Nickel laterite Part 2 – thermodynamic analysis of phase transformations occurring during reduction roasting

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Thermodynamic and phase transformation analyses of nickel laterite ores processed in industry have been carried out. The nickel in the laterite ores is principally associated with Fe rich goethite and serpentine particles. The thermodynamic analysis suggests that the nickel recovery from the Fe rich matrix is limited by equilibrium. The nickel recovery from the single phase serpentine/olivine appears to be higher for particles with Mg/Fe molar ratio <8. The nickel partitioning to the alloy phase is sensitive to the change of temperature and oxygen partial pressure both in the case of reduction roasting of Fe rich goethite and serpentine. It has also been shown in the current study that the optimum conditions for high nickel recovery from the Fe rich goethite and serpentine are different.

Keywords: Nickel laterite, Caron process, Thermodynamic of laterite reduction, Nickel partitioning

Introduction

Nickel laterite ores are used in industrial production of nickel metal through the Caron process.1 Nickel is extracted from the nickel laterite ores by reduction roasting followed by leaching in ammonium carbonate solution. Following purification of the leached liquor, an intermediate solid product of basic nickel carbonate is formed. This intermediate product is then further reduced through solid-gas reduction processes to obtain nickel metal product.

There have been a number of studies of the reduction roasting and leaching of limonitic and saprolitic ores2–7 that make up these nickel laterites. It is generally agreed that the nickel is associated with either goethite or serpentine minerals which, during reduction roasting, are transformed to magnetite and olivine respectively. Despite these previous works, only limited quantitative information is available on the nickel distribution between the various materials before and following the microstructural changes that occur as a result of reduction roasting and leaching.

In Part 1 of the paper,8 detailed characterisations of a particular nickel laterite ore samples processed under industrial conditions have been carried out. The results have provided detailed descriptions of the minerals present and their proportions in the laterite ores, and the changes that have taken place during the reduction roasting and leaching processes. The nickel was found to be associated predominantly with Fe rich matrix in the limonite composite materials, i.e. a mixture of fine goethite, serpentine and other silicate minerals. Nickel also associated with single phase serpentine/olivine particles and its composites in the saprolitic materials.

This study has also provided detailed information on the nickel distributions in the materials. In order to predict how these distributions change under the changing process conditions, information about the thermodynamic behaviour of these nickel bearing materials is required. There have been a number of studies of the thermodynamics of reduction roasting of laterite ores.6,11 however, in all of these studies ideal solution behaviour of the materials was assumed in all phases. This is clearly not the case in the actual systems; for example, the activity of NiO in (Mg, Ni)2SiO4 exhibits a strong negative deviation, i.e. $\gamma_{\text{NiO}} = 0.1$ at 1000°C.12 the activity of NiFe2O4 in spinel [NiFeO (Fe2O3)] at 1000°C is also reported to positively deviate from ideal, i.e. $\gamma_{\text{NiFeO}_2} = 1.1$ at 1000°C.13 The effects of minor impurity elements such as Al and Cr were also not considered in these previous modelling studies.

In Part 2 of the series of the paper, thermodynamic and phase transformation analyses of the materials during reduction roasting were carried out. The information on the characterised laterite materials described in Part 1, in conjunction with the information on the process conditions from industrial operations were used for the inputs of phase equilibria modelling using FactSage14 thermodynamic software and its optimised databases.15 The phases assemblages formed under specified temperatures and oxygen partial pressures were predicted; the results were then compared to the experimental measurements on the samples obtained the industrial operations.
Experimental

Materials

Nickel laterite ores used in the study were supplied by BHP Billiton Yabulu refinery and were obtained from locations in the plant along the process line, which include:

(i) ore feed, i.e. ore feed to multiple hearth roasters
(ii) reduced ore, i.e. ore from the exit of a cooler after multiple hearth roasters
(iii) leached reduced ore, i.e. residue from leaching carried out in laboratory. The details of the ores, in terms of bulk compositions, particle size distribution have been described in Part 1 of this series of papers.8

