REDUCTION OF A GARNIERITIC LATERITE ORE BY CO-CO₂ GAS MIXTURES

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ABSTRACT

In extraction of nickel from laterite ores, nickel has to be reduced to metallic form in pyrometallurgical processes. This paper studied the reduction of a garnieritic laterite ore in order to establish the extents and rates of reduction of nickel, cobalt and iron oxides under different conditions, reduction mechanisms, and the optimum conditions for selective reduction of nickel and cobalt oxides over iron oxides. The reduction of the garnieritic ore was examined at 700-900°C in the CO-CO₂ gas mixtures containing 20-70 vol% CO; the gas flow rate was varied in the range of 350-1050 mL/min.

A ferronickel alloy was formed by reduction of the metal oxides in the ore. The extent of reduction of nickel oxide increased with increasing temperature to 740 °C and then decreased with further increasing temperature. The extents of reduction of cobalt and iron decreased slightly with increase in temperature. Increase in CO concentration also promoted reduction of the metal oxides. When CO content was lower than 60 vol%, the extent of reduction of iron oxides was below 20%. Increase in CO concentration to 70 vol% sharply increased iron metallisation (>50%). Gas flowrate above 350 mL/min had a negligible effect on the ore reduction. The effect of ore size on the reduction of the metal oxides was insignificant. The optimal conditions for selective reduction of the laterite ore included temperature 740 °C and 60 vol% CO in the CO-CO₂ gas mixture.

1 INTRODUCTION

Nickel finds numerous applications, e.g., in stainless steel production and manufacture of industrial reactors, jet engines, cutlery, utensils, coinage, batteries, and catalysts [1]. Among these applications, nickel in stainless steel production accounts for nearly two thirds of global nickel production [1-2]. In recent years, rapid development and urbanization in developing countries have largely promoted nickel demand [3]. Currently, approximately 60% of nickel is produced from sulfidic ores, and 40% from laterite ores [4-6]. Nickel sulphide ores are increasingly depleted due to long-term exploitation and continuously decline in grade. Deeper underground mining increases the nickel production cost.

On the other hand, nickel in laterite ores takes up nearly 70% of world nickel reserve [5-6]. The capital weakness of sulphide ores and the predominance of nickel laterites reserve make laterite ores the increasingly important nickel source in the future.

Conventional processes in industrial nickel production include pyrometallurgical smelting processes, hydrometallurgical HPAL process, and Caron process [7]. Pyrometallurgical processes are more suitable for processing of saprolitic (serpentinic or garnieritic) laterite ores with high silica and magnesia content [8], in which nickel is concurrent with iron and magnesium in lattices of silicates. By contrast, hydrometallurgical and Caron technologies target processing of limonite laterites, in which nickel is mostly associated with goethite and relatively easy to be recovered. HPAL is superior in nickel and cobalt recoveries and has a good flexibility of feed ores. However, shortcomings of HPAL process are also known. High corrosion of autoclaves by leaching liquor necessitates the use of expensive construction materials such as titanium-lined or lead-lined autoclaves and causes extensive and expensive maintenance. The process consumes a considerable amount of sulphuric acid and generates liquid wastes whose disposal causes environmental concern. Sulphuric acid after leaching needs neutralization. A large amount of magnesium sulphate produced from digestion of hydrous magnesium silicates must be disposed of. Leaching liquor must be drained away into the ocean or precipitated and stored on land [9]. Smelting processes also achieve satisfactory production of nickel and cobalt but have been challenged by intensive energy consumption [9]. The average energy needed for nickel production from laterite ores is about 6.2-8.7 GJ per dry metric tonnage ore [4,10], which is regarded as costly for per unit nickel due to low nickel content of laterite ores (< 2%). Caron process which consists of both pyrometallurgical and hydrometallurgical processes, uses ammoniacal solution to leach out metals with a limited attack on silicates; therefore, the process can tolerate higher amount of magnesium. Its drawbacks such as low nickel recovery (~ 80%), intensive energy consumption, as well as the generated waste chemicals like ammoniacal solutions cannot be neglected [5,8].
Significant efforts have been devoted to technological advancement of nickel production from laterite ores. A modified Caron process was developed at BHP Billiton Yabulu refinery [7]. In this process, feed laterite ores are subjected to roasting reduction followed by ammoniacal leaching. Metallic iron formation is controlled so that nickel precipitation with iron hydroxide can be minimized resulting in Ni recovery improvement. Purwanto et al. [11] extracted Ni from selectively reduced laterite ore by sulphuric acid leaching; they reported that selective reduction can accelerate nickel extraction but suppress iron digestion. Kim et al. [12] concentrated nickel by roasting low-grade laterite ore separating the calcined ore with a magnetic separator. Li et al. [6] employed roasting reduction-magnetic separation to upgrade nickel and iron from laterite ores and received 83% nickel recovery for laterite reduced with sodium sulfate. Similarly, Zhu et al. [13] recovered ~92% nickel from a laterite ore reduced by coal with addition of 6% calcium sulfate to promote the growth of nickel metallic particles. These studies show that selective roasting reduction improve the efficiency of nickel recovery. However, the existing technologies have many challenges, including environmental concerns related to chemical wastes formation, deposition and energy consumption. Alternative technology for nickel production, examined in this project, includes selective reduction of laterite ores and carbonylation of reduced ores to extract nickel and cobalt. This paper studies reduction of laterite ore with the aim to determine the optimal conditions for selective reduction of nickel and cobalt oxides.

