

Experimental Study on Reduction-Magnetic Separation Process of Low-grade Nickel Laterite Ore

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Abstract: The reduction and magnetic separation of low-grade nickel laterite was studied at varying temperatures between 1325-1400°C and a weak magnetic field of 100 mT in order to acquire high grade concentrations. The influence of reduction temperature, percentage of CaO, and atomic ratio of C/O (carbon/oxygen) were investigated. According to the gas analysis, the reaction process was divided into two stages: the direct reduction had a greater advantage than the indirect reduction in the earlier stage when the temperature was low, and the direct reduction and the indirect reduction reacted together in the later stage when the temperature was high. The result indicated that reduction temperature of 1375°C, percentage of CaO of 12% and atomic ratio of C/O of 1.2, the grade of fine ore was improved up to 5.71%. At the same time, the recovery rate of nickel reached up to 96.35%.

Key words: low-grade, laterite, reduction-magnetic separation, nickel

1 Introduction

Nickel, known as "industrial vitamins", is a very important non-ferrous material. Under conditions of room temperature, nickel can make austenitic structure in steel be more stable, which leads to a steel with higher toughness and ductility. Nickel-based alloys not only have good performance in anti-corrosion and high temperature oxidation corrosion, but also have good mechanical strength and ductility [1], thus they are widely used in stainless steel, alloy steel, corrosion resistant alloys, batteries, electroplating, chemical industry, etc. Approximately 65% of the total metal nickel is consumed by the stainless steel industries. With the rapid development of the world's stainless steel industry, this will greatly promote and stimulate the consumption of nickel. Table 1.1 lists the global stainless steels yield in recent years [2].

Table 1.1 Global stainless steels yield /Kt

Region	2009	2010	Comparison,%	2010	2011	Comparison,%
Western Europe/ Africa	6449	7878	22.2	7878	7875	0.0
Central and Eastern Europe	237	340	43.2	340	387	14.1
America	1942	2609	34.4	2609	2486	-4.7
Asia (excluding China)	7472	9011	20.6	9011	8770	-2.7
China	8805	11256	27.8	11256	12592	11.9
Total	24904	31094	24.9	31094	32110	3.3

At present, identified land-based resources that average 1% nickel or greater containing at least 130 million tons of nickel, consist of sulfide ore (40%) and nickel laterite ore (60%). Table 1.2 lists the world mine production and reserves [3]. Historically, although laterite deposits are widely distributed, resource-rich, close to the surface, and large-scale, the smelting technology is complicated and costly, therefore approximately 60% of the world's production of nickel comes from sulfide ore. With the increasing depletion of sulfide ore, there is an increasing focus on the utilization of low-grade nickel laterite ore. With the development and improvement of the

smelting technology, laterite has shown a great deal of economic potential, the proportion of nickel production from laterite is increasing, and it has become an important source of the metal nickel. According to statistics, the proportion of the total metal nickel from laterite ore will exceed 50%.

At present, the typical metallurgical processes for laterite ores are pyrometallurgical processes, hydrometallurgical processes, and a combination of processes of metallurgical and mineral separation. Pyrometallurgical processes can be divided into the process which produces ferronickel by reduction smelting and the process of sulfide smelting to produce nickel matte by the output of products. Hydrometallurgical processes can also be divided into ammonia-ammonium carbonate leaching and high-pressure acid leaching. The combination of process of metallurgical and mineral separation can acquire the valuable products when the ores are separated after reduction roasting. Pyrometallurgical processes are short, but require high energy consumption. Hydrometallurgical processes don't require melting and can selective recovery of valuable metals, but have the disadvantages of reagent requirements and protection of the environment [4]. The combination of process of metallurgical and mineral separation is suited to deal with any type of nickel laterite ore and has the advantages of a short process, low energy conservation, etc., thus it is worth further research.

In this study, the reduction and magnetic separation of low-grade nickel laterite was studied in order to acquire the high grade concentrations. The influence of reduction temperature, reduction time, percentage of CaO, and atomic ratio of C/O (carbon/oxygen) were examined.

