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A Thermodynamic Analysis of the Selective Sulphidation of Nickel from a Nickeliferous Lateritic Ore

Abstract: The production of a nickel sulphide concentrate through selective sulphidation of a nickeliferous lateritic ore at temperatures lower than current smelting temperatures, is being studied as a potential production method for upgrading lateritic ores. The ability to produce such a nickel sulphide concentrate at economically attractive grades, while achieving reasonable nickel recoveries, relies on the conversion of the maximum amount of nickel oxide to sulphide, while minimizing the amount of iron sulphide. This paper examines the thermodynamic basis for this selective sulphidation. The analysis includes both pure component equilibrium as well as various solid and liquid solution phases, which are anticipated to set limits on the maximum achievable grade/recovery combinations. Thermodynamic calculations show that, for high iron limonitic ores, grades of up to 20 to 25 mass percent nickel should be possible, while maintaining recoveries of greater than 80 percent.

Keywords: thermodynamic analysis, nickel sulphide concentrate, sulphidation

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Introduction

The global consumption of nickel has grown tremendously since the 1940s, originally fuelled by World War II, and now by increased development and urbanization in China. The production methods and the types of nickel ores, which have been treated, have also changed over the past seventy years. Abundant high-grade sulphur deposits have become depleted and oxidic nickel ore bodies, which previously were not competitive with the treatment of sulphide ores, are now being considered with increasing interest. The relatively high abundance of nickel laterites is now beginning to translate into increased production from this oxidic ore type, which may be treated both by hydrometallurgical and pyrometallurgical methods. In fact, laterites account for approximately 70% of estimated resources, but only 40% of current production.

One of the major reasons that sulphides have accounted for a larger portion of production, when compared to lateritic ores, is due to their relative ease of processing. Nickel sulphide ores contain pentlandite, a mineral containing approximately 34 mass percent nickel. Pentlandite can be readily separated from the gangue components by flotation to produce a 10 to 14 mass percent nickel concentrate which is then smelted and converted to a matte for eventual conversion to high purity nickel products via a variety of process options. This ability to produce a nickel concentrate results in a much lower mass load to be treated in the subsequent high temperature and energy consuming smelting process. In contrast, thus far nickel laterites have not been amenable to significant physical upgrading and this inability to produce a nickel concentrate from a lateritic ore results in large quantities of material, which must be treated in the higher energy consuming pyrometallurgical and hydrometallurgical processes.

One potential avenue for the upgrading of nickeliferous ores is the selective conversion of the nickel oxide values within the ore to a nickel sulphide, while retaining the bulk of the iron as an oxide. Provided a suitable regime can be found to allow for selective sulphidation at temperatures lower than current smelting temperatures, significant energy and cost savings could be achieved. In addition to allowing for the upgrading of the nickel content, such a process has the added value of producing a concentrate, which is already commercially treated. The ability to selectively sulphidize nickel oxide relies heavily upon the thermodynamic stability of the nickel sulphide compared to its oxide, as well as the relative ease of nickel oxide sulphidation as compared to iron oxide sulphidation at temperatures between 773 to 1373 K. To the authors' knowledge, this subject has received little attention in the literature, although several papers have examined topics, which have some applicability to the current work, including studies on the partitioning of nickel between an oxy-sulphide liquid (oxygen enriched matte) and olivine at temperatures between 1473 and 1673 K [1, 2].

This paper will examine the thermodynamic partitioning of nickel and iron between relevant oxide and sulphide phases. The sulphidation of a limonitic-based laterite, which is composed of nickel and iron oxides, is studied although it should be possible to extend this technique to include magnesium and iron silicates, which are abundant in saprolitic-based laterites. The thermodynamics of the sulphidation of the pure nickel and iron oxide components are first discussed to provide a general argument for the suitability of the process. Then, the degree of selective sulphidation of the nickel, which can be achieved when converting the nickel oxides to sulphides in the presence of iron oxide, is examined in detail. The paper will also discuss several solution phases, which were found to be of importance and examine how these solution phases limit the extraction degree as a function of sulphide grade.

Thermodynamic calculations

There are a variety of pure components and solution phases in the Ni-Fe-S-O system. The pure components and solution phases, which were considered in the current paper, are outlined in Table 1.

