradually, but the solid phase temperature tends to decrease first and then increase. The centre of the symmetric stretching vibration band of the  $[SiO_4]^4$  tetrahedron in the slag system shifts to the low wavenumber region. The mole fraction of  $O^0$  in the slag continuously decreases, and the mole fraction of  $O^2$  and  $O^2$ - increases. The complex silicon-oxygen tetrahedron structure gradually disintegrates and the structural unit tends to be simple.

Keywords: CaO-SiO,-FeO-MgO slag system; Nickel slag; FeO content; Melting properties, Structure

### 1. Introduction

Nickel is one of the most important strategic metals in China, especially for the development of high-tech and green energy in the national defense and military industry, which is mainly used in steel, nickel based alloy, electroplating, battery, and other fields. At present, about 90 % of nickel production capacity is produced by the pyrometallurgical processes with nickel sulfide ore as raw material [1]. Jinchuan Group has built the largest nickel production base in China, known as "nickel capital"[2]. With the smelting of nickel, the production of iron-rich metallurgical slag increases year by year, because low nickel matte is produced by blowing oxygen into a flash furnace, separating nickel and iron from raw materials, and leaving a lot of Fe in molten slag. In the metallurgical nickel slag, Fe mainly exists in the olivine phase including fayalite or hortonolite [3]. FeO is the main phase according to the molecular theory of slag at high temperature [4]. Viscosity is one of the most important physical properties of slag affecting the course of the chemical reaction, mass transfer rate, and precipitation and growth of the slag,

and thus also the service life of the furnace lining. The content of FeO not only has a decisive effect on the melting properties of the slag but also on the viscosity, which in turn affects the reaction between the slag and the metal, which is related to metal smelting. Many scientists have researched the effect of FeO on the properties of the slag system. Chuang believed that the melting temperature and viscosity of CaO-SiO<sub>2</sub>-MgO-Al<sub>2</sub>O<sub>3</sub> slag system could be decreased by increasing the FeO content [5]. Jiang investigated the effect of FeO content on the viscosity of CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-FeO, and the results show that with increasing FeO content, the viscosity of CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-FeO slag system gradually decreases [6]. Accordingly, it is essential to understand the effects of FeO on the viscosity of nickel slag at high temperatures.

If the temperature of the slag system is below the critical viscosity temperature, the number and type of phases will have a great effect on the viscosity of the slag system. However, when the temperature of the slag system is higher than the critical viscosity temperature, the viscosity of the slag system is mainly affected by the structure of the molten slag [7]. The viscous flow properties of slag are

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Corresponding author: shenyy@lut.edu.cn

macroscopic representations of its microstructure. Therefore, it has valuable significance to research the effect of slag structure on viscosity. In practical application, the structure of slag is characterized by means of Raman, Fourier Transform Infrared Spectroscopy (FT-IR), X-ray Photoelectron Spectroscopy (XPS) [8].

Nickel slag has a complex composition and many impurity elements, among which CaO, FeO, SiO<sub>2</sub> and MgO have a specific gravity of up to 94 wt%[7]. Therefore, according to the nickel slag composition, it is simplified to the CaO-SiO<sub>2</sub>-FeO-MgO quaternary slag system. Factsage thermodynamic software is composed of a sequence of information database, processing modules and calculation modules. In addition to the calculation of multi-element and multiphase equilibrium, it can also carry out the calculation of phase diagram, dominant region diagram, and thermodynamic optimization. The thermodynamics and mineral transformation in phase diagram is predicted by FactSage [9-11].

In this study, the effect of FeO content on the melting characteristics and structure of CaO-SiO<sub>2</sub>-FeO-MgO slag system is investigated based on thermodynamic calculations and experiments with the nickel slag of water quenching furnace from Jinchuan Group as raw material. The main purpose of this study is to reveal the mechanism of the influence of FeO content on the viscosity of molten slag, to quantify the dependence of the corresponding viscosity temperature characteristics on FeO.

# 2. Experimental Procedure 2.1. Experimental Materials

These experimental slags were synthesized by reference of the component of nickel slag from flash furnace quenched by water. The chemicals used in the experiments such as CaO, SiO<sub>2</sub>, MgO, and FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O were all analytical reagent (CaO, SiO<sub>2</sub> and MgO: Sinopharm Chemical Reagent Co. Ltd. Shanghai, China; FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O: Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China).

