

Upgrading Low Nickel Content of Laterite-Graphite Pellets via Appropriate Calcinations Followed by Reduction

Jia-Shyan Shiau, Guan-Jhou Chen and Shih-Hsien Liu

Abstract—The appropriate carbothermic reduction parameters of low-grade laterite-graphite pellets and the influence of calcined temperature on these for upgrading the nickel (Ni) content in pellets were evaluated. Afterward, the impact of the additive (Na₂SO₄) on Ni grade and Ni recovery of calcined pellets at optimal reduction conditions was also investigated. XRD analysis, thermodynamic calculation, isothermal reduction experiment, BET-specific surface area analysis, bromine methyl alcohol solution analysis, and chemical composition analysis were used in order to obtain the associated parameters. In this study, it showed the improvement of Ni grade and Ni recovery rate of 673 K-calcined laterite-graphite pellets can respectively reach >30 mass% and 90.2 mass% under the conditions of reduction temperature = 1373 K, reduction time = 30 min, and the mole ratio of fixed carbon to reducible oxygen of iron and nickel in laterite nickel ore (C/O)=0.6. The reasons were proposed that the 673 K-calcined laterite ores have the highest specific surface area of 46.8 m²/g with pores in the size of 29.7 Å to provide faster Ni reduction at the initial stage followed by reduction. The addition of 5 mass% additive resulted in the best Ni grade of >30 mass % and the best Ni recovery rate of 93.8 mass % in pellets at the same reduction temperature, time and (C/O) molar ratio.

Keywords—laterite-graphite pellets, calcination, carbothermic reduction, nickel (Ni) content, additive.

1. INTRODUCTION

NICKEL(Ni) is an important strategic alloying metal with wide industrial applications. Nickel alloys are characterized by high strength and ductility as well as excellent corrosion and heat resistances. Its major application is for the smelting of steel and iron, especially for the manufacturing of stainless steel, which accounts for 61% of the total consumption of metallic nickel.[1-5] Approximately 60-70% of nickel reserves are nickeliferous laterite ores, from which only about 40% of the world nickel was produced. Nickel is associated mostly with iron oxides or silicate minerals as an isomorphism substitution in the lattice throughout the generation of laterite ores from weathered ultrabasic rocks. The properties of various layers within the laterite ore body are distinct. The limonite upper layer is characterized by the presence of goethite (FeOOH) and sometimes hematite (Fe₂O₃), which contains more iron and less nickel (about 0.8-1.5%), while the lower layer is rich in magnesium silicates, referred to as the saprolite layer, which is higher in nickel content (about 1.5-2.5%) as well as silica and magnesia contents. In addition, there is usually a transition layer between the limonite upper layer and the saprolite lower layer. Laterite ores are not amenable to concentration by physical beneficiation methods because of their complex mineralogy.[6-8]

It is both complex and capital intensive to concentrate nickel from laterite ores due to the inability to produce a high-grade concentrate, at present, for laterite ores treatment, it is crucial to apply chemical methods (pyrometallurgical or hydrometal-

lurgical) to alter the original mineralogy of laterite ores, such as reduction roasting-ammonia leaching (AL), high pressure acid leaching (HPAL), Caron process, atmospheric leaching, and rotary kiln-electric furnace (RKEF) process. The industrial application of hybrid hydrometallurgy-pyrometallurgy technology can be found in the Nippon Yakin Company's Oheya-ma smelting plant. Laterite nickel ore has many applications, and can be used to produce intermediate products like nickel oxide, nickel-sulfur or nickel iron alloy, of which the nickel-sulfur and nickel oxide can be used by nickel refineries to solve the problem of insufficient nickel sulfide. A nickel-iron alloy can also be used as a substitute for pure nickel addition in the manufacturing of stainless steel and low-nickel alloy steel.[9-13]

According to the Gibbs free energy of the Ellingham diagram, it indicates that the oxides in the lower part of the diagram will be stable and thus be difficult to reduce. In contrast, in the upper range of the Ellingham diagram, the existence of oxides causes higher free energy reaction, which then destabilizes the oxides, making them more readily reduced. From this concept, the selected reduction of oxides had been applied as usual, manufacturers can allow certain oxides to be reduced by controlling the temperature and reduced atmosphere, based on the associated Ellingham diagram. The reduction of the nickel oxide in laterite nickel ore will occur based on this mechanism with a carbothermic reduction experiment. In addition, by adjusting the added amount of reductant as well as reduction temperature and reduction time appropriately, one can control the reduction level of selected oxides, and the carbothermic reduction process of laterite nickel ore can be conducted in order to extract the metal phases of nickel and iron from the mineral phase.[14-18]

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Many researches on the thermal analysis of laterite nickel ore reported that the free water was removed at temperatures between 333 K and 383 K, dehydration occurs at 553 K, the serpentine phase transforms into enstatite and olivine at 898 K, and the recrystallization reaction happened at 1093 K.[19] Zevgolis et al[20] pointed out that a higher specific surface area is contributed to the carbothermic reduction of laterite nickel ore, and a lower reduction rate occurred at the limonite laterite nickel ore. Yang et al[21] proposed that garnieritic-type laterite nickel ore has a phase transformation at the calcining temperature of 873-973 K, and the accompanying increase in surface area and the generation of fine pores are also contributed to the carbothermic reduction. At the calcining temperature of 973-1123 K, laterite nickel ore will start its recrystallization, reducing its specific surface area and generating bigger pores, which are detrimental to the following carbothermic reduction.

J. Zhang et al.[22] studied the dehydration mechanism and reduction process dynamics of laterite nickel ore, and the results indicate that the dehydration of free water, the decomposition of goethite, the dehydroxylation reaction of kaolinite and serpentine as well as the second period reaction of dehydroxylation for the serpentine mineral, all take place in the heating process. The reduction of laterite nickel ore includes three stages. Chemical reaction is the controlling unit in the first stage, the activation energies of the precalcined and unroasted laterite nickel ores are 90.21 and 63.12 kJ/mol, respectively. Diffusion is the dominant link in the following two stages, in which the activation energy of laterite nickel ore gradually increases. As indicated by Li et al.,[23, 24] the addition of Na_2SO_4 to the carbon-bearing pellets of laterite nickel ore is beneficial to the reduction of nickel, resulting in a better nickel grade and recovery rate. Sun et al.[25] studied the influence of four additives (Na_2SO_4 , Na_2CO_3 , CaCO_3 and CaSO_4) on the carbothermic reduction of low-nickel high-iron laterite nickel ore. The results showed that Na_2SO_4 suppressed the reduction of iron, and that the dissolution of Na_2SO_4 could generate sulfur which would reduce the surface energy and melting point of the nickel-iron pellets, prompting the growth of the pellets and inducing their separation from other oxide-phase compositions. After being dissolved, Na_2SO_4 could generate alkaline oxides and sulfur. The sulfur would then react with iron to produce iron sulfide, suppressing the reduction of iron. Meanwhile, the alkaline oxides could improve the reduction effect on the carbothermic reduction.