2 EXPERIMENTAL

2.1 Material

The ore for which reduction was studied in this paper was an Australian garnieritic laterite ore; two size ranges were tested: 53-200 μm and <53 μm. The chemical X-ray fluorescence (XRF) analyses of the ore in these size ranges are presented in Table 1. The phases existing in the raw material were chlorite (Mg, Fe, Ni)$_2$(Si, Al)$_4$O$_{10}$(OH)$_8$, talc (Mg, Fe, Ni)$_2$SiO$_3$(OH)$_2$, quartz SiO$_2$, and hematite Fe$_2$O$_3$.

<table>
<thead>
<tr>
<th>Ore size (μm)</th>
<th>Ni</th>
<th>Mg</th>
<th>Si</th>
<th>Fe</th>
<th>Co</th>
<th>Al</th>
<th>Cr</th>
<th>Mn</th>
<th>LOI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;53</td>
<td>1.66</td>
<td>13.0</td>
<td>19.4</td>
<td>11.7</td>
<td>0.045</td>
<td>2.1</td>
<td>0.5</td>
<td>0.2</td>
<td>13.3</td>
</tr>
<tr>
<td>53-200</td>
<td>1.35</td>
<td>12.6</td>
<td>20.5</td>
<td>10.4</td>
<td>0.038</td>
<td>2.2</td>
<td>0.5</td>
<td>0.2</td>
<td>12.6</td>
</tr>
</tbody>
</table>

2.2 Reduction and Br-CH$_3$OH leaching

Ore reduction was examined in isothermal experiments at temperatures between 700 and 900°C, in the CO-CO$_2$ gas mixture with CO partial pressures of 0.2, 0.4, 0.6 and 0.7 atm. Reaction time was 60 min for most experiments except those examined the effect of flow rate on reduction; this duration was chosen because nickel and cobalt oxides reduction could be ensured to complete particularly in mild reducing atmospheres.

The reduction of the laterite ore was carried out in a horizontal tube furnace. Approximately 0.6 g of ore sample was contained in a ceramic boat and loaded into the cold end of an alumina tube. When the temperature reached the designated level, the system was flushed with argon (HP, > 99.99%) and the boat with the sample was pushed to the hot zone using a stainless steel wire. The temperature was monitored by a sheathed K-type thermocouple. After reduction, the sample was pulled out to the cold end and the CO-CO$_2$ gas was switched to argon.