FeO was prepared from  $FeC_2O_4 \cdot 2H_2O$  as following: 1) The  $Fe_2O_4 \cdot 2H_2O$  powder was heated at 1000°C for 2h in a high temperature tube furnace and protected with 300 mL/min of argon throughout the process. 2) After cooling with furnace, it was ground to below 200 mesh [12, 13]. The corresponding chemical equation was shown as follow.

$$FeC_2O_4 \cdot 2H_2O_{(s)} \rightarrow FeO_{(s)} + CO_{(g)} \uparrow + CO_{2(g)} \uparrow \\ + 2H_2O_{(g)} \uparrow$$
(1)

The other reagents were heated to 1000 °C in the muffle furnace for 2 hours to remove moisture and volatile impurities.

#### 2.2. Experimental Method

Based on the main chemical composition of nickel slag, CaO-SiO<sub>2</sub>-FeO-MgO quaternary slag system (it was uniformly referred to as slag system below) was taken as the object of study, for ignoring the influence of other groups. According to the previous research, the content of CaO, MgO and SiO<sub>2</sub> in slag system is determined to make sure (wCaO+wMgO)/ $wSiO_2$  unchanged at 0.90 [14, 15]. At the same time, FeO content was changed from 6.00 wt% to 46.00 wt%. The chemical composition of the slag system was designed as shown in Table 1.

### 2.2.1. Preparation of premelted slag

(1) The chemical reagents are weighed accurately in the composition shown in Table 1, then ground in an agate mortar until it is well mixed.

(2) The well-mixed powder samples were poured into the mould, pressed into a cylinder with a diameter of 30 mm and a height of 10 mm by a tablet machine under the pressure of 20 MPa, and then moved into the corundum crucible.

(3) The crucible containing sample was placed in a high-temperature tubular furnace with a protective gas (flow rate of Ar gas is 200 mL /min). The temperature was raised to 1550 °C at a heating rate of 4 °C/min and kept for 2 hours, then cooled to room temperature at a rate of 5 °C/min.

(4) The premelted slag was crushed and passed through a 200 mesh screen to obtain the particles about 0.074 mm in size.

#### 2.2.2. Determination of melting temperature

The melting temperature was measured by LZ-III Slag Melting Temperature Characteristic Tester. The test method of melting temperature is according to the standard as follows [16]: 1) accurately weighed 10 g processed premelted slag, placed it into the mould, and pressed it into a cylinder with a diameter of 3 mm and a height of 3 mm. 2) placed the prepared sample on the corundum gasket, started to deliver the sample after heating to 500 °C, and warmed up for 60 seconds after moving to the furnace port, and

 Table 1. Chemical composition of modified slag system

 (wt%)

Slag system	CaO	MgO	SiO <sub>2</sub>	FeO
S1	31.36	13.17	49.47	6.00
S2	28.02	11.77	44.21	16.00
S3	24.68	10.37	38.95	26.00
S4	21.35	8.97	33.68	36.00
S5	17.99	7.75	28.39	46.00



continued to deliver the sample until it reached the middle position of the furnace tube. 3) when the temperature rose to 700 °C, the computer automatically adjusted the position of the scale screen to record the original height of the sample clearly. With the heating rate of 5 °C/min, the height of the sample dropped to 75%, 50% and 25%, the corresponding temperature was the softening temperature, hemispheric temperature, and the flow temperature of the sample, respectively [17-18]. During the whole process, Ar was used as protective gas with the flow of 300mL/min. The details of the equipment had been introduced in the previous paper [7].

### 2.2.3. Measurement of Viscosity

Premelted slag of 130 g wasplaced into the mould and pressed into a cylinder with a diameter of 30 mm and a height of 10 mm under the pressure of 20 MPa by the tablet machine. Then it was placed into the corundum crucible with a diameter of 40 mm and a height of 120 mm. At last the corundum crucible containing the sample was placed into the RTW-16 High Temperature Melt Performance Tester, and heated up to 1500 °C and kept for 2 hours. In the cooling process, the viscosity of the slag was measured by rotating torque method. The whole process was protected by 1.5 L/min argon gas. Before measuring the viscosity of the sample, the viscosity constant "K" should be calibrated first via the experiment of castor oil as the labelling fluid for viscosity calibration [7].

### 2.2.4. Preparation of water quenching slag

10 g of premelted slag of was put into the corundum crucible. Platinum wire was used to hang the crucible in a vertical quenching furnace for heating. The temperature was raised to 1500 °C at a heating rate of 3 °C/ min, kept for 2 h, and then quenched with water. It was protected by 300 mL/min Ar throughout the entire process. The water-quenched slag sample was dried in a vacuum oven for 10 h, then crushed and sieved to 200 mesh (0.074 mm).

