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Thermodynamic Analysis of the Selective Reduction of a Nickeliferous Limonitic Laterite Ore by Hydrogen

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Abstract: Nickeliferous limonitic laterite ores are becoming increasingly attractive as a source of metallic nickel as the costs associated with recovering nickel from the sulphide ores increase. Unlike the sulphide ores, however, the laterite ores are not amenable to concentration by conventional mineral processing techniques such as froth flotation. One potential concentrating method would be the pyrometallurgical solid state reduction of the nickeliferous limonitic ores at relatively low temperatures, followed by beneficiation via magnetic separation. A number of reductants can be utilized in the reduction step, and in this research, a thermodynamic model has been developed to investigate the reduction of a nickeliferous limonitic laterite by hydrogen. The nickel recovery to the ferronickel phase was predicted to be greater than 95 % at temperatures of 673–873 K. Reductant additions above the stoichiometric requirement resulted in high recoveries over a wider temperature range, but the nickel grade of the ferronickel decreased.

Keywords: limonite, laterite, reduction, hydrogen, thermodynamics

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Introduction

The two major sources of nickel metal are the sulphide and the oxide ore deposits. While the oxide ores are more abundant, comprising about 70 % of the known world nickel resources, current primary nickel metal production is dominated by the nickel sulphides, which account for nearly 60 % of primary nickel production [1]. This disparity between known nickel resources and primary metal

production is a result of the challenges associated with concentrating and extracting the nickel content of the oxide ores. In the sulphide ores, nickel occurs as the discrete nickel sulphide mineral pentlandite $[(\text{FeNi})_9\text{S}_8]$, which is amenable to liberation and flotation to form a concentrate containing 6–15 % nickel. This concentrate can be produced close to the mine site before being sent for further processing, representing a significant cost savings. Conversely, in the oxide ores, nickel is typically found in solid solution with the iron hydroxides or incorporated into the magnesium silicate minerals and may only be beneficiated to a limited degree by screening [2]. Despite this, the growing worldwide demand for nickel metal, combined with the depletion of easily accessible sulphide ore deposits, has led to increased interest in developing the nickel oxide ore deposits.

The oxidic nickeliferous laterite ore deposits are composed of two major nickel-containing layers: an upper limonitic layer and a lower saprolitic layer. The limonitic layer occurs below the overburden and primarily consists of goethite $((\text{Fe,Ni})\text{O}\cdot\text{OH})$, with the nickel substituting for iron in the crystal lattice. These ores typically contain 1–1.6 % nickel and account for 60 % of the known nickel laterite resources. The saprolitic layer, also referred to as garnierite, occurs deeper in the deposit and is comprised of a mixture of iron oxides and magnesium silicate minerals. In this layer, the nickel typically substitutes for magnesium in the hydrated magnesium silicates $((\text{Mg,Fe,Ni})_3\text{Si}_2\text{O}_5(\text{OH})_4)$. Typical grades for the saprolitic ores vary from 2 % to 5 % nickel [3]. Globally, the average nickel grade in the nickel oxide ores is 1.3 % [1]. These ores also typically contain greater than 0.05 % cobalt [4].

As laterites are not amenable to conventional beneficiation methods, such as froth flotation, recovery of the nickel metal is typically achieved by hydrometallurgical and/or pyrometallurgical techniques applied to the whole ore. The limonites are traditionally leached, requiring elevated temperatures, pressures and acid consumption. This leaching process can then be followed by a smelting step to produce a ferronickel pig iron. The saprolites, on the other hand, are typically treated directly by

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pyrometallurgical techniques, such as smelting the ore to produce a ferronickel alloy. This is an energy-intensive process requiring elevated temperatures to dry the ore, reduce the metal oxides and melt the slag [4]. One alternative for both oxide ore types would be to perform a low temperature reduction process and then concentrate the ferronickel particles by physical separation processes such as magnetic separation. In this regard, it is of interest to understand the thermodynamics of the reduction process, in particular how the nickel grade and the recovery are affected by the reduction conditions.

The purpose of the present work was to expand the current body of existing knowledge with regards to the reduction of the oxide ores by determining the equilibrium products produced by reacting a typical nickeliferous limonitic laterite ore with hydrogen. First, the current thermodynamic and experimental information regarding the gaseous reduction of the nickeliferous limonitic laterite ores by hydrogen is reviewed. Second, based on the thermodynamic information available in the literature, a model is developed for the reduction of a typical nickeliferous limonitic laterite ore by hydrogen gas. Third, using the assay of a typical nickeliferous limonitic laterite ore, the equilibrium compositions of the products resulting from the reaction of the ore with hydrogen under various reducing conditions could be determined. In this manner, the effects of operating parameters, such as temperature and gas composition on both the nickel grade of the ferronickel alloy and the nickel recovery, could be determined. Finally, the use of hydrogen as the reducing gas is compared to carbon monoxide.

Previous thermodynamic studies

Thermodynamic studies of the gaseous reduction of nickeliferous laterite ores have previously been conducted by Canterford and Turnbull [5], Utigard and Bergman [6] and Valix et al. [7]. A review of these works has previously been given by Pickles and Elliott [8] with regards to reduction by carbon monoxide. Here, those aspects of these works that relate to reduction by hydrogen are discussed. In general, these authors note that the reducing atmosphere, and in particular the ratio of reductant to oxides, is the primary factor in determining the nickel grade in the ferronickel product. Lower reduction potentials, i. e. an increased CO₂:CO or H₂O:H₂ ratio in the reducing gas mixture, and low temperatures (<873 K) yielded the best selectivity. However, a decreased reduction potential required higher temperatures to achieve high conversion to metallic nickel. For all reduction

conditions studied, metallic nickel was only present in the ferronickel alloy phase.

Canterford and Turnbull and Valix et al. have both noted that at temperatures below 923–973 K, carbon monoxide provided better selectivity than hydrogen, producing a ferronickel with a significantly higher nickel grade, at the cost of a decreased nickel recovery [5, 7]. At temperatures above this range, both reducing gases behaved similarly, likely due to the complete reduction of all of the iron and nickel oxides in the ore. An equimolar blend of the two reducing gases showed intermediate behaviour below 923 K and identical behaviour to the pure gases above this temperature. Blending of CO or H₂ with CO₂ or H₂O was also predicted to improve selectivity by lowering the reduction potential of the gas mixture. Both Canterford and Turnbull and Valix et al. have noted 873 K as the optimum temperature for selective reduction in carbon monoxide based on the conversion of nickel oxide to metallic nickel, the nickel grade in the ferronickel, and the rate at which the reaction should proceed. At this temperature and with a stoichiometric addition of pure hydrogen, both groups of authors predicted a nickel metallization above 90 %.