The appropriate carbothermic reduction conditions include reaction temperature, heating time and carbon-oxygen (C/O) ratios which were evaluated at first, and the influence of calcining temperatures (673, 873 and 1173 K) on Ni grade and Ni recovery rate of the laterite-graphite pellets under fixed carbothermic reduction conditions was investigated subsequently in this study. Since the additive Na_2SO_4 was adopted to improve the nickel grade and recovery rate of laterite nickel ores,[25] therefore, this study focused on the optimal addition level for calcined laterite-graphite pellets that could yield the best nickel content in pellets to meet industrial standards: 15

mass% Ni grade and 85 mass% Ni recovery rate.

2. EXPERIMENTAL

2.1 Apparatus

The experimental flow chart of this research was shown in Fig. 1. The first step was to prepare the samples for the experiment. In order to conduct the calcination experiment, Indonesian limonite laterite nickel ores were pre-heated treatment at 673, 873 and 1173 K, each for 2 hours. The ores and reductants (graphite powder with 99.99% fixed carbon) were then separately ground into fine powders, which could pass through a 200-mesh sieve, and these were dried at 378 K until they had no free water. Next, the powders were mixed based on the calculated carbon-oxygen ratio (C/O), and the additive (Na_2SO_4) and binding agent (Bentonite) were then added. Finally, the powders were manually rolled into small pellets with a diameter of about 12 mm.

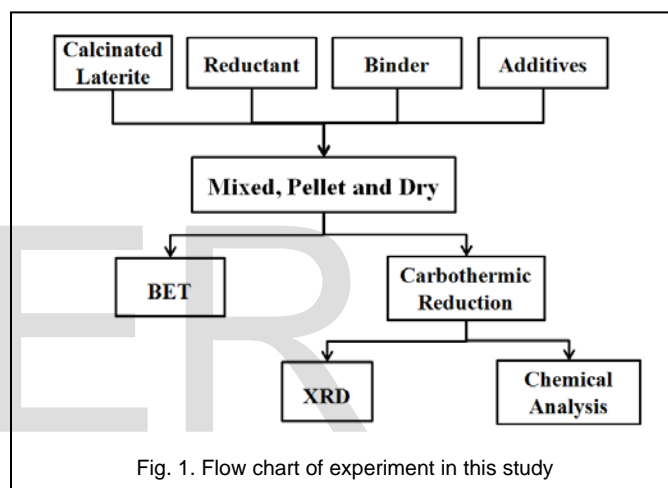


Fig. 1. Flow chart of experiment in this study

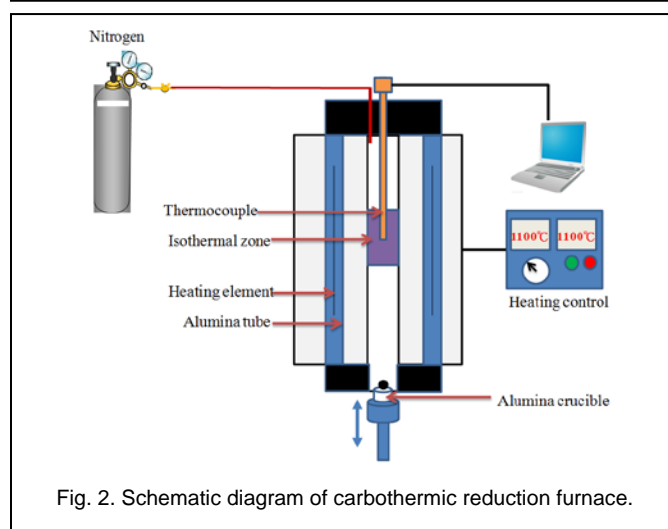
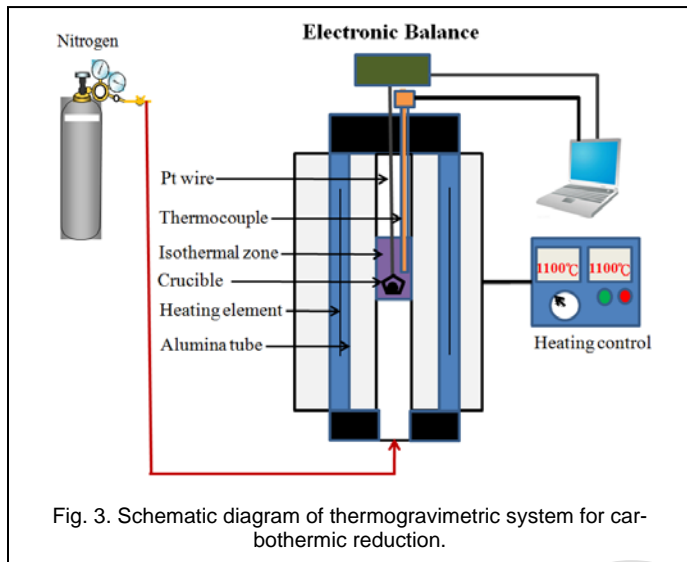


Fig. 2. Schematic diagram of carbothermic reduction furnace.

The procedures of the high temperature carbothermic reduction experiment are as follows: Let the inert gas (N_2 , 500 cc/min) flow into the muffle furnace; start the furnace and let the temperature rise to 1373 K. Put the sample pellets into the furnace; conduct the carbothermic reduction process and then, take the sample out of the furnace after the preset reaction

time is completed. Place the hot sample into a nitrogen-flowing cooling box until it is chilled to room temperature. A schematic diagram of the furnace was shown as Fig. 2. The isothermal reduction experiments were performed in a thermo-gravimetric system with the same furnace connected the electronic balance under the conditions of the inert gas flow and one pellet used at each experiment, shown as Fig. 3.