### 2.3. Calculation Method by FactSage

In this paper, the phase diagram at Ar atmosphere was calculated via the Phase Diagram Module in FactSage7.1. The precipitation of the slag system in equilibrium solidification process with different FeO content is calculated by Equilib Module. The oxygen partial pressure was not considered and set to 10<sup>-6</sup> atm in the calculation process via phase diagram module of Factsage.

### 3. Results and Discussion

# 3.1. Effect of FeO Content on Melting Characteristics of the Slag System

Figure 1 shows the phase diagram of the slag system under the Ar atmosphere with different FeO content. The component of the samples in the phase region is located "n". The primary crystal is melilite when FeO content is less than 16.00 wt% (Figure 1a, b). When FeO content is more than 26.00 wt%, the primary crystal is transformed into olivine (Figure 1c~e). It indicates that the precipitated primary phase changes from melilite to olivine with the increase of FeO content. However, "n" is located on the boundary between olivine and monoxide when FeO content is 46 % (shown in Figure 1e). At the same time, when FeO content is 6.00~46.00 wt%, the liquidus temperature of the component point "n" gradually decreases with the FeO content increase, and the area of the liquid phase gradually expands at the same temperature. This is mainly because FeO has a lower melting point and is easy to form a low melting point compound with other substances in the slag system, which acts as the slagging agent. As FeO content increases, the phase area becomes simpler: Olivine phase area gradually increases, the area of the phase of melilite, clinopyroxene, Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>8</sub>, tridymite, cristobalite and  $\beta$ -CaSiO<sub>2</sub> is gradually reduced; When FeO content reaches 36.00 wt%, the phase regions of melilite, α-CaSiO<sub>3</sub> and Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> disappear; When FeO content reaches 46.00 wt%, the phase regions of clinopyroxene,  $Ca_3MgSi_2O_8$  and  $\beta$ -CaSiO<sub>3</sub> disappear.

FactSage 7.1 was used to calculate the relationship between liquid phase content and temperature of the slag system with different FeO content, as shown in Figure 2; the effect of FeO content on the solidus temperature and liquidus temperature of the slag system was shown in Figure 3. The liquidus temperature of slag system decrease as FeO content increases from 6.00 wt% to 46.00 wt%; in contrast, the solid phase temperature decreases first and then increases. It should be noted that the range of 16.00~36.00 wt%, the liquidus temperature does not change significantly, but the solidus temperature decreases gradually. When FeO content is 36.00 wt%, the solidus temperature reaches its lowest point, which is 1169 °C; The temperature range of solidliquid two-phase coexistence region increases first and then decreases. The speculated reason is shown as follows: FeO has a low melting point and easily forms the low melting point compound with other substances in the slag system, resulting in the liquidus temperature of slag system decrease gradually. But when the content of FeO in slag system exceeds a certain amount, the slag system reflects the characteristics of olivine due to the increases olivine content.





Figure 1. Phase diagram of the slag system with different FeO; contents: (a) FeO=6.00 wt%; (b) FeO=16.00 wt%; (c) FeO=26.00 wt%; (d) FeO=36.00 wt%; (e) FeO=46.00 wt%



Figure 2. The content of liquid phase in the slag system with different temperature



Figure 3. Effect of FeO content on solidus temperature and liquidus temperature of slag system



Figure 4 shows the effect of FeO content on the melting temperature of slag system via experimentally determined. When FeO content is in the range of  $6.00 \sim 46.00$  wt%, the softening temperature, hemisphere temperature, and the flow temperature of the slag system gradually decrease with the increase of FeO content. This is mainly because FeO easily forms low-melting substance with CaO and SiO<sub>2</sub>, such as olivine, reducing the melting temperature of the slag system. Compared with Figure 3, it can be seen that the law of experimentally determined is consistent with the calculation result of FactSage 7.1, except for the FeO content of 46.00 wt%. Combined with the previous research, FactSage can be used to analyze the melting characteristics of slag system.



Figure 4. Effect of FeO content on the melting temperature of slag system

# 3.2. Effect of FeO content on the viscosity of the slag system

3.2.1. Effect of FeO content on the viscositytemperature curve of the slag system

Figure 5 shows the viscosity-temperature curve of the slag system with different FeO content via experimentally determined. It can be seen from the figure that the viscosity of the slag system decreases



Figure 5. Viscosity-temperature curve of slag system with different FeO content

with the increase of temperature. When FeO content is 6.00 wt%, the viscosity shows a significant downward trend with the temperature increase, but no mutation. When the temperature is above 1400 °C and FeO content is in the range of  $16.00 \sim 46.00 \text{ wt\%}$ , the viscosity tends to stabilize with the increase of temperature, which is caused by the change of the slag structure. If the temperature is lower than 1400 °C, the viscosity of the slag system changes significantly at different temperatures with the decrease of temperature due to the type and quantity of the precipitate phase of slag system. At the same time, acidic slag gradually changes to alkaline slag from the FeO content of 36.00%.

