Recovery of Fe, Ni, Co, and Cu from Nickel Converter Slag through Oxidation and Reduction

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The conventional method of nickel converter slag dilution is reduction–sulfurization by adding coal and pyrite into the slag. In this study, the effect of sulfur content in the initial slag ((pct S)0) on the slag dilution process was determined by producing metal, which is significantly different from the conventional method producing matte. Analysis of the nickel converter slag showed that nickel, cobalt, and copper were mainly present in the form of sulfides, which are difficult to separate from the slag. The NiO, CoO, and Cu2O in the slag are easily reduced into metal using carbon, while the presence of sulfur inhibits the reduction reaction. In a vertical resistance furnace, the desulfurized slags with different sulfur contents were reduced using carbon. The sulfur distribution rate increased with the decrease in (pct S)0, the distribution rate of nickel, cobalt, and copper decreased with the decrease in (pct S)0. The nickel recovery rate increased with the decrease in (pct S)0, while (pct S)0 almost had no effect on the recovery of iron, cobalt, and copper. The distribution rates of sulfur, nickel, and copper increased with the increase in mole ratio of carbon to reducible oxygen (nC/nO), while the distribution rate of iron and cobalt decreased with the increase in nC/nO. In addition, the recovery rates of iron, nickel, cobalt, and copper increased with the increase in nC/nO.

KEY WORDS: nickel converter slag; desulfurization; metal sulfide; reduction; desulfurized slag.

1. Introduction

When low-grade nickel matte is blown into a converter to produce high-grade nickel matte, a large amount of slag is generated, which contains many valuable elements, such as Ni, Co, and Cu.1) Generally, nickel converter slag is diluted in an electric dilution furnace by adding coal and pyrite, then the slag is discharged from the upper outlet of the furnace, and the matte is discharged from the lower outlet; however, the process requires a long treatment time and has a poor dilution effect because coal is always floating on the surface of the molten slag.2)

The FeOx–SiO2 slag system constitutes the main part of nickel converter slag, where a variety of metals exist in the dissolved state or as inclusions.3) Nickel mainly exists in the sulfide form (Ni3S2), while some of the nickel is dissolved in fayalite in the oxide form. Cobalt is mostly distributed in the silicate in the form of oxides (CoO), while almost all the copper is dispersed in the slag in the sulfide form (Cu2S). Owing to the violent agitation in the converter causing poor separation of the slag and matte, a large number of matte particles are dispersed in the molten slag even after dilution, which is the main reason for the loss of nickel and copper in nickel converter slag.4,5)

The key factors affecting the separation of matte from slag are the interfacial tension, density difference, and viscosity of slag.6,8) The interfacial tension between matte and slag determines the precipitation and growth of matte in molten slag. Reducing the Fe/SiO2 and improving the matte grade will increase the interfacial tension, which can promote the precipitation and growth of nickel matte.9) The low Fe/SiO2 grade and high matte grade causing a low slag density and high matte density, that is, a considerable density difference between matte and slag, can also enhance the matte drop settlement and shorten the dilution time. The lower viscosity of slag can improve its fluidity and reduce the resistance during matte particle movement in the slag, resulting in a better separation of matte from slag. The viscosity of slag will decrease with an increasing temperature and a decreasing Fe3O4 content. The viscosity of FeOx–SiO2 (Fe/SiO2 = 1.36) slag reduced from 0.120 Pa·s to 0.045 Pa·s with the temperature rising from 1 523 K to 1 773 K in a study by Chen et al.10) With the high oxygen potential in the converter, the FeO is easily oxidized into Fe2O3 and decomposition is difficult. The solid particles of Fe2O3 will significantly increase the viscosity of the slag and prevent the separation of the matte from the molten slag. In the slag dilution electric furnace, Fe3O4 in the slag can be reduced into FeO and the slag temperature rises through the input of electrical energy, both of which can significantly reduce the viscosity of the slag. If the slag is further reduced using carbon, there will be some liquid metals, which are easier to separate from the slag than from the matte. Compared to
the matte, the metal has higher Fe and lower S, that is, a greater density and greater interfacial tension than the slag (Table 1); as the slag is further reduced, the Fe$_2$O$_3$ and Fe/SiO$_2$ contents in the slag will decrease, then the viscosity decreases, and the interfacial tension increases.

