Metal Loss to Slag: Part II. Oxidic Dissolution of Nickel in Fayalite Slag and Thermodynamics of Continuous Converting of Nickel-Copper Matte

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$FeO-Fe_2O_3-SiO_2$ slags were equilibrated in pure nickel crucibles under a $CO-CO_2$ atmosphere. The Fe/SiO_2 ratios in the slag were fixed at 1.51 and 1.97 at temperatures of 1200 and 1300°C. The CO_2/CO ratios were varied up to values corresponding to magnetite saturation. On the basis of solubility data obtained, a computer model was developed to predict the solubilities of nickel and copper in slag during the continuous converting of nickel-copper matte. These are given as a function of five parameters: temperature, iron content and Cu/Ni ratio in the matte, partial pressure of SO_2 in the gas phase, and magnetite activity in the slag. The model is helpful in comprehending converting reactions and of practical applicability in optimizing the conventional as well as continuous converting processes.

THE concept of oxidic and sulfidic dissolution of copper in sulfur-containing slags has been developed in the previous work to explain the observed high solubilities of copper in reverberatory slags.[1] The distinction between oxidic and sulfidic dissolution of copper is only imaginary because copper in slag is assumed to be in the form of copper ion in both cases, but it nevertheless assists in understanding various aspects of copper loss to slag. On the basis of this concept, the sulfidic solubility of copper from high-grade matte decreases with decreasing activity of iron sulfide, or with increasing copper content of matte. Thus, it may be assumed that the metal losses to slag occur mainly in the oxidic form toward the finishing blow of nickel-copper matte converting. Under such conditions the dissolution of nickel and copper may be assessed based on solubility data established for sulfur-free slags. Data for copper solubility are available.[2,3,4] Nickel solubility was measured in the present study.

In the converting of nickel-copper matte, the temperature is normally about 1270°C[5] and typical Fe/SiO_2 ratios in the slag are 1.8 (Falconbridge)[5] and 2.0 (Copper Cliff).[6] The ratio is 1.5 in fayalite slag saturated with silica and magnetite.[7] These Fe/SiO_2 ratios suggest that the solubility of nickel in slag during converting cannot be investigated using silica crucibles. A condition close to silica saturation may prevail in reverberatory smelting, but in this the slag should contain sulfur. For silica-unsaturated fayalite slags, the choice of a crucible becomes somewhat more difficult. Fortunately, the solubility of nickel can be determined using a nickel crucible, which has the added advantage of being applicable not only to simple fayalite slag but also to alumina- or lime-bearing slags.

The experimental part of this study consisted of determining the nickel content in silica-unsaturated slag equilibrated with a pure nickel crucible under a $CO-CO_2$ atmosphere. The discussion includes a prediction of the solubilities of nickel and copper in slag under various conditions of bessemer matte converting.

EXPERIMENTAL

Two fayalite slags having Fe/SiO_2 ratios of 1.51 (33.8 pct SiO_2, 1.4 pct Fe_2O_3, 64.8 pct FeO) and 1.97 (28.2 pct SiO_2, 2.4 pct Fe_2O_3, 69.4 pct FeO) were prepared by premelting ferrous oxide, ferric oxide and silica (reagent grade) in iron crucibles under a neutral atmosphere.[1] Carbon monoxide (99.5 pct) was passed through packed towers of copper pellets (hydrogen-reduced BASF R3-11 catalyst) maintained at 300°C to remove oxygen, soda lime to remove carbon dioxide, and phosphorus pentoxide to remove water vapor. Carbon dioxide (99.99 pct) was similarly purified in the absence of the soda lime tower. The gases were then mixed. The CO_2/CO ratio in the gas mixture (total flow, 100 cc/min) was regulated with a bleeder system and monitored with capillary flowmeters. The nickel crucibles (12 mm ID, 15 mm OD, 40 mm high) were made by drilling pure nickel rod (99.5 pct).

The silica reaction tube assembly (52 mm ID, 58 mm OD, 580 mm long) is schematically shown in Fig. 1. The nickel crucible containing the slag melt (3 g) was held in a refractory holder and a Pt-Pt, 13 pct Rh thermocouple was positioned beside the crucible. The $CO-CO_2$ gas entered the reaction tube through an alumina tube (3 mm ID) placed 7 mm above the slag surface, swept over the melt surface and was vented.