Table 1.2 The world mine production and reserves

	Mine production		Reserves
	2010	2011	
Australia	170,000	180,000	24,000,000
Botswana	28,000	32,000	490,000
Brazil	59,100	83,000	8,700,000
Canada	158,000	200,000	3,300,000
China	79,000	80,000	3,000,000
Colombia	72,000	72,000	720,000
Cuba	70,000	74,000	5,500,000
Dominican Republic	---	14,000	1,000,000
Indonesia	232,000	230,000	3,900,000
Madagascar	15,000	25,000	1,600,000
New Caledonia	130,000	140,000	12,000,000
Philippines	173,000	230,000	1,100,000
Russia	269,000	280,000	6,000,000
South Africa	40,000	42,000	3,700,000
Other countries	99,000	100,000	4,600,000
World total(rounded)	1,590,000	1,800,000	80,000,000

2. Experimental

2.1. Characterization of the Materials

The chemical composition of the nickel laterite ore is listed in Table 2.1. The ore contained approximately 1.68 mass% Ni, 21.42 mass% Fe, 32.37 mass% SiO₂, and 22.95 mass% MgO,

which is typical of low-grade nickel laterite ore. XRD analysis (Fig.2.1) shows that the laterite ore is mainly composed of goethite, garnierite, kaolinite and clinochrysotile. In this study, graphite is used as the reductant, which contained approximately 99.5 mass% C. Calcium oxide was used as a flux.

Table 2.1 Chemical compositions of nickel laterite ore (unit: mass%).

O	Fe	Si	Mg	Al	Ni	Cr	Ca	Mn	Co	S	Ti	Zn
44.37	21.78	14.60	13.86	2.02	1.63	0.75	0.41	0.38	0.08	0.06	0.05	0.03

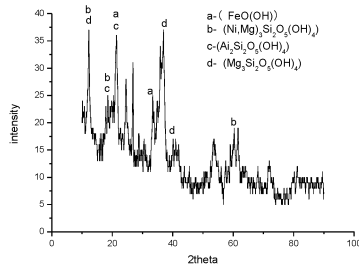


Fig.2.1 XRD pattern of the nickel laterite ore sample.

2.2. Experimental Methods and Processes

First, a large amount of free water in the laterite ore was taken off in the oven. After drying, the laterite ore was crushed and ground to 90 mass% passing 0.100mm. Then the ground laterite sample was mixed with graphite and calcium oxide to produce the pellets. The pellets were then heated at heating rate of 5°C/min in a high-temperature reactor shown in Fig.2.2. After reaching the given temperature, the pellets were kept at a given temperature for 300 minutes in order to make the material react fully. During the reaction, the reaction gas was detected by the gas analyzer. After roasting, the reduced pellets were cooled to room temperature under an Ar gas atmosphere. Lastly, the cooled pellets were crushed and ground to 95 mass% passing 0.100 mm and separated in a weak magnetic field of 100 mT to acquire the high grade concentrations. Fig.2.3 shows the process of the experiment.

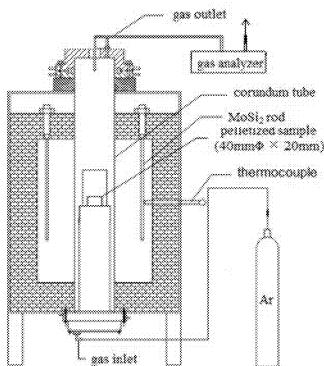


Fig.2.2 The high-temperature reactor.

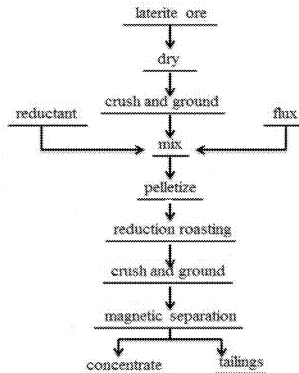


Fig.2.3 The process of the experiment.

3. Results and Discussion

In this study, the influence of reduction temperature, percentage of CaO, and atomic ratio of C/O (carbon/oxygen) are investigated in order to acquire the high grade concentrations. The experimental results are described in detail.

3.1 Beneficiation of Laterite Ore by Reduction and Magnetic Separation

3.1.1 Effect of Reduction Temperature on Reduction and Magnetic Separation

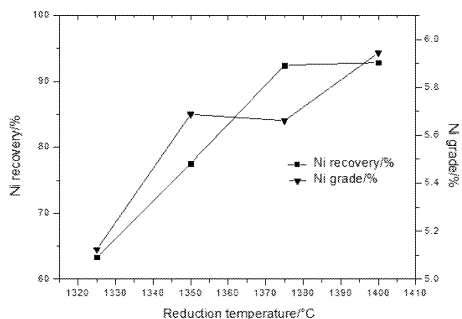


Fig.3.1 Effect of reduction temperature on reduction and magnetic separation.