2.2 Analysis Methods

Analysis of the iron samples was carried out as follow: (A) Compound analysis of the reduction products through the X-ray diffraction method; (B) Analysis of the nickel content through bromine methyl alcohol solution analysis; [11] (C) Chemical analysis of the content of each element through the Inductively Coupled Plasma (ICP-OES) method to calculate the nickel grade and recovery rate; (D) Measurement of the specific surface area of the pellets and their average pores size before reduction through BET specific surface area analysis (using a Surface Area & Mesopore Analyzer). The nickel grade and recovery rate were calculated using the following equations:

$$Ni_{grade}(\%) = \frac{M_{Ni}(\%)}{M_{Ni}(\%) + M_{Fe}(\%)} \times 100 \quad (1)$$

$$Ni_{recovery}(\%) = \frac{M_{Ni}}{T_{Ni}} \times 100 \quad (2)$$

MNi : Content of metal Ni
MFe : Content of metal Fe
TNi : Total content of Ni

2.3 Materials

Fig. 4 showed the results of differential scanning calorimetry analysis performed from room temperature to 1473 K at a rate of 10 K/min. The figure shows that laterite ore had three endothermic peaks (at 388, 657, and 794 K) and one exothermic peak (at 1059 K). These peaks were related to free water removal, losses of hydroxyls ($2\alpha\text{FeOOH} \rightarrow \alpha\text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$), crystal water evaporation and phase pyrolysis. According to the results in Figure 4, the calcination conditions were found

to be up to 1073 K of temperature and 2 hours heating time until the end of weight loss. Fig. 5 showed the results for XRD patterns of the sample before calcination. Diffraction peaks corresponding to hydroxide oxide [$\text{Fe}_{1.833}(\text{OH})_{0.5}\text{O}_{2.5}$], goethite [$\text{FeO}(\text{OH})$], siderite [$\text{Fe}(\text{CO}_3)$], magnetite [Fe_3O_4], and kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$] were found. Among these compounds, kaolinite and iron hydroxide oxide exhibit the primary peaks. Laterite ores have complex coexisting phases. XRD examination of calcined laterite ores identified the compounds as hematite ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite [Fe_3O_4].

Figs. 6(a) to 6(c) showed the XRD analysis results of limonite ore calcined at 673 K, 873 K and 1173 K, respectively. Fig. 6(a) indicated that after having been calcined at 673 K for 2 h the ore contains potassium magnesium silicate (K_2MgSiO_4), calcium silicate (Ca_2SiO_4), hematite ($\alpha\text{-Fe}_2\text{O}_3$), iron oxide ($\text{Fe}_{21.333}\text{O}_{32}$), quartz ($\alpha\text{-SiO}_2$) and magnetite (Fe_3O_4). As shown in Fig. 6(b), the major phases of limonite ore calcined at 873 K for 2 h are hematite ($\alpha\text{-Fe}_2\text{O}_3$), iron oxide ($\text{Fe}_{21.333}\text{O}_{32}$) and quartz ($\alpha\text{-SiO}_2$). Fig. 6(c) showed that when limonite ore is calcined at 1173 K for 2 h, the major phases are hematite ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4). Therefore, the calcined laterite ores had iron oxides as the major phases which be obtained by removal of the impurities and water from raw ore.

During the calcination at 673 K, it found that silicon dioxide was combined with other elements to form extra compounds. However, this was not the case when the calcining temperature was 873 K and above. As the calcining temperature rose, the phase components of the limonite ore became simpler, and the extra phases disappeared. After calcination, the iron oxides of the limonite ore were oxidized into Fe_2O_3 and Fe_3O_4 , which were more difficult to be reduced to an iron phase.

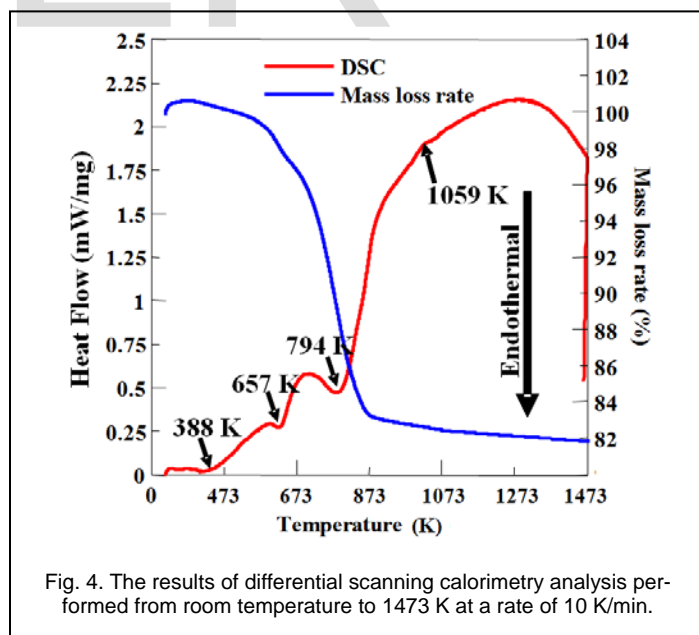


Table 1 showed the chemical analysis elements of limonite ore calcined under different temperatures. The contents of Ni, Fe_2O_3 , and FeO in the uncalcined limonite ore were 1.18 mass%, 59.7 mass % and 23.4 mass %, respectively, and they were 1.41 mass %, 59.3 mass % and 3.72 mass % for the 673 K-

calcined limonite ore, respectively. In the 873 K-calcined limonite ore, the contents of Ni, Fe₂O₃ and FeO were 1.37 mass %, 67.2 mass % and 0.37 mass %, respectively, and they were 1.28 mass %, 70.0 mass % and 0.12 mass % for the 1173 K-calcined limonite ore, respectively. As the temperature rose, the iron oxide phase was oxidized into Fe₂O₃. After calcination, the mass fractions of nickel and iron increased because of the removal of water and other impurities. In addition, Table 2 showed the chemical composition of bentonite, which is used as the binding agent for pelletizing.

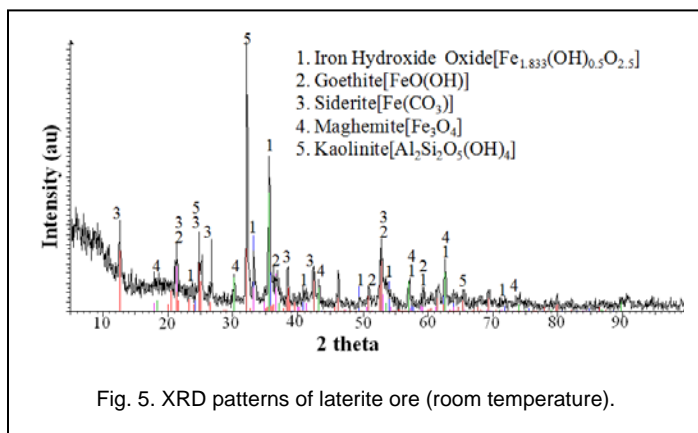


Fig. 5. XRD patterns of laterite ore (room temperature).