The sulfur present in the slag does not participate in the reduction reaction. NiO is extremely prone to reduction by CO, while Ni$_3$S$_2$ is difficult to reduce. The sulfur content in the slag increases the ratio between the sulfides and oxides of nickel, cobalt, and copper. Therefore, sulfur will remain in the melt during the reduction process. When the sulfur in metal is saturated, matte, which is easily dispersed in the slag, will precipitate. Therefore, if there is only metal and no matte in the reduction product, it is necessary to reduce the initial sulfur content in the slag. However, the reduction of sulfur will significantly increase the melting point of the alloy, which will cause poor separation of slag and metal. Hence, the sulfur content in the slag–metal system has a two-sided effect on the separation of metal elements. Studies on the effect of sulfur content on the distribution of metal elements have considerable significance for the recovery of metal elements from slag.

Based on the above discussion, if the sulfur in slag is oxidized into SO$_2$ and discharged, then oxides, such as FeO$_x$, NiO, CoO, and CuO, are reduced to their corresponding metals. From this, the following advantages can be achieved: (1) Forming the two phases of metal and slag, rather than matte and slag, causing an increase in interfacial tension and density difference; (2) reducing the oxidation of slag and FeO$_x$ content in slag, causing a decrease in slag viscosity, both of which are beneficial to the separation of metals from slag. In this study, nickel converter slag was desulfurized using Fe$_2$O$_3$, then the slags with different sulfur contents were analyzed. The slag was set in epoxy to form a polished cross-section and was analyzed using a Phenom Pro X scanning electron microscope (SEM) equipped with a wavelength dispersive X-ray spectroscopy (WDS) system. The raw materials and slag and alloy from the experiment were sent to the Testing Center of USTB Co., Ltd. for chemical analysis. The content of Fe$_2$O$_3$ in slag cannot be detected directly, but it can be calculated by detecting the total Fe and FeO in the slag.

### 2. Materials

Nickel converter slag from a domestic smelter factory (Jilin Jien Nickel Industry) was used in the experiments without dilution. The slag was cooled and directly taken to the laboratory for performing experiments. The nickel converter slag samples were dried for 6 hr at 383 K to remove any remaining moisture. The slag was crushed and ground until ≥ 95% of the particles became less than 100 mesh. This powder was then used for the subsequent analyses. The chemical compositions of the nickel converter slag determined via chemical analysis are listed in Table 2. Ferric oxide powder (pct Fe$_2$O$_3$ ≥ 99.0 wt.%) was used as the oxidizer, and graphite powder (pct C ≥ 99.0 wt.%) was used as the reducing agent.

#### 2.2. Experiments and Results

The microstructure of the lump of the dried nickel converter slag was analyzed. The slag was set in epoxy to form a polished cross-section and was analyzed using a Phenom Pro X scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS) system. The raw materials and slag and alloy from the experiment were sent to the Testing Center of USTB Co., Ltd. for chemical analysis. The content of Fe$_2$O$_3$ in slag cannot be detected directly, but it can be calculated by detecting the total Fe and FeO in the slag.

The experiments were conducted in a tubular furnace (with a maximum internal furnace temperature of 1 873 K) using Ar as the protective gas at 50 mL/min. Figure 1 shows a schematic illustration of the experimental setup. The sample mixture was placed in an alumina crucible (φ40 mm × 90 mm) and held in an alumina safety crucible (φ60

### Table 1. Chemical composition of nickel converter slag (wt.%).

| Element | Fe | Ni | Co | Cu | S | Fe$_2$O$_3$ | SiO$_2$ | CaO | MgO | Al$_2$O$_3$ |
|---------|----|----|----|----|---|----------|--------|-----|-----|----------|
| Value   | 43.20 | 3.51 | 0.60 | 0.92 | 1.53 | 3.06 | 29.20 | 0.11 | 0.83 | 0.48 |