Analysis techniques

Electron probe X-ray microanalyses (EPMA) were carried out using Superprobe JEOL 8200L (JEOL Ltd, Tokyo, Japan) equipped with five wavelength dispersive detectors. The EPMA analyses were operated at 15 kV accelerating voltage and probe current of 15 nA. Standards (MgO, quartz SiO2, hematite Fe2O3, chromite FeCr2O4, Al2O3 and NiO from Charles M. Taylor, Co., Stanford, CA) were used for the calibration of the EPMA measurements. Scanning electron microscopy (SEM) observations were carried out using Phillips XL-30 (Phillips, FEI Company, Hillsboro, OR) and cold field emission JEOL 6300/6400 with accelerating voltage of 15 and 20 kV. Elemental bulk analysis of the samples was carried out using the inductively coupled plasma atomic emission spectroscopy (ICP-AES) technique. The details of the sample preparations have been described in Part 1 of this series of papers.8

Thermodynamic models

Chemical thermodynamic predictions of the phases, their compositions and proportions formed under equilibrium conditions in the laterite ores during reduction roasting were carried out using FactSage24 thermodynamic software (version 5-5). Chemical compositions of the laterite ores, measured directly using EPMA and ICP-AES,8 were used for the input compositions for the thermodynamic calculations. Phases that contain the following oxides NiO, Fe2O3, MgO, Al2O3, Cr2O3 and SiO2 were considered. Fe–Ni alloy was considered to behave ideally, as has been reported by previous investigators.16

The appropriate optimised thermodynamic solution databases15 were used in the modelling; these include solution databases for ferronickel alloy (Fe–Ni); spinel \(((Fe^{2+}, Ni^{2+}, Mg^{2+})[Fe^{3+}, Al^{3+}, Cr^{3+}]}_{2}O_{2}\); monoxide (wustite) \([Fe, Mg, NiO]_{2}\); olivine (Mg, Fe, Ni)2SiO4; pyroxene \([Mg, Fe, Ni]SiO3\); hematite (corundum) \([Fe, Al, Cr]_{2}O_{3}\); quartz [SiO2]. The ferronickel (Fe–Ni) alloy solution model was introduced by the authors in the package following an ideal solution between solid Fe and Ni. The proportion of the phases, nickel distribution between phases, and nickel concentration in the phases present at equilibrium were calculated at various partial pressures of oxygen at a temperature of 740°C. This temperature was chosen to reflect the typical peak temperature of the materials during the industrial reduction roasting at the Yabulu operation.

Results and discussion

Nickel distribution and nickel recovery

A summary of the nickel distribution and nickel recovery in the selected major nickel bearing particles/ phases in the ore feed, reduced ore, and leached ore, as measured by EPMA, is shown in Table 1. A more detailed description of the nickel distribution in the particles/phases has been described elsewhere.5 In the ore feed, the nickel was mainly present in the Fe rich matrix of the limonite composite particles (~47-4%) and in the serpentine particles (~33-5%). In the reduced ore, 52-8% of the nickel was in the Fe rich matrix and 19-8% was in the single phase olivine particles.

The far right column in Table 1 shows the nickel recovery from each phase. The number was calculated from the difference between the nickel concentration in the reduced and in the leached ore, divided by the concentration in the reduced ore, multiplied by 100%. It can be seen that upon leaching, most of the nickel in Fe rich limonite matrix materials was leached out; with average nickel recovery of 86–93%. The nickel recoveries from the magnetite phase were also quite high, i.e. 85–93%. The nickel recoveries from the olivine and olivine composite particles, however, were quite low, i.e. 18–52%. After leaching, most of the remaining nickel was associated with olivine and its composites. The nickel bulk composition in the leached ore sample measured by ICP-AES analysis was 0.38 mass-%Ni, in which 72.8% of this was in the olivine and its composites.

Goethite to magnetite transformation

Microstructural changes

It can be seen from Table 1 that the major nickel bearing phase is the Fe rich matrix in the limonite composite particles. As has been described in the previous work this Fe rich matrix is a mixture of fine goethite (major) and serpentine (minor) as well as other trace minerals, contributing to the majority of Ni in the ore feed.

