Iron Recovery from Nickel Slag by Aluminum Dross: A Static Model from Industrial Practice View

Guangzong Zhang, Nan Wang, Min Chen, Xiaoao Li, Hui Li, Ying Wang, and Yanqing Cheng

Abstract Nickel slag can be recycled as one of excellent secondary sources due to valuable iron resource. A static model of recycling nickel slag by aluminum dross was established based on material balance and non-isothermal thermodynamic calculations. Discussions had been carried out under different basicities of the modified slags and the reduction degree of 'FeO,' and the results showed that the dosage of nickel slag, aluminum dross, and modifier is 55.60%, 28.82%, and 15.58%, respectively, at the basicity of modified slag of 1.0. The non-isothermal thermodynamic model indicated that an increment of slag temperature from 114.3 to 430.2 K could be obtained with the reduction process, which not only signified the superiority of aluminothermy, but also laid a foundation for the industrial practice.

Keywords Nickel slag · Aluminum dross · Material balance calculation · Non-isothermal thermodynamic model

Introduction

Nickel slag can be recycled as one of excellent secondary sources due to valuable iron resource [1–3]. The iron content in quenched nickel slag from flash smelting can be as high as 50 wt%, which is the main reason why so many researchers have paid their attentions on its recycling in past years. Compared with stockpiling in heaps in the open air, iron exaction is no doubt an efficient way to reduce environmental pollution and resource waste.

Pyrometallurgical methods have the advantages in slag treatment, which can avoid the waste water produced by hydrometallurgy as well as make the full use of the considerable heat carried by molten slag [4–6]. Different from carbothermic reduction, aluminothermic reduction that is treated as a self-sustaining technique has been used in today's recovery, such as copper slag recycling [7–9]. However, aluminum dross from aluminum industries is used as the reductant in this work, and the higher Al

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G. Zhang · N. Wang (✉) · M. Chen · X. Li · H. Li · Y. Wang · Y. Cheng
School of Metallurgy, Northeastern University, Liaoning 110819, China
e-mail: wangn@smm.neu.edu.cn

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content of ~35 wt% promotes a substitution of pure aluminum shots, where it should be mentioned that the contents of hazardous elemental N, Cl, and F in aluminum dross can meet the emission standard for harmless treatment after washing treatment and the high-temperature process [10]. Therefore, recycling nickel slag by aluminum dross can realize the full use of the metallurgical solid wastes as well as the environmental protection.

Thermal effect in waste treatment has always been a key issue for researchers, because the proper utilization of slag melt and application of exothermic property of aluminothermic reaction can both facilitate energy conservation. However, the thermodynamic foundations underlying the current recycling is still not clear, especially for the industrial practice, the dosage of reactants and the heat input that required has never been studied.

The objective of this work is to discuss the evolution of slag compositions and slag temperature based on the static model, which is established according to the calculations of material balance and non-isothermal thermodynamic model. Dependences of slag-composition variation on basicity of the modified slag and on the reduction degree of ‘FeO’ are analyzed to lay a foundation for the high-temperature experiment. Also, the heat energy underlying molten nickel slag with different discharge temperatures, the dependence of heat energy of slag system on reduction degree of ‘FeO’ and the slag temperature change under different basicities of the modified slag are successively discussed to evaluate the ‘waste heat utilization’ and the exothermic effect of aluminothermic reaction on slag treatment.

Experimental

Nickel slag raw material was obtained during flash smelting and was supplied by a domestic nickel plant, the compositions of which is shown in in Table 1. It could be found that the mass fraction of ‘FeO’ is as high as 51.31 wt%, much higher than the average grade of iron ore in China (~27 wt%). Combined with nickel slag, the compositions of aluminum dross that was collected from an aluminum enterprise are also listed in Table 1. The content of metallic Al in aluminum dross is 33.14 wt%, and the lower contents of F, K, and Cl (~0.14%) can be ignored due to the process conditions without soluble-salt addition, which indicates that aluminum dross can be used as the reductant in slag treatment [11].