#### Table 2. Melt density and interfacial tension of alloy–slag system.

| Parameter            | Value            | Melt System                         | Reference |
|----------------------|------------------|-------------------------------------|-----------|
| Density $\rho_{\text{mat}}$ (g/cm$^3$) | 3.68–3.69          | FeO$_x$–SiO$_2$–Al$_2$O$_3$       | S. W. Ip$^{11}$ |
|                      | 3.61–3.69          | FeO$_x$–SiO$_2$–MgO                 | S. W. Ip$^{11}$ |
|                      | 2.794–2.836        | FeO$_x$–SiO$_2$–CaO–Al$_2$O$_3$     | H. Sun$^{32}$ |
| Density $\rho_{\text{mat}}$ (g/cm$^3$) | 3.82–5.18          | Fe–Ni–S                           | S. W. Ip$^{11}$ |
|                      | 5.18–5.25          | Fe–Cu–Ni–S                        | S. W. Ip$^{11}$ |
|                      | 3.92–5.59          | Ni–Cu–S                           | J. E. Mungall$^{11}$ |
| Density $\rho_{\text{metal}}$ (g/cm$^3$) | 7.1–8.0           | Ni–Cu–Fe                           | J. Brillo$^{11}$ |
|                      | 6.905–7.25         | Fe                               | A. Sharan$^{11}$ |
|                      | 7.60–7.73          | Ni                               | A. Sharan$^{11}$ |
|                      | 7.22–7.62          | Co–Cu–Fe                          | J. Brillo$^{11}$ |
| Interfacial Tension $\gamma_{\text{mat-slag}}$ (N/m) | 0.005–0.180        | Fe–Ni–S & FeO$_x$–SiO$_2$–Al$_2$O$_3$ | S. W. Ip$^{11}$ |
|                     | 0.026–0.192        | Fe–Ni–S & FeO$_x$–SiO$_2$–MgO      | S. W. Ip$^{11}$ |
| Interfacial Tension $\gamma_{\text{metal-slag}}$ (N/m) | 0.960–1.670      | Fe–Ni & CaO–SiO$_2$–Al$_2$O$_3$   | A. Sharan$^{11}$ |
|                     | 1.049–1.133        | Fe–Ni & CaO–SiO$_2$–Al$_2$O$_3$    | H. Sun$^{30}$ |
mm × 150 mm) to protect the furnace tube from inner crucible failure. The furnace temperature was increased from room temperature (approximately 298 K) to 1 273 K at a rate of 10 K/min. The crucible containing the sample was placed in the tubular furnace at 1 273 K for 30 min; then the temperature was further increased to 1 573 K in 60 min and kept at 1 573 K for 30 min.

The Fe₂O₃ (0–40.0 g) and nickel converter slag (100.0 g) were mixed, and the mixture in the alumina crucible was placed in the furnace at 1 273 K. Then the temperature was further increased to 1 573 K and maintained for 60 min. Then the desulfurized slag was quenched. Part of the cooled desulfurized slag was used for analyses and the other part was used as the material for the next carbon thermal reduction experiment.

It was assumed that iron, nickel, cobalt, and copper in the desulfurized slag existed as Fe₂O₃, FeO, NiO, CoO, and Cu₂O when participating in the carbothermal reduction reaction. The gaseous product of the reduction reaction was only CO. The concentration of the added carbon powder is expressed as the mole ratio of carbon to reducible oxygen (n_C/n_O) instead of mass% to meaningfully represent the significance of the carbon addition. In the (n_C/n_O) value,