Pure goethite, FeO.OH, consists essentially of layers of hexagonal close packed oxygen ions, with the iron ions occupy half of the octahedral interstices; with unit cell parameters as follow: \(a=9.94 \text{ Å}, b=9.49 \text{ Å}, c=3.02 \text{ Å}(Z=4)\). Upon dehydration in air, goethite is transformed to hematite through the following reaction

\[2\text{FeO.OH} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \] (1)

In the present study, the goethite present in the laterite ore contains nickel. Upon reduction roasting in mildly reducing conditions, such as the conditions in the industrial process at Yabulu, it appeared that the goethite was transformed into magnetite rather than to hematite, following reaction (2)

\[6\text{Fe, NiO} + 2\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} + 1/2\text{O}_2 \] (2)

Ni–Fe alloy was also observed to nucleate from the magnetite, which can be represented by the following overall reaction

\[\text{Fe, Ni}_2\text{O}_4(s) \rightarrow 3\text{Ni, Fe}_\text{alloy} + 2\text{O}_2 (g) \] (3)

The nickel therefore distributed between the magnetite and the Ni–Fe alloy phase. The transformations were supported by the SEM, EPMA and synchrotron X-ray powder diffraction (SXRD) results.5
Figure 1 shows the typical changes of the microstructure of the Fe rich matrix in the limonite composite particle in the ore feed, reduced ore and leached ore. In the ore feed the majority of the goethite was in the form of plate-like, or needle-like, bright particles with a size varying from submicrometre to tens of micrometres, as shown in Fig. 1a. The large dark grey phase shown in Fig. 1a is serpentine particle.

Upon reduction roasting, the plate-like goethite was transformed into plate-like magnetite, as shown in Fig. 1b. In addition, magnetite formation within some of the olivine phase (which was transformed from serpentine) was observed, also shown in Fig. 1b. From Fig. 1b, it also appeared that the dehydration and dehydroxylation of the goethite and serpentine in Fe rich matrix during the reduction roasting generated cracks/fissures across the matrix, and in between mineral grains.

Upon leaching, some of the limonite composite particles retained their structure (Fig. 1c, top) while others disintegrated, forming agglomeration smaller particles held together by less dense Fe rich matrix (Fig. 1c, bottom).

In some smaller limonite particles, it appeared that the goethite was transformed into networks of magnetite forming a porous magnetite upon reduction, as shown in Fig. 2b. The SXRD results suggest the formation of Ni–Fe alloy upon reduction roasting and SEM results suggest that this phase was formed on the free surfaces of the magnetite particles. Considering the porous structure that allows the delivery of fresh reducing gas into the interior of the particles, it is very likely that some alloy particles were also interspersed within this porous magnetite, for example, on the surface in the inner pores. These porous magnetite particles retained their shape upon leaching, as shown in Fig. 2c.

### Thermodynamic predictions

The major component of the reduced ore was the Fe rich matrix (a mixture of fine magnetite and fine olivine, which were transformed from fine goethite and serpentine). This component contains nickel of ~52.8% of the total nickel in the ore.

The thermodynamic prediction of the Fe rich matrix in the ore was carried out by considering the average composition of the Fe rich matrix in the reduced ore measured directly using EPMA, i.e. 73.1 mass-%Fe₂O₃, 23.3 mass-%MgO, 6.8 mass-%SiO₂, 1.2 mass-%Cr₂O₃, 4.0 mass-%Al₂O₃ and 2.41 mass-%NiO. Figure 3a shows the calculated phase equilibria at temperature of 740°C in the Fe rich matrix as a function of partial pressure of oxygen. At high oxygen partial pressures, \( p_{O_2} \) > 1.01 × 10⁻¹³ Pa (10⁻¹⁸ atm), the phases present were spinel and olivine. Upon decreasing the \( p_{O_2} \), Fe–Ni alloy and monoxide solid solution was formed at \( p_{O_2} = 1.01 \times 10^{-13} \) Pa (10⁻¹⁸ atm) and 3.2 × 10⁻¹⁵ Pa (10⁻¹⁹.5 atm) respectively. The monoxide became unstable as the partial pressure of oxygen was reduced below \( p_{O_2} = 1.8 \times 10^{-10} \) Pa (10⁻²⁰.⁷⁵ atm). Monoxide was found to be stable only in the range of \( p_{O_2} = 3.2 \times 10^{-17} \) Pa (10⁻¹⁹ atm) to 1.8 × 10⁻¹⁶ Pa (10⁻²⁰.⁷⁵ atm).