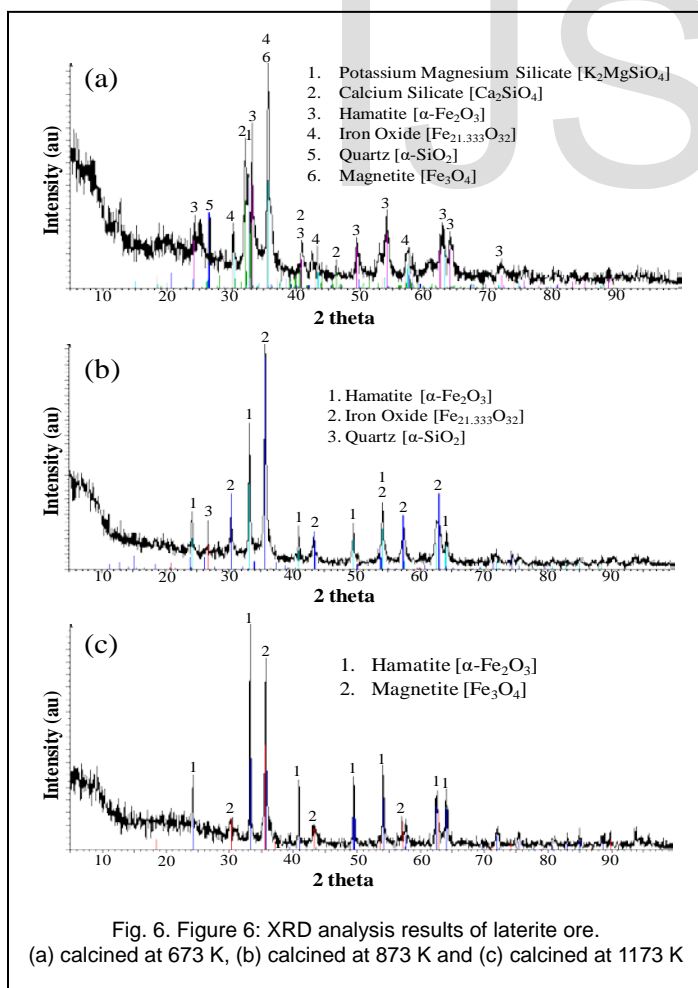


Fig. 6. Figure 6: XRD analysis results of laterite ore.

(a) calcined at 673 K, (b) calcined at 873 K and (c) calcined at 1173 K

TABLE 1

Chemical analysis of laterite ores calcined at different temperatures.(unit: mass %)

Calcining Temp.	P	S	Ni	Co	CaO	MgO	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	FeO	TFe	Na ₂ O	MnO	ZnO
298 K	0.01	0.02	1.18	0.16	0.15	4.41	4.50	10.2	59.68	23.4	41.1	0.02	1.27	0.04
673 K	0.01	0.02	1.41	0.13	0.25	5.64	4.78	11.05	59.31	3.71	44.4	0.02	1.24	0.04
873 K	0.01	0.02	1.37	0.13	0.26	6.10	5.17	11.93	67.21	0.37	47.3	0.02	1.35	0.05
1173 K	0.01	0.02	1.28	0.01	0.20	6.11	5.24	11.98	69.68	0.12	49.0	0.01	0.04	0.04

TABLE 2

Chemical composition of bentonite.(unit: mass %)

Elemental	P	S	CaO	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	Na ₂ O
Bentonite	0.03	0.37	4.63	1.25	12.94	62.78	0.62	1.69

3. RESULTS AND DISCUSSIONSECTIONS

3.1 Cross section observation of laterite-graphite pellets before and after calcinations

Cross-sectional images of reduced laterite-graphite pellets with calcined or uncalcined (30 min reduction) were shown in Fig. 7. The uncalcined laterite pellets had two regions at 1073-1173 K, namely a dense outer layer and a porous core. The calcined pellets at 1073-1373 K had a dense outer layer and a loose core. The calcined ore at 1373 and 1473 K did not have a core any more.

With increasing temperature, the inward diffusion of the dense area led to the gradual disappearance of the loose area. The metallic phase became liquid at the soft melting temperature, and the pellets shrank at 1473 K. A whole pellet had pieces of dense pellets and cracks. This porous structure led to poor heat transfer due to degraded heat conduction. It demonstrates that the sintering led to the formation of two regions, namely a dense area in the outer layer of the pellet and a loose area in the core of the pellet for the carbothermic reduction.

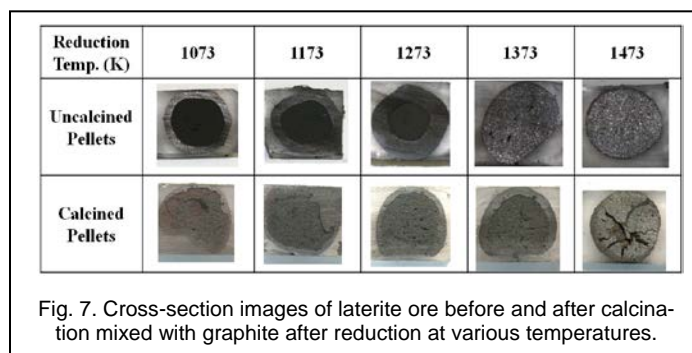


Fig. 7. Cross-section images of laterite ore before and after calcination mixed with graphite after reduction at various temperatures.

The diffraction patterns of uncalcined laterite reduced at 1273 K for 30 min were shown in Fig. 8. Fig. 8(a) showed that the main phases of the outer layer of the pellet were Fe₂O₃, SiO₂ and FeO after reduction, and those of the core of pellet were Fe_{0.97}12O, SiO₂, Fe₃N, and Fe₂SiO₄ as Fig. 8(b). It found that Fe₂O₃ was in outer-layer of pellet, for the reason that the pellet was exposed to the air and re-oxidation occurred. The

XRD comparison of the outer and inner pellets was found to be very similar to the peak intensity, and the same phase was shown in the outer-layer and core of pellet corresponds to the same theta after reduction.

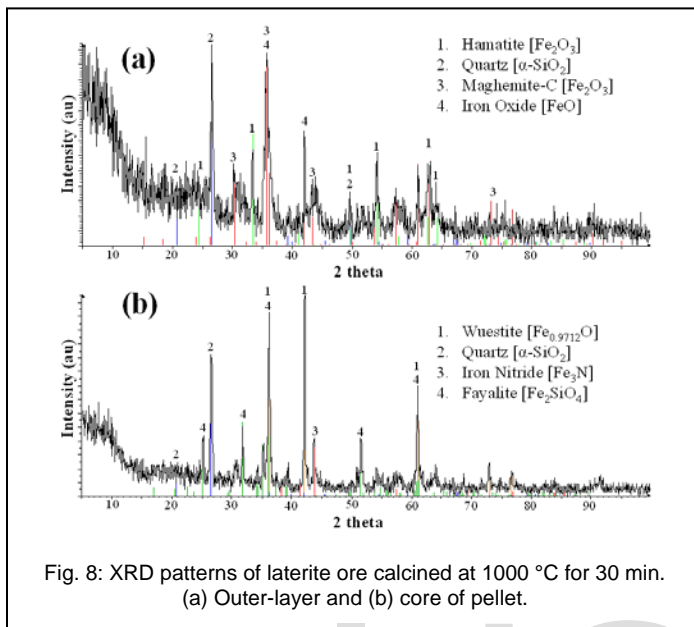


Fig. 8: XRD patterns of laterite ore calcined at 1000 °C for 30 min. (a) Outer-layer and (b) core of pellet.