Pure components

The potential for selective sulphidation of nickel oxide from iron oxide relies on the increased stability of nickel sulphide compared to iron sulphide for a given sulphidizing atmosphere. The relative stabilities of the various oxides and sulphides are generally considered in terms of a sulphur or oxygen potential, or equivalently in terms of the relative partial pressures of S_2 and SO_2. Consider the reaction of nickel oxide with gaseous sulphur to form nickel disulphide:

$$4NiO + 5S_2(g) \rightarrow 4NiS_2 + 2SO_2(g) \tag{1}$$

The equilibrium constant K_I for this reaction may be written as:

$$K_I = \frac{p_{SO_2}{}^2 a_{NiS_2}{}^4}{p_{S_2}{}^5 a_{NiO}{}^4} \tag{2}$$

The sulphur and oxygen potential of the system are not independent of each other and are related through the following equilibrium:

$$S_2(g) + 2O_2 \rightarrow 2SO_2(g) \tag{3}$$

For which the equilibrium constant can be written as:

$$K_{II} = \frac{p_{SO_2}{}^2}{p_{S_2} p_{O_2}{}^2} \tag{4}$$

For a given sulphur partial pressure and system pressure, the partial pressures of sulphur dioxide and oxygen are uniquely determined. Equations 2 and 4 can be rearranged and the partial pressures of sulphur dioxide and oxygen expressed in terms of the partial pressure of sulphur and the total pressure of the system as follows:

$$p_{SO_2} = K_{II} \frac{\sqrt{p_{S_2}}(P_{total} - p_{S_2})}{1 + K_{II}\sqrt{p_{S_2}}} \tag{5}$$

$$p_{O_2} = P_{total} - K_{II} \frac{\sqrt{p_{S_2}}(P_{total} - p_{S_2})}{1 + K_{II}\sqrt{p_{S_2}}} - p_{S_2} \tag{6}$$

Substitution of Equations 2, 5 and 6 into 4 and assuming unit activity for the condensed phases, results in the fol-

Pure Components [13]		Spinel [9]	High Temperature Pyrrhotite [4]	Liquid [11]	
NiO	Fe_3O_4	$NiFe_2O_4$	NiS	Ni	Fe
Ni_3S_2	Fe_2O_3	Fe_3O_4	FeS	NiS	FeS
NiS	$Fe_{0.877}S$		VaS	NiO	FeO
NiS_2	FeS_2			$Ni_{0.25}S_{0.25}O$	$FeO_{1.5}$
$NiSO_4$	$FeSO_4$				$Ni_{0.25}S_{0.25}O$
					FeOS

Table 1: Summary of phases and components considered in the current study. The reference numbers indicate the source of the thermodynamic data.

lowing expression, which determines the critical sulphur partial pressure at which both phases coexist:

$$P_{total} = \sqrt{\frac{K_I}{K_{II}}} p_{S_2}{}^{2} + p_{S_2} + K_{II} p_{S_2}{}^{2.5} \tag{7}$$

Once the sulphur potential is calculated through the solution of Equation 7, the ratio of the partial pressure of sulphur to sulphur dioxide can be determined. This ratio provides an overall measure of the strength of the sulphidizing environment required to convert the nickel oxide into a nickel sulphide. Similar procedures were used for the calculation of the remaining oxide/sulphide, oxide/oxide and sulphide/sulphide equilibria, and used for the determination of a window through which selective sulphidation of nickel oxide may occur, with limited sulphidation of the iron oxides.

Nickel and iron solid solution phases

There are a variety of solid solutions which may form in the nickel-iron-sulphur-oxygen system. Examination of the ternary phase diagrams, showed that for temperatures in the range of 673 to 773 K, relatively rich nickel phases such as pentlandite may form, along with an iron-nickel monosulphide solid solution [3, 4]. At temperatures above 883 K, pentlandite is no longer stable and a heazlewoodite solid solution phase $(Ni, Fe)_3S_2$ may form, along with an iron-rich monosulphide solid solution [5]. The partitioning of iron and nickel between these phases and an iron/nickel spinel solid solution will place thermodynamic limitations on both the overall degree of nickel extraction and the achievable grade of the nickel sulphide which may be formed due to the departure of activities from unity. It is therefore useful to examine the partitioning of nickel and iron between the relevant solution phases.

Monosulphide solid solution/spinel equilibrium

At temperatures above 723 K, it is expected that a spinel will coexist with the dominant sulphide phase, which, under the conditions of interest will be a monosulphide solid solution. The distribution of nickel and iron between the two phases will be determined through the following exchange reaction:

$$NiFe_2O_4 + FeS \rightarrow Fe_3O_4 + NiS \tag{8}$$

Both NiS and FeS are in a single solution phase and $NiFe_2O_4$ and Fe_3O_4 form a solid solution in the spinel phase. The equilibrium expression for this reaction can be written as:

$$K_{III} = \frac{a_{Fe3O4} a_{NiS}}{a_{NiFe2O4} a_{FeS}} \tag{9}$$

An analysis of the Gibbs phase rule indicates that for the two solid solutions coexisting with a gas phase there are three independent variables, temperature, pressure and a compositional variable. Once the temperature, pressure and the fraction of nickel in the sulphide phase are specified, the equilibrium is fully determined. Thus, for a specific grade of nickel within the sulphide phase, the partitioning between the spinel and sulphide phase is fully determined.