### Table 3. Experimental data of oxidation and reduction.

| No. | Addition of Fe₂O₃/g | Desulphurized slag/wt.% | Separation Temperature T/K | Mass of slag/g | Slag composition after separation/wt.% | Mass of alloy/g | Alloy composition after separation/wt.% |
|-----|---------------------|------------------------|-----------------------------|----------------|---------------------------------------|----------------|---------------------------------------|
|     |                     |                         |                             |                | (pct Fe) (pct Ni) (pct Co) (pct Cu) (pct S) (pct SiO₂) (pct S) |                | (pct Fe) (pct Ni) (pct Co) (pct Cu) (pct S) |
| 1   | 0                   | 1.50                    | 52.82                        | 3.17           | 1 773                                 | 0.1            | 90.20                                 | 44.37                        |
| 2   | 0.2                 | 84.29                   | 42.46                        | 0.30           | 3.17                                  | 1.14           | 32.57                                 | 7.93                         |
| 3   | 0.3                 | 77.81                   | 40.02                        | 0.32           | 0.13                                  | 1.33           | 37.75                                 | 17.14                       |
| 4   | 0.4                 | 71.15                   | 36.95                        | 0.36           | 0.11                                  | 1.29           | 41.29                                 | 22.18                       |
| 5   | 0.4                 | 84.26                   | 42.52                        | 0.32           | 0.18                                  | 1.33           | 34.85                                 | 12.29                       |
| 6   | 0.4                 | 77.69                   | 40.10                        | 0.32           | 0.13                                  | 1.33           | 37.81                                 | 17.12                       |
| 7   | 0.4                 | 71.32                   | 36.86                        | 0.33           | 0.10                                  | 1.28           | 34.86                                 | 12.23                       |
| 8   | 5                   | 1.41                    | 51.63                        | 6.49           | 1 773                                 | 0.1            | 90.15                                 | 44.34                        |
| 9   | 0.2                 | 84.89                   | 44.27                        | 0.26           | 0.17                                  | 1.29           | 33.20                                 | 11.64                       |
| 10  | 0.2                 | 84.93                   | 44.19                        | 0.23           | 0.17                                  | 1.29           | 33.19                                 | 11.72                       |
| 11  | 0.2                 | 91.06                   | 47.23                        | 0.25           | 0.28                                  | 0.92           | 29.69                                 | 7.11                         |
| 12  | 0.2                 | 84.32                   | 45.27                        | 0.21           | 0.15                                  | 0.98           | 32.06                                 | 12.24                       |
| 13  | 0.4                 | 70.42                   | 39.50                        | 0.19           | 0.07                                  | 0.95           | 38.39                                 | 22.98                       |
| 14  | 0.4                 | 90.90                   | 47.23                        | 0.17           | 0.27                                  | 0.91           | 29.74                                 | 7.28                         |
| 15  | 0.2                 | 84.12                   | 45.22                        | 0.14           | 0.17                                  | 0.98           | 32.14                                 | 12.45                       |
| 16  | 0.4                 | 69.99                   | 39.24                        | 0.10           | 0.06                                  | 0.97           | 38.63                                 | 23.43                       |
| 17  | 0.86                | 53.32                   | 8.47                         | 1 773          | 0.2                                  | 84.39          | 46.79                                 | 12.02                       |
| 18  | 0.2                 | 84.07                   | 46.71                        | 0.11           | 0.14                                  | 0.84           | 30.90                                 | 12.35                       |
| 19  | 0.59                | 54.18                   | 8.94                         | 1 773          | 0.2                                  | 86.20          | 48.13                                 | 10.15                       |
| 20  | 0.2                 | 83.72                   | 47.54                        | 0.10           | 0.12                                  | 0.59           | 29.84                                 | 12.62                       |
| 21* | 30                  | 0.40                    | 52.53                        | 13.49          | 1 773                                 | 0.1            |                                                     |                             |
| 22* |                     | 0.2                     |                              |                |                                       |                |                                       |                             |
| 23* |                     | 0.4                     |                              |                |                                       |                |                                       |                             |
| 24  | 1 823               | 0.1                     | 91.92                        | 51.78          | 0.18                                  | 0.26           | 0.35                                  | 25.11                       |
| 25  | 1 823               | 0.2                     | 84.19                        | 49.96          | 0.10                                  | 0.12           | 0.22                                  | 27.42                       |
| 26  | 1 823               | 0.4                     | 68.78                        | 44.30          | 0.09                                  | 0.05           | 0.13                                  | 33.56                       |
| 27* | 40                  | 0.33                    | 50.45                        | 18.08          | 1 773                                 | 0.2            |                                                     |                             |
| 28  | 1 823               | 0.2                     | 84.79                        | 52.15          | 0.10                                  | 0.12           | 0.22                                  | 25.40                       |

Note: * the samples of alloy and slag from experiment of NO. 21, 22, 23, and 27 have poor separation, and the alloy contains a large amount of slag, so there is no experimental data here.
Reducible oxygen (O) is the total amount of oxygen present in the form of Fe₂O₃, FeO, NiO, CoO, and Cu₂O.

With the n_C/n_O ratio kept constant at 0.1, 0.2, 0.3, and 0.4, the desulfurized slag and carbon powder were mixed, and the mixture in the alumina crucible was placed in the furnace at 1 273 K. Then the temperature was further increased to 1 573 K and maintained for 30 min. Because of the poor separation of the metals from the slag at 1 573 K, the furnace temperature was continually increased to 1 773 K or 1 823 K in 30 min and then held for 15 min to ensure that the metal was well separated from the slag. After reduction and separation, the sample was quenched and used for analysis.