The crucible was held at constant temperature (±0.5°C) for 20 to 42 h under constant $CO-CO_2$ flow conditions. There was excellent agreement between results obtained for 20 and 42 h, indicating that the shorter period was sufficient to establish equilibrium (Table I). The equilibrium slag composition was approached only from the low oxygen potential side to avoid the precipitation of metallic nickel in the slag. After equilibration the furnace was lowered, and the reaction tube assembly was quenched from the outside with an air blower. Nickel in the slag was analyzed by

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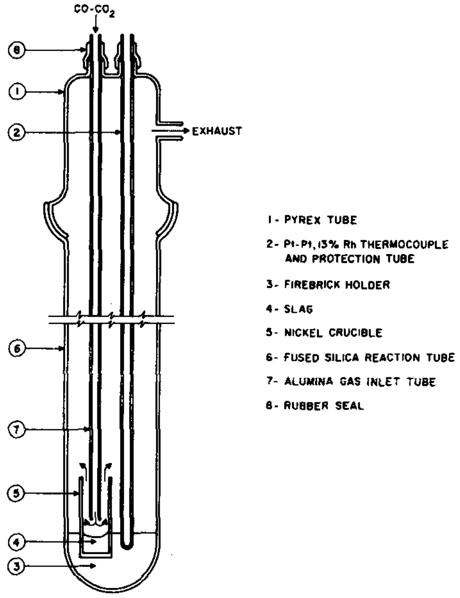

Fig. 1—Reaction tube assembly.

the dimethylglyoximate method, while the silica was determined gravimetrically. Ferric ion as magnetite was analyzed by the conventional titration method which involved leaching of the slag sample with hydrochloric acid under a stream of pure CO_2 gas.

RESULTS

The experimental results are shown in Table I. Excellent agreement between results for tests with different equilibration times indicates not only that the equilibria were successfully attained but also that the temperature fluctuation was small enough to prevent the precipitation of metallic nickel in the slag.

Since solubilities of nickel were found to be dependent on the oxygen potential, the metal is assumed to dissolve in the slag in the oxidic form (NiO). The CO_2/CO ratios may be related to the activity of NiO as follows.[8]

$$Ni(s) + CO_2 = NiO(s) + CO$$

$$\Delta G^\circ = 9{,}050 + 2.80\,T \text{ (cal/mole)} \qquad [1]$$

$$K = \frac{a_{NiO}}{a_{Ni}} \times \frac{CO}{CO_2} \qquad [2]$$

When the oxygen potential is sufficiently high, the activity of iron in the slag is negligibly small. According to Michal and Schuhmann,[8] at a CO_2/CO ratio of 2, for example, the activity of iron is less than 0.07 in silica-saturated slag at 1300°C. When the oxygen potential becomes low, the nickel crucible in contact with the molten slag begins to form a thin layer of Ni-Fe alloy and a_{Ni} cannot be regarded any longer as being approximately unity. For this reason, solubility measurements at CO_2/CO ratios lower than 2.0 were avoided in the present experiments. Under the present experimental conditions it may be assumed that $a_{Ni} \approx 1$. Then, from Eqs. [1] and [2],

$$a_{NiO} = 0.01107\,(CO_2/CO) \qquad (1200^\circ C) \qquad [3]$$

$$a_{NiO} = 0.01348\,(CO_2/CO) \qquad (1300^\circ C) \qquad [4]$$

The calculated oxide activities are shown in Table I and Fig. 2.

The weight percent nickel in the slag was found to be a smooth function of a_{NiO} except at the highest CO_2/CO ratios in each series of experiments. This deviation is due to the onset of magnetite saturation. The dissolution of NiO in the slag can be expected to cause magnetite saturation at lower CO_2/CO ratios. According to Michal *et al*,[9] the CO_2/CO ratios corresponding to