The influence of reduction temperature on reduction and magnetic separation was examined by carrying out the experiment at 1325°C, 1350°C, 1375°C, and 1400°C with the atomic ratio of C/O at 1.4 and the percentage of CaO at 12%.

The results are presented in Fig.3.1. It can be seen that the recovery and grade of nickel improves with increasing reduction temperature. When the reduction temperature was 1325 °C, the grade and recovery of the nickel were 5.12% and 63.36% respectively, while the reduction temperature was up 1400°C, the grade and recovery of the nickel were up to 5.94% and 91.65% respectively. During the experiment, the molten state of the material was observed when the reduction temperature was at 1400 °C and there was some ferronickel particles after reduction roasting at the same time. We conclude that the higher reduction temperature is beneficial to reduction and magnetic separation of laterite ore. This phenomenon is attributed to the fact that reduction temperature has an important impact on aggregation and grew up in the grains of ferronickel in the reaction. The larger the grains of ferronickel, the greater the degree of separation of valuable metal and gangue will be, which improves the separation of slag and iron and improves the recovery of valuable metals.

When the reduction temperature was very low, the growth rate of ferronickel crystal nucleus was also very low, which caused the diameter of ferronickel particles to be very small. The reason for this was that the temperature was low in the pellets, which led to the transfer and congregation process of iron and nickel metals to be very slow. The separation of ferronickel alloy and slag was very difficult. The recovery of nickel was much lower. When the temperature reached to about 1400°C, the molten slag and ferronickel particles began to form, the kinetic process of transfer was accelerated, and the bigger particles of ferronickel alloy came into existence and made the recovery rate of nickel maintain at a higher level. The bigger the molten slag was, the more difficult the separation of the metal and slag, and the higher the energy consumption. According to the targets of both efficiency and emission, the optimum reduction temperature was 1375°C. At

this condition, the recovery rate of nickel reached 92.46%.

3.1.2 Effect of the Atomic Ratio of C/O on Reduction and Magnetic Separation

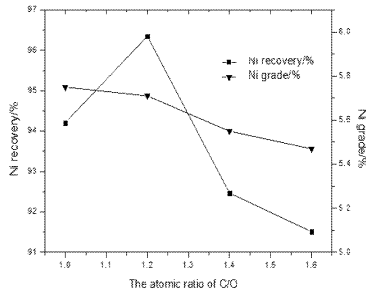


Fig.3.2 Effect of the atomic ratio of C/O on reduction and magnetic separation.

The influence of the atomic ratio of C/O on reduction and magnetic separation was carried out at the ratios of 1.0, 1.2, 1.4, and 1.6, with the reduction temperature of 1375°C and the percentage of CaO of 12%.

The results are presented in Fig.3.2. With increasing atomic ratio of C/O, the grade and recovery of the nickel significantly increased and then decreased. When the atomic ratio of C/O was 1.2, the maximum grade and recovery of the nickel reached 5.71% and 96.35% respectively. Meanwhile, it was found that there were some ferronickel particles after reduction roasting when the atomic of C/O was low. This phenomenon was attributed to the fact that excessive residual carbon in the phase was detrimental to the agglomeration of the grains of ferronickel [5].

In this study, anthracite was a reducing agent, which mainly improved the reducing atmosphere inside the pellets which promoted reduction of iron oxide, nickel oxide and thus produced a large amount of ferronickel crystal nuclei inside the pellets which was good to the agglomeration of the grains of ferronickel. In addition, the carbon penetrated into ferronickel, which reduced the melting temperature of ferronickel. As a result, there was some metal molten phase in the pellets, which is advantageous for the promotion of agglomeration. However with increasing atomic ratio of C/O, the excessive residual carbon disperses inside the pellets, which increases the viscosity of the slag and hinders the metal phase aggregation. This reduces the recovery rate of nickel.

In order to have a clear understanding on the effect of excessive carbon on the recovery rate of nickel, we selected several groups with high atomic ratio of C/O to study. The results are presented in Fig.3.3. We found that the recovery rate of nickel was very low. According to the result, the optimum atomic ratio of C/O was 1.2.

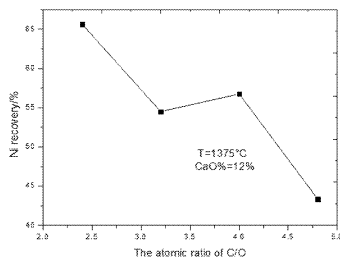


Fig.3.3 Effect of the atomic ratio of C/O in higher level on nickel recovery.

