

THE RECOVERY OF FERRO-NICKEL FROM SAPROLITE ORES USING REDUCTION ROASTING

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ABSTRACT

Lateritic ores represent an increasing source of supply of nickel to world markets. The mineralogy of these ores is complex but can be broadly considered as consisting of limonitic (oxide) and saprolitic (silicate) minerals. The achievement of high metal recoveries from saprolite ores poses a particular problem and relatively little is known of the fundamental reactions taking place during pyrometallurgical reduction.

Recent experimental studies have been undertaken to determine the microstructural and phase transformations occurring during the reduction roasting of well-characterised nickel-containing saprolite ore. Selected lizardite samples have been treated at temperatures between 500°C to 800°C in controlled gas mixtures and process conditions, and nickel recoveries determined through the use of leaching tests on reduced samples. Phase and microstructural changes have been characterised using X-ray powder Diffraction (XRD), High Resolution Scanning Electron Microscope (HRSEM) and Transmission Electron Microscope (TEM) techniques.

A complex series of phase and microstructure changes has been observed involving: i) the dehydration of serpentine, ii) the formation of a high-silica amorphous phase, iii) the nucleation and recrystallisation of forsterite (Olivine), and iv) the formation of Ni-Fe nanoparticles. The metal recovery is shown to be dependent on thermal history, peak temperature, time and reduction potential of the gas. The findings of the study reveal for the first time evidence of Ni-Fe alloy formation under these conditions and have important implications for the design and operation of reduction roasting operations for ferro-nickel production.

KEYWORDS: *Ferronickel, reduction roasting, kinetics, saprolite.*

1. INTRODUCTION

Nickel laterite ores, which account for approximately 80% of world's nickel reserves [1], are now becoming increasingly important for the world's nickel supply as nickel demands have grown in the recent decades [2].

The Caron process, which involves reduction roasting of the ore followed by ammonical leaching of reduced ore, is one of the ways in which nickel laterite can be treated [3]. It has been successfully used in processing the iron-rich limonitic part of the nickel laterite ore body. Reserves of limonite ores are, however, limited and there are large deposits of saprolitic ores (with high Mg and Si content) that cannot currently be economically processed by the Caron process.

Previous investigations on the treatment of saprolite ore using the Caron process have suggested the reduction roasting process may consist of a series of chemical reactions and phase transformations; these reactions may involve dehydration of hydrous-silicate, metallisation of nickel from de-hydrated silicate matrix and re-crystallisation of de-hydrated silicates [4-5]. Nevertheless, these underlying reaction mechanisms and their influences on final nickel recovery are not well understood.

The current article outlines recent research on the reduction roasting of saprolite ore utilizing

modern analytical skills and equipment to reveal possible mechanisms of reduction of nickel from saprolite, and how this process is controlled by accompanying reactions or transformations.

2. EXPERIMENTAL

2.1. Material

Ring-milled saprolite ore was supplied by BHP Billiton Yabulu Refinery, Townsville, Queensland, Australia. In the current study, this saprolite was further sieved to obtain a portion with particle size less than 38 μm as starting material. The bulk composition of this saprolite ore was analyzed by ICP-AES in Yabulu Refinery and reported in table 1.

Table 1: Bulk composition of saprolite supplied by BHP Billiton Yabulu Refinery

Element	Ni	Co	Fe	Mg	Si	Al	Cr	Mn	Ca	Zn
wt%	1.41	0.05	6.30	18.10	16.02	0.31	0.38	0.11	0.03	0.01

The phases present in the saprolite ore have been identified by X-ray diffraction and the proportion of each phase was estimated from Electron Probe Micro-Analysis (EPMA) as shown in table 2.