3.2 Selection of appropriate reduction conditions of laterite-graphite pellets

In order to select the appropriate reduction temperature and C/O of laterite-graphite pellets, this study used a thermodynamic calculation tool (FactSage) to evaluate the Ni and Fe content after theoretical reaction based on the raw data of laterite ore, additive and reductant in Table 1 and Table 2. Fig.9(a) showed the Ni recovery and the Ni grade, respectively, and it indicated that metallic Ni begins to form at 973 K, and the Ni recovery rises very rapidly to 98% with ranged 973 K to 1573 K at C/O molar ratio of 0.3, then remains relatively constant. For C/O additions in the range of 0-1.5, in each case, the formation of Ni metal occurs at about 973 K. After an initial rapid increase in the Ni recovery in all cases, the rate of increase in Ni recovery with increasing temperature begins to slow down, levels off and the Ni recovery decreases with increasing C/O. The initial common curve for Ni recovery corresponds to the consumption of solid carbon, once the carbon is consumed, the rate of Ni recovery decreases with increasing C/O, reaches a maximum, and then begins to decrease as some Ni is reoxidized into the magnesium silicate. These results would indicate that C/O ranged 0.3 to 0.9 molar ratio, nickel recoveries of about 98% could be achieved. With regard to the grades, they follow a common curve corresponding to the consumption of the solid carbon. For low carbon additions, once the carbon is consumed, the grades increase, while at high C/O additions the grades decrease drastically, then level off. Higher C/O additions result in increased nickel recovery but lower nickel grades. For a C/O addition greater than that required for very high nickel recovery, the grade is decreased due to increased reduction of iron oxide to metallic iron.

Fig. 9(b) showed that Fe recovery rate increased with in-

creasing C/O molar ratio, and this also has a negative effect on Ni grade. Since Iron is co-reduced with nickel to produce a ferronickel alloy in pellets, the grade of the ferronickel is initially high at about 85%, reflecting the relative ease of reduction of the nickel oxide to nickel in comparison to the reduction of iron oxide to iron. However, with increasing temperature the grade drops rapidly due to increasing production of metallic iron and at 973 K as shown in Fig. 9(c), the grade reaches a relatively constant value of 20% ranged from 973 K to 1473 K. The temperature range over which the nickel grade is high is relatively narrow and corresponds to the range of increasing recovery of nickel.

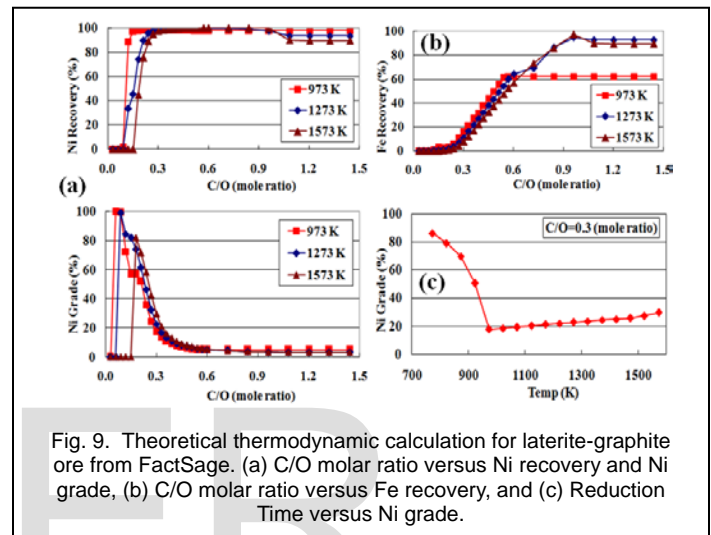


Fig. 9. Theoretical thermodynamic calculation for laterite-graphite ore from FactSage. (a) C/O molar ratio versus Ni recovery and Ni grade, (b) C/O molar ratio versus Fe recovery, and (c) Reduction Time versus Ni grade.

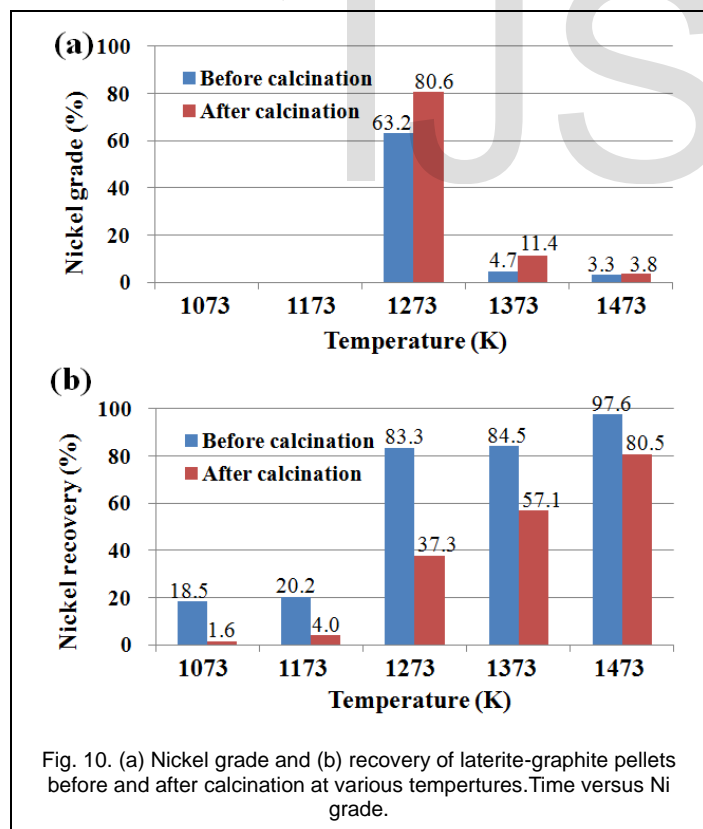
Chemical analysis of laterite samples before and after calcination (calcining temperature, 1173 K; time, 2 hours) followed by reduction at various temperatures was shown in Table 3. The results show that the iron phase had not been reduced at 1073-1173 K. When the laterite-graphite pellets were reduced at 1273 K, the nickel and iron metal phase obviously reduced, and these results obtained the nickel and iron content to calculate the nickel grade and the nickel recovery. The nickel grade and recovery of laterite-graphite pellets before and after calcination at various temperatures were shown in Fig. 10. Fig. 10(a) shows that the nickel grade decreased with increasing reduction temperature. The metallic nickel and iron content increased with increasing reduction temperature, and thus the nickel grade decreased. The nickel grade of calcined laterite was better than that of uncalcined laterite. Fig. 10(b) showed that the nickel recovery increased with increasing reduction temperature. The nickel recovery of uncalcined laterite was better than that of calcined laterite.