3.1.3 Effect of the Percentage of CaO on Reduction and Magnetic Separation

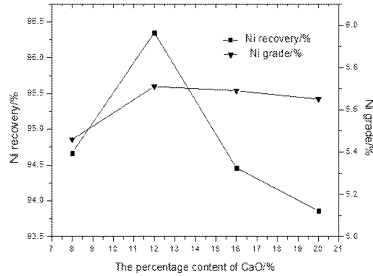


Fig.3.4 Effect of the percentage of CaO on nickel recovery.

The influence of the percentage of CaO on nickel recovery was carried out at 8%, 12%, 16%, and 20% with a reduction temperature of 1375 °C and atomic ratio of C/O of 1.2.

The results are presented in Fig. 3.4. It can be seen that the recovery of nickel first increased and then decreased with increasing percentage of CaO. The maximum recovery of nickel was 94.45% when the percentage of CaO was 12%.

During the reduction process of laterite nickel ore, complex silicate containing nickel and iron oxide decomposed into simple nickel oxide at first. Then the simple oxide is reduced by the anthracite. The study shows that suitable additives can improve the reduction of laterite. During the reduction roasting, the right amount of calcium oxide can accelerate the decomposition of complex silicate containing nickel and iron: $\text{CaO} + \text{NiO} \cdot \text{SiO}_2 = \text{CaO} \cdot \text{SiO}_2 + \text{NiO}$ [6]. This improves the activity of NiO, and it is reduced to metallic easily. In addition, calcium oxide with several mineral can form some materials which have the lower melting temperature. As a result, there is some molten phase in the pellets, which is advantageous for the promotion of agglomeration. So the recovery rate of nickel increased at the beginning with increasing percentage of CaO. However the absorbing ability to calcium oxide for each mineral is different [7]. When there is excessive residual calcium oxide in the phase, the excessive residual calcium oxide disperses inside the pellets, which increases the viscosity of the slag and hinders the metal phase aggregation. This is detrimental to the agglomeration of the grains of ferronickel. This leads to the recovery rate of nickel decreasing with further increasing percentage of CaO. According to the result, the optimum percentage of CaO was 12%.

3.2 Characterization of the Fine Reduced Laterite Ore by Magnetic Separation

In order to find out the phase composition of fine laterite ore reduced with reduction temperature of 1375 °C, the atomic ratio of C/O of 1.2, and the percentage of CaO of 12%, the samples were examined by X-Ray fluorescence(XRF), X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS). The chemical compositions of the fine ore by reduction-magnetic separation was shown in Table 3.1, the XRD pattern of fine ore by reduction-magnetic separation was seen in Fig.3.5, and the SEM pattern of fine ore by reduction-magnetic separation was shown in Fig.3.6 and the chemical compositions of observed district in SEM pattern was shown in Table 3.2.

As shown in Table 3.1, the fine ore achieved effective separation between the valuable metals and gangue. The Ni and Fe grades were 5.71% and 75.02% respectively, and the corresponding Ni and Fe recoveries were 96.35% and 93.02% respectively. As seen from the XRD pattern of fine

ore in Fig.3.5, the main material is ferronickel alloy and the rest is $(Mg,Fe)_2SiO_4$ and $CaSiO_3$, etc. in fine ore. As seen in SEM pattern of fine ore and the chemical compositions of observed district, we can find that a small amount of gangue embedded cloth in ferronickel alloy.

Table 3.1 Chemical compositions of fine ore (unit: mass%).

Fe	O	Ni	Mg	Si	Cr	Ca	Al	V	Mo	S
75.02	7.22	5.71	4.27	3.90	1.52	1.29	0.86	0.049	0.0418	0.039

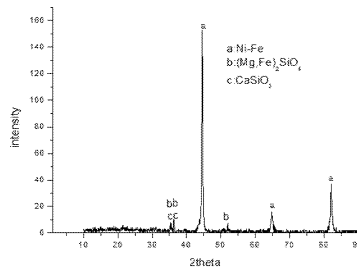


Fig.3.5 XRD pattern of the fine ore by magnetic separation of laterite reduced.

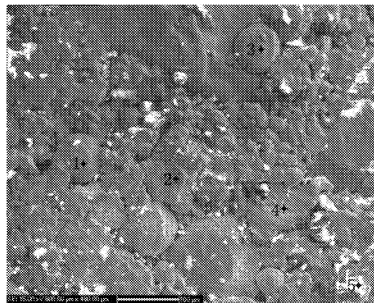


Fig.3.6 SEM pattern of the fine ore by magnetic separation of laterite reduced.

Table 3.2 Chemical compositions of observed district.