3. Results and Discussion

3.1. Phase Characteristics

The nickel converter slag was mainly composed of FeO–SiO₂. The SEM images of its microscopic morphology are shown in Fig. 2 and the elemental concentrations measured via EDS are given in Table 4. Fayalite (Fe₂SiO₄) is the dominant phase of the nickel slag, as seen in zones 2 and 2’ in the SEM images. A spinel (FeO), located inside the fayalite phase, was also observed (in zones 1 and 1’ in Fig. 2) with a grain size of approximately 50 μm. Copper matte, with a grain size of approximately 10 μm, was scattered throughout the slag, as seen in zones 4 and 4’. A small amount of a glassy phase was also observed (zones 3 and 3’ in Fig. 2), which was mainly distributed around the edges of the fayalite phase. Hence, it is clear that nickel was partially present in the fayalite and spinel phases in the form of oxide, cobalt was relatively well dispersed without any obvious aggregation, and copper mainly existed in the form of sulfide with obvious aggregation. The elemental distribution of nickel, cobalt, and copper in nickel converter slag, obtained at the Beijing General Research Institute of Mining & Metallurgy, is similar to that in a previous study25,29 and is given in Table 5.

3.2. Oxidation and Desulfurization

When the sulfur content of the molten steel is low (0.005–0.52 wt.%), it can be removed by adding CaO. This leads to the formation of the slag in the form of CaS.27 However, when the sulfur content of the slag is relatively high, gasification desulfurization is often used to oxidize the S²⁻ ions in the slag to SO₂, which can be removed from the slag in the form of SO₂ gas.28 Blowing air into the molten copper slag can rapidly reduce the sulfur content from 0.52 wt.% to less than 0.01 wt.%29 while the ferric oxide (Fe₂O₃ or Fe₃O₄) in the slag can be used for desulfurization at the experimental temperature of 1 573 K. A high sulfur content (1.53 wt.%) was used in this study to investigate the desulfurization effect of Fe₂O₃ (a weak oxidizer) on the nickel converter slag.

3.2.1. Effect of Fe₂O₃ Addition on Slag Properties

As the proportion of the FeO–SiO₂ melted in the nickel converter slag was over 80 wt.%, the melting point of the nickel converter slag used in the experiment was determined using the FeOₓ–Fe₂O₃–SiO₂ melts.30 The results from the FactSage calculations (The initial input components are given in Table 1, and m is the amount of added Fe₂O₃.) show that the melting point of the slag changed with the addition of Fe₂O₃, as shown in Fig. 3. Adding a small quantity of ferric oxide (< 6 wt.%) can reduce the melting point of the slag; however, when 6–40 wt.% ferric oxide was added, the melting point of the slag began to increase. Although the increase in the slag melting point did not have any significant influence on the desulfurization or reduction reactions, the subsequent separation of the metal from the slag will be degraded. Figure 2 shows that the quantity of ferric oxide should be less than 15 wt.% at 1 573 K, which can ensure that the slag has good fluidity. However, to analyze the effect of adding ferric oxide over a larger range, the amount of ferric oxide added in this experiment ranged

![Fig. 2. SEM micrographs of untreated, drying nickel converter slag. The numbers show points where EDS analyses were undertaken, the results of which are given in Table 4.](image)

Table 4. Distribution of elements in nickel converter slag, where the points are those shown in the SEM images in Fig. 2.

| Points   | Element/wt.%   | Fe  | O   | Si  | Ni  | Co  | Cu  | S   |
|----------|----------------|-----|-----|-----|-----|-----|-----|-----|
| A-1#     |                | 65.9| 26.1| 2.6 | 4.5 | 0.5 | 0.4 | –   |
| A-2#     |                | 54.2| 28.6| 13.8| 2.7 | 0.7 | –   | –   |
| A-3#     |                | 38.4| 37.7| 22.4| 0.6 | 0.6 | 0.3 | –   |
| A-4#     |                | 15.1| 8.9 | 2.7 | 3.5 | 54.5| 15.4| –   |
| B-1#     |                | 67.2| 24.4| 2.7 | 3.8 | 0.6 | 1.2 | 0.1 |
| B-2#     |                | 56.2| 27.7| 14.0| 1.3 | 0.2 | 0.2 | 0.3 |
| B-3#     |                | 32.0| 38.1| 23.2| 0.2 | 5.2 | 1.2 | –   |
| B-4#     |                | 20.2| 8.7 | 2.3 | 2.5 | 48.8| 17.4| –   |