TABLE 3

Chemical analysis of laterite ore before and after calcination at various temperatures

Reduction Temp. (K)	1073		1173		1273		1373		1473	
Calced	N	Y	N	Y	N	Y	N	Y	N	Y
T-Fe	43.3	41.8	43.6	42.0	45.6	43.2	52.8	46.3	59.0	50.8
Fe	0	0	0	0	0.64	0.12	25.1	6.2	46.8	33.7
T-Ni	1.24	1.23	1.24	1.24	1.32	1.34	1.48	1.40	1.64	1.53
Ni	0.23	0.07	0.25	0.05	1.1	0.5	1.25	0.8	1.6	1.32

J. Yang[21] determined when the roasting temperature increased up to 1073 K, the sintering had a prevailing effect on pore size and surface area. Coalescence of small pores into large ones increased the pore size and decreased surface area, which was particularly profound in sample calcined at 1123-1273 K. Calcination for 30-60 min at these temperatures resulted in significant increase in pore size and decrease in surface area. E. N. Zevogolis[20] indicated that the poor reducibility occurred because of the lower specific surface area of ore. From this study, it found that the Ni grade was increased by reduction of iron, and the Ni recovery was decreased by decreased surface area. Compared with laterite reduced without calcination, the Ni grade increased from 4.7% to 11.4% and the recovery of Ni decreased from 84.5% to 57.1% for the calcined laterite, and the appropriate reduction temperature (1373 K) was selected based on the obviously increase of the Ni grade and accepted Ni recovery.



3.3 Effects of calcined temperatures followed by carbothermic reduction

According to previous related research,[23, 25] the reduction

efficiency of laterite nickel ore calcined at 873-1273 K is good, while that for limonite-type laterite nickel ore is still not suitable for reduction even after being calcined. Therefore, this research investigated the effects of calcining temperatures (673, 873 and 1173 K) on the appropriate reduction parameters. Table 4 showed the chemical composition of limonite ore calcined at three temperatures and reduced under optimal reduction conditions. It shows that the metallic nickel content declined from 1.29 mass % to 0.99 mass % as the calcining temperature increased. Therefore, the calcined temperature was 673 K, the best nickel recovery rate was obtained and relatively less metallic iron was produced. Meanwhile, the nickel grade decreased in the range of 22.1-30 mass% as the calcined

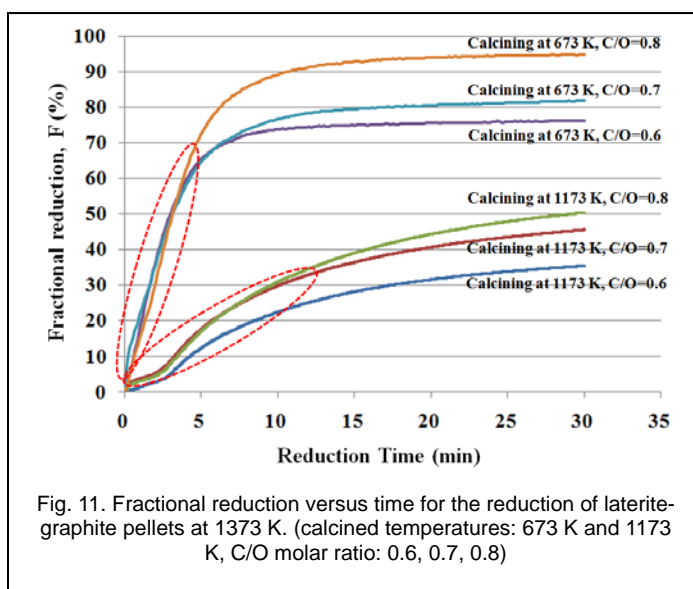
TABLE 4

Chemical composition results of laterite ore calcined at different temperatures and reduced under optimal reduction conditions.(unit: mass %)

Calcining Temp. (K)	TNi	Ni	TFe	FeO	Ni Grade	Ni Recovery
673	1.43	1.29	47.9	46.0	> 30	90.2
873	1.44	1.05	47.9	46.2	> 30	72.9
1173	1.26	0.99	47.7	52.6	22.1	78.6

temperature increased because the metallic iron was gradually reduced from its oxides leading to a decline in the nickel grade. The nickel recovery rate first declined from 90.2 mass % to 72.9 mass % and then rose to 78.6 mass % along with the rising temperature.

In order to understand why the higher Ni grade of laterite-graphite pellets occurred at the lower calcined temperature (673 K), The isothermal carbothermic reduction experiment was conducted in this study, and the result of laterite-graphite pellets with the calcined temperatures of 673 K and 1173 K, C/O molar ratio of 0.6 to 0.8, reduction temperature of 1373 K were shown as Fig. 11.



Where F is the fractional reduction using the following relation[26]: $F = (\text{mass of oxygen removed from the sample}) / (\text{initial mass of oxygen and fixed carbon})$. It shows that the reduction degree of the Fe and Ni is greatly affected by the calcined temperatures, and the calcined pellets (at 673 K) were

obviously faster reduced than the calcined pellets (at 1173 K), however, the increase of the reduction degree slowed down when the reduction time was close to 15-20 min. In this study, the well known unreacted shrinking core model was used to analyze the results[27] and a graphic of the relationship between the reduction degree and the reduction time was made, namely $1-(1-F)^{1/3}$ vs. reduction time, as shown in Fig. 12. It was seen that the solid-state reduction of the laterite pellets with graphite at 1373 K is controlled by interface chemical (reduction) reaction during the initial stage of 5 min. Table 5 showed the results of the BET analysis of the carbon-containing pellets of limonite ore calcined at three temperatures. It indicates that as the calcining temperature rose, the specific surface area first increased from 25.5 m²/g to 46.8 m²/g and then, decreased to 12.5 m²/g; and the average pore size first decreased from 31.0 Å to 29.7 Å and then, increased to 61.5 Å.

TABLE 5

BET analysis results of laterite ore calcined at different temperatures.