No.	Fe	Ni	Cr	Si	Mg	O	C
1	80.77	10.94	0	1.15	0.83	6.30	0
2	77.99	9.94	0	0	0	12.07	0
3	82.28	9.16	3.69	1.04	0	3.85	0
4	82.45	0	13.03	1.00	0	3.51	0
5	2.81	0	1.45	21.88	9.47	50.90	13.46

3.3 The Gas Analysis of Reduced Laterite Ore

During the experimental process, the gas of reduced laterite ore with reduction temperature of 1375°C , the atomic ratio of C/O of 1.2, and the percentage of CaO at 12% was detected by a gas analyzer, which helped clearly show the reaction process in the pellets. The change of volume fraction of CO , CO_2 with increase of the reduction temperature is shown in Fig.3.6.

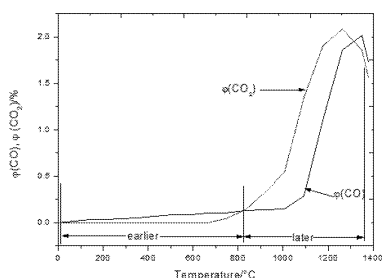


Fig.3.7 The change of volume fraction of CO, CO₂ with increase of the reduction temperature.

As shown in Fig.3.7, according to the gas analysis, there were two stages during the reaction process.

Early on, the volume fraction of CO was slightly more than the volume fraction of CO₂, but they were small in total. We considered that the direct reduction ($\text{NiO}+\text{C}=\text{Ni}+\text{CO}\uparrow$, $3\text{Fe}_2\text{O}_3+\text{C}=2\text{Fe}_3\text{O}_4+\text{CO}\uparrow$, $\text{Fe}_3\text{O}_4+\text{C}=3\text{FeO}+\text{CO}\uparrow$, $3\text{FeO}+\text{C}=2\text{Fe}+\text{CO}\uparrow$) had a greater advantage than the indirect reaction ($\text{NiO}+\text{CO}=\text{Ni}+\text{CO}_2$, $\text{FeO}+\text{CO}=\text{Fe}+\text{CO}_2$, $3\text{Fe}_2\text{O}_3+\text{CO}=2\text{Fe}_3\text{O}_4+\text{CO}_2$, $\text{Fe}_3\text{O}_4+\text{CO}=3\text{FeO}+\text{CO}_2$) during this stage when the temperature was lower. This phenomenon was attributed to the fact that diffusion of the gas became the limiting element of the reaction in the earlier portion. The reason for this was that there was almost no gap because of reducing agent and oxide close contact fully inside the pellets. And during this stage, the temperature was low in the pellets, which led to the diffusion of the gas was very slow.

Then, with increasing reduction temperature, the volume fraction of CO, CO₂ increased rapidly in the later portion. It was also found that the volume fraction of CO₂ was much larger than CO. This was due to the diffusion of the gas got faster and the reducing gas was in close contact with the oxides inside the pellets. This was the main reason that the volume fraction of CO₂ was much larger than the volume fraction of CO. There was excessive residual carbon, which promoted the boudouard reaction ($\text{C}+\text{CO}_2=2\text{CO}$, $\Delta_r G^0=166550-171\text{T J/mol}$). This was the primary reason that the volume fraction of CO₂ increased first before CO (Fig.3.7) in the later portion. It was concluded that there was direct reaction and indirect reaction at the same time and they promoted each other in the later portion.

4. Conclusion

For low-grade nickel laterite, the reduction and magnetic separation was studied at temperatures of 1325-1400°C with a weak magnetic field of 100 mT in order to acquire the high grade concentrations. The influence of reduction temperature, the percentage of CaO, and the atomic ratio of C/O (carbon/oxygen) were investigated for reduction and magnetic separation. During the experimental process, the gas of reduced laterite ore was detected by the gas analyzer. The fine ore was characterized by X-Ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS). The following words summarize this study.

(1) According to the gas analysis, the reaction process was divided into two stages: the direct reduction had a greater advantage in the earlier stage when the temperature was low, and there was the direct reaction and the indirect reaction at the same time in the later stage when the

temperature was high.

(2) The result indicated that optimum reduction temperature was 1375°C, the optimum percentage of CaO was 12%, and the optimum atomic ratio of C/O was 1.2, resulting in the grade of fine ore of 5.71%. At the same time, the recovery rate of nickel was 96.35%.

(3) The nickel and iron in the fine ore basically existed in alloy state, and a small amount of gangue embedded cloth in ferronickel alloy.

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