The thermodynamic description of the monosulphide phase has been previously described by using the following expression [4]:

$$\begin{aligned} G_{mss} = {} & y_{Ni} G^{o}_{NiS} + y_{Fe} G^{o}_{FeS} + y_{Va} G^{o}_{VaS} \\ & + RT(y_{Ni} \ln y_{ni} + y_{Fe} \ln y_{yFe} + y_{Va} \ln y_{Va}) \\ & + y_{Ni} y_{Va} \sum_{n \geq o} {}^{n} L_{(Ni,Va:S}(y_{Ni} - y_{Va})^{n} \\ & + y_{Fe} y_{Va} \sum_{n \geq o} {}^{n} L_{(Fe,Va:S}(y_{Fe} - y_{Va})^{n} \end{aligned} \tag{10}$$

where the departure from ideal stoichiometry (metal to sulphur molar ratio of one) is accommodated by the inclusion of vacancies in the metal lattice (denoted VaS). The parameters used in this model can be found in the literature [4, 6, 7].

The activity coefficients and therefore the activities of the components can be determined from Equation 10 through the application of the following equation from Berman and Brown [8]:

$$RT \ln \gamma_i = G^{xs} + \sum_{\substack{n=1 \\ n \neq m}}^{nc} x_n \left(\frac{\partial G^{xs}}{\partial x_m} \right)_{\substack{x_q = x1 \ldots x_{nc} \\ x_q \neq x_n x_m}} \tag{11}$$

where x_i are the mole fractions of NiS, FeS and VaS, which are equivalent to the site fractions (y_i) in Equation 10. G^{xs} represents the excess Gibbs Free Energy of mixing, which for the monosulphide solution is represented by the last two terms in Equation 10.

The presence of magnetite allows for some solubility of nickel oxide within the spinel phase as trevorite $(NiFe_2O_4.)$ The overall activity of magnetite and trevorite within the spinel phase has been described by Pelton et al [9] using the following expressions:

$$a_{Fe_3O_4} = \frac{27}{4}\frac{(1-x_{NiFe_2O_4})(2-x_{NiFe_2O_4})^2}{(3-x_{NiFe_2O_4})^3} \tag{12}$$

$$\mathrm{a}_{\mathrm{NiFe_2O_4}} = 4\frac{(\mathrm{x}_{\mathrm{NiFe_2O_4}})(2-\mathrm{x}_{\mathrm{NiFe_2O_4}})}{(3-\mathrm{x}_{\mathrm{NiFe_2O_4}})^2} \tag{13}$$

Substitution of the activity of Fe_3O_4 and $NiFe_2O_4$ from Equations 12 and 13 and rearrangement of Equation 9 allows the equilibrium mole fraction of $NiFe_2O_4$ to be written in terms of the activities of NiS and FeS and the equilibrium constant as follows:

$$x_{NiFe_2O_4} = \frac{3}{2}\frac{27a_{NiS}+16K_{III}a_{FeS}-\sqrt{81a_{NiS}+480a_{NiS}a_{FeS}K_{III}+256K_{III}{}^2a_{FeS}{}^2}}{27a_{NiS}+16K_{III}a_{FeS}} \tag{14}$$

The overall sulphur potential and oxygen potential are fixed and can be determined through the following equilibrium, combined, with Equation 4, as discussed in the previous section:

$$Fe_3O_4 + 5S_2 \rightarrow 6FeS + 4SO_2 \tag{15}$$

The overall activity of the vacancies, and thus the vacancy concentration of the monosulphide solution (mss) is determined by the sulphur potential of the system, through the following equilibrium:

$$2VaS \rightarrow S_2(g) \tag{16}$$

This equilibrium reaction leads to the following expression for the activity of the vacancies in the monosulphide solution written in terms of the sulphur potential calculated from the solution of Equations 4 and 15 and also in terms of the equilibrium constant for Equation 16 (denoted K_{IV}).:

$$a_{VaS} \rightarrow \sqrt{\frac{p_{S_2}}{K_{IV}}} \tag{17}$$

For a specific mole fraction of nickel within the monosulphide solution, the system is fully determined and the partitioning of nickel and iron between the monosulphide solution and spinel, along with the excess sulphur concentration in the monosulphide solution can be determined. The equilibrium composition was determined using a least squares routine in MATLAB™.