From thermodynamic calculations and mass/heat balances of the input and output streams of the gas components of the reactor in the actual process; the effective reduction potential inside the reactor was

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**Table 1** Summary of nickel distribution and nickel recovery in selected major particles and in their phase constituents, in ore feed, reduced ore and leached ore samples, measured by EPMA

<table>
<thead>
<tr>
<th>Phase/mineral group name</th>
<th>Particle</th>
<th>Ore feed</th>
<th>Reduced ore</th>
<th>Leached ore</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ni/total</td>
<td>Ni/total</td>
<td>Ni/total</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Percentage of Ni, %</td>
<td>Percentage of Ni in phase, %</td>
<td>Percentage of Ni, %</td>
</tr>
<tr>
<td>Fe rich matrix</td>
<td>1: limonite composite particles</td>
<td>1.59</td>
<td>1.91</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>1a: agglomerates</td>
<td>0.37</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2: magnetite (Fe, Ni)O₃·Fe₂O₃</td>
<td>0.77</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3: magnetite with chromite inclusions</td>
<td>0.29</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4: magnetite with chromite inclusions</td>
<td>0.27</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5: magnetite</td>
<td>0.27</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>6: magnetite</td>
<td>0.14</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7: magnetite</td>
<td>0.35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>8: olivine</td>
<td>0.35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>8a: olivine-serpentine composite</td>
<td>0.27</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>8b: olivine with magnetite inclusions</td>
<td>0.14</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
estimated to be in the range of $p_{O_2} = 5.7 \times 10^{-15} \text{ Pa} (10^{-19.25} \text{ atm})$ to $3.2 \times 10^{-15} \text{ Pa} (10^{-19.5} \text{ atm})$ at 740°C. Under this range of condition, the thermodynamic predictions suggested that the stable phases were olivine, spinel and Fe–Ni alloy. The monoxide phase was not stable in this range of oxygen partial pressures.

Figure 3b shows the equilibrium nickel distributions among the phases present, i.e. spinel, olivine and Fe–Ni alloy. It can be seen clearly that the amount of nickel that reported to alloy was critically dependent on the gas atmosphere. In the oxygen partial pressure range of interest, the fraction weight of nickel reporting to the Fe–Ni alloy out of total nickel in the Fe rich matrix of the ore was between 0.87 and 0.92. Assuming that all the nickel in the Fe–Ni was leached out during the subsequent leaching process and the extraction of the nickel was mainly from the alloy; these values of fraction weight also represent the effective nickel recovery. These values were, within the experimental uncertainties, in agreement with the observed overall nickel recoveries from the Fe rich matrix in the leached ore measured using EPMA, i.e. between 86 and 93% recovery (see Table 1 and the double shaded box in Fig. 3b).

The above results suggested that the Ni recovery from the Fe rich matrix in the reduced ore in the conditions of interest was limited by chemical equilibrium and was determined by the nickel partitioning to the nickel alloy phase. The fine sizes of the magnetite and olivine phases in the Fe rich matrix facilitated the maximum recovery of nickel from this mixture. Additional nickel recovery required further reduction in the effective partial pressure of oxygen, i.e. less than $p_{O_2} = 3.2 \times 10^{-15} \text{ Pa} (10^{-19.5} \text{ atm})$ at 740°C.