Table 1 Chemical compositions of nickel slag and aluminum dross (wt%)

Compositions	‘FeO’	CaO	MgO	SiO_2	Al_2O_3	Al	AlN	Na_2O	Ni	Co	Cu	S
Nickel slag	51.31	3.58	8.41	31.60	–	–	–	–	0.16	0.08	0.22	1.20
Aluminum dross	–	2.04	6.97	10.12	40.83	33.14	4.85	2.05	–	–	–	–

Modeling Construction

When aluminum dross is added to the molten nickel slag, aluminothermic reaction as expressed in Eq. (1) will occur at the interface between aluminum and molten slag [12]. Based on mass conservation, the input and output of each element are analyzed, and the material calculation during the melting reduction can be realized.

$$\begin{aligned}&\mathrm{Al(l)} + 1.5\mathrm{FeO(l)} = 1.5\mathrm{Fe(l)} + 0.5\mathrm{Al_2O_3}(s),\\&\Delta G^{\theta} = -444,428.5 + 89.55T\ \mathrm{J \cdot mol^{-1}}\end{aligned} \tag{1}$$

Taking element Al as an example, the source contains Al, Al_2O_3, and AlN in aluminum dross and the output includes the left element Al in slag, the Al_2O_3 formed during reaction and the AlN that did not participate in the reaction. The balance equation is shown as follow:

$$\begin{aligned}&m(\mathrm{Al})_{\text{Aluminum dross}} + m(\mathrm{Al_2O_3})_{\text{Aluminum dross}} + m(\mathrm{AlN})_{\text{Aluminum dross}}\\&\quad = m(\mathrm{Al})_{\text{Slag}} + m(\mathrm{Al_2O_3})_{\text{Slag}} + m(\mathrm{AlN})_{\text{Slag}}\end{aligned} \tag{2}$$

Slag compositions during current reaction is dominated by oxides of CaO, SiO_2, ‘FeO,’ Al_2O_3, and MgO, and the mass fraction of each oxide can be calculated according to Eq. (3):

$$\begin{aligned}&w(\mathrm{MeO, Me = Ca, Si, Al, Fe, Mg})\\&\quad = \frac{\text{Mass of MeO in slag system after reaction}}{\text{Total mass of slag system after reaction}} \times 100\%\end{aligned} \tag{3}$$

Slag temperature during recycling will have an important influence on the kinetic conditions of the reduction and the separation of reduced product from slag in later period. From the perspective of thermodynamics, the aluminothermic reaction is a strongly exothermic process, a considerable heat energy will be released into slag pool, as shown in Eq. (1). However, the endothermic effect of the modifier and aluminum dross dissolutions should also be taken into account, which makes the heat-balance calculation more important.

Based on 100 kg of nickel slag, analysis of energy conservation is carried out upon established non-isothermal thermodynamic model, as shown in Eq. (4) [11].

$$\begin{cases} Q_{\text{input}} = \sum \dfrac{m_i}{M_i} \Delta H_i \\ Q_{\text{output}} = \sum \displaystyle\int_{T_0}^{T} C_{\mathrm{p},j} \cdot m_j + Q_{\text{heat loss}} \\ Q_{\text{input}} - Q_{\text{output}} = \dfrac{\mathrm{d}T}{\mathrm{d}m}\left(m_{\mathrm{Fe}} C_{\mathrm{p,Fe}} + m_{\text{slag}} C_{\mathrm{p,slag}}\right) \end{cases} \tag{4}$$

where Q_{input} and Q_{output} is the heat input and heat output per unit mass of the slag system, respectively, and Q_{input} includes the heat generated from aluminothermic reaction and the CaO modification, while Q_{output} includes the heat loss during recycling and the dissolution of aluminum dross and CaO (kJ kg^{-1}), m_i and m_j represent the masses of reactants (i refers to Al and the modifier CaO, j refers to the aluminum dross and the modifier CaO), and m_{Fe} and m_{slag} are the mass of the generated iron liquid and slag system, respectively (kg); M_i is the molar mass (g mol^{-1}), and ΔH_i is the enthalpy change of reaction (kJ mol^{-1}); T and T_0 is the slag and the room temperature (298 K), respectively (K); $C_{\text{p},j}$, $C_{\text{p,Fe}}$, and $C_{\text{p,slag}}$ are the capacities of reactants, the generated iron liquid and the slag, respectively (kJ K^{-1} kg^{-1}), which can be obtained from Eq. (5) [13].

$$C_{\text{P}} = A_1 + A_2 \times 10^{-3} T + A_3 \times 10^{5} T^{-2} + A_4 \times 10^{-6} T^{2} + A_5 \times 10^{8} T^{-3} \quad (5)$$

where A_1, A_2, A_3, A_4, A_5 are the coefficients relevant to the capacities and T is the temperature of the oxide, the iron or the slag (K).