Liquid phase

The formation of a sulphide matte with appreciable quantities of dissolved oxygen is possible at the oxygen and sulphur potentials, which are being considered, and will form from magnetite/monosulphide phase assemblages between 1223 K and 1323 K [10]. The partitioning of nickel between the liquid phase and the spinel phase is an important consideration and can be represented by Equation 18. This Equation is similar to Equation 8, which was used to define the exchange reaction between the spinel and the monosulphide solid solution. The species in brackets denote those that are dissolved within the liquid phase.

$$NiFe_2O_4 + (FeS) \rightarrow Fe_3O_4 + (NiS) \tag{18}$$

The thermodynamic properties of the sulphur-oxygen liquid have been described by Kress [11] using an associated solution model, which considers the liquid to be composed of ten species. The overall Gibbs Free Energy of the phase was described using the general Margules expansion represented by Equation 19 where x_i represents the mole fraction of the individual species in the matte.

$$G_{mss} = \sum_{i=1}^{n} x_i G_i^o + \sum_{i=1}^{n} x_i RT\,ln(x_i) + \sum_{i=1}^{n}\sum_{j=i}^{n}\sum_{k=1}^{n} W_{ijk}x_i x_j x_k \tag{19}$$

The parameters for the model have been reported by Kress [11]. In the model, the ternary terms, $i = j = k$ and the case where $i \neq j \neq k$ were not included. The chemical potentials of the individual species can be determined by application of Equations 17 to 19 to give the following expression for the chemical potential of species i as derived by Kress [12]:

$$\mu_i = \mu_i{}^o + RT\,ln(x_i) + \sum_{j}^{n}\sum_{k}^{n} W_{jk}\left(\frac{Q_{ijk}x_j x_k}{x_i} - 2x_j x_k{}^2\right) \tag{20}$$

Q_{ijk} is defined as $\delta_{ij} + 2\delta_{ik}$ where $\delta_{ij} = 1$ if $i = j$ and 0 if $i \neq j$.

The number of species in the liquid phase is greater than the number of components, therefore the equilibrium speciation of the liquid for a given temperature and composition was determined by minimizing the Gibbs Free Energy of the liquid. A minimization routine was programmed in MATLAB™, following the method outlined by Kress [12]. Examination of the Gibbs phase rule indicates that when the temperature, total pressure and the mole fraction of nickel in the liquid are defined, the equilibrium between the gas phase, spinel and liquid is fully determined.

The solubility of oxygen in the liquid matte in equilibrium with the spinel can be determined by ensuring that the activity of magnetite, which can be calculated using Reaction 2, is equal to the activity of the magnetite which is determined through solution of the matte/spinel equivalent of Equation 15, previously used to define the monosulphide/spinel equilibrium. The equation utilized is as follows:

$$8(FeO_{1.5})+(Fe)\rightarrow Fe_3O_4 \tag{21}$$

Results and discussion

Pure components

Figure 1 shows the ratio of the pressures of sulphur to sulphur dioxide required for the sulphidation of iron and nickel oxides to sulphides, as well as the relative stabilities of the various sulphide species at 1 atmosphere pressure. In general, it can be seen that the nickel sulphides form at lower sulphur potentials than the iron sulphides. At temperatures between 573 and 723 K both the iron and the nickel oxides that have formed during the dehydroxylation of the ore will react with elemental sulphur to form sulphides:

$$4NiO+5S_2(g)\rightarrow 4NiS_2+2SO_2(g) \tag{22}$$

$$4Fe_2O_3+12S_2(g)\rightarrow 8FeS_2+6SO_2(g) \tag{23}$$

At temperatures below 946 K, these sulphides should not coexist thermodynamically with the oxides, instead the sulphides should react with the corresponding oxides to form sulphates. Given the solid state nature of the reactants and also the low temperatures, there are severe kinetic limitations on the reaction rates.