Figure 3c shows the predicted equilibrium concentrations of nickel in the phases present at various oxygen partial pressures. It can be seen that pure nickel was formed at $p_{O_2} = 1.01 \times 10^{-13} \text{ Pa} (10^{-15} \text{ atm})$. As the oxygen partition pressure was decreased below this critical condition, both nickel and iron, present in the spinel and monoxide phases, were progressively transformed to the alloy. The concentration of nickel in the alloy decreased as the oxygen partial pressure was decreased. Thus, while total nickel recovery as alloy increased with decreasing oxygen partial pressure, this was accompanied by increased iron metal formation. In an industrial context, there are disadvantages associated with the more formation of iron since upon leaching,
Figure 3c also shows the Ni concentration in the Fe rich matrix as a function of oxygen partial pressure. This value was determined by dividing the total weight of Ni in the spinel, olivine and monoxide by the total weight of spinel, olivine and monoxide. At the oxygen partial pressure range of interest, the mean Ni concentration in the Fe rich matrix was $0.2 - 0.3$ mass-%. These values were also in good agreement with the EPMA measurements of the Ni concentration in the Fe rich matrix both in the intact and disintegrated limonite composite particles in the leached ore, i.e. 0.14–0.27 mass%Ni (see Table 1 and the double shaded box in Fig. 3c). This again supports the idea of the process being limited by the chemical equilibrium.

Results of EPMA and SXRD$^5$ confirm that in the case of reduction roasting of the ore under the conditions studied, magnetite is formed rather than hematite, following reaction (2). The current thermodynamic prediction shows an agreement with these characterisation results, that is no hematite/corundum $[Fe, Al, Cr]_2O_3$ was formed at the conditions of interest.

The effect of temperature on the amount of nickel reporting to the alloy, calculated using FactSage thermodynamic software, is shown in Fig. 4. It can be seen that the nickel partitioning was very sensitive to the change of temperature. The equilibrium was moved to higher oxygen partial pressures as the temperature was increased, which indicates that based on thermodynamic properties alone, carrying out the process at higher temperatures (at the same oxygen partial pressure) results in more nickel reporting to the alloy. For example, at $pO_2 = 3.2 \times 10^{-15}$ Pa ($10^{-19.5}$ atm), the fraction of nickel as metallic form was 0.46 when the process was carried out at 700°C. By increasing the temperature to 740°C, the fraction of nickel as metallic form increased from 0.46 to 0.92.

The effect of particle size
The effect of particle size on the nickel recovery from magnetite particles was evaluated by comparing the remaining average nickel concentration in the particles of various sizes in the leached ore sample, measured using EPMA. In Fig. 5, the effect of magnetite particle size on the remaining average nickel concentration in the magnetite particles in the leached ore is shown. Higher nickel concentration indicates lower nickel recovery from the particles.

It appeared that lower nickel recovery was occurred in the larger magnetite particles. However, it should be noted that the magnetite particles with a size $>100$ μm were mainly dense crystalline magnetite that were
already present in the form of magnetite in the original ore. The majority of the single phase magnetite was the porous magnetite particles of size 50 \( \mu \text{m} \) and less, which was transformed from the goethite phase upon reduction roasting following reaction (2).

Investigation of the nickel profile in the large dense crystalline magnetite particles in the reduced ore and leached ore showed that the nickel concentration was relatively high and uniform (see Fig. 6). This may indicates that upon leaching no nickel was extracted from these dense magnetite particles. These results suggest that nickel recovery directly from dense magnetite is quite unlikely in the conditions studied, i.e. kinetically unfavourable.

On the other hand, the nickel concentrations in the small porous magnetite particles (which were transformed from goethite upon reduction roasting) in the leached ore were very low (<0.08 mass-%NiO) indicating high nickel recovery. The porous structure together with its small size particle facilitated good contact with the leaching solution resulting in the maximum nickel recovery from these particles.

**Serpentine to olivine transformation**

**Microstructural changes**

It has been reported by previous investigators that serpentine (lizardite) upon heating in air is transformed to olivine at \( \sim 600 \degree \text{C} \), through the following reaction

\[
2\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 (s) \rightarrow \\
3\text{Mg}_2\text{SiO}_4 (s) + \text{SiO}_2 (s) + 4\text{H}_2\text{O} (g)
\]

An endothermic peak in the differential thermal analysis curve for serpentine at about 700–800 \degree \text{C} is associated with the removal of structural water, and the exothermic peak at 800–820 \degree \text{C} related to the recrystallisation of olivine.