Results and Discussion

Dependence of Slag-Composition Variation on Basicity of the Modified Slag

Table 2 shows the slag compositions and the dosage of reactants under different modification conditions. As basicity of the modified slag increases from 0.5 to 1.5, the mass fractions of SiO_2, MgO, and 'FeO' in the modified slag gradually decrease, while the mass fractions of CaO gradually increase. In addition, combining the mass fraction of 'FeO' in the modified slag and Eq. (1), the dosage of aluminum dross under different basicities is calculated, which lays a foundation for the high-temperature experiments. It can be seen that the dosage of aluminum dross decreases from 31.59 to

Table 2 Chemical compositions of the modified slags and the percentages of reactants (mass fraction/%)

Basicity of modified slags	Slag compositions					Dosage of reactants		
	w (SiO_2)	w (Al_2O_3)	w (CaO)	w (MgO)	w ('FeO')	Nickel slag	Aluminum dross	CaO
0.5	29.50	0.00	14.76	7.85	47.89	60.96	31.59	7.45
0.75	27.48	0.00	20.61	7.31	44.60	58.15	30.14	11.71
1.0	25.71	0.00	25.71	6.84	41.74	55.60	28.82	15.58
1.25	24.16	0.00	30.20	6.43	39.22	53.26	27.60	19.14
1.5	22.78	0.00	34.17	6.06	36.98	51.11	26.49	22.40

26.49% with the increasing basicity of modified slag. Moreover, the dosage of nickel slag, aluminum dross, and modifier is 55.60%, 28.82%, and 15.58%, respectively, at the basicity of the modified slag of 1.0.

Dependence of Slag-Composition Variation on Reduction Degree of ‘FeO’

Figure 1 shows the mass-fraction variation of oxides with the reduction degree of ‘FeO,’ where Fig. 1a shows the mass-fraction variation of all components under basicity of 1.0 and Fig. 1b shows the changes of ‘FeO,’ Al_2O_3, and CaO under basicity of 0.75, 1.0 and 1.25, respectively. As shown in Fig. 1a, the mass fraction of ‘FeO’ in slag gradually decreases from 41.61% as the increasing reduction degree, yet the mass fraction of Al_2O_3 gradually increases, and it can reach up to 35.81% in secondary slag. Simultaneously, the contents of SiO_2 and MgO increase slightly, while the content of CaO remains unchanged. Based on the tendency of curves in Fig. 1b, CaO content in slags gradually increases with the increasing basicity at a fixed ‘FeO’ reduction degree. Taking the modified slag as an example, the mass fraction of CaO is 20.61%, 25.71%, and 30.20%, respectively, from the basicity of 0.75 to 1.25. In contrast, the contents of ‘FeO’ and Al_2O_3 in the slag decrease with the increasing basicity. The mass fractions of ‘FeO’ and the Al_2O_3 in modified and secondary slags are 44.60%, 41.74%, 39.22%, and 38.20%, 35.81%, 33.72%, respectively, under the three slag basicities.

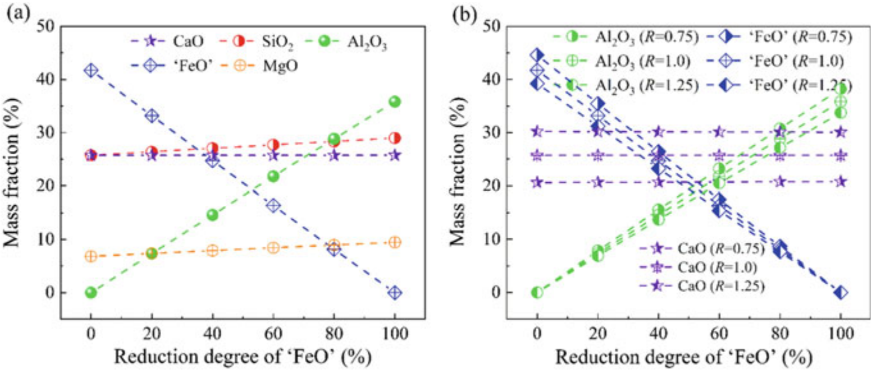


Fig. 1 Slag composition evolution of MeO (Me = Ca, Si, Al, Fe, Mg) with ‘FeO’ reduction degree. **a** $R = 1.0$; **b** $R = 0.75$, 1.0 and 1.25. (Color figure online)