Table I. Experimental Results

Exp No.	Temp, °C	Fe/SiO_2 Ratio in Slag	CO_2/CO	a_{NiO} Calculated	Slag Analysis, Pct			Calculated Composition, Pct		
					Ni	Fe_3O_4	SiO_2	NiO	Fe_2O_3	FeO
1	1200	1.51	2	0.0227	0.63	–	32.0	0.8	–	–
13*	1200	1.51	2	0.0227	0.59	2.3	33.4	0.8	1.6	64.2
6	1200	1.51	3	0.0340	0.79	2.9	32.5	1.0	2.0	64.5
2	1200	1.51	5	0.0567	1.29	4.8	32.2	1.6	3.3	62.9
3	1200	1.51	10	0.1134	1.98	5.8	33.2	2.5	4.0	60.3
5	1200	1.51	15	0.1701	2.36	9.7	32.5	3.0	6.7	57.8
4	1200	1.51	20	0.2268	2.90	6.0	31.6	3.7	4.1	60.6
15	1200	1.51	30	0.3402	2.80	8.2	31.6	3.6	5.7	59.1
16	1300	1.51	2	0.0271	0.87	3.8	32.3	1.1	2.5	64.1
17	1300	1.51	5	0.0677	2.23	5.9	31.6	2.8	4.1	61.5
18	1300	1.51	20	0.2708	7.55	10.5	29.8	9.6	7.3	53.3
19	1300	1.51	50	0.6770	9.86	11.9	28.7	12.6	8.2	50.5
9	1200	1.97	2	0.0227	0.40	6.8	26.4	0.5	4.7	68.4
7	1200	1.97	3	0.0340	0.70	–	–	0.9	–	–
12*	1200	1.97	3	0.0340	0.68	7.6	–	0.9	5.3	–
8	1200	1.97	5	0.0567	1.16	9.4	26.4	1.5	6.5	65.6
10	1200	1.97	10	0.1134	3.28	–	–	4.2	–	–
11	1200	1.97	15	0.1701	3.93	12.9	23.8	5.0	8.9	62.3
14	1200	1.97	30	0.3402	4.25	14.5	25.0	5.4	10.0	59.6
20	1300	1.97	2	0.0271	0.84	9.2	27.5	1.1	6.3	65.1
21	1300	1.97	5	0.0677	2.08	9.2	26.6	2.7	6.3	64.4
22	1300	1.97	10	0.1354	4.42	12.5	25.1	5.6	8.6	60.7
23	1300	1.97	20	0.2708	7.71	14.8	23.5	9.8	10.2	56.5
24	1300	1.97	40	0.5416	10.2	15.1	23.3	13.0	10.4	53.3

*42 h equilibration; otherwise 20 h.

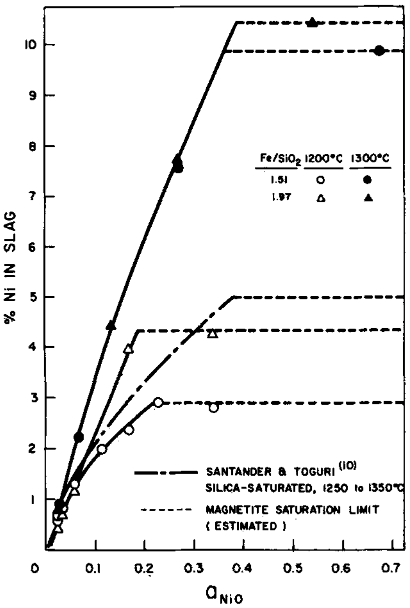

Fig. 2—Solubility of nickel in fayalite slag as a function of activity of NiO.

silica and magnetite saturation in fayalite slag at 1200 and 1300°C are about 30 and 60, respectively. Using Eqs. [3] and [4], the NiO activities corresponding to silica and magnetite saturation at 1200 and 1300°C are estimated to be within the range:

a_{NiO} (magn. satn.) < 0.33 (1200°C)

a_{NiO} (magn. satn.) < 0.80 (1300°C)

On this basis, the apparent deviation of the nickel concentration at the highest oxygen potentials may be interpreted as indicating magnetite saturation. The actual saturation limit probably corresponds to a_{NiO} intermediate to the highest and the second highest oxygen potentials in each series of experiments. For oxygen potentials higher than that for magnetite saturation the slag will eventually be covered by a magnetite layer and the reaction will practically cease owing to slow diffusion through the solid magnetite layer. From the phase rule it can be shown that the results obtained at oxygen potentials above those for magnetite saturation are meaningless. In order to accurately locate the magnetite saturation limits, the CO_2/CO ratio should be varied by small increments between the second highest and the highest oxygen potentials in each series of experiments.