Calcining Temp. (K)	Surface Area (m ² /g)	Average pore radius (Å)
298	25.5	31.0
673	46.8	29.7
873	30.7	44.9
1173	12.5	61.5

The results show that the lattice of the uncalcined limonite ore whose specific surface area was smaller, contained free water, crystal water and hydrogen cations. When the calcining temperature was 673 K, dehydroxylation occurred, removing some crystal water and hydrogen cations, leaving pores with similar sizes and thus increasing the specific surface area. Under a calcining temperature at 873 K, phase transformation of limonite ore began, and its serpentine phase transformed to olivine and enstatite, decreasing the specific surface area and slightly enlarging the pore size. Recrystallization started at 1173 K, and a sintering effect occurred in the interior of the pellets, making the pore size bigger and resulting in a large loss of specific surface area. The whole process was illustrated in Fig. 13. According to the reaction formula $2\alpha\text{FeOOH} \rightarrow \alpha\text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$, the hydrogen cations and crystal water contained in the lattice are removed by the temperature effect (at 673 K), resulting in more fine gaps among the lattice and increasing the specific surface area, which would be beneficial to the spread of gas and eventually speed up the reduction of nickel. A reduction temperature of 1373 K was too low for the iron compound to be fully reduced into metallic iron. Therefore, the best nickel grade (>30 mass %) and recovery rate (90.2 mass %) for limonite ore can be obtained when it is calcined at 673 K in advance, and then, reduced under optimal reduction parameters (a reduction temperature of 1373 K, a reduction time of 30 min and a carbon-oxygen ratio of 0.6).

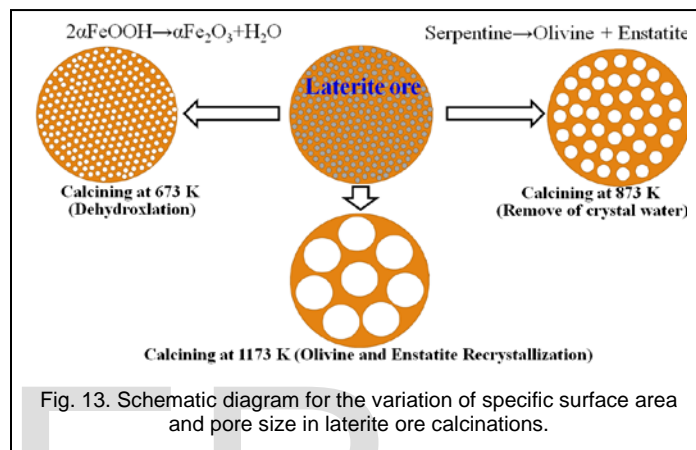


Fig. 13. Schematic diagram for the variation of specific surface area and pore size in laterite ore calcinations.

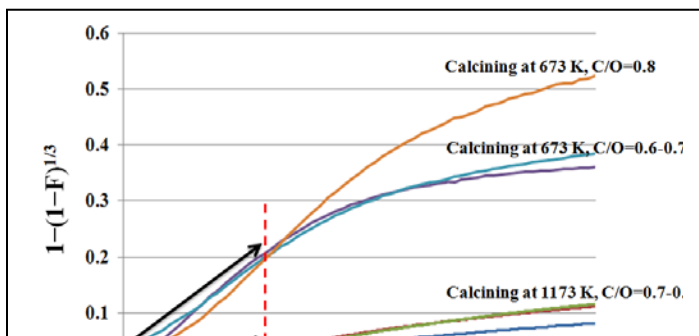
3.4 Effects of additives on Ni grade and Ni recovery during carbothermic reduction

In order to improve limonite ore calcined at 873 K and 1173 K and to make the nickel grades and recovery rates reach 15 mass % and 85 mass %, respectively, as required by industrial standards, the researchers proposed the Na₂SO₄[22-26] which could effectively increase the reduction of metallic nickel. This study thus probed the effects of different amounts of Na₂SO₄ on the nickel grade and recovery rate of limonite ore which was calcined at different temperatures in advance and then reduced under optimal reduction parameters. Table 6 showed the chemical analysis results of calcined (673, 873 and 1173 K) limonite ore which was reduced under optimal reduction parameters.

TABLE 6

Chemical analysis results of laterite ore calcined at different temperatures after being reduced under optimal reduction parameters and with additives of various amounts. (unit: mass%)

Calcining Temp. (K)	Additive Content (%)	TNi	Ni	TFe	FeO	Fe	Ni Grade	Ni Recovery
673	0	1.43	1.29	47.9	46.0	0.36	> 30	90.2
	5	1.45	1.36	48.7	49.9	0.60	> 30	93.8
	10	1.44	1.40	48.1	54.3	1.32	21.6	97.2
873	0	1.44	1.05	47.9	46.2	0.92	> 30	72.9
	5	1.45	1.37	48.9	52.7	2.69	> 30	94.5
	10	1.46	1.50	48.7	52.0	7.39	16.5	100
1173	0	1.26	0.99	47.7	52.6	3.49	22.1	78.6
	5	1.20	1.26	48.5	53.5	4.0	23.1	100
	10	1.29	1.48	47.7	45.0	6.14	17.4	100



The results indicated that the metallic nickel content of 673 K-calcined limonite ore increased from 1.29 mass % to 1.40 mass %, as the amount of Na₂SO₄ added rose during the reduction process. For 873 K-calcined limonite ore, the metallic nickel content grew from 1.05 mass % to 1.50 mass % along with the increase of Na₂SO₄ during the carbothermic reduction process. Furthermore, the increase of Na₂SO₄ during the carbothermic reduction process of 1173 K-calcined limonite ore caused the metallic nickel content to rise from 0.99 mass % to 1.48 mass %. Generally speaking, the metallic nickel content of limonite ore (calcined at 673 K, 873 K and 1173 K) grew along with the increase in Na₂SO₄ in the carbothermic reduction process. Therefore, it is deduced that the Na₂SO₄ in the reduction process could effectively reduce the ore back to a metallic nickel phase.

The results also showed that the nickel grade of 673 K-calcined limonite ore increased to 21.6 mass % with an increase in the amount of Na₂SO₄ added during the reduction process. 873 K-calcined limonite ore displayed a similar trend, as its nickel grade increased to 16.5 mass % as the amount of Na₂SO₄ added increased. However, the 1173 K-calcined limonite ore presented a different pattern; its nickel grade first rose from 22.1 mass % to 23.1 mass % and then descended to 17.4 mass % as the amount of Na₂SO₄ added increased. When the amount of additive increased, it was easier to reduce the ore to a metallic iron phase, causing the nickel grade to decline. After being reduced, the nickel recovery rate of 673 K-calcined limonite ore increased from 90.2 mass % to 97.2 mass % as the added amount of Na₂SO₄ increased. The 873 K-calcined limonite ore showed a similar trend; its nickel recovery rate after reduction rose from 72.9 mass % to 100 mass % as the addition of Na₂SO₄ increased. This was also the case for the 1173 K-calcined limonite ore, whose nickel recovery rate grew from 78.6 mass % to 100 mass % with a rise in the amount of Na₂SO₄ added during the reduction process. It is thus concluded that Na₂SO₄ could prompt effective displacement of the metallic nickel, increasing its content and recovery rate.[25]