The reduced ore samples were leached in a Br-CH$_3$OH solution, in which metallic nickel, cobalt, and iron were attacked by the leachant whereas unreduced oxides retained in the solid phase. Approximately 0.5 g of reduced ore was added to 50 mL Br-CH$_3$OH leaching solution containing 2.5 mL of bromine and 47.5 mL of anhydrous methanol [14]. Leaching was performed isothermally in a water bath at 70 °C for 90 min.

2.3 XRD identification

The change in the phase composition of reduced samples was examined using Philips X’pert Multipurpose X-ray Diffractometer with Cu Kα radiation. The XRD spectra were recorded at angles (2θ) between 4 and 64°. The XRD data were processed using Highscore Plus 3.0 in combination with ICDD Powder Diffraction File 2 Database (2008), ICDD Powder Diffraction File 4+/Minerals 2013 RDB and American Mineralogist Crystal Structure Database (September 2013).
2.4 SEM/EDS analysis

The morphology and elemental composition of phases in the reduced samples were observed by a Hitachi 3400 I scanning electron microscope (SEM) equipped with a Bruker Quantax 400 energy dispersive spectrometer (EDS). The instrument was operated at a 20 KV accelerating voltage and a 60 mA probe current. The reduced samples were mounted into epoxy resin, and the cross-sections were ground, polished and then carbon coated for the analyses.

2.5 ICP-AES measurement

Concentrations of nickel, cobalt and iron in solutions resulting from leaching of reduced samples were measured by ICP-AES (Perkin Elmer 7300DV). The relative standard derivation (RSD) of all the ICP-AES measurements of iron, nickel, and cobalt remains within 1-2% and their corresponding detection limits are 40 ppb, 8 ppb, and 5 ppb, respectively. The extent of reduction of Ni, Co and Fe, (Ri), Ni and Co grade(Gi) and selectivity (Si) of nickel and cobalt oxides reduction were defined by Equations (1), (2), and (3) as follows:

\[
R_i = \frac{C_i \times n \times 100\%}{(W_i \times m / V)}
\]

\[
G_i = \frac{W_i \times R_i \times 100\%}{(\sum W_i \times R_i)}
\]

\[
S_i = \frac{R_i}{R_{Fe}}
\]

where: \(i\) represents Ni, Co and Fe; \(C_i\) (ppm or mg/L) isthe concentration of element \(I\) measured by ICP-AES; \(n= 10\) is the dilution times; \(W_i\) is the content of \(I\) in the original ore as shown in Table 1; \(m\) is the mass of the leached reduced sample; \(V=0.25L\) is the volume of the solution.

3 RESULTS AND DISCUSSION

3.1 XRD and SEM/EDS phase analyses of the reduced ore

The XRD patterns of the ore component 53-200 μm reduced with 700 mL/min gas containing 60 vol% CO-40 vol% CO₂ at 740 and 850 °C for 60 min are presented in Fig. 1. Both reduced samples contain talc and quartz as present in the original samples and new phases olivine \((\text{Mg, Fe, Ni})_2\text{SiO}_4\), pyroxene \((\text{Mg, Fe, Ni})\text{SiO}_3\), wustite \(\text{Fe}_2\text{O}_3\) and ferro-nickel \(\text{Fe-Ni}\). The sample reduced at 740 °C contained partially dehydrated chlorite \((\text{Mg, Fe, Ni})_3(\text{Si, Al})_4\text{O}_{10}(\text{OH})_2\) which disappeared after reduction at 850 °C.

**Figure 11**: XRD analysis of 53-200 μm ore reduced at 740 and 850 °C in 60 vol% CO-40 vol% CO₂

Fig. 2 shows the BSE micrographs of the reduced laterite samples. Fig. 2(a) and (b) are the overview with lower magnifications. The phases present in the reduced ore are consistent with those determined by XRD, including talc, partially dehydrated chlorite, pyroxene, olivine, quartz and wustite. Alloy particles could not be observed in the overview images (×210) but are visible at higher magnifications (Fig. 2(c), (d) and (e)). These fine ferro-nickel alloy particles at nano-scale size (around 100-300 nm) disperse throughout the silicate (pyroxene) matrix, suggesting simultaneous reduction of iron and nickel (cobalt) from the lattice of the solid solution of siliceous phases. Although EDS quantitative
analysis of these fine bright particles with submicron size was inconclusive, Fe-Ni alloy identified by XRD combined with similar observations on Fe-Ni particles distributed in silicate phases by Bunjaku et al. [15] and Li et al. [16] support the presence of the metallic product.