Table 5. Elemental distribution of nickel, cobalt, and copper in nickel converter slag.

| Reference | Ni distribution wt.% | Oxide       | Cu distribution wt.% |
|-----------|----------------------|-------------|----------------------|
| J. Peng25 | 58.48                | 40.78       | 68.03                |
| Z. Yu26  | 51.64                | 48.36       | 12.82                |
|          | 53.04                | 46.96       | 15.33                |
| Present study | 6.36                | 94.64       | 53.04                |
| J. Peng25 | 15.33                | 84.67       | 15.33                |
| Z. Yu26  | 12.82                | 87.18       | 12.82                |
| Present study | 87.37                | 12.63       | 87.37                |
from 0–40 wt.%. 

3.2.2. Influence of Fe$_2$O$_3$ on Residual Sulfur in Slag

According to the elemental analysis results (Table 5), the proportions of nickel, cobalt, and copper existing in the form of oxides are 50%, 85%, and 10% respectively, and the rest is sulfide. The remaining sulfur is in the form of FeS. The input composition is as given in Table 6 when using FactSage to simulate the desulfurization process by adding Fe$_2$O$_3$. The other parameters such as the amount of Fe$_2$O$_3$ (0–40 g), temperature (1 573 K), and partial pressure of SO$_2$ (0.01–0.5 atm) can be set during the calculation. Then the residual sulfur content in the slag was calculated and compared with the experimental result, which is shown in Fig. 4.

The content of Fe$_2$O$_3$ in the initial slag is less, its activity is low, and it is not sufficient to react with the sulfur in the slag. However, when the Fe$_2$O$_3$ increases or the ratio of Fe$^{3+}$/Fe$^{2+}$ becomes high, the oxidation of the slag is enhanced and the sulfur in the slag can be oxidized into SO$_2$. The chemical reaction equation is

$$3\text{Fe}_2\text{O}_3 + \text{MeS} \rightarrow 6\text{FeO} + \text{MeO} + \text{SO}_2 \quad \text{(1)}$$

The increase in Fe$_2$O$_3$ will accelerate the transformation of sulfide to oxide, and the sulfur will be removed in the form of SO$_2$. In addition, the decrease of SO$_2$ in gas, that is low p$_{\text{SO}_2}$, will also promote Eq. (1) to the right and accelerate the desulfurization process.

Highly oxidized and low-melting-point slags are beneficial for converting metal sulfides to metal oxides, consistent with previous reports. In the calculations using FactSage, the standard Gibbs free energy curve shows that carbon can react with the oxides, in the order of Cu$_2$O, NiO, CoO, FeO, and Fe$_2$SiO$_4$, instead of sulfides.

However, with further increase in the content Fe$_2$O$_3$ (20–40 wt.%), the residual sulfur decreases slowly. According to Fig. 4, with the addition of Fe$_2$O$_3$ in the range of 20–40 wt.%, the slag melting properties deteriorate. The migration of sulfur atoms in the slag will be weakened; then the contact between sulfur and oxygen in the slag is limited, which results in a sulfur removal less than that calculated using FactSage 7.1.

3.3. Reduction and Separation

Nickel, cobalt, and copper mainly exist as oxides and sulfides in slags. Under high-temperature conditions (> 1 523 K), they primarily exist as NiO, CoO, Cu$_2$O, Ni$_3$S$_2$, CoS, and Cu$_2$S. Under the experimental temperatures used here, the main reaction products of the sulfides and oxides with carbon were CS$_2$ and CO, respectively. The main reactions and products of the carbothermal reduction reaction are shown in Fig. 5; these are calculated using the Reaction module in FactSage. The standard Gibbs free energy curve shows that carbon can react with the oxides, in the order of Cu$_2$O, NiO, CoO, FeO, and Fe$_2$SiO$_4$, instead of sulfides.