The XRD analysis results of limonite ore calcined at different temperatures (673, 873 and 1173 K) and then, reduced under optimal reduction parameters and with different amounts of additive were shown in Fig. 14. Figure 14(a) indicated that after being reduced, the major phases of the 673 K-calcined limonite ore were Fe₂SiO₄, Fe_{0.9712}O and (Fe, Mg)₂SiO₄. However, XRD peaks corresponding to the Fe-phase appeared as the amount of Na₂SO₄ increased. Figures 14(b) and (c) also showed a similar pattern in which the peaks corresponding to the metallic iron increased as the amount of Na₂SO₄ increased. The experimental results show that the addition of Na₂SO₄ could aid in the reduction of calcined limonite ore to metallic nickel and iron, increasing the nickel recovery rate. This is because the sodium salts combined with the aluminum and silicon in the mineral phase, forming aluminum-silicon-sodium salts and displacing the metallic nickel and iron phases, while the sulfur combined with the iron to form iron sulfide, suppressing the reduction of the metallic iron.[25]

Based on the above experimental results and discussion, our study found that the appropriate reduction conditions of 1173

K-calcined limonite ore are 1373 K for the reduction temperature, 30 min for reduction time and 0.6 for the carbon-oxygen ratio, which contribute to the best nickel grade of 22.1 mass % and recovery rate of 78.6wt%. Furthermore, the results of carbothermic reduction process of limonite ore calcined at different temperatures (673, 873 and 1173 K) discovered that 673 K-calcined limonite ore experienced a dehydroxylation, creating a higher specific surface area and smaller pores, which represent better activity beneficial to the spread of gas during the following carbothermic reduction process. They could consequently cause a better reduction of metallic iron and nickel, effectively cutting energy consumption. 673 K-calcined limonite ore, after being reduced, had a nickel grade better than 30 mass %, and its nickel recovery rate could reach 90.2 mass %. Finally, from the effects with the addition of different amounts of Na₂SO₄ on limonite ore calcined at different temperatures (673, 873 and 1173 K), it noted that the amount of Na₂SO₄ was increased with the decreased nickel grade and the increased recovery rate, and these meet the requirements of industrial standards: 15 mass % for nickel grade and >85 mass % for recovery rate.

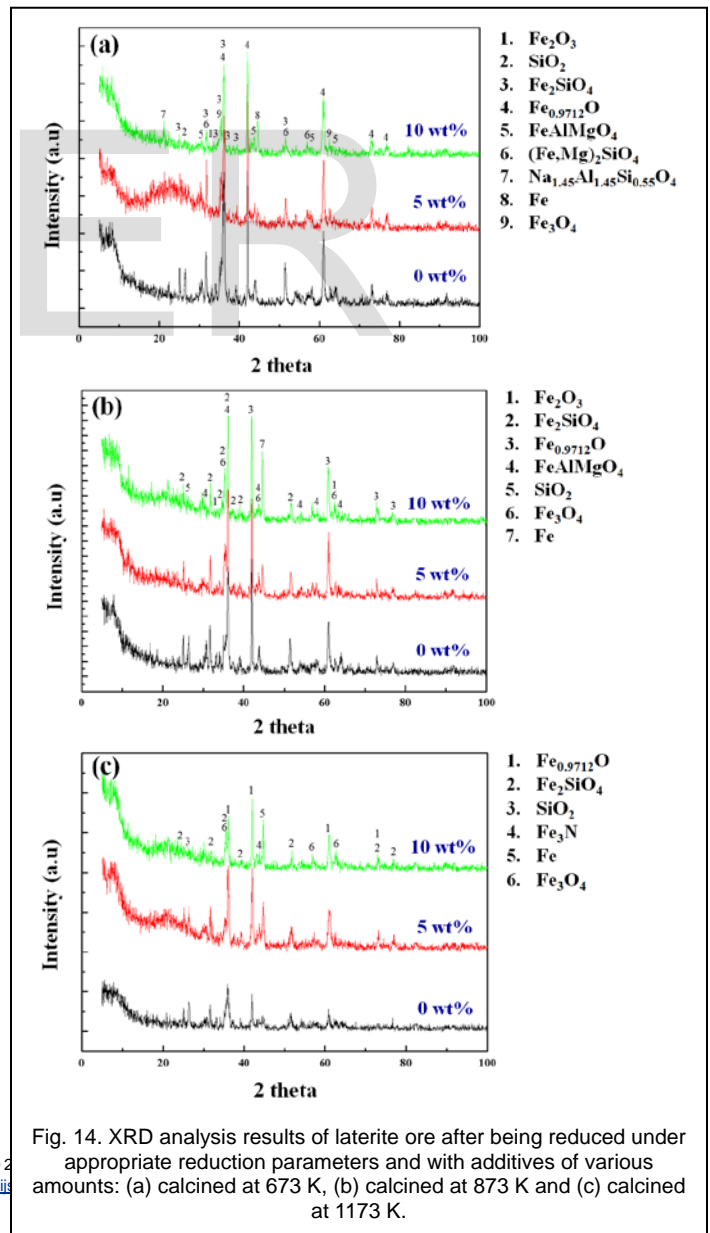


Fig. 14. XRD analysis results of laterite ore after being reduced under appropriate reduction parameters and with additives of various amounts: (a) calcined at 673 K, (b) calcined at 873 K and (c) calcined at 1173 K.

4. CONCLUSION

This study focus on three parts. First, to evaluate the appropriate carbothermic reduction parameters for the laterite-graphite pellets and their impact on the Ni grade and Ni recovery rate. Second, to investigate what role the calcination temperature plays in the reduction rate of calcinated pellets, and to find the ways to upgrade the Ni content in pellets followed by reduction under optimal parameters. Finally, additives were used to improve the Ni recovery rate. The conclusions of this work are presented as follow:

- (1) The improvement of Ni grade and Ni recovery rate of laterite-graphite pellets by using 673 K calcination temperature could respectively reach >30 mass% and 90.2 mass% under the conditions of reduction temperature = 1373 K, reduction time = 30 minutes, and a carbon-oxygen (C/O) molar ratio of 0.6.
- (2) The 673 K-calcined laterite ores had the highest specific surface area of 46.8 m²/g with pores in the size of 29.7 Å to provide a faster Ni reduction at the initial stage of carbothermic reduction.
- (3) The addition of 5 mass% additive resulted in the best Ni grade of >30 mass % and the best Ni recovery rate of 93.8 mass % in pellets at the same reduction temperature, time and (C/O) molar ratio.

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