Figure 12: (a) and (b) overview of BSE images of phases in the reduced ore. 1 wustite, 2 modified chlorite, 3 olivine, 4 pyroxene, 5 talc, and 6 quartz. (c), (d) and (e) embedded Fe-Ni particles at higher magnifications of 1,000, 5,000, and 12,000.

Detailed morphologies of the other phases, both nickeliferous minerals and non-nickel carriers are presented in Fig. 3. After reduction, numerous tiny pores were created across the modified chlorite particles (Fig. 3(a)) as a result of removal of combined water in chlorite structure, which brought about significant changes in the surface area, pore size and volume. Pyroxene particles, shown in Fig. 3(b), exhibited a more porous structure with larger pores and cracks on the surface and in the interior of the mineral. This may mean that nickel and cobalt within this phase are easier to be accessed by the gaseous reductant. However, a compact structure of olivine (Fig. 3(c)) with much lower porosity means
less likelihood of nickel and cobalt yield from this mineral phase. Talc particles, slightly more heat-resistant, maintained its structure and morphology after reduction (Fig. 3(d)). Quartz remained a dense structure while the iron oxide inclusion in the silicate matrix seem not to change significantly in morphology while being reduced to wustite (Fig. 3(e) and (f)).

Figure 13: Morphology of major phases in the reduced laterite; (a) chlorite, (b) pyroxene (c) olivine, (d) talc, (e) quartz and (f) wustite inclusion

The EDS analyses of these major minerals in the ore, presented in Table 2, indicate that all of the silicate phases contain magnesium, iron and nickel, which suggests that these three elements coexist in silicate lattices to form solid solutions. EDS examination on quartz reveals the average composition approaches to its stoichiometry, which implies there is no reduction occurring to this mineral. For iron oxides embedded into silicate matrix, the constituents after reduction fit to wustite; this shows that iron metallization from this oxide inclusion was inhibited in selective reduction.
Table 2: Average compositions of major phases in reduced laterite ore (at 740 °C in 60 vol% CO)

<table>
<thead>
<tr>
<th>Phase</th>
<th>O</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>quartz</td>
<td>50.2</td>
<td>63.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>wustite</td>
<td>23.9</td>
<td>52.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>olivine</td>
<td>38.5</td>
<td>53.6</td>
<td>25.3</td>
<td>22.1</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>pyroxene</td>
<td>42.2</td>
<td>56.8</td>
<td>19.8</td>
<td>17.4</td>
<td>3.7</td>
<td>3.0</td>
</tr>
<tr>
<td>talc</td>
<td>42.3</td>
<td>58.4</td>
<td>16.0</td>
<td>14.1</td>
<td>4.2</td>
<td>3.4</td>
</tr>
<tr>
<td>chlorite</td>
<td>41.9</td>
<td>55.8</td>
<td>26.1</td>
<td>22.8</td>
<td>0.4</td>
<td>0.3</td>
</tr>
</tbody>
</table>

3.2 Effect of gas flow rate

The effect of gas flow rate on Ni, Co, and Fe metallization in laterite reduction at 700 °C is given in Fig. 4. It is seen that at 700 °C the rate of Ni, Co and Fe oxides reduction (change in the extent of reduction per unit time) did not depend on the gas flow rate. It can be noticed that at this temperature, completion of reduction of nickel and iron oxides required longer time (at least 60 min) than that of cobalt oxide reduction at all gas flow rates in the reduction experiments. Overlapping of the reduction rate curves of a specific metal oxide at the experimental flow rates suggests that external mass transfer of gaseous reactants did not contribute to the reduction rate control at 700 °C.