In the ore used in the present study, the nickel was also associated with nickel olivine. This olivine was transformed from serpentine upon reduction roasting following a similar reaction as above, i.e.

\[
2(\text{Mg, Fe, Ni})_3\text{Si}_2\text{O}_5(\text{OH})_4 (s) \rightarrow \\
3(\text{Mg, Fe, Ni})_2\text{SiO}_4 (s) + \text{SiO}_2 (s) + 4\text{H}_2\text{O} (g)
\]

This transformation was supported by the SXRD and EPMA results.

In the reduced ore, single phase olivine particles contributed to \( \sim 19-5\% \) of the nickel out of the total nickel in the ore. In the ores used in the present study, the olivine was present in diverse and complex structures, and varying chemistry; but principally in the form of dense and vein-like structures (intertwined platelike and dense olivine with porous olivine in between). The variations in the structure and chemistry were due to the difference in the stage of the alteration/weathering of the original ore. Figure 7 shows the change in the microstructures of the serpentine/olivine particles upon reduction roasting and leaching. The EPMA and XRD results suggest that the serpentine particles were transformed to olivine upon reduction roasting following reaction (5). In some of the olivine particles (minor), formation of magnetite
in the fissures of the vein-like olivine and from within the dense olivine were observed, as shown in Fig. 7b. This was observed in olivine particles with high concentration of iron (fayalite olivine).

Similar complex olivine microstructures as in the reduced ore were observed in the leached ore indicating that there was no significant change of the microstructure of the olivine particles upon leaching, as shown in Fig. 7c.

**Thermodynamic predictions**

Thermodynamic predictions were carried out on the single phase olivine, using the composition measured using EPMA, i.e. composition of 38.8 mass-%MgO, 46.9 mass-%SiO₂, 11.7 mass-%Fe₂O₃, 0.1 mass-%Cr₂O₃, 0.4 mass-%Al₂O₃ and 2.07 mass-%NiO.⁸

The EPMA results of the reduced ore indicate that the serpentine was transformed into olivine upon reduction roasting as in reaction (5); only a trace amount of pyroxene was observed. This indicates that there was no long range diffusion of metal cations taking place during thermal treatment that would enable significant changes in Mg/Si or Fe/Si ratios to take place. In modelling the phase equilibria, pyroxene phase was set as metastable phase. The calculated phase equilibria at 740°C, showing the main phases present, are shown in Fig. 8a. In the PₓOᵧ range of interest, only olivine (~85%), SiO₂ (~13%) and Fe–Ni alloy (~1%) were present.

The equilibrium nickel distributions between olivine and Fe–Ni alloy are shown in Fig. 8b. In the PₓOᵧ range of interest, the calculated weight fraction of nickel in the alloys compared to total nickel were 0.45–0.58 respectively under these conditions. The nickel recovery from single phase olivine particles, as measured by EPMA, was quite low, i.e. ~18% (see Table 1 and the double shaded box in Fig. 8b).

The equilibrium concentration of nickel in the alloy and olivine at various oxygen partial pressures is shown in Fig. 8c. Similar to the case of reduction of Fe rich matrix, initially the formed alloy was rich with nickel, however as the oxygen partial pressure was decreased more iron from the olivine report to the alloy, therefore the nickel concentration in the alloy was decreased.

The calculated equilibrium nickel concentration in the single phase olivine at PₓOᵧ = 3.2 × 10⁻¹⁵ Pa (10⁻¹⁹.⁵ atm) was 0.84 mass-%Ni; also shown in Fig. 8c. The average nickel concentration of the single phase olivine particles in the leached ore measured using EPMA was 1.34 mass-%Ni (see Table 1 and the double shaded box in Fig. 8c). Considering this and the low nickel recovery (measured using EPMA), it appeared that in the case of single phase olivine not all of the potential extractable nickel was leached out upon leaching.