Utigard and Bergman considered the reduction of a saprolitic ore by a mixture of H₂ and CO₂ [6]. According to their model, at a H₂:CO₂ ratio of 1.6 and temperature of 873 K, no metallic iron should be formed and the nickel recovery should reach about 50 %, while at the same gas ratio and a temperature of 1,273 K, the nickel recovery should reach about 90 %. They also noted that metallic iron should not be formed at a gas ratio below 1.6 and that a higher ratio resulted in an increased rate of and extent of metallization. These findings are in general agreement with those of Canterford and Turnbull and Valix et al., who found that lower temperatures and reductant gas ratios should promote greater selectivity of the nickel oxide over the iron oxide and therefore generate a higher grade ferronickel. However, the conclusion that a pure nickel metal product may be formed under specific conditions directly contradicts the findings of both Canterford and Turnbull and Valix et al. [5, 7].

The consensus of these works is that truly selective reduction of a limonitic ore by hydrogen is not thermodynamically favourable. However, partially selective reduction should be possible and optimization of the reduction conditions should allow a high nickel grade ferronickel to be produced with a satisfactory nickel recovery. An optimum temperature range for the processing of limonitic laterites is noted around 873–973 K, with lower temperatures promoting higher selectivity at the cost of a decreased rate of reaction. Higher H₂O:H₂ ratios

are also expected to produce more selective conditions, with best results expected if the amount of reductant is close to the stoichiometric requirement. In general, it is also expected that reduction of the laterite ore by hydrogen will provide decreased selectivity but increased recovery at low temperatures, when compared to reduction by an equivalent amount of carbon monoxide.

Previous experimental work

Experimental studies have been conducted on the application of hydrogen as reducing agent for nickel laterite ores or similar materials by De Graaf, Kawahara et al., Cores et al., Utigard and Bergman, Antola et al. and Utigard et al. [6, 9–13]. In general, these experimental works appear to be consistent with the thermodynamic predictions available in the literature. An optimum temperature range for the selective reduction of a limonitic laterite by hydrogen of 823–923 K has been noted by De Graaf [9]. A similar temperature range is noted for the synthetic nickel oxide–iron oxide mixtures studied by Cores et al. and for the high nickel calcine studied by Utigard et al. [11, 13]. In the case of the saprolitic ores, Kawahara et al. and Utigard and Bergman have noted a higher optimum temperature of about 1,073 K, which supports the recommendation from Valix and Cheung and Rhamdhani et al. that the best results may be achieved from processing the two ore types separately at different temperatures [6, 10, 14, 15].

De Graaf and Antola et al. have also made comparisons between hydrogen and carbon monoxide for the reduction of a limonitic laterite [9, 12]. At temperatures below about 923 K, carbon dioxide is reported to provide greater selectivity than an equimolar amount of hydrogen, yielding a higher grade ferronickel but a lower nickel recovery. Above this temperature, the two gases appear to behave similarly. A slightly lower optimal reduction temperature (823–923 K) has been noted for the application of hydrogen as a reducing agent compared to carbon monoxide (873–923 K). Otherwise, these authors note similar behaviour for both gases, with increasing temperature and increasing carbon monoxide or hydrogen content in the reducing atmosphere, decreasing selectivity and yielding a lower grade ferronickel, while slightly increasing nickel recovery. Cores et al. also compared hydrogen and carbon monoxide as reductants for synthetic mixtures of nickel oxide and magnetite and noted that the reaction rate for hydrogen appeared to be higher than for carbon monoxide [11]. Finally, Antola et al. reported that carbon deposition was observed at temperatures below

973 K when using carbon monoxide as the reductant, which would make hydrogen an attractive alternative for this application [12].

Equilibrium considerations

A description of the equilibrium model has been given previously for application to the sulphidation of a limonitic laterite ore, the solid-state reduction of a limonitic laterite ore by carbon and the gaseous reduction of a limonitic ore by carbon monoxide [8, 16, 17]. In the present paper, the model has been extended to the solid-state gaseous reduction of a nickeliferous limonitic laterite ore by hydrogen. Therefore, only a summary of the pertinent features of the model is provided here as well as any changes necessary to modify the model for gaseous reduction by hydrogen. The Equilibrium module of HSC Chemistry[®] 6.1 was utilized to calculate the multi-component equilibrium composition using the Gibbs free energy minimization method [18]. The nickeliferous limonitic laterite ore was assumed to be comprised of the following elements: Mg, Si, Fe, Ni, Co, H and O. When these seven elements were input to the Equilibrium Composition calculations program of HSC Chemistry[®] 6.1, a list of 173 possible species was generated. However, the majority of these are unstable under the conditions in the current gaseous reduction process and therefore, only the 26 species shown in Table 1 were utilized. The species were grouped into three phases: gases, oxides (including monoxide (FeO–NiO–CoO) and spinel (Fe₃O₄–NiFe₂O₄–CoFe₂O₄)) and ferronickel alloy (Fe–Ni–Co). As previously described, the non-ideal behaviour of the various species was taken into account by including activity coefficients for the species in the monoxide and spinel and also for those in the alloy, taken from the literature [19, 20]. The ore composition was assumed to be as follows (in mass %): 95.37 % FeO·OH, 0.26 % MgO, 2.66 % SiO₂, 1.57 % NiO and 0.14 % CoO.

Table 1: Phases and species utilized in the equilibrium calculations for the reduction of the nickeliferous limonitic laterite ore by hydrogen.

Gases	Oxides	Oxides	Oxides	Oxides	Alloy
O ₂	CoO	FeO·OH	MgFe ₂ O ₄	NiO	Fe
H ₂	Co ₃ O ₄	2FeO·SiO ₂	MgO	SiO ₂	Ni
H ₂ O	2CoO·SiO ₂	FeSiO ₃	MgSiO ₃	NiFe ₂ O ₄	Co
	FeO	Fe ₂ SiO ₄	Mg ₂ SiO ₄	Fe ₃ O ₄	
	Fe ₂ O ₃	Fe ₂ MgO ₄	2NiO·SiO ₂	CoFe ₂ O ₄	

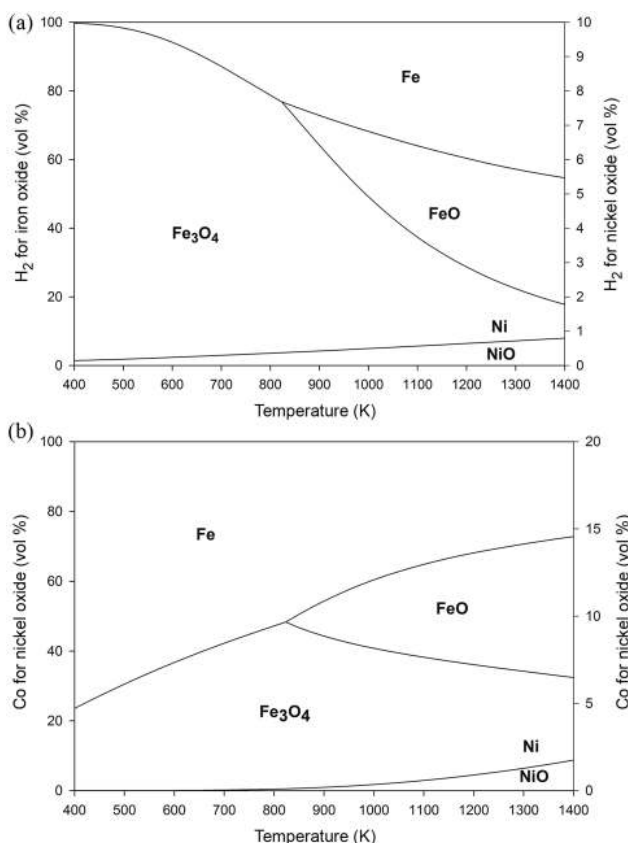


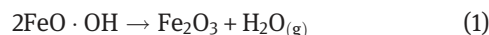
Figure 1: Stability diagrams for Fe–O and Ni–O in hydrogen (a) and carbon monoxide (b).