Figure 6 shows the influence of FeO content on the viscosity of slag system at different temperatures. When the temperature of 1400~1500 °C and FeO content of 6.00~46.00 wt%, with the increase of FeO content at the same temperature, the slag viscosity gradually decreases. When FeO content decreases from 26.00 wt% to 6.00 wt%, the precipitated solid phase changes the slag system from molten state to heterogeneous state, which leads to the sharp increase of viscosity value. When FeO content increases from 6.00 wt% to 26.00 wt% at the temperature of 1500 °C, the viscosity is reduced from 0.394 Pa·s to 0.134 Pa·s. When FeO content continues to increase to 46.00 wt%, viscosity decreases slowly to 0.096 Pa.s. This can provide a basis for nickel sulfur smelting and slag discharge in flash furnace.



Figure 6. Relationship between FeO content and viscosity at different temperatures

### 3.2.2. Effect of FeO Content on the critical viscosity temperature of slag system

The viscosity increases gradually when the slag is cooled from the liquid phase. Critical viscosity temperature  $(T_{\rm ev})$  refers to a critical point of the temperature in the cooling process that the viscosity will increase rapidly [19].  $T_{\rm ev}$  indicates a point of abrupt change in the viscosity-temperature relationship. This temperature is recognized as a sharp



break in the viscosity-temperature curve and marks the division between crystal-affected viscosity and viscosity not affected by the presence of crystals [20]. In order to measure the viscosity of molten slag, the temperature of slag system must be much higher than the critical viscosity temperature, or even the fully liquid phase [21]. In this study, the method of determining the critical viscosity temperature is to make two tangents on the viscosity-temperature curve, and the temperature corresponding to the intersection of the tangents is the critical viscosity temperature [22]. Figure 7 shows the critical viscosity temperature of the slag system with different FeO content determined by the viscosity-temperature curve.

The comparison of the critical viscosity

temperature and the flow temperature of the slag system is shown in Figure 8. When FeO content is 6.00~46.00 wt%, the critical viscosity temperature gradually decreases with the increase of FeO content, which is in line with the flow temperature of the slag system. When FeO content is 6.00 wt%, 16.00 wt%, 26.00 wt%, 36.00 wt%, and 46.00 wt%, the corresponding critical viscosity temperatures are 1340 °C, 1301 °C, 1284 °C, 1270 °C, and 1263 °C, respectively. And the critical viscosity temperature of the slag system is lower than the flow temperature, which is consistent with the actual situation. It reveals that the viscosity will increase and the fluidity will become worse due to the precipitation of the solid phase when the temperature is lower than the flow temperature. When the precipitated solid phase



Figure 7. Critical viscosity temperature of slag system with different FeO content: (a) FeO=6.00 wt%; (b) FeO=16.00 wt%; (c) FeO=26.00 wt%; (d) FeO=36.00 wt%; (e) FeO=46.00 wt%



Figure 8. Comparison of the critical viscosity temperature and the flow temperature of slag system with different FeO content

reaches a certain amount, the solid phase will start to separate from the liquid phase slag, and the viscosity will increase rapidly.

# *3.2.3.* Effect of phase precipitation with different FeO content on the viscosity of slag system

Figure 9 shows the effect of phase precipitation on the viscosity of slag system with different FeO content. The phase precipitation at different temperature is calculated by FactSage 7.1. The molten slag with 6.00 wt% FeO precipitates melilite, clinopyroxene, and the  $\lambda$ -CaSiO<sub>3</sub> in the process of cooling down. The primary phase "melilite" is precipitated when the temperature is 1340°C. As the temperature decreases, the viscosity value increases



*Figure 9.* Effect of phase precipitation on viscosity of the slag system with different FeO content: (a) FeO=6.00 wt%; (b) FeO=16.00 wt%; (c) FeO=26.00 wt%; (d) FeO=36.00 wt%; (e) FeO=46.00 wt%



significantly. When FeO content is 16.00 wt%, melilite as the primary phase is precipitated in the slag at the temperature of 1301°C. When FeO content is 26.00 wt% and 36.00 wt%, olivine begins to precipitate in the slag first. And when the temperature drops to 1284°C and 1270°C, the viscosity increases sharply. According to the calculation of FactSage, olivine precipitates at this time is 24.47 wt% and 35.32 wt%, respectively, indicating that the olivine phase separated from the liquid slag is at 1284 °C and 1270°C. When FeO content is 46.00 wt%, olivine precipitates in the slag first, and then monoxide appears. When the temperature drops to 1263°C, the viscosity increases sharply. At this time, 24.89 wt% of olivine and 3.24 wt% of monoxide has precipitated which leads to the abrupt change of slag viscositytemperature curve.