The predictions of the effect of temperature on the fraction of nickel reporting to the alloy in the case of reduction roasting of serpentinite, calculated using FactSage thermodynamic software: oxygen partial pressures of interest (shaded) are in range of PₓOᵧ=5.7 × 10⁻¹⁵ Pa (10⁻₁⁹.⁵ atm) to 3.2 × 10⁻¹⁵ Pa (10⁻₁⁹.⁵ atm) at 740°C
Comparison of Ni partitioning to alloy in the case of Fe rich matrix and olivine particles

Figure 10 shows the comparison of nickel partitioning to alloy at various oxygen partial pressures, calculated using FactSage thermodynamic software, in the case of reduction roasting of Fe rich matrix and single phase serpentine (olivine): temperature $740 \, ^\circ C$; oxygen partial pressures of interest (shaded) are in range of $p_{O_2} = 5.7 \times 10^{-5} \, Pa (10^{-19.5} \, atm)$ to $3.2 \times 10^{-15} \, Pa (10^{-19.5} \, atm)$.

Comparison of Ni partitioning to alloy in the case of Fe rich matrix and olivine particles

Figure 10 shows the comparison of the nickel partitioning in the alloy in the case of reduction roasting of Fe rich matrix and single phase serpentine/olivine at $740 \, ^\circ C$. The thermodynamic prediction results showed that at the same oxygen partial pressure the equilibrium nickel partitioning to the alloy for Fe rich matrix and serpentinite/olivine was not the same. It can be seen that at $p_{O_2} = 3.2 \times 10^{-15} \, Pa (10^{-19.5} \, atm)$, the fraction of nickel reporting to alloy in the case of Fe rich matrix was 0.92, while in the case of serpentinite/olivine was only 0.58. In the case of serpentinite/olivine, the oxygen partial pressure need to be decreased to $p_{O_2} = 1.01 \times 10^{-16} \, Pa (10^{-21} \, atm)$ to get the same nickel partitioning as in the case of Fe rich matrix. This result may indicate that separate reduction atmosphere of the two laterite ores (hydroxide and silicate) at different conditions (in a more reducing atmosphere in the case of silicate ore) then remixing the ores prior to leaching may be beneficial to achieve better nickel recovery.

Effect of particle size

Figure 11 shows the effect of particle size on the nickel recovery from single phase olivine particles. The results may suggest that the larger particles had lower remaining nickel concentrations (or higher nickel recovery) compared to the smaller particles. If the extraction were determined by kinetics of leaching, e.g. by a shrinking core model, this was the opposite of what was expected, i.e. higher nickel recovery from the smaller particles. It should be noted, however, that other factors (such as the physical and chemical characteristics of the particles) were not considered in the plot.

Further investigations on the nickel profiles across the olivine particles in the leached ore were carried out. Figure 12 shows examples of some nickel profiles observed in some of the olivine particles in the leached ore. It can be seen that the average nickel concentration varies from one particle to another regardless of the size of the particle. For example, two olivine particles of a similar size (particles 2 and 3 in Fig. 12a) may have two different nickel concentrations. Particles 1 and 4, as shown in Fig. 12, are larger and have a lower average nickel concentration compared to the particle 3 (Fig. 12a). Particle 4, which has a size comparable to particle 1 but exhibit a less dense structure, has an average nickel concentration of two times higher than that of particle 1. Another interesting observation from this study is that the nickel profiles across the olivine particles in the reduced and leached ores, in general, are uniform.

The nickel recovery from the olivine particles can also be affected by the physical characteristics of the particles, for example detailed microstructure (dense, vein-like), porosity and crystallinity; as well as their chemical (composition) characteristics. These characteristics are affected by the level of alteration (weathering) of the original saprolite particles. Geologists use a scale from 0 for fresh rock to 5 for earthy materials to provide a simple classification of the alteration stages of laterite materials. The alteration stages can roughly be identified by the chemistry of the saprolites, i.e. by the molar ratio of Mg/Fe in the crystalline solid.

To evaluate the effect of alteration stage on the nickel recovery, the nickel concentration in the reduced and the leached ore was plotted against the molar ratio of Mg/Fe, as shown in Fig. 13. The open triangles and the closed circles are the actual nickel concentration data measured using EPMA for the reduced ore and the leached ore respectively. The differences between these may indicate the extent of nickel recovery upon leaching. The numbers 1–5 represent the alteration stages based on the Mg/Fe ratio. Although the plot is indicative, certain trend can be observed from Fig. 13. It can be seen that the olivine with Mg/Fe ratios <8 appeared on average to have better nickel recovery compared to olivine with Mg/Fe ratios >8.