Heat Energy Underlying Molten Nickel Slag with Different Discharge Temperatures

According to Eq. (1), the relationship between the heat energy carried by 100 kg of molten nickel slag and its discharge temperature is calculated, as shown in Fig. 2. With temperature increasing from 1573 to 1633 K, the heat energy carried by the molten nickel slag gradually increases from 115.49 × 10^3 to 121.46 × 10^3 kJ. In addition, the ratio of the heat energy carried by initial molten nickel slag to the heat required for different reduction temperatures is also shown. Taking the reduction temperature of 1773 K as an example, the ratio varies in the range of 75.54–79.44%, which undoubtedly reflects the great value of 'waste heat utilization' during recycling metallurgical waste slags. As the reduction temperature increases from 1673 to 1873 K, the heat required to melt the nickel slag also increases, and the ratio under the same discharge temperature decreases as a consequence. For instance, the heat energy carried by molten nickel slag with discharge temperature of 1573 K accounts for 80.96%, 75.54%, and 70.79% under the three reduction temperatures, respectively.

Dependence of Heat Energy on Reduction Degree of 'FeO'

Table 3 shows the heat-balance calculation results of slag system under basicity of the modified slag of 1.0, and Fig. 3 shows the proportions of heat input and heat output of the slag system accordingly. For the heat input of slag system, the exothermic heat of aluminothermic reaction gradually increases from 0.00 to 211.14 × 10^3 kJ with the increasing reduction degree of 'FeO.' As shown in Fig. 3a, the proportion occupies

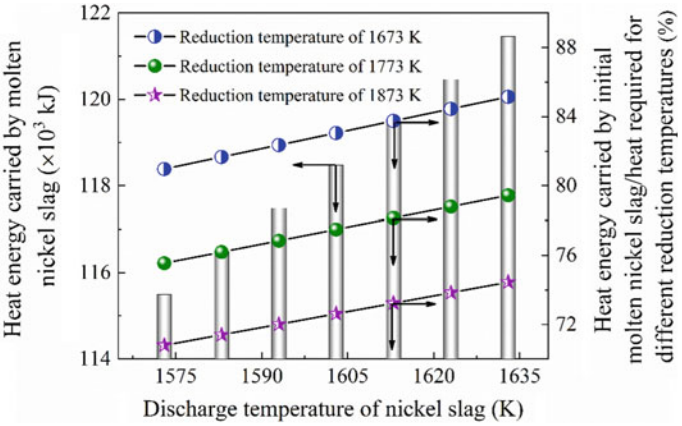


Fig. 2 Relationship of heat energy and the output temperature for 100 kg of nickel slag. (Color figure online)

Table 3 Calculation results of heat energy balance with modified basicity of 1.0

Reduction degree of 'FeO'(%)	Discharge temperature of nickel slag (K)	Heat input (× 10^3 kJ)			Heat output (× 10^3 kJ)		ΔQ (× 10^3 kJ)	Slag temperature (K)
		Heat energy carried by the molten nickel slag	Aluminothermic reaction	Exothermic effect of modification	Endothermic heat of dissolution of the modifier and aluminum dross	Heat loss		
0	1573	115.49	0.00	70.47	36.66	14.93	18.88	1687.29
20			42.22		58.61	16.96	37.12	1780.95
40			84.44		82.06	18.84	54.02	1854.50
60			126.70		106.61	20.61	69.96	1913.79
80			168.92		131.94	22.30	85.16	1962.50
100			211.14		157.87	23.92	99.82	2003.24

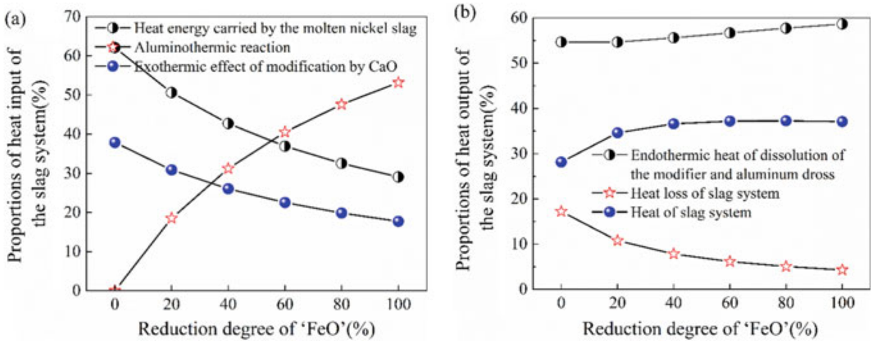


Fig. 3 Percentages of heat input and heat output of slag system with modified basicity of 1.0. (Color figure online)