### Table 6. Input composition during calculations using FactSage.

| Element | Value |
|---------|-------|
| Ni$_3$S$_2$ | 2.39 |
| NiO | 2.23 |
| CoS | 0.14 |
| CoO | 0.65 |
| Cu$_2$O | 1.04 |
| CuS | 0.10 |
| FeS* | 1.76 |
| FeO** | 51.36 |
| Fe$_2$O$_3$ | 3.06 |
| SiO$_2$ | 29.2 |
| Al$_2$O$_3$*** | 8.07 |

Note: * sulfur balance; **iron balance, except for FeS and Fe$_2$O$_3$, other iron elements exist in the form of FeO; *** total slag is 100 g, and other substances in the slag are calculated by Al$_2$O$_3$. 

Fig. 3. Phase diagram of the FeO–Fe$_2$O$_3$–SiO$_2$ system (obtained from FactSage).

Fig. 4. Effect of adding Fe$_2$O$_3$ on the residual sulfur in the slag.

Fig. 5. Standard Gibbs free energy of several sulfides and oxides.
3.3.1. Residual Sulfur vs. Element Distribution

The sulfur in slag mainly combines with nickel, cobalt, copper, and iron. In addition, a higher sulfur content in the initial slag (\((\text{pct } S)_0\)) before reduction indicates that the sulfides of nickel, cobalt, and copper are higher. Theoretical analysis based on Fig. 5 shows that sulfides are difficult to reduce using carbon. It can be presumed that the increase in the sulfur content in slag will hinder the reduction of nickel, cobalt, and copper to metal. By reducing the residual sulfur content, the influence of residual sulfur on the separation and extraction of nickel, cobalt, and copper can be studied through the distribution rates of sulfur, iron, nickel, cobalt, and copper after reduction.

There are various metals in nickel converter slag, such as iron, nickel, cobalt, copper, and sulfur. The distribution rate of element \(M (M = S, \text{Fe, Ni, Co, and Cu})\) is defined as

\[
L_M = \frac{(\text{pct } M)}{[\text{pct } M]} \times 100\% \quad (2)
\]

where \(L_M\) is the distribution rate of element \(M (M = S, \text{Fe, Ni, Co, and Cu})\) between slag and metal (%); \((\text{pct } M)\) is the mass percentage of element \(M\) in slag (wt.%); \([\text{pct } M]\) is the mass percentage of element \(M\) in metal (wt.%).

Figure 6 shows the influence of the sulfur content in slag on the distribution rates of sulfur, iron, nickel, cobalt, and copper after reduction at 1 773 K and 1 823 K. Figures 6(a-1) and 6(a-2) show that the sulfur distribution rate \((L_S)\) increases with the decrease in the sulfur content in the initial slag. This trend is similar at different temperatures (1 773 K and 1 823 K) and different values of \(n_C/n_O\) (C/O = 0.1, 0.2, and 0.4). Figures 6(b-1) and 6(b-2) show that the change in the sulfur content in the initial slag has almost no effect on the iron distribution rate at 1 773 K and 1 823 K. The distributions of nickel, cobalt, and copper decrease with...
the initial sulfur content, that is, nickel, cobalt, and copper tend to be enriched in metal, but the distribution rate does not change when the sulfur content is less than 0.86 wt.%. (When \(\text{pct S}_0\) is less than 0.59 wt.%, the metal cannot completely separate from the slag after reduction at 1 773 K.) When \(\text{pct S}_0\) is in a range of 0.86–1.50 wt.%, the distribution rates of nickel and copper reduce significantly while the cobalt distribution rate does not decrease significantly. According to Figs. 6(c-1), 6(c-2), 6(d-1), 6(d-2), 6(e-1), and 6(e-2), the change in the nickel and copper distribution rates increases with \(n_C/n_O\).

### 3.3.2. Residual Sulfur vs. Metal Recovery

An alloy containing iron, nickel, cobalt, and copper can be obtained through the reduction of nickel slag. The recovery rate of metal should be more objective than the distribution rate to measure the extraction of metals. Therefore, the relationship between metal recovery and the initial sulfur content in slag is studied, as shown in Fig. 7.