The variations in the nickel recovery with different Mg/Fe ratios may also be attributed to the thermodynamic characteristic of the olivine, in particular the activity of NiO in the olivine. The activity of NiO is affected by the composition of the olivine, thus also affected by the Mg/Fe ratio in the olivine. From previous investigation, it is clear that the activity of NiO in the solid (Mg,Ni)2SiO4 varies with varying Mg concentration. However, there is no data available to the
public on the variations of NiO activity with Fe and Mg concentrations in the (Fe,Ni)$_2$SiO$_4$ and (Mg,Fe,Ni)$_2$SiO$_4$.

It has been described in the previous section that the measured nickel recovery in the olivine particle was lower than the equilibrium nickel recovery calculated using FactSage. The measured nickel concentration in the olivine was also higher than that of predicted equilibrium nickel concentration. These results may suggest that the nickel extraction from the olivine was limited by kinetics (for example diffusion limited) rather than by equilibrium. However, evidences of kinetic limited process were not observed in the olivine particles. These include the uniform nickel profiles that were observed in the reduced and leached olivine particles; the higher nickel recoveries from the larger olivine particles compared to from the smaller olivine particles; and the fact that NiO activity may vary depending on the Mg/Fe ratio in the olivine particles. No experimental work has been reported on the effect of Mg/Fe ratio in the NiO activity in solid olivine [(Mg,Fe,Ni)$_2$SiO$_4$]. Previous studies on the phase equilibria between liquid FeO–MgO–SiO$_2$ slag and liquid Fe–Ni alloy at 1500°C suggest that NiO activity coefficient, $\gamma_{\text{NiO}}$, in the slag varies with varying FeO concentration. This may indicate that a similar variation applies in the case of solid olivine.

The above results indicate that the factors affecting the nickel recovery from olivine particle are quite complex; it is not only affected by its size but also by other factors (and the interrelationship between these) such as:

(i) the physical characteristics of the particles, for example detailed microstructure (dense, vein-like), porosity and crystallinity

(ii) the chemical characteristics, such as Mg/Fe ratio

(iii) the thermal history of the materials (e.g. reduction roasting)

(iv) the details of leaching practices.

From the current studies it is still not clear whether the nickel extraction from the single phase olivine particles is controlled by equilibrium or kinetics. However, it is apparent that the effect of Mg/Fe ratio in the solid (Mg,Fe,Ni)$_2$SiO$_4$ on the activity of NiO is worthy of further research.

Other single phase particles

Other single phase particles in the ores include magnetite, chromite and silica particles. The results of comparison of the microstructure of single phase magnetite, chromite and silica particles in the ore feed, reduced ore and leached ore suggest that these large...
single phase particles do not undergo any transformation upon reduction roasting and leaching.

Summary
Detailed characterisation of processed laterite ores obtained from industry has been carried out in the current studies and quantitative descriptions of these materials have been developed. These results have been used for the basis of phase transformations and thermodynamic analyses.

The nickel in the ore is present in the Fe rich matrix (a mixture of fine magnetite and olivine) and olivine particles. In the case of Fe rich matrix, it appears that the formation of Fe–Ni alloy (which directly affect the nickel recovery upon leaching) from this mixture is limited by equilibrium. At the conditions of interest, all of the extractable nickel (from thermodynamic point of view) has been extracted from Fe rich matrix. Further nickel recovery from this requires further reduction of effective oxygen partial pressure.

In the case of nickel extraction from single phase olivine particles, it is still not clear whether the process is limited by kinetics or equilibrium. The nickel recovery from the single phase olivine particles appear to be complex and affected by a number of factors such as its chemical and physical characteristics. It appears that nickel recovery is better for single phase olivine with Mg/Fe ratio <8.

The thermodynamic predictions show that the nickel partitioning to the alloy phase is sensitive to the change of temperature both in the case of reduction of Fe rich matrix and single phase olivine. It has been shown that this nickel partitioning to the alloy in the case of reduction roasting of Fe rich matrix and single phase olivine is different. It has been shown in the current studies that separate reduction roasting treatment of the high and low silicate laterite ores is beneficial to obtain maximum nickel recovery.

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