### 3.3. Effect of FeO content on the structure of slag system

Figure 10 shows the FT-IR spectra of slag system with different FeO content. When the temperature of molten slag is higher than critical viscosity temperatures, the structure has a significant effect on the viscosity. The main melt structure in acid slag is  $[SiO_4]^4$ .  $[SiO_4]^4$  tetrahedron symmetric stretching vibration zone is between 800~1250 cm<sup>-1</sup> that is divided into four categories of Si-O zones: (Q<sup>3</sup>, layered) 1100~1150 cm<sup>-1</sup>, (Q<sup>2</sup>, chain) 950~980 cm<sup>-1</sup>,  $(Q^1, dimer)$  900~920 cm<sup>-1</sup>, and  $(Q^0, monomer)$ 850~880 cm<sup>-1</sup> [23, 24]. Q<sup>3</sup>, Q<sup>2</sup>, Q<sup>1</sup>, and Q<sup>0</sup> represent that the amount of oxygen atoms linked to each silicon atom is 3, 2, 1, and 0, respectively. It indicates that FeO content has a great influence on the slag structure. When FeO content is in the range of 6.00~46.00 wt%, the centre position of the  $[SiO_4]^{4-}$ tetrahedral symmetrical stretching vibration band shifts to lower wave number with the FeO content increase. The Si-O bands corresponding to Q<sup>0</sup> and Q<sup>1</sup> gradually approach the centre of the [SiO<sub>4</sub>]<sup>4-</sup> tetrahedral symmetric stretching vibration band and the depth of valley gradually deepen. The Si-O bands corresponding to  $Q^3$  gradually moves away from the centre of the [SiO4]4- tetrahedral symmetric stretching vibration band and the depth of valley gradually becomes shallower.  $Q^2$  does not change significantly. It indicates that as FeO content increases, the silicate network structure gradually develops from complex to simple [25]. This is mainly because FeO is the basic oxide, as a network modifier, which destroys the silicate network structure and decomposes the siliconoxide anion group. With the increase of FeO content, the connection mode of silicon-oxygen tetrahedral gradually changes from layered (Q<sup>3</sup>) to chain (Q<sup>2</sup>), then to dimer (Q<sup>1</sup>), and finally decomposed into monomer (Q<sup>0</sup>). The viscosity of slag decreases gradually as the structure of melt becomes simpler [26].

On the other hand, the type of oxygen atom is often used to describe the structure of the molten slag. There are three types of oxygen, shown as follows: 1)  $O^0$  named bridging oxygen where the oxygen atom is connected to two silicon atom. 2) O<sup>-</sup> named nonbridging oxygen where the oxygen atom is connected to a silicon atom. 3) O<sup>2-</sup> named free oxygen where the oxygen atom is not connected to the silicon atom [27]. The schematic disintegration of the silicate structure by FeO is shown in Figure 11. Free oxygen can be generated from FeO in the molten slag and enter the silicate system, meanwhile destroying the bridge oxygen bonding in the silicate structure. The



Figure 10. FT-IR spectra of slag system with FeO content



Figure 11 Schematic disintegration of silicate structure by FeO



complicated silicate network structure changes into a simple silicate structure and a large number of nonbridged oxygen appears for this reason. For instance, as combining with the free oxygen released by the FeO, the main structure of  $[Si_3O_9]^{6-}$  decomposes into a dimeric structure of  $[Si_2O_7]^{6-}$  and a monomeric structure unit of  $[SiO_4]^{4-}$ , while the cation of Fe will act as a balancing charge.

The peaks of  $O_{1s}$  in the XPS spectrum are fitted and decomposed into peaks corresponding to three different types of oxygen atoms in order to analyze the effect of FeO content on oxygen atoms in the slag; the results as shown in Figure 12. The XPS peak has been calibrated through Au calibration. The ratio of the integrated acreage of different types of oxygen atoms peak to the integrated acreage of the  $O_{1s}$  peak is used to obtain the mole fraction. Table 2 reveals the location of  $O^0$ ,  $O^-$ ,  $O^{2-}$  and the mole fractions after fitting the oxygen atom peaks with different FeO content.