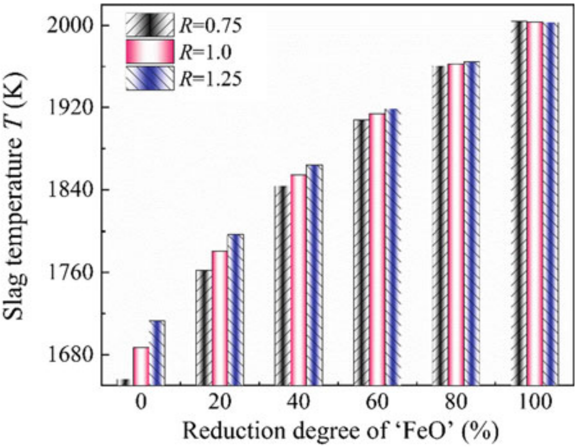
heat input of slag system from 0.00 to 53.17%. At the same time, the proportion of heat carried by molten nickel slag accounts for 62.10–29.08% of heat input, which plays dominant role before the reduction degree of 'FeO' of 55.33% and indicates the importance of 'waste heat utilization' in reducing energy consumption.

Combining Table 3 with Fig. 3b, the endothermic heat of dissolution of the modifier and aluminum dross varies from 36.66×10^3 to 157.87×10^3 kJ with the increase of the reduction degree of 'FeO,' which accounts for 54.65–58.63% of heat output of the system. Under the effect of heat input and output, the heat of slag system increases from 18.88×10^3 to 99.82×10^3 kJ, causing an increase in slag temperature from 1687.29 to 2003.24 K. Furthermore, the temperature increase of modified slag can be attributed to the exothermic effect of modification. Larger CaO addition under higher slag basicity induces a larger heat release and temperature increase.

Slag Temperature Change Under Different Basicities of Modified Slag

Figure 4 shows the slag temperature change with the reduction degree of 'FeO' under different basicities of modified slag of 0.75, 1.0, and 1.25, where the discharge temperature of nickel slag is set as 1573 K and the heat loss during the reaction is calculated as 10% of the physical heat of the whole slag system [11]. It can be seen that the slag temperature under the three basicities of modified slag gradually increases with the reduction degree of 'FeO.' Taking the basicity of 1.0 as an example, slag temperature changes from 1687.29 to 2003.24 K as mentioned above, 114.29–430.24 K higher than the discharge temperature of 1573 K. In addition, slag temperature increases in the range of 83.22–430.73 K and 140.16–429.80 K under basicities of 0.75 and 1.25, respectively. From the perspective of industrial practice,

Fig. 4 Slag temperature change under different basicities of modified slag. (Color figure online)



both the 'waste heat utilization' and the exothermic effect of aluminothermic reaction play a very important role in increasing the temperature of molten pool, laying a foundation for the high-valued utilization of metallurgical solid wastes.

Conclusions

Based on iron recovery from nickel slag by aluminum dross, the evolution of slag compositions and slag temperature based on the established static model have been discussed, and the following conclusions can be drawn:

(1) Material balance calculations show that the dosage of nickel slag, aluminum dross, and modifier is 55.60%, 28.82%, and 15.58%, respectively, at the basicity of modified slag of 1.0. As the reduction degree of 'FeO' increases, the mass fraction of 'FeO' in slag gradually decreases from 41.61%, yet the mass fraction of Al_2O_3 gradually increases, which can reach up to 35.81% in secondary slag.

(2) Calculation of non-isothermal thermodynamic model indicates that the heat energy carried by the 100 kg of molten nickel slag gradually increases from 115.49×10^3 to 121.46×10^3 kJ with discharge temperature increasing from 1573 to 1633 K. For reduction temperature of 1773 K, the ratio of the heat energy carried by initial molten nickel slag to the heat required for different reduction temperatures varies in the range of 75.54–79.44%, reflecting the great value of 'waste heat utilization' during recycling metallurgical waste slags.

(3) The proportion of exothermic heat of aluminothermic reaction occupies the heat input of slag system from 0.00 to 53.17%. For 100 kg of molten nickel slag, the heat of slag system increases from 18.88×10^3 to 99.82×10^3 kJ under the effect of heat input and output, which causes an increment of slag temperature from 114.3 to 430.2 K with the reduction process.

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