The silica content of the slag was found to decrease slightly with increasing Fe_3O_4 and NiO contents or increasing oxygen potential (Table I). While the magnetite content increases from 6.8 to 12.9 pct (1200°C, $Fe/SiO_2 = 1.97$), for example, the nickel content increases almost ten times from 0.43 to 3.97 pct. The solubility of nickel therefore appears to be very sensitive to the magnetite content of the slag. The magnetite solubility limits for nickel-free fayalite slag with $Fe/SiO_2 = 1.97$ are about 22 pct at 1200°C and 34 pct at 1300°C.[7] Comparison with the present data indicates that nickel dissolution decreases the magnetite content at the solubility limits, suggesting that NiO replaces Fe_3O_4. This is shown graphically in Fig. 3. The effect of the silica content of the slag is often discussed in relation to metal losses in the slag, but a comparison between two different conditions is meaningful only when the activity of magnetite is kept constant. Fig. 3 shows that the solubility of NiO in slag is simultaneously dependent upon the silica and magnetite contents.

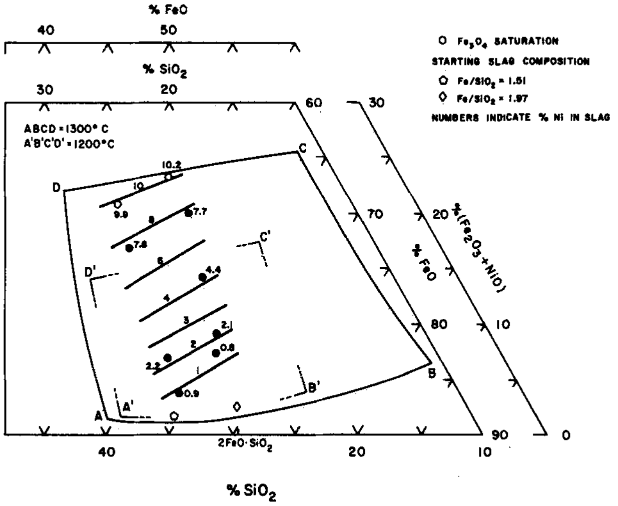

Fig. 3—Solubility of nickel as a function of SiO_2 and FeO contents of slag (1300°C). *ABCD* indicates the homogeneous slag range of the $FeO-Fe_2O_3-SiO_2$ system.[7]

For practical purposes it is much more convenient to express the solubility in terms of weight percent instead of mole fraction. The present results at 1200 and 1300°C are summarized by the equation:

$$\text{pct Ni} = a_{\text{NiO}}\,[(53.6 - 18.0Q) + (-20.9 + 18.0Q)t] + a^2_{\text{NiO}}\,[(-371.6 + 204.0Q) + (356.8 - 204.0Q)t] \qquad [5]$$

$$t \equiv [T(\text{K}) - 1473]/100; \quad (1.4 < Q < 2.1)$$

where Q refers to the Fe/SiO_2 ratio in slag.

Santander and Toguri[10] measured the solubility of nickel in silica saturated fayalite slags at 1250 and 1350°C. In view of the fact that the Fe/SiO_2 ratio in silica-saturated slags varies from 1.21 for iron saturation to 1.56 for magnetite saturation at 1300°C,[7] it is not possible to directly compare their results with the present data for which the ratios were held constant. However, their empirical relationship,

$$\text{pct Ni} = 9.6\,a_{\text{NiO}}^{2/3} \qquad [6]$$

gives 5.0 pct Ni for the assumed magnetite saturation limit at 1300°C ($a_{\text{NiO}} = 0.38$), which compares with 10.3 pct Ni by extrapolation of the present data. Although Eq. [6] violates thermodynamic principle as it yields $\gamma^{\circ}_{\text{NiO}} = 0$ in the infinitely dilute solution range, the relation is plotted in Fig. 2 for comparison in the higher concentration range.

It is evident from Fig. 2 that the solubility of nickel clearly approaches zero when the activity of the oxide approaches zero. This suggests that nickel can be dissolved by the slag only after being oxidized, and therefore it may be concluded that there is no appreciable solubility of Ni as neutral metallic atoms under the present experimental conditions. Consequently, Eq. [5] may be applied to any practical conditions regardless of whether or not a separate metallic nickel phase is present in equilibrium with the slag. The equation may also be interpolated for other temperatures and

Fe/SiO_2 ratios, and possibly be extrapolated for a small range of these parameters.