The recovery rate of element \(M (M = S, \text{Fe, Ni, Co, and Cu})\) is defined as

\[
R_M = \frac{m_a \cdot \text{[pct } M\text{]}}{m_a \cdot \text{[pct } M\text{]} + m_s \cdot \text{[pct } M\text{]}} \times 100\% \tag{3}
\]

where \(R_M\) is the metal recovery rate (%); \(m_a\) is the mass of obtained alloy (g); \(m_s\) is the mass of slag after reduction, and \(m_0 = m_s - \Delta m - m_a\) (\(m_0\) is the mass of slag before reduction (g); \(\Delta m\) is the loss in weight after the reduction (g)).

Figure 7 shows the relationship between the recovery rates of iron, nickel, cobalt, and copper and the sulfur content in slag.

### 3.3.3. Mole Ratio of Carbon to Oxygen \((n_C/n_O)\) vs. Element Distribution

The mole ratio of carbon to oxygen \((n_C/n_O)\) has an important influence on the reduction of iron, nickel, cobalt, and copper. In this study, the distributions of iron, nickel, cobalt, and copper were examined at different temperatures and sulfur contents. Figure 8 shows that the mole ratio of carbon to oxygen has different effects on the distributions of iron, nickel, cobalt, and copper at different temperatures (1 773 K and 1 823 K) and sulfur contents in slag (\(\text{pct } S_0 = 0.33–1.50\text{ wt.%)}. According to Figs. 8(a-1) and 8(a-2), the distribution rate of sulfur increases with \(n_C/n_O\) at low values of \(n_C/n_O\) ranging from 0.1–0.2. Then, the distribution rate of sulfur is almost unchanged at high values of \(n_C/n_O\) ranging from 0.3–0.4. According to Figs. 8(b-1) and 8(b-2), the distribution rate of iron decreases with the increase in \(n_C/n_O\), steeply at first and then gradually. This is similar to the trend observed for cobalt. According to Figs. 8(c-1) and 8(c-2), the distribution rates of nickel and copper increase with \(n_C/n_O\), but the trend is significantly different at different temperatures and sulfur contents in slag.
3.3.4. Mole Ratio of Carbon to Oxygen (n_C/n_O) vs Metals Recovery

Figure 9 shows that the recovery rates of iron, nickel, cobalt, and copper increase with the mole ratio of carbon to oxygen (n_C/n_O). Figures 9(a-1) and 9(a-2) show a linear relationship between n_C/n_O and the iron recovery rate, while the growth trend curve of nickel, cobalt, and copper recovery is steep at first (n_C/n_O = 0.1–0.2) and then gradual (n_C/n_O = 0.2–0.4).

Figure 8 shows that the distributions of nickel and copper increase. However, according to Fig. 9, the recovery ratios of nickel and copper will decrease. According to Eqs. (2) and (3), the relationship between R_M and L_M is

\[ R_M = \frac{1}{1 + \frac{m_s}{m_a} L_M} \]  

Even though L_M increases with n_C/n_O, \( \frac{m_s}{m_a} \) decreases simultaneously. The accumulation of L_M and \( \frac{m_s}{m_a} \) affects R_M and not just L_M.

4. Conclusions

Nickel converter slag is mainly composed of FeO–SiO_2 and contains large amounts of valuable metals such as iron, nickel, cobalt, and copper. Nickel is mainly present in the form of fayalite and spinel, cobalt is relatively well dispersed in the form of oxides, and copper primarily exists in the form of sulfides with evident aggregation.

With the addition of Fe_2O_3 in the range of 0–6 wt.%, the slag melting point decreases and then increases. The sulfur content in slag decreases with the addition of Fe_2O_3, and the residual sulfur in slag can be reduced to 0.33 wt.%. The sulfur distribution rate increases with the decrease in the sulfur content in the initial slag. The distributions of...
nickel, cobalt, and copper decrease with the initial sulfur content. The nickel recovery rate increases with the decrease in the initial slag sulfur content. The trend becomes gentle when (pct S)_0 is in a range of 0.33–0.86 wt.%. The sulfur content in the initial slag has almost no effect on the recovery of iron, cobalt, and copper. The distribution rates of sulfur, nickel, and cobalt increase with the mole ratio of carbon to oxygen (nC/nO), while the distribution rates of iron and cobalt decrease with the increase in nC/nO. In addition, the recovery rates of iron, nickel, cobalt, and copper increase with nC/nO.

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