Figure 1(a) shows the combination of the Fe–O and Ni–O stability diagrams for hydrogen as the reducing agent and assumes pure metal and pure oxide phases. In comparison to iron oxide, nickel oxide is relatively easily reduced to nickel metal and thus nickel oxide is only stable in the lower right portion of the diagram. Magnetite occupies the majority of the left side of the diagram and is stable over a wide range of hydrogen contents. At low temperatures, metallic iron only exists at very high hydrogen contents. Magnetite can be converted to wustite by increasing the temperature and/or increasing the amount of hydrogen in the gas phase. Higher hydrogen volumes are required at lower temperatures than at higher temperatures. In a similar manner to magnetite, wustite can be converted to metallic iron by further increasing the temperature and/or the proportion of hydrogen in the gas. Also, the proportion of hydrogen in the gas that is required to reduce wustite to metallic iron decreases with increasing temperature. Therefore, based on these results, it should be possible to selectively reduce nickel and produce magnetite or wustite depending on the reduction temperature and the gas composition, with

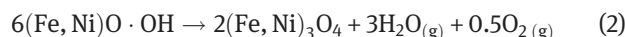
the formation of metallic iron being avoided. It can be noted that although wustite can be produced at high temperatures, reversion to magnetite could occur during cooling.

It is of interest to ascertain the differences between hydrogen and carbon monoxide as potential reducing agents for the nickeliferous limonitic laterite ores and also to establish any possible advantages of combining hydrogen with carbon monoxide. In a manner similar to the stability diagram for reduction with hydrogen given in Figure 1(b), the Fe–O and Ni–O stability diagrams for carbon monoxide as the reducing agent are provided in Figure 1(b). In carbon monoxide, the production of metallic iron from magnetite or wustite is favoured by both increasing temperature and increasing amounts of carbon monoxide, while in hydrogen, metallic iron formation is promoted by increasing temperature and decreasing amounts of hydrogen. In both cases, metallic nickel is produced at low amounts of reducing gas and wustite is formed from magnetite with increasing temperature and decreasing amounts of hydrogen or carbon monoxide. In hydrogen and at low temperatures, magnetite exists over a wide range of hydrogen to water vapour ratios, while in carbon monoxide, over a similar temperature range, magnetite exists at low carbon monoxide to carbon dioxide ratios and metallic iron at moderate-to-high ratios. It is noteworthy that the conditions for the formation of wustite are similar in both cases. Thus, in a process where the objective is to avoid magnetite formation and produce both wustite and metallic nickel, the temperatures and the amounts of reducing gas required for both hydrogen and carbon monoxide would be expected to be similar.

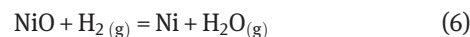
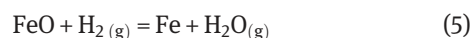
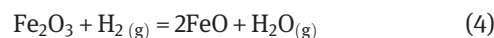
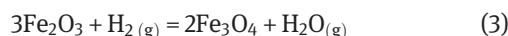
The goethite present in the limonitic ore will be converted into hematite under oxidizing conditions as follows:



while under reducing conditions, magnetite will form as follows:



The reactions for the reduction of pure iron oxide and pure nickel oxide in the ore by hydrogen are as follows:



and the reactions for the reduction of nickel ferrite to nickel and magnetite, nickel and wustite, and nickel and metallic iron are as follows:

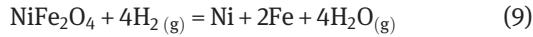
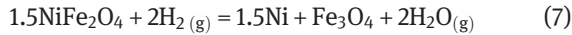


Figure 2 shows the standard-free energy changes for the hydrogen reduction reactions involving the formation of nickel metal (Reactions 6–9). The values for the reduction of nickel oxide to nickel metal (Reaction 6) are somewhat negative but show only a slight decrease with increasing temperature. On the other hand, the reactions for the reduction of nickel ferrite to nickel and magnetite, or wustite or metallic iron, all decrease rapidly at similar rates with increasing temperature. Consequently, selective reduction of nickel ferrite should occur in preference to the reduction of nickel oxide. Additionally, at the proposed reduction temperature of about 873 K, the values for the reduction of nickel ferrite to wustite are slightly lower than those for magnetite but close to those for reduction to metallic iron. Therefore, although the reduction of nickel ferrite to nickel and wustite is thermodynamically feasible, some magnetite and possibly metallic iron could also be formed. The above analysis assumes that the activities of the condensed species are unity and in actual systems, this will not be the case as various solid solutions are possible. However, it would be expected that by controlling the reducing conditions with regards to temperature and gas composition, some degree of selective reduction could be achieved.

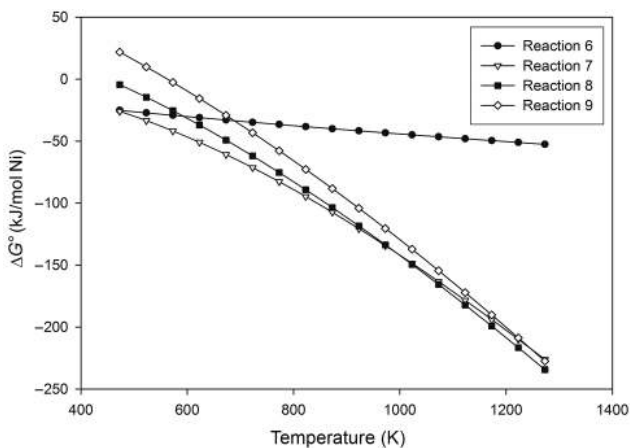


Figure 2: Standard-free energy changes (ΔG°) for the reactions involving nickel.

Results and discussion

Under actual reaction conditions, the system would not be closed and both the free and the majority of the combined water in the ore would be removed and leave the system at temperatures below the reduction temperature. Therefore, calculations were performed for the calcined ore assuming all free and chemically bound water had been removed. An uncalcined or partially calcined ore containing crystalline water would be expected to behave as a calcined ore in a mixed H₂O:H₂ atmosphere with a lower reduction potential.