THERMODYNAMICS OF CONTINUOUS Ni-Cu MATTE CONVERTING

Choice of Variables

To analyze thermodynamically the bessemerization process three phases may be assumed; gas, slag and matte. The gas phase consists of SO_2, S_2, O_2, and N_2. Nitrogen may be excluded by considering it as a neutral diluent. When the activity of FeS is small, as in the final stage of Ni-Cu matte converting, sulfidic dissolution can be neglected, and therefore the slag phase is represented by the system FeO-Fe_2O_3-SiO_2-NiO-$CuO_{0.5}$, neglecting constituents such as Al_2O_3 and CaO. The matte phase may be represented by the system Cu-Ni-Fe-S. Although, by analogy with copper mattes,[11] oxygen or iron oxides may dissolve in nickel matte as well, their concentration is assumed to be smaller than in copper matte owing to a tendency for nickel atoms to form NiO and to separate out in the slag. In other words, it is iron sulfide in matte that tends to dissolve iron oxides as a result of the strong affinity between iron sulfide and oxides in the molten state.[12] Accordingly, the solubility of oxygen may be neglected here, especially for converter mattes in which the iron concentration is very low.

On the basis of the phase rule, there are five degrees of freedom (F) in the present system which consists of three phases and six components (Ni, Cu, Fe, S, O, SiO_2): $F = 6 + 2 - 3 = 5$. Most conveniently, the following five variables may be chosen: temperature (T), partial pressure of SO_2 (p_{SO_2}), activity of magnetite ($a_{Fe_3O_4}$), wt pct Cu/wt pct Ni ratio in matte, and wt pct Fe in matte. A value for p_{SO_2} is estimated on the assumption that all of the oxygen introduced by the converting air reacts with the melt.[13] About one third of the oxygen of the inlet air is fixed as iron oxides in the slag. In the particular case of blowing with air (21 pct O_2), the maximum value of p_{SO_2} is approximately 0.15 atm. The activity of magnetite can be estimated from the Fe_3O_4 content of the slag using Fig. 5 as a guide.[14] The activity of Fe_3O_4 depends largely on temperature and only slightly on the Fe/SiO_2 ratio in the slag.

In practice, the bath temperature varies considerably during converting, from about 1200°C initially to 1260 to 1270°C toward the end of the blow.[6] The Cu/Ni ratio also changes as nickel is more readily lost to the slag than is copper. The magnetite activity also changes considerably, being low in the initial stage and becoming higher, sometimes to the point of saturation, in the final stage. Moreover, converting is normally a batch process involving successive matte charging and slag skimming. In this sense, the present thermodynamic analysis is more pertinent to the steady state existing in continuous converting rather than in conventional converting.

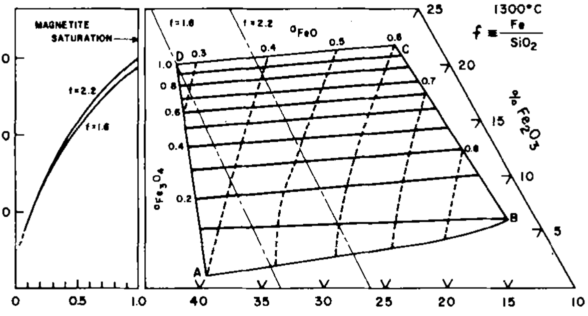

Fig. 4—Activity of magnetite in FeO-Fe_2O_3-SiO_2 slag at 1300°C. After Korakas.[14]

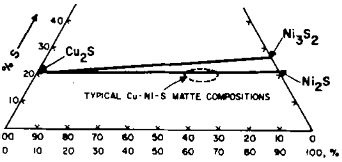

Fig. 5—Portion of the Cu-Ni-S system showing the improved representation of commercial matte compositions by the Cu_2S-Ni_2S rather than the Cu_2S-Ni_3S_2 pseudo-binary system. Typical Cu-Ni-S matte compositions, after Boldt and Queneau.[6]

The relation between the NiO activity and pct Ni in slag has been given by Eq. [5], whereas the $CuO_{0.5}$ activity has been related to the weight percent of copper in a sulfur-free slag by a temperature-independent equation:[1]

$$\text{pct Cu} = 35.9 a_{CuO_{0.5}} \qquad [7]$$

Eq. [7] was originally derived for silica-saturated fayalite slags, but the equation may be applied to silica-unsaturated slags as an approximation. Thus, if the activities of NiO and $CuO_{0.5}$ can be calculated as a function of the above-defined five variables, the corresponding contents of nickel and copper in slag can be calculated. The present problem is therefore reduced to calculation of the activities of NiO and $CuO_{0.5}$ for a given set of five variables.