Table 2: Major phases present and proportion estimation

Phase/Mineral Name	Ideal Chemical Formula	Estimated Proportion, wt%
Serpentine	$(\text{Mg,Fe,Ni,Al})_2(\text{Al,Si})_2\text{O}_5(\text{OH})_4$	90.7%
Olivine	$(\text{Mg,Fe,Ni})_2\text{SiO}_4$	1.7%
Pyroxene	$(\text{Mg,Ni,Fe,Ca})\text{SiO}_3$	1.0%
Spinel	$(\text{Mg,Fe})\text{O}(\text{Cr,Fe,Al})_2\text{O}_3,$ $(\text{Fe,Mn,Ni})\text{OFe}_2\text{O}_3$	1.6%
Quartz	SiO_2	5.0%

2.2. Reduction experiment

Reduction roasting experiments were carried out in an electrically-heated tube furnace inside a quartz tube, using a top-blown fluidizing particle technique. A schematic representation of the reduction apparatus is shown in figure 1. The reducing gases were introduced through a 5-mm-inner diameter (ID) alumina injection tube from the top, blowing and circulating the particles at the bottom of a 30-mm-diameter closed-end quartz tube. The flow rate of the introduced gases was controlled at 300mL/min. An electrically-driven mechanical vibrator was connected to the quartz tube through a steel frame; the agitation of the quartz tube improved the circulation of the particles in the reaction vessel during the reduction process and enhanced the contact between gases and particles.

3 grams ($\pm 0.01\text{g}$) of sample were inserted into the quartz tube and placed in the tube furnace after the furnace was heated to the desired temperature. After reduction, the quartz tube containing the sample was quickly removed and cooled down by applying flowing water to the outside of the tube. The flow of reducing gases was maintained during cooling. Alcohol was added into the quartz tube after it cooled down to room temperature to prevent the sample from being

exposed to the air and re-oxidation of the reduced sample. The sample then was removed from the quartz tube and stored in sealed plastic containers awaiting further analysis.

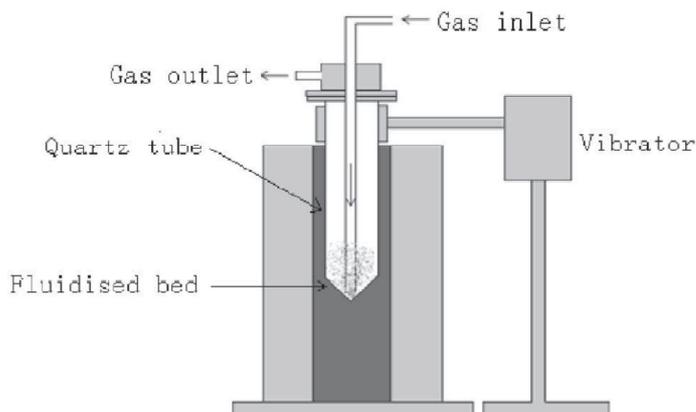


Figure 1: Schematic of the fluidized bed for saprolite reduction roasting

2.3. Analysis techniques

Reduced Pulverised Saprolite samples were sent to BHP Billiton Yabulu Refinery for leaching and chemical analysis. The reduced ores were leached in a mixed aqueous solution of ammonia and ammonium carbonate aerobically for an hour followed by 3 days anaerobic leaching. Ni recovery was calculated on the basis of ICP-AES analysis of the leached ore. Small portions of reduced ore and leached ore were reserved for X-ray powder diffraction (XRD) and TEM analysis. The reduced and leached saprolite ore samples were suspended in ethyl-alcohol and the suspension was dropped onto 200-mesh copper grids coated with hollow carbon film for high resolution SEM and TEM analysis. Fractured serpentine rock was placed on the carbon stub and subjected to microstructure analysis.

The microstructure of samples was investigated using scanning electron microscopy (SEM). (FE-SEM JEOL 890 and PHILIPS XL-30 with accelerating voltage of 20 keV) Transmission electron microscopy (PHILIPS F20 with accelerating voltage of 200 keV) combined with energy dispersive X-ray (EDX) techniques were used to identify the formation and compositions of Ni-Fe alloy. Phase identification by X-ray powder diffraction (XRD) analysis was carried out using Bruker D8 Advance X-Ray diffractometer with a Cu K α radiation source.