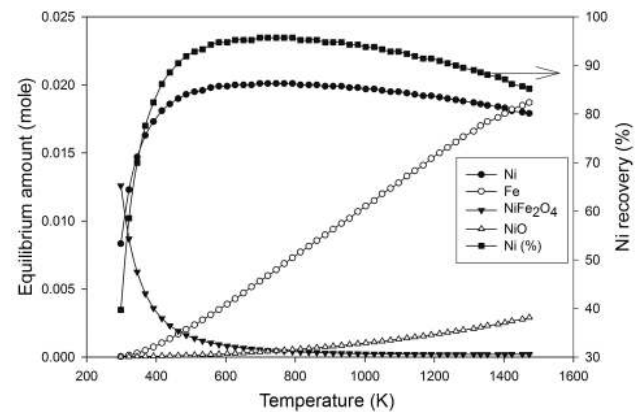


Figure 3: Effect of temperature on the amounts of the nickel-containing species, the nickel recovery and the amount of metallic iron for reduction of the ore in hydrogen at a reductant to ore ratio of 0.558 kmol/100 kg.

Figure 3 shows the equilibrium amounts of the nickel-containing species plus iron for a hydrogen addition of 0.558 kmol/100 kg of calcined ore. This hydrogen addition and ore composition was used as the base case for all further modelling. This hydrogen addition corresponds to the stoichiometric requirement for the reduction of all of the nickel oxide to nickel metal (0.021 kmol H₂), and for the decomposition of the goethite and subsequent reduction of the hematite to wustite (0.537 kmol H₂), as described by the following reaction:

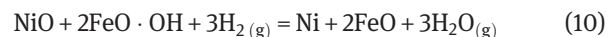


Figure 4 shows the ferronickel composition for the same conditions as in Figure 3. Both metallic nickel and iron begin to form at low temperatures. With increasing temperature, the amount of nickel ferrite decreases quickly while the amount of nickel metal increases correspondingly. Over the temperature range of 673–973 K, the nickel recovery was relatively constant at about 95%. The

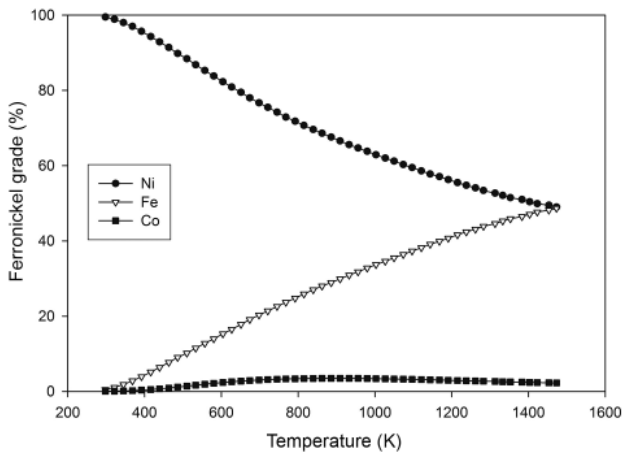


Figure 4: Effect of temperature on the composition of the ferronickel alloy for reduction of the ore in hydrogen at a reductant to ore ratio of 0.558 kmol/100 kg.

amount of nickel oxide increases slowly with temperature, leading to reduced nickel recovery at high temperatures. The amount of iron increases continuously with temperature rather than following the amount of nickel and, consequently, as shown in Figure 4, the nickel content of the ferronickel decreases continuously with temperature, while the iron content shows a corresponding continuous increase. For the optimum reduction temperature range of 673–873 K, the nickel grade of the ferronickel was in the range of 68–78%. It should be noted that while there is a thermodynamic optimal point at 733 K for the recovery of nickel to the ferronickel phase, several previous researchers have suggested that kinetic limitations may prevent the practical use of any temperature below 873 K. Recent kinetic studies on the hydrogen reduction of a mixed nickel–iron oxide (10.47% Ni, 49.27% Fe) similar to the species considered in the current study have confirmed this. Yu et al. [21] have shown that while reduction of the oxide begins at temperatures as low as 623 K, satisfactory rates of reaction cannot be achieved at temperatures below 873 K. At this temperature, recovery of nickel to the ferronickel should be similar to that predicted at the optimum, but the expected grade will have significantly decreased due to the continued reduction of the iron oxides to metallic iron.

Figure 5 shows the behaviour of the major iron-containing species. Goethite disappears at low temperatures, which results in an increase in the amount of magnetite. Above about 473 K, the amount of magnetite decreases with increasing temperature. Correspondingly, the amount of wustite increases continuously and rapidly with increasing temperature. It is noteworthy that for reduction temperatures of 773 K

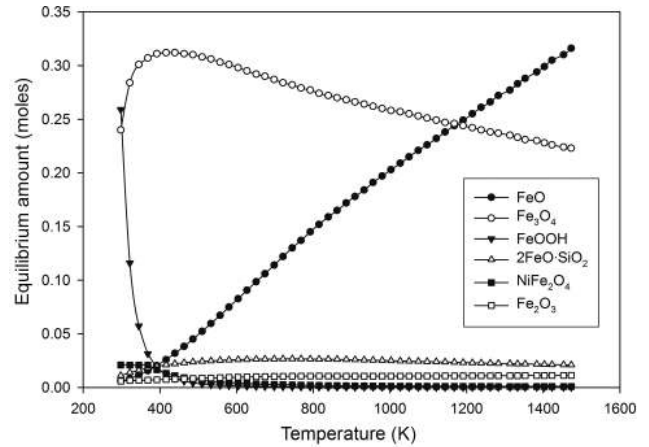


Figure 5: Effect of temperature on the amounts of the iron oxide-containing species for reduction of the ore in hydrogen at a reductant to ore ratio of 0.558 kmol/100 kg.

and above, magnetite is present in significant amounts. The amount of magnetite only becomes less than the amount of wustite, on a mole basis, above about 1,173 K. The amounts of 2FeO·SiO₂ and Fe₂O₃ are present in only small amounts across the whole temperature range.

Figure 6 shows the changes in the gas composition and also log P_{O_2} as a function of temperature for reduction of the calcined ore. There is a continuous decrease in the amount of hydrogen and a corresponding continuous increase in the amount water vapour with increasing temperature. As the temperature increases, nickel oxide and the various iron oxides are reduced by hydrogen and this results in an increasing amount of water vapour.

Figures 7 and 8 show the effect of temperature on the nickel recovery and grade, respectively, for various

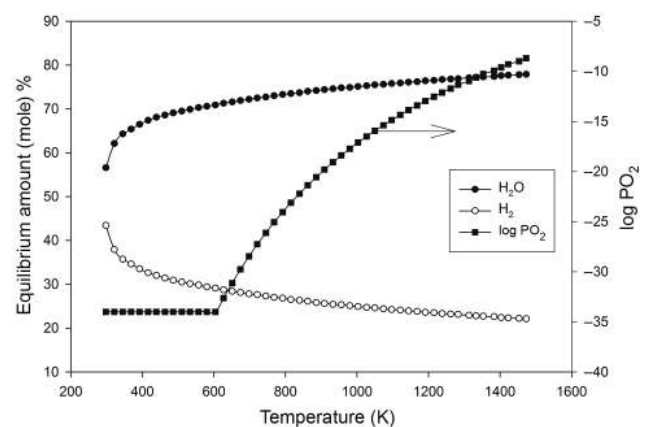


Figure 6: Effect of temperature on the gas composition and log P_{O_2} at a reductant to ore ratio of 0.558 kmol/100 kg.