Figure 13 shows the effect of FeO content on the mole fraction of different kinds of oxygen atoms in water quenching slag samples. When FeO content is  $6.00{\sim}46.00$  wt%, with FeO content increases, the mole fraction of O<sup>0</sup> continuously decreases, but the mole fraction of O<sup>-</sup> and O<sup>2-</sup> continuously increases. It indicates that the complex silicon-oxygen tetrahedron structure gradually disintegrates and the structural unit tends to be simple. It leads to a gradual decrease in viscosity, which is consistent with the results obtained by FT-IR spectra and the viscosity experiment.



*Figure 12.* The XPS peaks fitting spectrum of O<sub>1s</sub> in water quenching slag samples with different FeO content: (a) FeO=6.00 wt%; (b) FeO=16.00 wt%; (c) FeO=26.00 wt%; (d) FeO=36.00 wt%; (e) FeO=46.00 wt%



FeO	$O^0$		O <sup>-</sup>		O <sup>2-</sup>	
Content(wt%)	Position (eV)	Mole fraction	Position (eV)	Mole fraction	Position (eV)	Mole fraction
6.00	532.35	49.76%	531.29	33.45%	530.40	16.79%
16.00	532.25	47.62%	531.25	34.62%	530.38	17.76%
26.00	532.18	43.86%	531.23	34.87%	530.39	21.27%
36.00	532.13	41.63%	531.18	36.56%	530.33	21.80%
46.00	532.27	38.46%	531.29	36.94%	530.21	24.60%

Table 2. Fitting positions and mole fractions of different types of oxygen atoms in slag system with different FeO content



Figure 13. Curves of the mole fractions of different types of oxygen atoms with FeO content

### 4. Conclusion

As the FeO content increases, the precipitated primary phase changes from melilite to olivine. The liquidus temperature tends to decrease, and the solid phase temperature first decreases and then increases. The softening temperature, hemispherical temperature and slag system flow temperature all show a decreasing trend.

(2) The FeO content has a significant effect on the slag viscosity. As the FeO content increases, the viscosity and critical viscosity temperature of the slag system gradually decrease. The critical viscosity temperature of the slag system is mainly affected by the type and amount of solid precipitatates.

(3) The FeO content has a significant effect on the slag structure. With increasing FeO content, the centre of the symmetric stretching vibration band of the  $SiO_4$ ]<sup>4-</sup> tetrahedron in the slag system shifts to the low wave number region. The mole fraction of O<sup>0</sup> in the slag continuously decreases, and the mole fraction of O<sup>-</sup> and O<sup>2-</sup> increases. The complex silicon-oxygen tetrahedral structure gradually disintegrates and the structural unit tends to be simple.

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#### **Author's Contributions**

Y.-T. Ma: organization; P. Yang, B.-G Lu, Y.-L. Dou, J.-K. Tian, W.-B. Guo, Z.-Q. Zhang: experiment, test and validation; Y.-Y. Shen: writing-original draft.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Reference

- D. S. Wu, Summarization on the developments of nickel smelting technique, Hunan Nonferrous Metals, 27(01) (2011) 17-19+47. (In Chinese)
- [2] Z. Q. Yang, Y. Q. Wang, Q. Gao, H. Wang, Present research situation and prospect of nickel utilization of wastes in filling mining technology in jinchuan mine, Multipurpose Utilization of Mineral Resources, (3) (2017) 22-28. https://doi.org/10.3969/j.issn.1000-6532.2017.03.003
- [3] Y. Y. Shen, M. Chen, Y. Y. Zhang, Influence of temperature control system on the crystallisation behaviour of magnetite phases in nickel Slags, Steel Research International, 89 (2017) 1700300. https://doi.org/10.1002/srin.201700300
- [4] Y. W. Tian, X. J. Zhai, K. R. Liu, A concise course of metallurgical physical chemistry, Chemical Industry Press, Beijing, 2007, 119-122. (In Chinese)
- [5] H. C. Chuang, W. S. Hwang, S. H. Liu, Effects of basicity and FeO content on the softening and melting temperatures of the CaO-SiO<sub>2</sub>-MgO-Al<sub>2</sub>O<sub>3</sub> slag system, Materials Transactions, 50 (6) (2009) 1448-1456. https://doi.org/10.2320/matertrans.MRA2008372
- [6] L. Jiang, Fundamental research on the structure and viscosity of molten CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-FeO slag,