3. RESULTS

3.1. Phase transformations

Ring-milled saprolite samples (<38 μ m) were subjected to X-ray diffraction analysis after reduction at temperatures in the range of 500°C to 800°C for 15 minutes in 15%H₂ in N₂. The diffraction pattern of the original saprolite sample (figure 2) shows the presence of serpentine (lizardite) and small amounts of quartz and olivine. Some broadening of the lizardite peaks indicates low crystallinity and variable composition nature of the lizardite. With the increase of the reduction temperature, the lizardite peak intensity is decreased progressively and cannot be detected after reduction is carried out at 650°C. In the temperature range from 650°C to 800 °C olivine XRD peaks are found to grow with increasing reduction temperature. The formation of taenite (Fe-Ni alloy) and quartz is not identified by X-ray diffraction.

3.2. Microstructure change

The layered morphology of the "as received" serpentine is revealed by SEM, which is consistent with the crystal structure of this phase (figure 3). Very fine pores with diameter less than 0.2 μm in the original serpentine, which may due to the weathering process, can be seen at high magnification. After 10mins reduction at 500°C, cracks and fissures can be seen to have formed on the serpentine surface and pores with diameter from 0.5 to several microns in selected areas of the surface. With further increase of reduction temperature, the breakdown of serpentine progresses and produces more cracks and pores. At 700°C, the intermediate structure of decomposed serpentine is strongly altered and previously formed pores become progressively coarse. Nucleation and re-crystallization and appears to have taken place at 800°C, this is associated with a reduction in pore surface area.

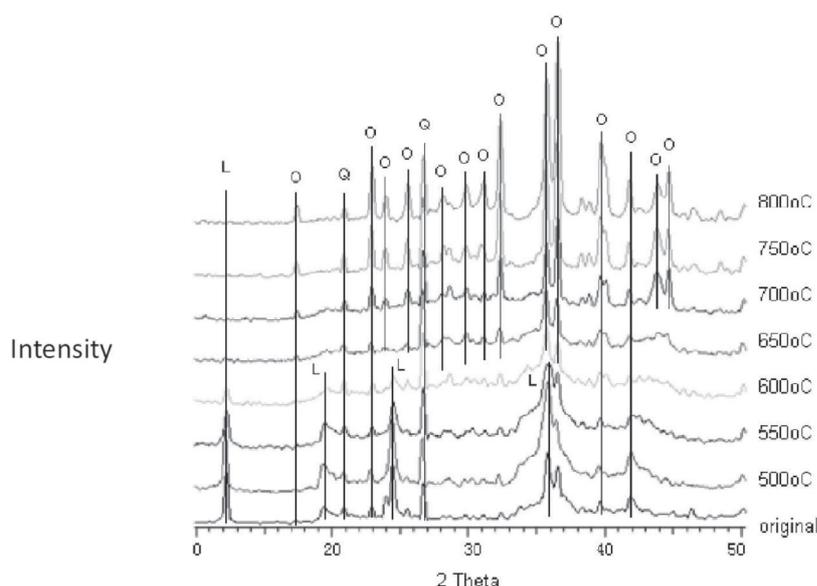


Figure 2: XRD patterns of reduced Saprolite at different reduction temperature in 15% H_2 in N_2 for 15mins (Legend: L-lizardite, O-olivine, Q-quartz. Radiation: Cu- $\text{K}\alpha$)

3.3. Observation of the formation of Fe-Ni alloy

Though the formation of Ni-Fe alloy after reduction roasting has been suggested in a previous study [7], there has not been any direct evidence showing the morphology and size of the formed Ni-Fe alloy. The alloy phase cannot be resolved using electron probe x-ray analysis (EPMA) [8]. In the current study, both High Resolution Scanning Electron Microscope (HRSEM) and Transmission Electron Microscope (TEM) were utilized to analyze the reduced and leached ore samples.

Figure 4 shows HRSEM images of reduced ore, precipitates with particle size of approximately 10-20 nm can be clearly identified forming on the surface of the ore matrix when reduced at 700°C and 800°C (figure 4b-c). The backscattered electron image (Figure 4d) indicates these precipitates consist of elements having mean atomic number greater than in the ore matrix.