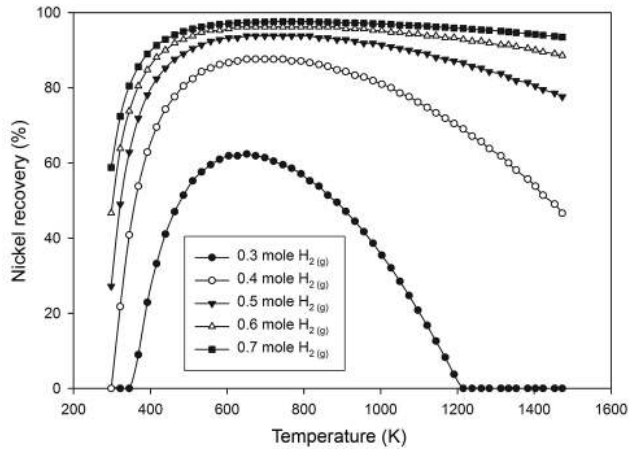


Figure 7: Effect of temperature on the nickel recovery for reduction of the calcined ore for various amounts of hydrogen per 100 kg of ore.

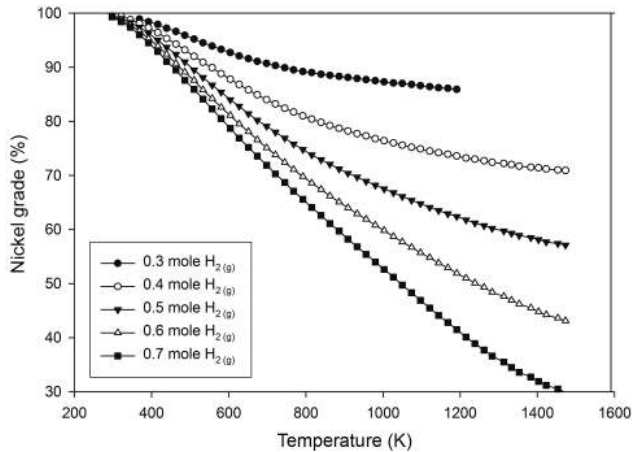


Figure 8: Effect of temperature on the nickel grade of the ferronickel for reduction of the calcined ore for various amounts of hydrogen per 100 kg of ore.

hydrogen additions. With increasing hydrogen addition, reduction occurs at lower temperatures, higher recoveries are achieved over a wider temperature range and the maximum recovery is maintained over a wider temperature range. The grade decreased with increasing temperature, with generally a more rapid decline at lower temperatures than at higher temperatures. At low temperatures and below the temperature of maximum nickel recovery, the decrease in grade is due to the increased amount of iron produced. At higher temperatures and for low hydrogen additions, the recovery of nickel decreases at a rate similar to that of iron and thus the grade remains relatively constant. On the other hand, at higher temperatures and for high hydrogen additions, the nickel

recovery remains high, but the amount of iron increases with temperature and thus the grade decreases. This decrease in grade also corresponds to a decrease in the magnetite content of the reduced material, which is of benefit if a magnetic separation method is to be used to recover the ferronickel product.

Figure 9 shows the effect of $H_2O:H_2$ ratio on both the nickel recovery and the grade of the ferronickel alloy, again for 0.558 kmol of $H_2/100$ kg of ore at 733 K, which is the temperature of maximum recovery. The nickel recovery decreased linearly with increasing $H_2O:H_2$ ratio, while the grade increased relatively quickly at low ratios and then began to level off at higher ratios. At low ratios, the grade increased relatively rapidly with increasing ratio as a result of a faster decrease in the iron recovery, in comparison to that of the nickel. As the ratio increased, the iron recovery decreased more slowly in comparison to that of nickel and thus, the nickel grade changed more slowly. For reasonable nickel recoveries in the range of 85–95%, only modest gains in the grade could be made by increasing the $H_2O:H_2$ ratio and this was at the expense of the nickel recovery. Thus, operation at low ratios leads to high nickel recoveries but still relatively high grades.

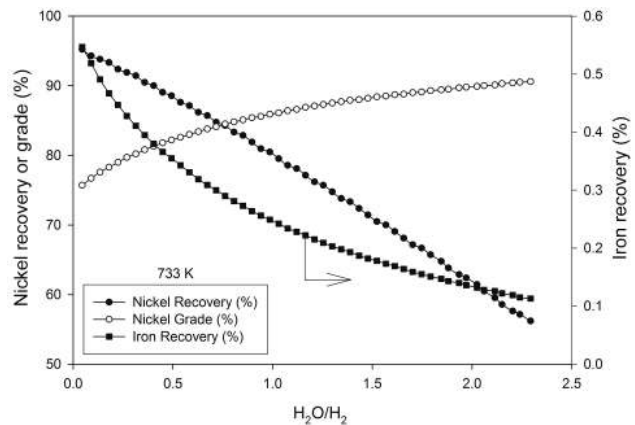


Figure 9: Effect of H_2O/H_2 ratio on the nickel grade of the ferronickel and also the nickel recovery at 733 K in hydrogen at a reductant to ore ratio of 0.558 kmol/100 kg. Also included is the iron recovery.

In an actual orebody, the composition of the ore can vary, in particular the nickel oxide and iron oxide contents. Figure 10(a) and Figure 10(b) shows the effects of the nickel oxide and the hematite contents of the ore on the nickel recovery and the grade of the ferronickel, respectively, at a reduction temperature of 733 K and a hydrogen addition of 0.558 kmol $H_2/100$ kg of ore. An increase

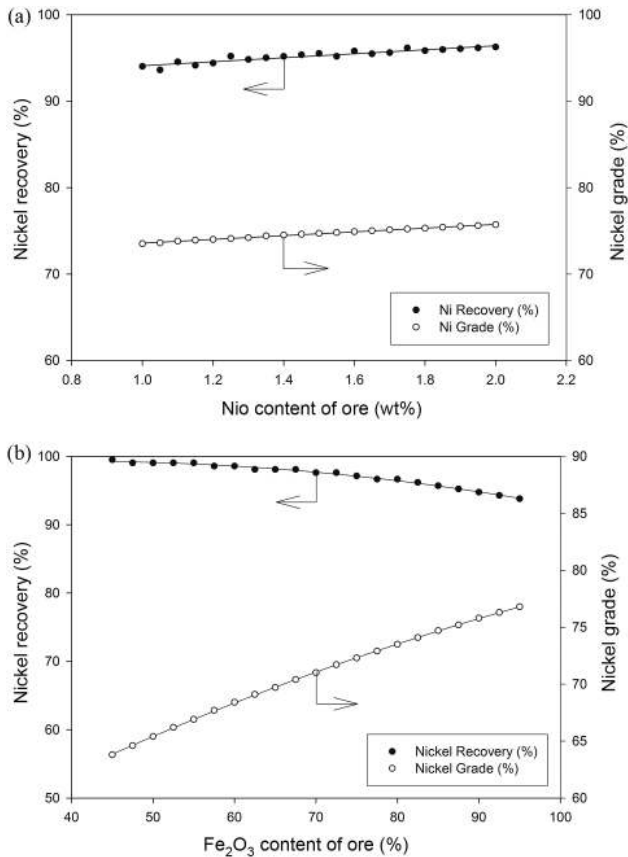


Figure 10: Effect of NiO content of the ore (a) and Fe₂O₃ content of the ore (b) on the nickel recovery and nickel grade of the ferro-nickel for reduction of the calcined ore in hydrogen at a reductant to ore ratio of 0.558 kmol/100 kg and a reduction temperature of 733 K.