Figure 14: Effect of reducing gas flow rate on reduction of Ni, Co and Fe oxides in the ore

Figure 15: Correlation of Ni, Co, Fe metallisation with CO partial pressure of reducing gases

Flow rate experiments at 800 and 900 °C further confirmed that increase in the gas flow rate from 700 to 1050 mL/min had little effect on the rate and extent of reduction. Li [17] reported that maintaining CO/CO₂ gas mixture (25 vol% CO - 75 vol% CO₂) at flow rate higher than 2200 mL/min ensured the external mass transfer would not be the rate controlling step in reduction of pelletized laterite ore. This gas flow rate threshold was much higher than the value obtained in the current study, and the difference may be due to the different ore compositions and particle sizes (e.g., powder versus pellet) and reactor dimensions. Using gas flow rate above these thresholds means shifting the rate determining step to other factors such as intrinsic reactions and/or internal diffusion. Thus, gas flow rate of 700 mL/min was used in experimental study of the effects of temperature and other parameters on the reduction of laterite ore.

3.3 Effect of CO partial pressure

The effect of CO partial pressure on the reduction of laterite ore was studied at 740 °C. In these experiments, the ore with 53-200 μm was used and CO concentration in the CO-CO₂ gas mixture was adjusted at 20, 40, 60 and 70 vol%. The reduction extents of Ni, Co and Fe in 60-min experiments at different CO partial pressures are shown in Fig. 5. The reduction extents of nickel, cobalt and iron at CO partial pressure of 0.2 atm were 70, 83 and 7%, respectively. Increase in the CO partial pressure to 0.6 atm increased these figures correspondingly to 85%, 99% and 16%. Further increase in the carbon monoxide partial pressure to 0.7 atm did not facilitate reduction of nickel and cobalt oxides, but had a strong effect on iron oxides reduction of which the extent increased to approximately 55%. The significant increments in nickel and cobalt metallisation between 0.2 and 0.6 atm of CO partial pressure shows that 20 - 40 vol% CO in the CO-
CO₂ mixture was not high enough for desirable nickel and cobalt extraction, though 10 vol% CO in reducing gases is theoretically favourable in thermodynamics to the reduction of their oxides at the temperature of interest.

The XRD patterns of the samples of 53-200μm laterite ore reduced at 740 °C at different CO partial pressures are presented in Fig. 6. All reduced samples contain ferronickel (Fe-Ni-Co alloy), quartz, pyroxene, olivine, chloride and talc. Magnetite was only detected in the ore reduced by the gas with 20 vol% CO; wustite was not observed in the ore reduced by 70 vol% CO–30 vol% CO₂ gas, but exists in the XRD spectra of other samples. Peaks of Fe-Ni alloy strengthen with increasing the partial pressure of CO. When the ore was reduced in the gas atmosphere with 20 vol% CO, reduction of hematite mostly proceeded to magnetite. Wustite was not observed in the ore reduced in this atmosphere and peaks of the metal phase are weak. In reduction of the ore by the gas containing 60 and 70 vol% CO, iron oxides were partially reduced to metallic iron (Fe-Ni-Co alloy), whose peaks in the XRD spectra become stronger. The Fe-Ni peak at 2θ=44.3° was gradually shifted to lower diffraction angle as CO concentration increased from 20 to 70 vol%. This change was caused by increased iron content in the Fe-Ni-Co alloy.

Figure 16: XRD patterns of samples reduced at 740 °C in CO/CO gas mixtures with different CO content

Antola et al. [18] indicated that gas composition is a decisive parameter affecting reduction degree of nickeliferous ores and diluted CO concentration in reducing gas retards the nickel reduction from low-grade nickel laterite ores. There seems to be a difference between the theoretical gas concentration and experimental reducing power of the gas. The discrepancies between theoretical prediction and reality of reduction of nickel and cobalt oxides in the laterite probably result from the fact that nickel and cobalt do not occur as pure oxides in the ore but as solid solutions with iron and magnesium in silicates. Magnesium and/or iron partially substitute nickel in octahedral positions, forming complex silicate isomorphism that can be more difficult to reduce in mild reducing conditions. However, high CO partial pressure in a reducing gas was verified by Antola et al. [18] to forward metallic iron precipitation, and slightly lower reduction potentials and prolonged time have been advised to choose for nickel production from oxidic nickel ore. In this study, higher CO partial pressure than 0.60 atm did not strengthen nickel and cobalt reduction, suggesting that 60 vol% CO is optimal for Ni and Co extraction from the ore.