Figure 5 shows an example of the original and reduced ores viewed using Transmission Electron Microscope (TEM). In comparison with original ore, images of the reduced ore at all temperatures show the formation of spherical precipitates with precipitate size increasing with the increase of reduction temperature. Combined EDS and analysis shows there is a great enrichment of

Ni and Fe in these precipitates (figure 6a), indicating a formation of Ni-Fe alloy. A selected area diffraction (SAD) pattern of a single particle of Ni-Fe alloy is shown in figure 6b, indicating a face-centred cubic structure with unit cell dimension consistent with Ni-Fe alloy formation.

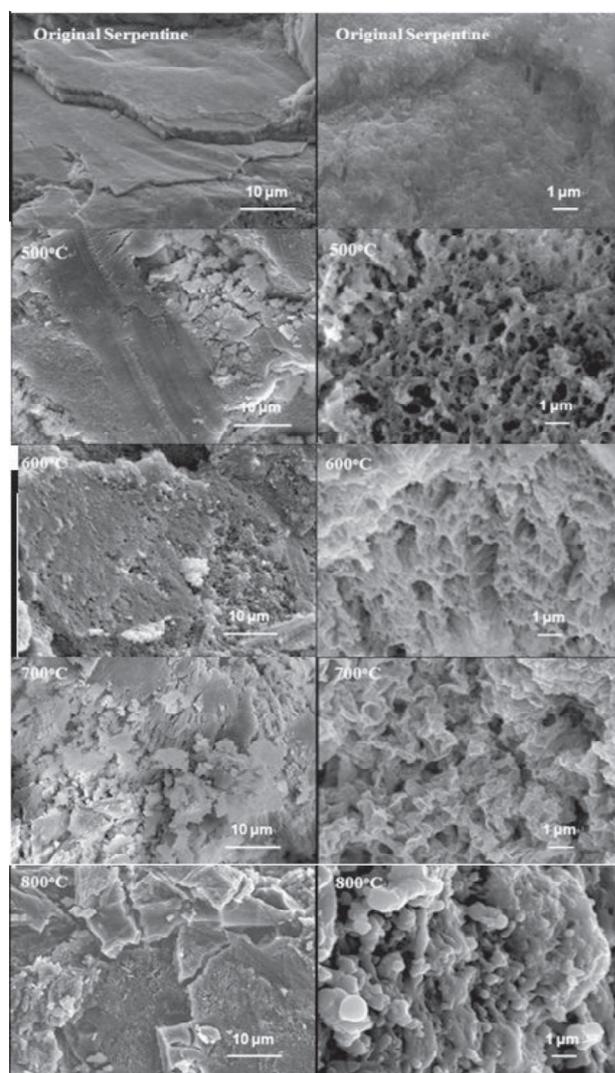


Figure 3: SEM micrographs showing changes in serpentine microstructure during reduction at various temperatures (Samples reduced in 15% H_2 in N_2 for 15 mins)

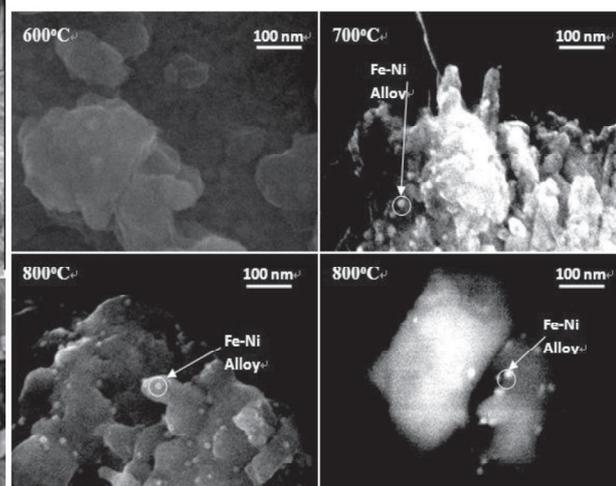


Figure 4: HRSEM imaging of reduced serpentine in 15% H_2/N_2 for 30mins at various temperatures showing the formation of Ni-Fe alloy particles (a,b,c: secondary electron image; d: backscattered electron image)

3.4. Leaching of Fe-Ni alloy

The leached ore samples have been examined under both HRSEM and TEM. It can be seen from HRSEM micrographs (figure 7), precipitates *on the surface* of the ore matrix formed after reduction at all temperatures have been all removed by the leaching process.