in the nickel oxide content of the ore in the range of 1–2%, results in modest increases in the recovery from about 94–96% and the nickel grade from about 74–76%. On the other hand, increasing the amount of iron oxide in the ore from 45% to 95% results in a decrease in the nickel recovery from 99% to 94%. The nickel grade increases with increasing iron oxide, since the conditions become more oxidizing and the recovery of metallic iron decreases more rapidly than that of metallic nickel.

The current model appears to be in general agreement with the predictions made in previous thermodynamic studies. Increasing temperature corresponded to a decrease in ferro-nickel grade but an increase in recovery. An increase in the H₂O:H₂ ratio in the reduction gas had the opposite effect, increasing the ferro-nickel grade but decreasing the nickel recovery to the ferro-nickel phase. However, the optimal temperature for selective reduction of 733 K predicted by the current model is lower than the range of 823–873 K predicted by other researchers [5–7].

Comparison of hydrogen with carbon monoxide

In a manner similar to Figure 7, the equilibrium nickel and iron recoveries for a carbon monoxide addition of 0.558 kmol/100 kg of ore have been investigated previously and the results are compared to those for hydrogen in Figure 11 [8]. Again, in a manner similar to hydrogen, the amount of carbon monoxide is the stoichiometric requirement for the reduction of all of the nickel oxide to nickel metal (0.021 kmol CO) and also for the reduction of the hematite to wustite (0.537 kmol CO). In both cases, metallic iron formation occurs simultaneously with that of nickel and a ferro-nickel alloy is produced. In carbon monoxide, the nickel recovery curve is characterized by a relatively sharp peak and the iron recovery follows the nickel recovery. However, the alloy forms at lower temperatures in hydrogen than in carbon monoxide. In comparison to carbon monoxide, the curve for hydrogen is broader and extends over a wider temperature range. In hydrogen, the amount of iron tends to increase continuously with temperature, and this can be contrasted with carbon monoxide, where the iron recovery follows the nickel recovery. The maximum nickel recovery was slightly lower for hydrogen than for carbon monoxide, but the temperature of maximum recovery was significantly lower for hydrogen. Figure 12 compares the grade of the ferro-nickel alloy produced in carbon monoxide with the results for hydrogen. In carbon monoxide, the nickel grade decreases until the temperature of maximum recovery since the iron recovery increases more quickly than the nickel. However, past this

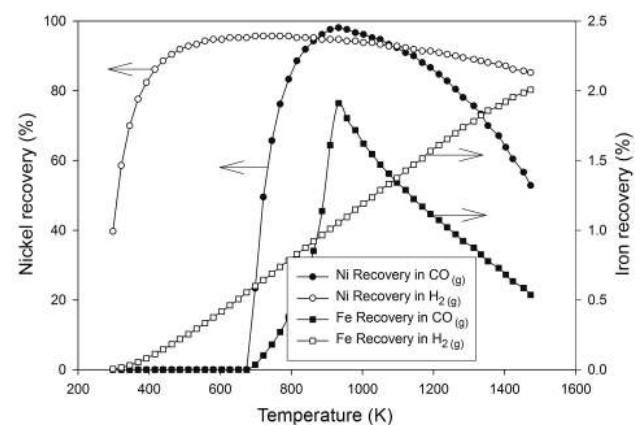


Figure 11: Effect of temperature on the nickel and iron recoveries as a function of temperature for reduction of the ore in pure carbon monoxide or pure hydrogen at a reductant to ore ratio of 0.558 kmol/100 kg.

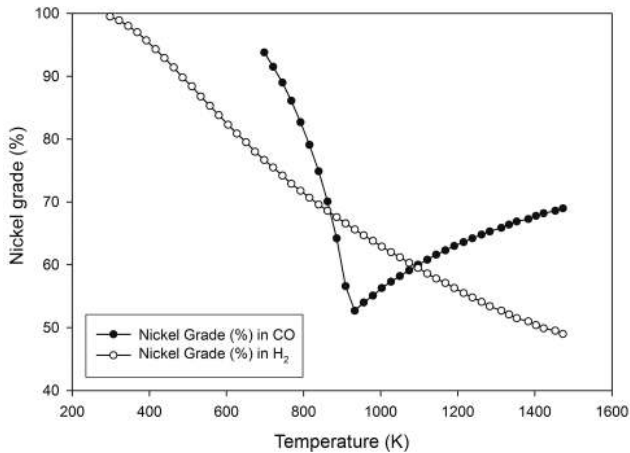


Figure 12: Effect of temperature on the nickel grade of the ferronickel as a function of temperature for reduction of the ore in pure carbon monoxide or hydrogen at a reductant to ore ratio of 0.558 kmol/100 kg.

temperature, the nickel grade increases since the nickel recovery decreases more quickly than the iron recovery. On the other hand, in hydrogen, the nickel grade decreases continuously with increasing temperature, due to the increasing iron recovery with increasing temperature.

Figure 13 compares the equilibrium amounts of CO and CO_2 or H_2 and H_2O for reduction by hydrogen at 0.558 kmol of CO or H_2 as a function of temperature for the calcined ore. Also included are the $\log P_{O_2}$ values. For carbon monoxide at low temperatures, the equilibrium is mainly determined by the presence of carbon; as the temperature increases to the temperature of maximum nickel recovery of about 933 K, then the amount of

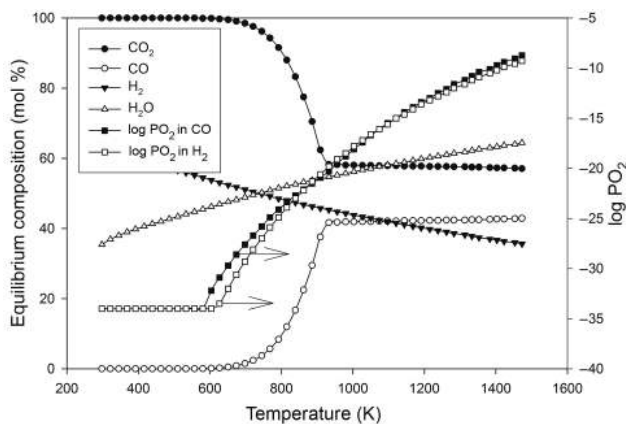


Figure 13: Effect of temperature on the composition of the gas phase ferronickel alloy for reduction of the calcined ore in pure carbon monoxide or pure hydrogen at a reductant to ore ratio of 0.558 kmol/100 kg. Also included are the $\log P_{O_2}$ values for carbon monoxide and hydrogen.