3.4 Effect of reduction temperature

The effect of temperature on reduction of 53-200 μm laterite ore was studied in the temperature range 700-900 °C with CO partial pressure of 0.6 atm. The extents of reduction of nickel, cobalt and iron oxides at different temperatures for 60 min are presented in Fig.7. The reducibility of nickel oxide increased with increasing temperature from 700
to 740 °C but decreased with further increasing temperature to 800 °C and above. As a result, the extent of reduction of nickel oxide reached the maximum of 85% at 740 °C. The reduction of cobalt oxide was close to 100% at 700-800 °C and gradually dropped to about 90% with increasing reduction temperature to 900 °C. Iron metallization monotonically decreased with increasing temperature from 700 to 900 °C. The maximum reduction of iron oxides, 23%, was produced at 700 °C.

Table 3: Effect of temperature on Ni and Co grade of ferronickel alloy and selectivity of reduction

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>G_Ni (%)</th>
<th>G_Co (%)</th>
<th>S_Ni</th>
<th>S_Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>31.0</td>
<td>1.9</td>
<td>3.5</td>
<td>7.6</td>
</tr>
<tr>
<td>740</td>
<td>41.3</td>
<td>2.3</td>
<td>5.6</td>
<td>10.9</td>
</tr>
<tr>
<td>800</td>
<td>44.8</td>
<td>3.0</td>
<td>6.6</td>
<td>15.8</td>
</tr>
<tr>
<td>850</td>
<td>56.0</td>
<td>5.4</td>
<td>11.1</td>
<td>37.8</td>
</tr>
<tr>
<td>900</td>
<td>59.1</td>
<td>6.0</td>
<td>13.0</td>
<td>47.0</td>
</tr>
</tbody>
</table>

A low extent of iron metallization was achieved by controlling the CO partial pressure not exceeding the boundary for wustite reduction in CO/CO₂ (~60 vol%~70 vol% CO in CO₂). The drop in nickel production over increasing temperature indicates that the reduction of nickel oxide is hindered by high temperature; this is probably caused by substantial formation of olivine and recrystallization of this phase up to 810 °C (Equations (4) and (5)). The formation of olivine tends to integrate nickel into the silicate lattices to form solid solutions [21]. The activity of nickel oxide in the silicate solid solutions negatively deviates from ideal solutions [22], which impairs its reducibility.

\[(\text{Mg, Fe, Ni})_2\text{Si}_2\text{O}_5(\text{OH})_2 = 2(\text{Mg, Fe, Ni})\text{O} + (\text{Mg, Fe, Ni})\text{Si}_2\text{O}_5 + 2\text{H}_2\text{O}\]  
\[(\text{Mg, Fe, Ni})\text{O}_2 + 2(\text{Mg, Fe, Ni})\text{Si}_2\text{O}_5 = 3(\text{Mg, Fe, Ni})\text{Si}_2\text{O}_4 + \text{SiO}_2\]  

As shown in Fig. 1, the phases in the reduced ore at 850 °C are similar to those reduced at 740 °C, including talc, olivine, pyroxene, wustite, quartz, and ferronickel. The distinction is that partially dehydrated chlorite was found in the sample reduced at 740 °C but not at 850 °C. This change has been found to associate with complete decomposition of chlorite between 700 and 800 °C [23-24]. Besides, talc retained at 850°C but its 006 peak (20=28.7°) disappeared during reduction at high temperature.
ning reduction at this temperature; this peak has been reported by Yang et al. [24] to survive up to 900-1000 °C in the annealed laterite, suggesting talc is less heat-resistant in reducing atmosphere than in inert gases. Weakened ferronickel peaks at 850 °C imply that nickel, iron and cobalt metallization particularly the former two from their oxides were weakened at higher temperatures, which conforms to the ICP-AES analyses of reduced ores given in Fig. 7. More importantly, olivine reflections were reinforced at 850 °C, and therefore more nickel suffers from consolidation of this conservative phase from which it is difficult to reduce.