Solution Model for Ni-Cu Matte

Activity measurements for Ni-Cu-Fe-S (-O) mattes are not available, and therefore some assumptions will be made to relate matte composition to the activities of the constituents. Nickel-copper matte has generally been dealt as a ternary sulfide mixture: Ni_3S_2-Cu_2S-FeS. Since molten sulfides have a remarkable solubility for metals as well as metalloids, this conventional way of representing nickel matte has no physico-chemical meaning and is only an approximation to express the composition of actual mattes. Commercial nickel mattes contain excess nickel, which gives rise to a deviation from the binary Ni_3S_2-Cu_2S system. By choosing Ni_2S as a constituent, the composition of commercial sulfur-deficient mattes can be expressed far more satisfactorily, as is shown in Fig. 5. The misleading choice of liquid Ni_3S_2 as a nickel matte constituent was conventionally made in view of the absence of thermodynamic data for Ni-S melts, when the free energy data for solid Ni_3S_2 could be used by extrapolating to liquid temperatures. However, presently available data for Ni-S melts[15] allow the free energy of formation of liquid Ni_2S to be calculated, as shown in Appendix I and Table II.

The pseudo-binary Cu_2S-Ni_3S_2 and Ni_3S_2-FeS systems have been erroneously assumed to be ideal solutions[16,17] in analogy with the Cu_2S-FeS system[18] which was observed not to depart too far from ideality due to a stable quasi-lattice of sulfur atoms (ions) in the melt. The assumption of ideality may be applied to the Cu_2S-Ni_2S pseudo-binary with respect to both metal and sulfur sublattices, but it should not be applied to the Cu_2S-Ni_3S_2 pseudo-binary. In this case neither metal nor sulfur quasi-sublattices of constituents are common, and the larger molecule of Ni_3S_2 contains five atoms compared with the Cu_2S molecule which contains three atoms. In the Ni_2S melt the molar volumes of Ni, S and Ni_2S are 6.2, 12.8 and 25.2 cc/mole at 1100°C, respectively,[19] while the molar volume of a Ni_3S_2 melt is as large as 45 cc/mole. In the Cu_2S melt the molar volumes of Cu, S and Cu_2S are 8.0, 14.8 and 30.8 cc/mole at 1200°C, respectively.[19] It is therefore possible to assume approximately ideal mixing between Cu_2S (30.8 cc/mole) and Ni_2S (25.2 cc/mole), but mixing between Cu_2S and Ni_3S_2, with Ni_3S_2 possessing a 1.5 times larger volume than Cu_2S, cannot be considered ideal even on the basis of the configurational entropy alone.

According to Darken and Schwerdtfeger,[20] Raoultian ideality for a pseudo-binary A_uX_v-B_uX_v, where all the A and B atoms are interchangeable on the A-B sublattice but no X atoms can occupy the A-B sublattice, should be expressed by

$$a_{B_uX_v} = N^u_{B_uX_v}$$

where N refers to the mole fraction. For the Cu_2S-Ni_2S system,

$$a_{Ni_2S} = N^2_{Ni_2S} \tag{8}$$

$$a_{Cu_2S} = N^2_{Cu_2S} \tag{9}$$

Then, in analogy with Cu_2S-FeS melt,[18] the activity of FeS is given by

$$a_{FeS} = N_{FeS} \tag{10}$$

The mole fraction of the molecular constituents Ni_2S, Cu_2S and FeS can easily be expressed in terms of the Cu/Ni ratio and pct Fe in the matte.