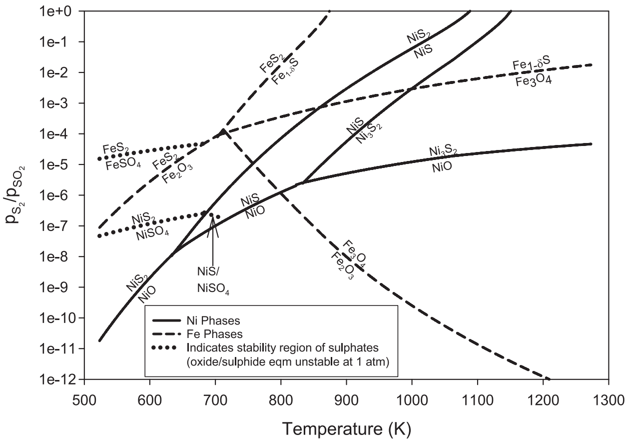

Fig. 1: Calculated stability diagram for the Fe-S-O and Ni-S-O systems at 1 atm total pressure

As the temperature is further increased, the sulphur potential required to maintain both the pyrite (FeS_2) and the nickel disulphide increases and, provided there is still hematite (Fe_2O_3) present, the pyrite will decompose to pyrrhotite ($Fe_{1-\delta}S$) at approximately 723 K. In a similar temperature regime, the reduction of hematite to magnetite (Fe_3O_4) becomes possible through either direct reduction via sulphur or through the solid state reaction with existing pyrite or pyrrhotite as follows (note: δ is used to describe the range of pyrrhotite stoichiometry)

$$12Fe_2O_3+S_2\rightarrow 8Fe_3O_4+2SO_2(g) \tag{24}$$

$$16Fe_2O_3+FeS_2\rightarrow 11Fe_3O_4+2SO_2(g) \tag{25}$$

$$Fe_2O_3+\frac{1}{10-4\delta}Fe_{1-\delta}S\rightarrow\frac{7-3\delta}{10-4\delta}Fe_3O_4+\frac{1}{10-4\delta}SO_2(g) \tag{26}$$

Further increases in temperature promote the formation of more metal-rich nickel sulphide phases, from NiS_2 to NiS, and finally to Ni_3S_2. An examination of the pure components suggests there is considerable opportunity for the selective sulphidation of a nickel oxide from an iron oxide, however the solid solutions, which can form will impact both the phase composition of the nickel sulphide, as well as limit the overall nickel conversion and the grade of sulphide that is achievable. This analysis also reveals that the dominant phases of interest, in terms of partitioning of nickel and iron, will be between the spinel phase, the monosulphide solid solution and possibly heazlewoodite.

Spinel/monosulphide equilibrium

Figure 2 shows the equilibrium mole fraction of the spinel phase, trevorite, as a function of the nickel to iron ratio in the monosulphide solution for temperatures between 1073 and 1323 K. The nickel content in the spinel increases with increasing sulphide grade as a result of the equilibrium established by Reaction 8. The deviation from a molar ratio of sulphur to metal of unity in the mss solution is shown in Figure 3 as a function of the iron to nickel ratio in the mss phase for temperatures between 1073 and 1373 K. The increased nickel content results in a weaker sulphidizing environment and therefore a smaller deviation from the stoichiometric monosulphide. Additionally, higher temperatures promote the formation of a near stoichiometric monosulphide solution.

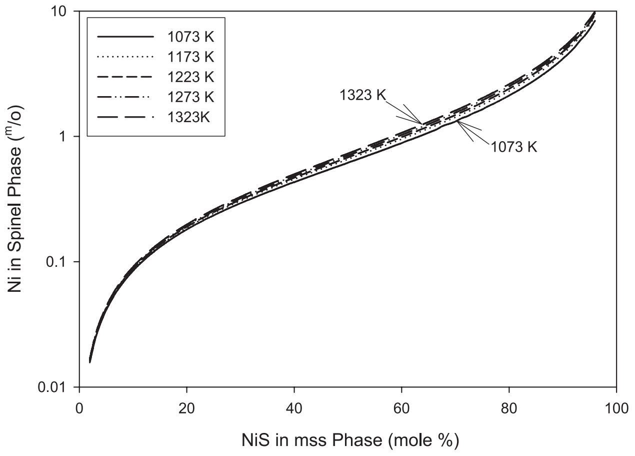

Fig. 2: Equilibrium mass percent of nickel in the spinel phase as a function of the mole fraction nickel monosulphide in the mss solution at various temperatures

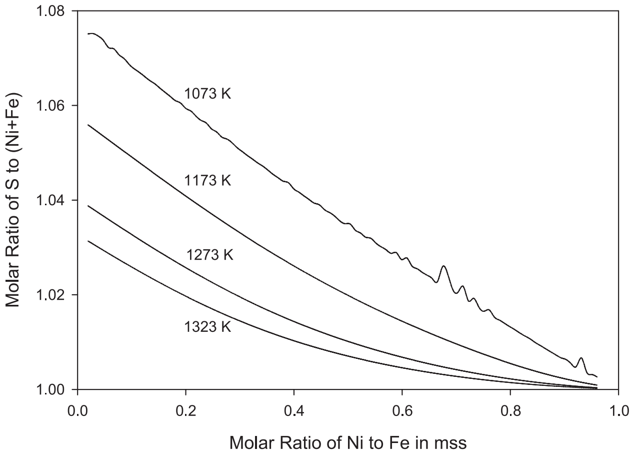

Fig. 3: Sulphide composition as a function of nickel content in the mss solution at various temperatures