On the other hand, after leaching, it appears that Ni-Fe enriched precipitates have been removed throughout the bulk material when reduced at 600°C. However, despite dissolution from the surface they remain within the ore matrix when reduced at 800°C (figure 8).

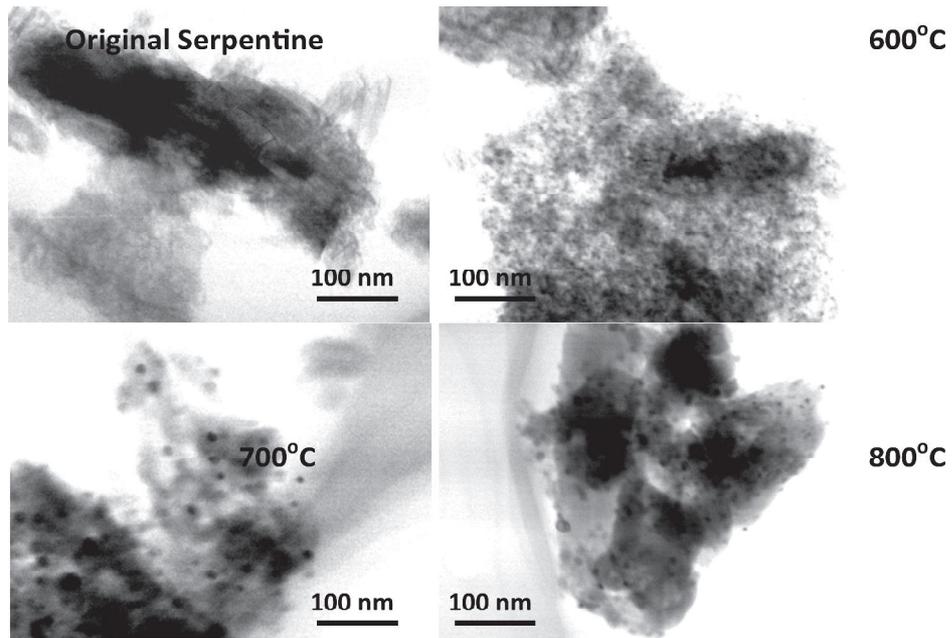


Figure 5: TEM imaging of reduced serpentine in 15 % H₂/N₂ for 30mins at various temperatures showing the formation of Ni-Fe alloy particles (Bright Field)