Chongqing University, Chongqing, 2015. (In Chinese)

- [7] Y. Y. Shen, J. K. Chong, Z. N. Huang, Viscosity and structure of a CaO-SiO<sub>2</sub>-FeO-MgO system during a modified process from nickel slag by CaO, Materials, 12 (2019) 2562. https://doi.org/10.3390/ma12162562
- [8] X. Dai, J. Bai, Q. Huang, Z. Liu, X. J. Bai, R. G. Cao, X. D. Wen, W. Li, S. Y. Du, Viscosity temperature properties from molecular dynamics simulation: The role of calcium oxide, sodium oxide and ferrous oxide, Fuel, 237 (2019) 163-169. https://doi.org/10.1016/j.fuel.2018.09.127
- [9] W. J. Song, L. H. Tang, X. D. Zhu, Y. Q. Wu, Y. Q. Rong, Z. B. Zhu, S. Koyama, Fusibility and flow properties of coal ash and slag, Fuel, 88 (2) (2008) 297-304. https://doi.org/10.1016/j.fuel.2008.09.015
- [10] W. J. Song, L. H. Tang, X. D. Zhu, Y. Q. Wu, Y. Q. Rong, Z. B. Zhu, S. Koyama, Flow properties and rheology of slag from coal gasification, Fuel, 89 (7) (2009) 1709-1715.
  - https://doi.org/10.1016/j.fuel.2009.07.013
- [11] W. J. Song, L. H. Tang, X. D. Zhu, Y. Q. Wu, Y. Q. Rong, Z. B. Zhu, S Koyama, Effect of coal ash composition on ash fusion temperatures, Energy&Fules, 24 (1) (2010) 182-189. https://doi.org/10.1021/ef900537m
- [12] Y. Gao, C. Duan, Y. Yang, R. Dong, C. Yang, C. Hong, Effect of applied voltage on electroreduction with controlled oxygen flow of molten slag containing FeO at 1723 K, ISIJ International, 55 (11) (2015) 2273-2282. https://doi.org/10.2355/isijinternational.ISIJINT-2014-826
- [13] C. Y. Sun, X. M. Guo, Electrical conductivity of MO (MO = FeO, NiO)-containing CaO-MgO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag with low basicity, Transactions of Nonferrous Metals Society of China, 21 (7) (2011) 1648-1654. https://doi.org/10.1016/S1003-6326(11)60909-6
- [14] G. Z. Li, Y. Y. Shen, Y. B. Ma, Effect of basicity on precipitation and growth of magnetite phase from modified molten nickel slag, The Chinese Journal of Process Engineering, 17 (04) (2017) 791-796. https://doi.org/10.12034/j.issn.1009-606X.216377
- [15] Y. Y. Shen, Z. N. Huang, Y. Y. Zhang, Transfer behavior of Fe element in nickel slag during molten oxidation and magnetic separation processes, Materials Transactions, 59 (10) (2018) 1659-1664. https://doi.org/10.2320/matertrans.M2018002
- [16] Standard Test Method for Fusibility of Coal and Coke Ash, ASTM International, 05 (06) (2003) 1-4. https://doi.org/10.1520/D1857-03
- [17] A. Boccaccini, B. Hamann, Review in situ hightemperature optical microscopy, Journal of Materials Science, 34 (1999) 5419-5436. https://doi.org/10.1023/A:1004706922530
- [18] L. Wang, C. Zhang, D. Cai, J. Q. Zhang, Y. Sasaki, O. Ostrovski, Effects of CaO/SiO<sub>2</sub> ratio and Na<sub>2</sub>O content on melting properties and viscosity of SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O mold fluxes, Metallurgical and Materials Transactions B, 48 (2016) 516-526. https://doi.org/10.1007/s11663-016-0816-5
- [19] P. Y. Hsieh, K. S. Kwong, J. Bennett, Correlation between the critical viscosity and ash fusion temperatures of coal gasifier ashes, Fuel Processing Technology, 142 (2016) 13-26. https://doi.org/10.1016/j.fuproc.2015.09.019
- [20] W. J. Song, Y. H. Dong, Y. Q. Wu, Prediction of temperature of critical viscosity for coal ash slag, Aiche