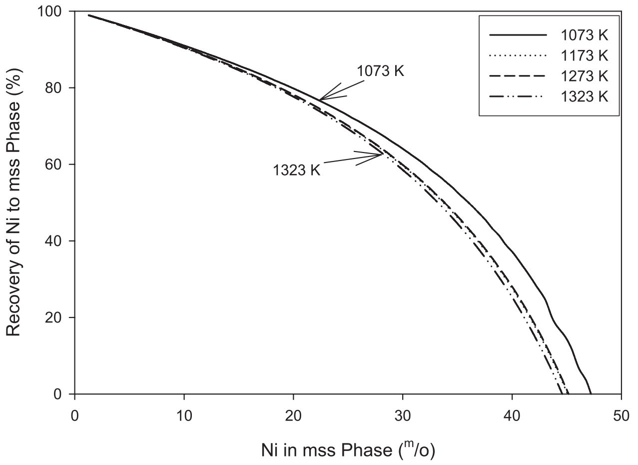

Fig. 4: Maximum nickel recovery as a function of nickel sulphide grade at various temperatures

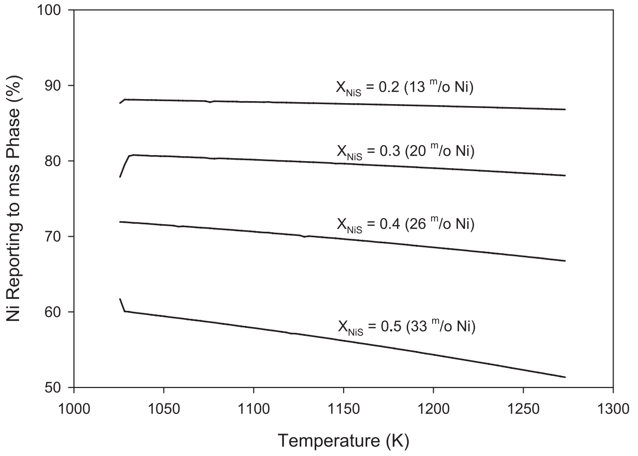

Fig. 5: Maximum nickel recovery as a function of temperature for various nickel grades

It is useful to consider the impact that the residual nickel in the spinel phase will have on possible grade recovery combinations. The extent of nickel conversion to sulphide will dictate the maximum recovery that could be achieved for a specific nickel grade. The ideal grade recovery curves, shown in Figure 4, were created for a hypothetical nickel-iron oxide with an iron to nickel mass ratio of 47, which corresponds to an equivalent nickel grade of 1.5 mass percent. The calculations indicate that at above 20 mass percent nickel grade in the sulphide, the achievable recovery drops very quickly. As a result, grades above 20 to 25 mass percent nickel will most likely result in too low a recovery to be considered under any practical conditions. Temperature has little impact on the partitioning of the nickel between the phases. This is evident in Figure 5, which shows the recovery of nickel as a function of temperature for several possible nickel sulphide grades.

An examination of Figure 1 shows that pure nickel monosulphide decomposes to heazlewoodite at approximately 973 K in the presence of magnetite. The temperature at which this happens in the presence of the monosulphide solid solution will depend on the activity of nickel monosulphide in the mss phase and the corresponding partial pressure of sulphur according to:

$$6NiS \rightarrow 2Ni_3S_2 + S_2(g) \tag{27}$$

The activity of heazlewoodite can be calculated as a function of the nickel content in the monosulphide phase. Figure 6 shows the activity of Ni_3S_2 as a function of nickel

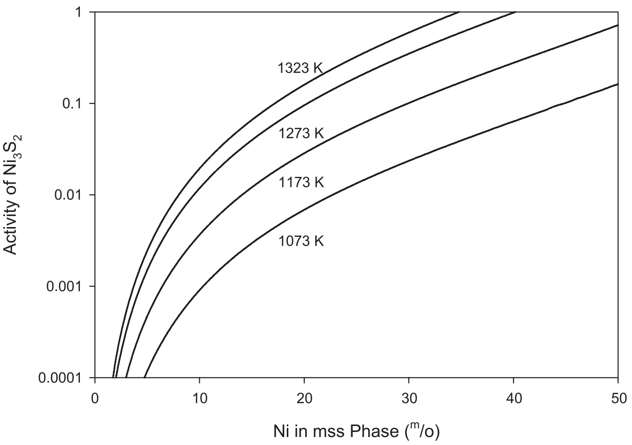

Fig. 6: Activity of Ni_3S_2 as a function of nickel content in mss phase at various temperatures.