3.5 Effect of ore particle size

The effect of particle size on the ore reduction was studied using samples of two sizes, 53-200 μm and < 53 μm at 740 °C and 850 °C in the 60 vol% CO-40 vol% CO₂ gas mixture. The extents of reduction of nickel, cobalt and iron oxides are presented in Fig. 8.

The extents of reduction of nickel and iron oxides were inversely affected by ore particle size; finer ore (< 53 μm) had higher yields of nickel and iron, although the effect of the ore size on iron oxide reduction was not as significant as nickel oxide reduction. More than 90% nickel oxide was reduced from the finer ore but the coarser ore (53-200 μm) achieved lower (85%) extent of reduction at 740 °C. The effect of the ore size on the iron oxide reduction was not strong, as the extent of iron oxide reduction was low. The extent of reduction of cobalt oxide in the coarse ore was higher than in the fine ore.

3.6 The mechanism of laterite ore selective reduction

The extraction of nickel and cobalt from garnieritic laterite ores consists of dehydration of hydrous silicates and selective reduction reactions. At lower temperatures, nickeliferous chlorite commences dehydrating from about 600 °C and gradually decomposes to amorphous forsterite and enstatite, in which loosely bonded nickel and cobalt oxides and their silicates are readily reduced. During reduction, a small amount of iron oxide is reduced to metallic state. Metalized nickel and iron form solid ferronickel alloy. Production of the alloy lowers the activity of iron which is favourable to further reduction of wustite [21]. Iron oxide reduction from fayalite (Fe₃SiO₄) is thermodynamically infeasible under the experimental conditions of this investigation. Nickel and cobalt containing minerals are reducible in the form of amorphous metasilicates and orthosilicates resulting from dehydration at lower temperatures before being transformed to crystalline solid solutions.

When temperature is increased up to 800 °C, reduction reactions are affected by the phase transformation and crystallization. Proximate ionic radii of magnesium, iron, and nickel increase the occurrence of Mg-Fe-Ni solid solution [21]. The activity of nickel oxide in Mg₂SiO₄-Ni₂SiO₄ solution has strong negative deviations from the ideal (Raoultian) solution [22]. As temperature is elevated, more nickel is incorporated into the solid solutions, resulting in a higher fraction of nickel oxide unreducible. This has been verified by decrease in the extent of nickel oxide reduction with increasing temperature above 740°C.

4 CONCLUSIONS

The reduction of an Australian garnieritic laterite ore was examined at different conditions. It was found that the optimal reduction conditions were temperature at 740°C and 60 vol% CO in the CO-CO₂ gas mixture. Gas flow rate did not show visible effect on the ore reduction in the range of 350 – 1050 mL/min. The reducibility of nickel and cobalt oxides decreases with increasing temperature above 800 °C. The metallization of Ni, Co and Fe increased with CO partial pressure; the reduction of iron oxide sharply increased when CO concentration was above 60 vol% which made reduction of nickel and cobalt oxides nonselective. Olivine formation, recrystallization and integration of nickel into the lattice at high temperatures (800 °C and above) render nickel and cobalt oxides less reducible, causing decreased yields of these metals. The selection of the reduction conditions may need to compromise between maximum nickel and cobalt production and the selectivity of reduction of nickel and cobalt oxides to reach best benefit from laterite ore processing.

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5 REFERENCES

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Energy efficiency and environmental friendliness are the future of the global Ferroalloy industry

May 31-June 4, 2015
Kiev, Ukraine

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