Journal, 57 (10) (2011) 2921-2925. https://doi.org/10.1002/aic.12500

- [21] H. C. Chuang, W. S. Hwang, S. H. Liu, Effects of basicity and FeO content on the softening and melting temperatures of the CaO-SiO<sub>2</sub>-MgO-Al<sub>2</sub>O<sub>3</sub> slag system, Materials Transactions, 50 (6) (2009) 1448-1456. https://doi.org/10.2320/matertrans.MRA2008372
- [22] S. Vargas, F. J. Frandsen, K. Dam-Johansen, Rheological properties of high-temperature melts of coal ashes and other silicates, Progress in Energy and Combustion Science, 27 (2001) 237-429. https://doi.org/10.1016/S0360-1285(00)00023-X
- [23] H. Park, J. Y. Park, G. H. Kim, I. Sohn, Effect of TiO<sub>2</sub> on the viscosity and slag structure in blast furnace type slags, Steel Research International, 83 (2012) 150-156. https://doi.org/10.1002/srin.201100249
- [24] B. O. Björkman, G. Eriksson, E. Rosén, A generalized approach to the flood-knapp structure based model for binary liquid silicates: Application and update for the PbO-SiO<sub>2</sub> System, Metallurgical and Materials Transactions B, 15 (1984) 511-516. https://doi.org/10.1007/BF02657381
- [25] X. M. Lv, X. W. Lv, L. W. Wang, J. Qiu, M. Liu, Viscosity and structure evolution of the SiO<sub>2</sub>-MgO-FeO-CaO-Al<sub>2</sub>O<sub>3</sub> slag in ferronickel smelting process from laterite, Journal Of Mining And Metallurgy Section B-Metallurgy, 53 (2) 2017 147-154. https://doi.org/10.2298/JMMB150911002L
- [26] J. H. Park, D. J. Min, H. S. Song, Amphoteric behavior of alumina in viscous flow and structure of CaO-SiO<sub>2</sub>(-MgO)-Al<sub>2</sub>O<sub>3</sub> slags, Metallurgical and Materials Transactions B, 35 (2004) 269-275. https://doi.org/10.1007/s11663-004-0028-2
- [27] C. Fincham, F. D. Richardson, The behaviour of sulphur in silicate and aluminate melts, Proceedings Of The Royal Society A: Mathematical, Physical And Engineering Sciences, 223 (1152) (1954) 40-62. https://doi.org/10.1098/rspa.1954.0099



### UTICAJ FeO SADRŽAJA NA SVOJSTVA TOPLJENJA I STRUKTURU NIKLOVE ŠLJAKE

### Y.-T. Ma <sup>a</sup>, P. Yang <sup>b</sup>, B.-G Lu <sup>a</sup>, Y.-L. Dou <sup>a</sup>, J.-K. Tian <sup>b</sup>, W.-B. Guo <sup>b</sup>, Z.-Q. Zhang <sup>b</sup>, Y.-Y. Shen <sup>b,\*</sup>

<sup>a</sup> Ltd., Jinčang, Glavna državna laboratorija za sveobuhvatnu primenu nikl-kobalt resursa, Jin čuan Group Co., Kina

<sup>b</sup> Lanzhou tehnološki univerzitet, Fakultet za nauku o materijalima, Glavna državna laboratorija za naprednu obradu i recikliranje obojenih metala, Lanzhou, Kina

### Apstrakt

Topljenjem u proizvodnji nikla nastaje velika količina niklove šljake, koja sadrži dosta Fe u obliku FeO. Termodinamičkim proračunima i eksperimentima istražen je uticaj sadržaja FeO na svojstva topljenja i strukturu niklove šljake, koristeći kao sirovinu vodom hlađenu niklovu šljaku, koja je pojednostavljena do sistema šljake CaO-SiO<sub>2</sub>-FeO-MgO. Rezultati su sledeci: sa povećanjem sadržaja FeO, istaložena primarna faza prelazi iz melita u olivin. Temperatura likvidusa, temperatura omekšavanja, hemisferna temperatura, temperatura protoka, viskozitet i temperatura kritične viskoznosti sistema šljake imaju tendenciju da se postepeno smanjuju, ali temperatura čvrste faze ima tendenciju da se prvo smanji, a zatim poveća. Centar simetrične vibracione zone istezanja [SiO<sub>4</sub>]<sup>4</sup>-tetraedra u sistemu šljake pomera se u oblast niskog talasnog broja. Molski udeo  $O^0$  u šljaci kontinuirano opada, a molski udeo  $O^-$  i  $O^{2-}$  raste. Složena struktura silicijum-kiseonik tetraedra postepeno se dezintegriše i strukturna jedinica teži da bude jednostavna.

Ključne reči: CaO-SiO,-FeO-MgO sistem šljake; Niklova šljaka; Sadržaj FeO; Svojstva topljenja; Struktura