carbon monoxide increases rapidly and carbon dioxide is consumed [8]. Above this temperature, the amount of carbon monoxide decreases slightly while the amount of carbon dioxide increases to some extent due to the reduction of some magnetite to wustite. On the other hand, the amounts of both metallic nickel and iron are decreasing. For the case of hydrogen, the amount of hydrogen continuously decreases with temperature while the amount of water vapour increases across the whole temperature range. As a result, the formation of metallic iron continues even at high temperatures, while nickel is oxidized. This behaviour can also be explained in terms of the behaviour of the $\log P_{O_2}$ values. In carbon monoxide, the $\log P_{O_2}$ value is slightly higher both at lower temperatures and also at higher temperatures, than in hydrogen. Consequently, ferronickel formation occurs at lower temperatures in hydrogen, than in carbon monoxide. At higher temperatures, the higher oxygen potential in carbon monoxide results in oxidation of the iron, but not in hydrogen. As a result, once above the maximum recovery temperature, the nickel grade of the ferronickel will be lower in hydrogen than in carbon monoxide.

Figures 14 and 15 show the effect of hydrogen additions to carbon monoxide, represented in terms of the hydrogen to carbon monoxide ratio, on the nickel recovery and the grade of the ferronickel. As noted previously, the addition of hydrogen lowers the initial temperature of ferronickel formation and hence, higher recoveries are achieved at lower temperatures. Furthermore, the temperature range over which high nickel recoveries can be achieved is extended both at low and high temperatures.

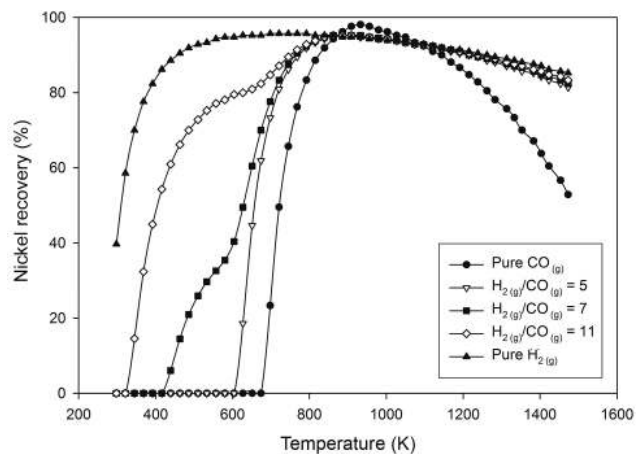


Figure 14: Effect of temperature on the nickel recovery for reduction of the calcined ore in pure carbon monoxide, pure hydrogen and various hydrogen to carbon monoxide ratios at a reductant to ore ratio of 0.558 kmol/100 kg.

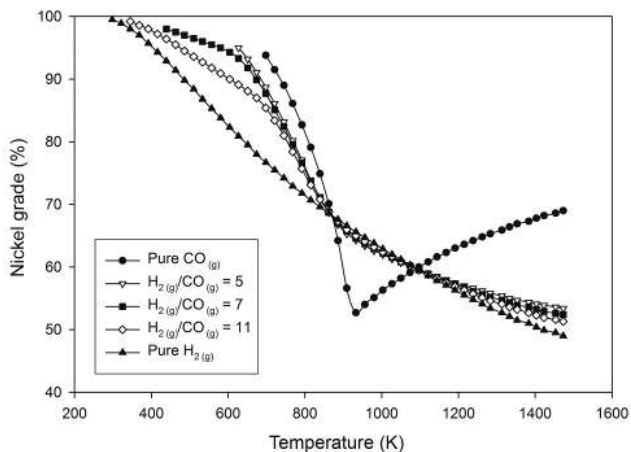


Figure 15: Effect of temperature on the nickel grade of the ferronickel for reduction of the calcined ore in pure carbon monoxide, pure hydrogen and various hydrogen to carbon monoxide ratios at a reductant to ore ratio of 0.558 kmol/100 kg.

On the other hand, the maximum recoveries are slightly higher in carbon monoxide. For gas compositions rich in hydrogen, the general trend is a decrease in grade with increasing temperature due to the formation of increasing amounts of iron. For gas compositions rich in carbon monoxide, the grade decreases at lower temperatures due to increased reduction of iron, but then increases at higher temperatures due to the preferential oxidation of the iron. At low temperatures and for a given temperature, the grade increases somewhat with increasing carbon monoxide to hydrogen ratio. At intermediate and higher temperatures, the grades in hydrogen and carbon monoxide are similar for a given temperature, except when the gas composition approaches that of pure carbon monoxide.

Comparison of model with experimental results

Although a number of experimental studies have been performed on the reduction of laterites by carbon monoxide and/or hydrogen, there is a paucity of experimental information regarding the effect of variables, in particular temperature, on the recovery of nickel to the ferronickel phase and the grade of the ferronickel alloy for the limonitic laterites [6, 9–13]. De Graaf [9] investigated the reduction of both a limonitic laterite ore (Manuran) and two silicate laterite ores by carbon monoxide and/or hydrogen and reported the effect of temperature. The CO₂:CO ratio and the H₂:H₂O ratio were 1.2. The limonitic laterite ore composition was as

follows (in mass %): 1.3% Ni, 48.7% Fe, 2.1% SiO₂, 5.6% Al₂O₃, 0.6% MgO and LOI of 13.7%. In order to accommodate this ore composition in the model, the iron was assumed to be present as FeO·OH and Al₂O₃ was added. De Graaf did not provide results for the effect of temperature on the nickel recovery for hydrogen reduction of Manuran ore. Therefore, the present results for hydrogen are compared to his results for carbon monoxide and also to the previously determined model results for carbon monoxide [8] as shown as in Figure 16. For the conditions chosen, it can be seen that the experimental and model results for carbon monoxide generally agree across the whole temperature range with a maximum recovery noted in the temperature range of 873–923 K. In this range, the model recoveries for both carbon monoxide and hydrogen are around 95%, but the curve for hydrogen reduction exhibits only a slight optimum at the lower temperature range of 773–823 K. However, the recovery is essentially independent of temperature. This reflects the fact that hydrogen provides more reducing conditions which, at all temperatures, minimizes the oxidation of nickel and results in high nickel recoveries across the whole temperature range.