Analysis of the System

The free energy changes and equilibrium constants at 1300°C for the reactions involved in the system are shown in Table II.[21] As an example of the analytical method employed, the calculation will be carried out for the following case:

i) temperature = 1300°C
ii) Cu/Ni (matte) = 0.45
iii) pct Fe (matte) = 1.0
iv) $p_{SO_2} = 0.15$ atm
v) $a_{Fe_3O_4} = 1.0$ (magnetite saturation)

Conditions ii) and iii) yield the following matte composition:

1.0 pct Fe
53.6 pct Ni
24.1 pct Cu
21.3 pct S

In terms of the mole fraction of each molecular constituent, we have

$$\begin{aligned} N_{FeS} &= 0.027 \\ N_{Ni_2S} &= 0.687 \\ N_{Cu_2S} &= 0.286 \end{aligned} \tag{11}$$

By the virtue of Eqs. [8], [9] and [10], we have

$$a_{FeS} = N_{FeS} = 0.027 \tag{12}$$

$$a_{Ni_2S} = N^2_{Ni_2S} = 0.472 \tag{13}$$

$$a_{Cu_2S} = N^2_{Cu_2S} = 0.082 \tag{14}$$

From the equilibrium constant of reaction [9] of Table I, and with the insertion of conditions iv) and v) and Eq. [12], we obtain

$$K_9 = \frac{a^{10}_{FeO}p_{SO_2}}{a^3_{Fe_3O_4}a_{FeS}} = \frac{a^{10}_{FeO} \times 0.15}{1.0 \times 0.027}$$

or

$$a_{FeO} = 0.522 \tag{15}$$

From the equilibrium constant for reaction [10], and the above value of a_{FeO}, we obtain

$$K_{10} = \frac{a^4_{FeO}}{a_{Fe_3O_4}a_{Fe}} = \frac{(0.522)^4}{1.0 \times a_{Fe}}$$

or

$$a_{Fe} = 1.10 \times 10^{-2} \tag{16}$$

Substituting Eqs. [12] and [16] into the expression for the equilibrium constant of reaction [3], we obtain

$$K_3 = \frac{a_{FeS}}{a_{Fe}p^{1/2}_{S_2}} = \frac{0.027}{1.1 \times 10^{-2} \times p^{1/2}_{S_2}}$$

or

$$\begin{aligned} p^{1/2}_{S_2} &= 1.65 \times 10^{-2} \\ p_{S_2} &= 2.74 \times 10^{-4} \end{aligned} \tag{17}$$

Substituting condition iv) and Eq. [17] into the equilibrium constant for reaction [8], we obtain

$$K_8 = \frac{p_{SO_2}}{p^{1/2}_{S_2}p_{O_2}} = \frac{0.15}{1.65 \times 10^{-2} \times p_{O_2}}$$

or

$$\begin{aligned} p^{1/2}_{O_2} &= 2.24 \times 10^{-4} \\ p^{1/4}_{O_2} &= 1.49 \times 10^{-2} \end{aligned} \tag{18}$$

Substituting Eqs. [14] and [17] into the equilibrium constant for reaction [2], we obtain

$$K_2 = \frac{a_{Cu_2S}}{a^2_{Cu}p^{1/2}_{S_2}} = \frac{0.082}{a^2_{Cu} \times 1.65 \times 10^{-2}}$$

or

$$a_{Cu} = 0.100 \tag{19}$$

Substituting Eqs. [13] and [17] into the equilibrium constant of reaction [1], we obtain

$$K_1 = \frac{a_{Ni_2S}}{a^2_{Ni}p^{1/2}_{S_2}} = \frac{0.472}{a^2_{Ni} \times 1.65 \times 10^{-2}}$$

or

$$a_{\mathrm{Ni}} = 0.282 \qquad [20]$$

Substituting Eqs. [18] and [20] into the equilibrium constant for reaction [7], we obtain

$$K_7 = \frac{a_{\mathrm{NiO}}}{a_{\mathrm{Ni}}\, p_{\mathrm{O_2}}^{1/2}} = \frac{a_{\mathrm{NiO}}}{0.282 \times 2.24 \times 10^{-4}}$$

or

$$a_{\mathrm{NiO}} = 5.97 \times 10^{-2} \qquad [21]$$

Finally, from the insertion of Eqs. [18] and [19] into the equilibrium constant of reaction [6], we obtain

$$K_6 = \frac{a_{\mathrm{CuO_{0.5}}}}{a_{\mathrm{Cu}}\, p_{\mathrm{O_2}}^{1/4}} = \frac{a_{\mathrm{CuO_{0.5}}}}{0.100 \times 1.49 \times 10^{-2}}$$