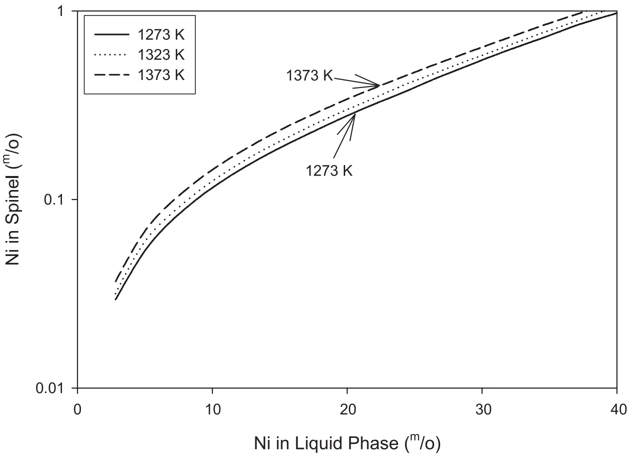

Fig. 7: Mass percent of nickel in the spinel phase versus the nickel grade in the liquid phase at various temperatures.

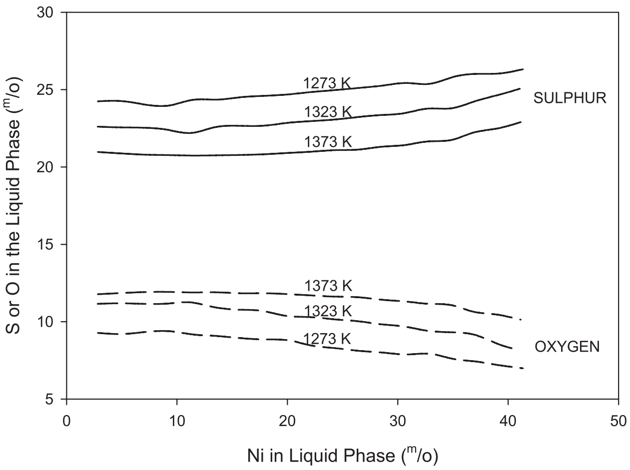

Fig. 8: Oxygen and sulphur contents of liquid matte in equilibrium with the spinel phase at various temperatures

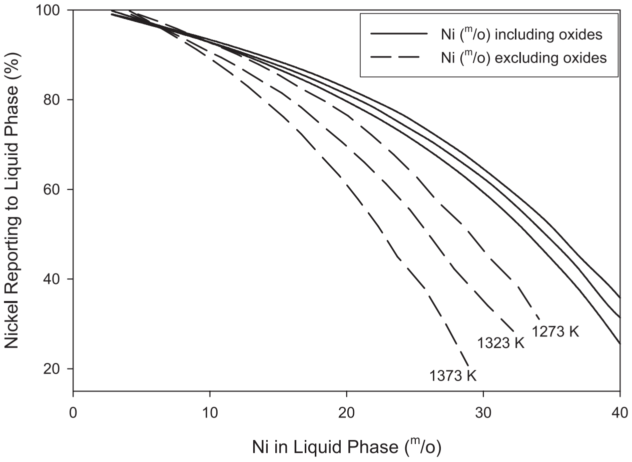

Fig. 9: The maximum recovery of nickel to the liquid phase versus nickel grade in the liquid phase at various temperatures

content. At a Ni_3S_2 activity of unity, this phase will begin to form. It is apparent that the ability of the nickel monosulphide to form a solution with iron sulphide pushes the formation of heazlewoodite to higher temperatures with this phase not beginning to form until 25 mass percent nickel at higher temperatures (i.e. 1273 to 1323 K) and 40 to 45 mass percent nickel at temperatures near 1073 K. An examination of the typical equilibrium content of nickel in the spinel phase at these higher nickel grades suggests that heazlewoodite will not be a relevant phase of interest if a reasonable conversion of nickel to the sulphide phase is desirable.