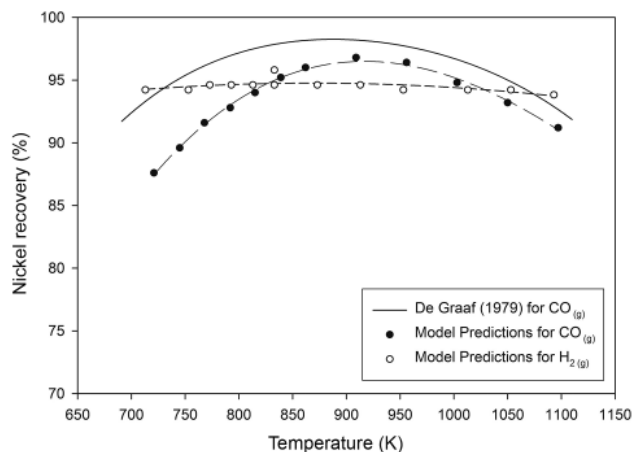


Figure 16: Comparison of the model predictions for the hydrogen reduction of Manuran ore with those previously predicted for carbon monoxide and also the experimental results of de Graaf for reduction in carbon monoxide [8, 9].

Conclusions

- (1) The utilization of hydrogen as a reducing agent for a nickeliferous limonitic laterite ore was studied using the Equilibrium Module of HSC Chemistry[®] 6.1. Activity coefficient data from the literature for

various species were also incorporated into the model. As in previous studies, the results showed that iron was simultaneously reduced with nickel to produce a ferronickel alloy under all conditions considered. The nickel grade of the alloy and the nickel recovery were determined by the reductant to ore ratio and the temperature.

- (2) For the calcined ore with a hydrogen addition of 0.558 kmol/100 kg of ore, over the temperature range of 673–873 K, the nickel recovery was relatively constant at about 95%, in comparison to a maximum recovery of 81% at 673 K for the uncalcined ore. The amount of nickel oxide increased continuously with temperature and as a result, the nickel recovery decreased at high temperatures. The amount of metallic iron also increased continuously with increasing temperature, leading to a decrease in nickel grade. Additionally, under these reduction conditions, the majority of the iron was present as magnetite, which is a significant concern if a magnetic separation method is to be used to recover the ferronickel.
- (3) With increasing reductant to ore ratio, reduction occurred at lower temperatures and the recovery of nickel to the ferronickel increased at a given temperature. Also, as the reductant to ore ratio increased, higher recoveries were maintained over a wider temperature range and consequently the maximum recoveries were maintained over an extended temperature range. In general, the grade decreased with increasing temperature, with generally a more rapid decline at lower temperatures than at higher temperatures. For 0.558 kmol of H₂/100 kg of ore at the optimum reduction temperature of 733 K, the nickel recovery decreased with increasing H₂O/H₂ ratio, while the grade increased relatively quickly at lower ratios and then began to level off at higher ratios.
- (4) A comparison was made between the reduction of the nickeliferous limonitic laterite ore with hydrogen or carbon monoxide and various combinations. The general trends for reduction in hydrogen were similar to those in carbon monoxide. However, in hydrogen, reduction occurred at lower temperatures and both the maximum recovery and the temperature required for maximum recovery were lower for hydrogen than for carbon monoxide. The temperature range over which high nickel recoveries could be achieved was much wider for hydrogen than for carbon monoxide. In carbon monoxide, the iron recovery followed the nickel recovery while in hydrogen, the amount of iron continuously increased with temperature and consequently, the

grade of the ferronickel decreased with increasing temperature. In general, lower grades could be achieved in hydrogen than in carbon monoxide but the recoveries were higher.

- (5) The model results were compared to the experimental results in carbon monoxide from De Graaf's research. Both the experimental and also previous model results for carbon monoxide exhibited a maximum recovery from about 873–923 K. However, for hydrogen, the model results exhibited only a slight maximum from about 773–823 K and the recoveries were essentially independent of temperature. Again, this reflects the more reducing conditions for reduction by hydrogen, which favours lower reduction temperatures and higher recoveries at low temperatures.

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References

- [1] A.D. Dalvi, W.G. Bacon and R.C. Osborne, Prospectors & Developers Association, Association of Canada International Conference, March 7–10, 2004, Toronto, PDAC, Toronto (2004), pp. 1–27.
- [2] K. Quast, J.N. Connor, W. Skinner, D.J. Robinson and J. Addai-Mensah, *Miner. Eng.*, 79 (2015) 261–268.
- [3] C.R.M. Butt and D. Cluzel, *Elements*, 9 (2013) 123–128.
- [4] A. Oxley and N. Barcza, *Miner. Eng.*, 54 (2013) 2–13.
- [5] B.J.H. Canterford and A.G. Turnbull, *Proc. Australas. Inst. Min. Metall.*, 275 (1980) 43–51.
- [6] T. Utigard and R.A. Bergman, *Metall. Mater. Trans. B*, 23B (1992) 271–275.
- [7] M. Valix, W.H. Cheung, P.D. Dan and G.A. Foulds, Proceedings of the 23rd Australasian Conference on Chemical Engineering, September 24–27, 1995, Adelaide, Australia, Institute of Engineers Australia, Barton (1995), pp. 142–146.
- [8] C.A. Pickles and R. Elliott, *Miner. Process. Extr. Metall.*, 124 (2015) 208–216.
- [9] J.E. De Graaf, *Hydrometallurgy*, 5 (1979) 47–65.
- [10] M. Kawahara, J.M. Toguri and R.A. Bergman, *Metall. Mater. Trans. B*, 19B (1988) 181–186.
- [11] A. Cores, A. Formoso, M. Larrea and J. Ortiz, *Ironmaking Steelmaking*, 16 (1989) 446–449.
- [12] O. Antola, L. Holappa and P. Paschen, *Miner. Process. Extr. Metall. Rev.*, 15 (2013) 169–179.
- [13] T. Utigard, G. Plascencia, T. Marin, A. Warner, J. Liu, A. Vahed and M. Muinonen, *Can. Metall. Q.*, 44 (2005) 421–428.

- [14] F. O'Connor, W.H. Cheung and M. Valix, *Int. J. Miner. Process.*, 80 (2006) 88–99.
- [15] M.A. Rhamdhani, P.C. Hayes and E. Jak, *Miner. Process. Extr. Metall.*, 118 (2009) 129–145.
- [16] C.A. Pickles, C.T. Harris, J. Peacey and J. Forster, *Miner. Eng.*, 54(9) (2013) 52–62.
- [17] C.A. Pickles, J. Forster and R. Elliott, *Miner. Eng.*, 65 (2014) 33–40.
- [18] A. Roine, *HSC Chemistry 6.0 - User's Guide*, Outokumpu Research Oy, Pori, Finland, 2006.
- [19] A.D. Pelton, H. Schmalzried and J. Sticher, *J. Phys. Chem. Solids*, 40 (1979) 1103–1122.
- [20] L.J. Swartzendruber, V.P. Itkin and C.B. Alcock, *Phase Equilib. Diffus.*, 12 (1991) 288–312.
- [21] D. Yu, M. Zhu, T.A. Utigard and M. Barati, *Miner. Eng.*, 54 (2013) 32–38.