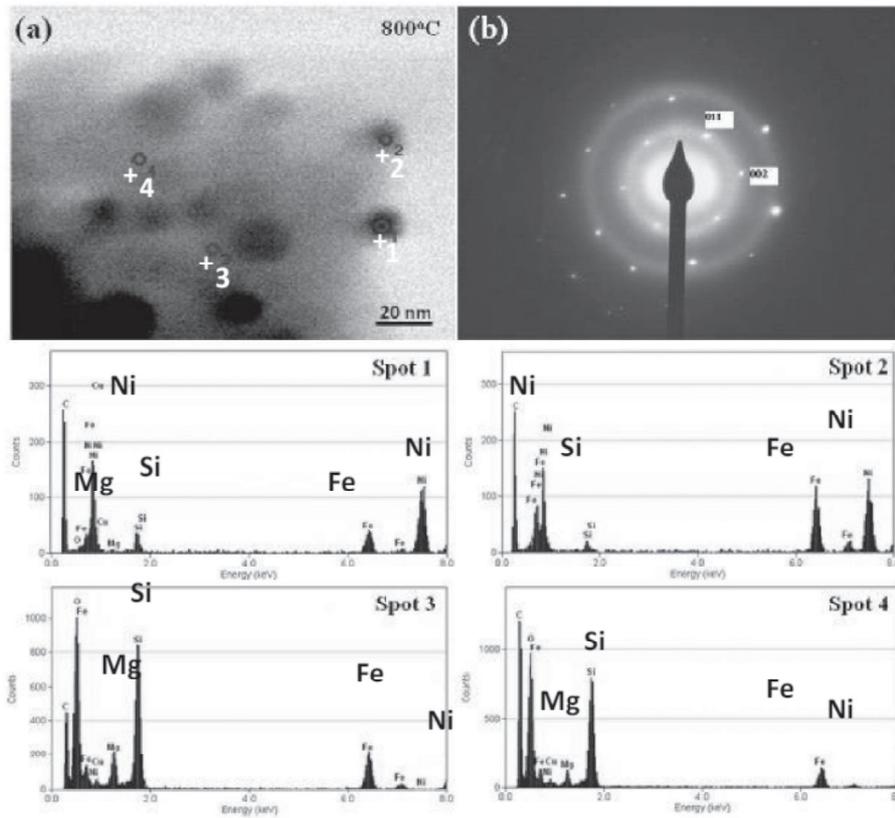


Figure 6: a) EDS analysis of reduced serpentine in 15 % H₂/N₂ for 30mins at 800°C; b) SAD pattern of formed Ni-Fe alloy

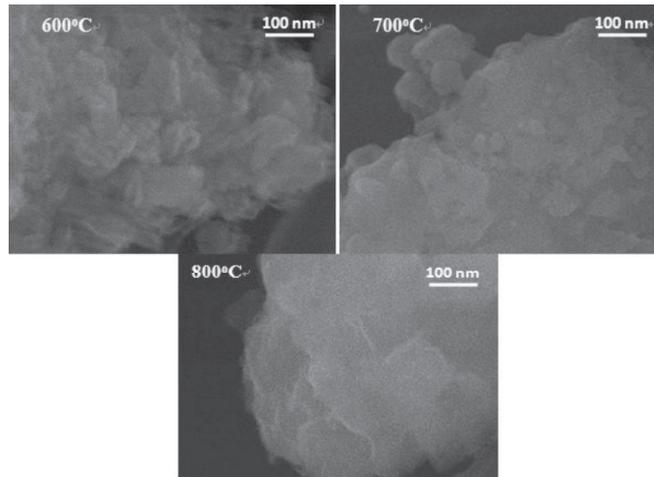


Figure 7: HRSEM imaging of the surfaces of leached serpentine previously reduced in 15 % H_2/N_2 for 30mins at various temperatures

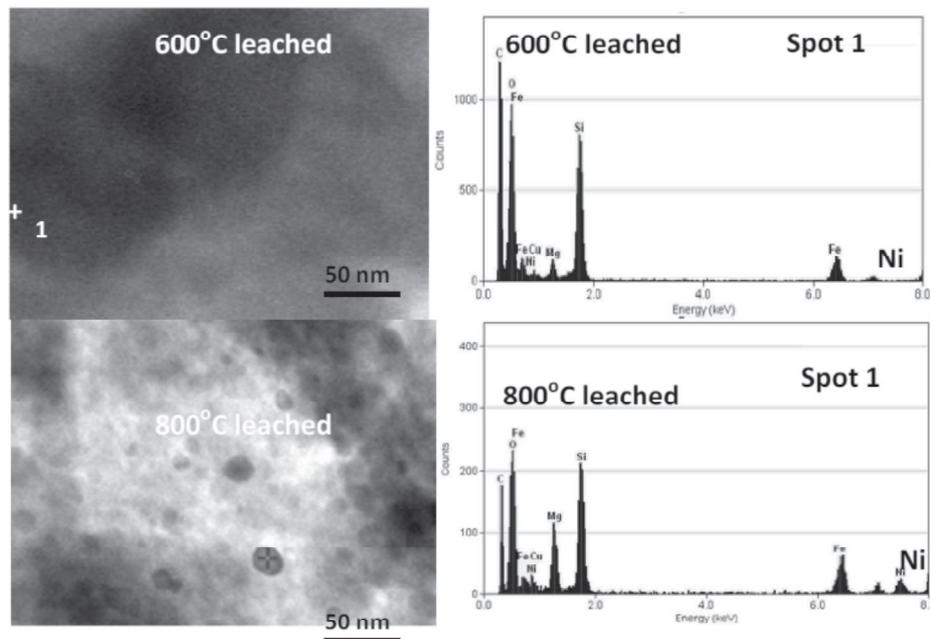


Figure 8: EDS analysis of leached serpentine previously reduced in 15 % H_2/N_2 for 30mins at 600°C and 800°C

3.5. Ni recovery

Ni recovery following leaching of reduced saprolite is plotted on figure 9 against reduction temperature between 500-800°C. It can be seen that Ni recovery increases with increase of reduction temperature, and reaches to maximum at 700°C-750°C; a significant decrease in Ni recovery is found when reduction temperatures are higher than 750°C. At reduction temperature range from 500°C to 650°C, Ni recovery increases with increase of reduction time, however, long reduction times in the temperature range from 700°C-800°C have a negative effect on the Ni recovery.