In a manner similar to the spinel/mss equilibrium it is useful to examine the implications of the nickel partitioning between the matte and the spinel phase. Figure 7 shows the mass percent of nickel that remains in the spinel phase as a function of the nickel grade within the liquid phase. The higher the nickel grade, the higher the residual nickel content in the spinel phase, which is a direct result of exchange Reaction 18. The overall liquid composition changes as a function of temperature, and to a lesser extent the nickel content in the liquid. Figure 8 shows the mass percent of dissolved oxygen and sulphur as a function of composition for temperatures between 1273 and 1373 K. The dissolved oxygen content is in the same range as reported by Doyle and Naldrett [2] and also Naldrett [11].

Figure 9 presents the maximum achievable nickel conversion to the liquid phase versus the nickel grade of the liquid phase. The starting nickel content in the oxide was the same as the value used previously. The first set of curves shows the bulk nickel grade including the dissolved iron oxide components, whereas the second set of curves includes only the sulphide components, assuming the iron oxide was able to precipitate from the liquid as magnetite during cooling. The results indicate that for an overall nickel oxide conversion of over eighty percent, the bulk nickel grade of the liquid is limited to between 15 to 20 mass percent, which corresponds to a nickel grade on a sulphide only basis of between 25 to 30 mass percent.

It was found that during the calculation of the equilibrium composition of mattes containing high nickel contents in the liquid phase that the results were numerically unstable. In order to examine the potential reason for this, the system was tested for a miscibility gap. Two liquids were assumed to coexist in equilibrium with magnetite at a total pressure of 1 atm. The coexistence of two liquids requires that the activities of all components be equal. For the current conditions this implies that two additional constraints must be included during the equilibrium calculations, namely:

$$a_{FeS}{}^{L1} = a_{FeS}{}^{L2} \tag{28}$$

$$a_{NiS}{}^{L1} = a_{NiS}{}^{L2} \tag{29}$$

The additional constraints imposed by Equations 28 and 29 remove all degrees of freedom regarding the liquid compositions, and for a fixed temperature and pressure the composition of both liquids are uniquely determined.

The two liquid compositions, which were found to satisfy Equations 28 and 29 in addition to the conditions previously specified are shown in Table 2 for the three different temperatures. The first liquid represents a nickel-rich phase with little oxygen solubility and a bulk composition very close to the liquid heazlewoodite phase found in the Fe-Ni-S phase diagram, whereas the second phase is very close to a mixture of iron-rich monosulphide solid solution with dissolved magnetite. This phase separation is not surprising, as the partitioning of nickel and iron between a (Fe, Ni)$_3$S$_2$ phase and monosulphide solution phase is seen in the Fe-Ni-S phase diagram. Additionally, there is a strong positive Gibbs Free Energy of mixing between oxygen and nickel compounds in the solution, which represents a driving force for their separation. The formation of a second liquid occurs at nickel contents similar to those found in the mss/spinel/heazlewoodite equilibrium previously discussed. A more detailed study of the miscibility gap was not done, since the liquid separation occurs in an area that is not relevant to the current area of study as the residual nickel within the trevorite at these compositions would be on the order of 1 mass percent. With typical ore grades of only 1 to 1.5 mass percent, little or no recovery would be achieved.

Conclusions

An examination of the pure component thermodynamics reveals a strong driving force for the selective sulphidation of nickel oxide from a lateritic ore while leaving the bulk of the iron as an oxide. Further study of the solution phases within the Ni-Fe-S-O system reveals the overall conversion of nickel to a sulphide must be balanced by the quantity of iron that is also converted to sulphide. At high nickel grades the recovery of the nickel to sulphide decreases dramatically. At these high nickel grades the formation of a nickel-rich heazlewoodite phase, which coexists with the monosulphide phase is possible as is the formation of two immiscible liquids. These phases will not likely appear in the sulphidation regimes of interest due to the low recovery of nickel which would be achieved at the higher nickel grades required for the formation of these phases. The thermodynamic analysis suggests that the maximum bulk nickel grade that could be achieved, while at the same time requiring that eighty percent of the nickel be converted to a sulphide, is approximately 20 to 25 mass percent nickel.

	1273 K		1323 K		1373 K	
	Liquid 1	Liquid 2	Liquid 1	Liquid 2	Liquid 1	Liquid 2
Mass% Ni	64.48	26.02	62.62	23.68	58.56	21.94
Mass% Fe	6.95	41.32	8.55	44.11	12.71	46.44
Mass% S	28.54	25.25	28.55	23.41	27.63	21.22
Mass% O	0.02	7.46	0.26	8.83	1.11	10.41
a_{FeS}	0.24	0.23	0.23	0.23	0.20	0.19
a_{NiS}	0.26	0.27	0.26	0.26	0.25	0.25

Table 2: Liquid compositions on either side of the calculated miscibility gap

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