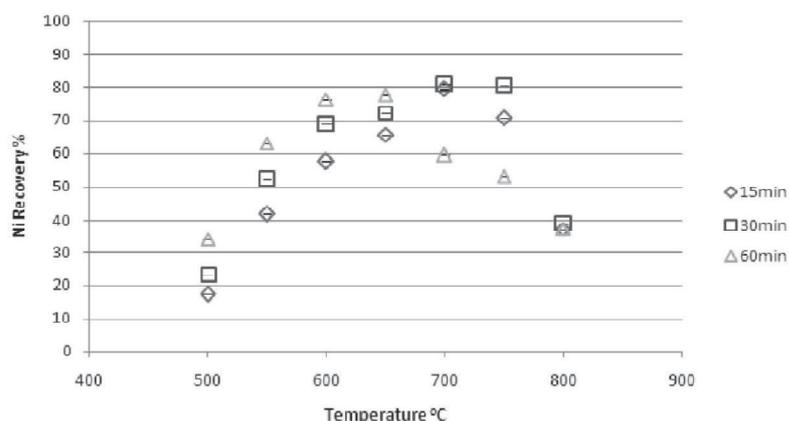


Figure 9: Ni recoveries from roasted/leached saprolite as a function of reduction temperature and time in 15 % H_2/N_2

4. DISCUSSION AND INDUSTRIAL IMPLICATIONS

Analysis of roasted/leached samples indicates there is a dramatic increase of Ni recovery from 500°C to 600°C, which suggests the reduction proceeds significantly once serpentine crystal structure is destroyed. Formation of pores with breakdown of serpentine, which leads to larger surface area for reaction, may also accelerate the reduction process. Low Ni recovery was found at reduction temperatures higher than 750°C. Stevens et al [10] suggested that dissolution of nickel in the recrystallised olivine phase renders it inert and prevents its reduction and extraction. However, a different phenomenon was observed in current study. After reduction at 800°C, a large amount of Ni-Fe alloy precipitates were found to be present after reduction and showed no sign of Ni dissolution in olivine phase. After leaching, Ni-Fe alloy precipitates formed on the surface were removed; however, TEM analysis suggests that there is still significant fraction of alloy remaining physically trapped, i.e., encapsulated, in the olivine matrix.

4.1. Processing temperature

The results from the present study show that the maximum Ni recoveries from the roast/leach Caron Process are obtained for roasting temperatures in the range of 600-700°C; further increase in reduction temperature leads to a large decrease in the recovery. The nominal maximum reduction temperature of the ore in the Herschoff reduction roaster at Queensland Nickel Yabulu Refinery is controlled at 750-780°C. At this temperature range, it has been shown in present study, the sintering of decomposed ore material and recrystallisation of the olivine becomes phase significant. Although Ni in the ore may still be reduced at the higher temperature, it has been shown that a large proportion of the reduced Ni alloy cannot be recovered from the saprolite through ammonical leaching since the nano-sized alloy particles become encapsulated in the olivine matrix.

4.2. Residence time

In the current industrial process at Queensland Nickel Yabulu Refinery, the ore is fed into the roaster and gradually heated up as the ore descends under gravity through the furnace. The average residence time of the ore at temperatures between 600 and 780°C is about 50 minutes. In present study, it has been found that nickel recovery increases with increase of reduction time at temperature range between 500°C to 600°C, prolonged heating at temperature above 600°C does not improve or has negative effect on the nickel recovery due to the progressive sintering of the ore and

recrystallisation of the olivine phase that is formed during the reduction roast. There would appear to be no net benefit in increasing the residence time of the ore in the reduction roasting stage.

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