or

$$a_{\mathrm{CuO_{0.5}}} = 1.07 \times 10^{-2} \qquad [22]$$

The $CuO_{0.5}$ activity given by Eq. [22] may be converted to the solubility of copper in slag by means of Eq. [7]. The value of $a_{\mathrm{CuO_{0.5}}} = 0.0107$ thus corresponds to 0.39 pct Cu in slag. The NiO activity given by Eq. [21] may be converted to the solubility of nickel in slag by means of Eq. [5], or, by using the curves in Fig. 2. The solubility of nickel at 1300°C is seemingly independent of the Fe/SiO_2 ratio in slag, and the NiO activity of 0.0597 corresponds to 1.9 pct Ni in slag. The calculated results for the above example are all summarized in Table III.

The nickel solubility below 1300°C is dependent upon the Fe/SiO_2 ratio in slag, as seen in Fig. 2. It is to be noted that the Fe/SiO_2 ratio in the above analysis is not an independent variable on the basis of the phase rule, but is a function of the five variables defined above. This is readily understood from Fig. 4 in which only one value of the Fe/SiO_2 ratio is given for a given set of $a_{\mathrm{Fe_3O_4}}$ and a_{FeO}. Thus, in accordance with Eq. [5], it is convenient to express Q as a function of $a_{\mathrm{Fe_3O_4}}$ and a_{FeO} which are given by condition v) and Eq. [15], respectively. Using activity data[1,14] as well as the present experimental results, the relationship may be roughly approximated by

$$Q = (0.48 - 0.78t) - (2.20 - 1.50t)\,a_{\mathrm{Fe_3O_4}} + (1.80 + 3.72t)\,a_{\mathrm{FeO}} + (6.90 - 2.42t)\,a_{\mathrm{Fe_3O_4}}a_{\mathrm{FeO}} \qquad [23]$$

Appendix I. Thermodynamic Properties[15] of Ni_2S (l) used to Calculate

$$2\,\mathrm{Ni}(s) + \tfrac{1}{2}\,\mathrm{S_2}(g) = \mathrm{Ni_2S}(l)$$

$$\Delta G_T^\circ = -28{,}090 + 6.17\,T\ \text{(cal/mole)}$$

Temperature, °C	$p_{\mathrm{S_2}}^{1/2}$, (atm)$^{1/2}$	a_{Ni}	K*	ΔG_T°† (cal/mole)
1100	2.43×10^{-3}	0.556	1.32×10^{3}	−19,610
1000	8.30×10^{-4}	0.634	3.00×10^{3}	−20,250
900	2.55×10^{-4}	0.711	7.74×10^{3}	−20,870
800	6.50×10^{-5}	0.809	2.35×10^{4}	−21,460

$$^*K = \frac{1.0}{a_{\mathrm{Ni}}^2\, p_{\mathrm{S_2}}^{1/2}}$$

$$^\dagger\Delta G_T^\circ = -4.575\,T \log K$$

Although the Fe/SiO_2 ratio-independent expression, Eq. [7], has been used for copper as an approximation, a dependency similar to Eqs. [5] and [23] may also exist for copper solubility. In the case of copper, however, the experimental problem of a suitable crucible becomes very serious for silica-unsaturated slags, although it may be surmounted by the use of a technique such as levitation.

In order to calculate other sets of data similar to the above example, a computer program was written in Waterloo Fortran language. The computer program can be run for any condition, and several built-in DO-loops allow systematic coverage of a wide range of conditions. It is possible to optimize the process by running the program for various conditions of interest. An example of the computer printout is given in Table IV. The value of FE/SIL indicates the Fe/SiO_2 ratio in slag. If the slag composition exceeds the normal highest limit of silica content the computer prints −0.00 as FE/SIL, whereas 0.00 is printed if the slag composition exceeds the normal lowest limits of silica content. Those conditions may not be practiced without a drastic modification of slag constitution.

DISCUSSION

Conventional converting of nickel-copper matte is a batch or discontinuous operation. In Falconbridge practice,[6] for example, five ladles of blast furnace matte are blown initially, and then one to two ladles of the slag are skimmed off. More low grade matte is added to the converter, followed by further blowing. Slag skimming and matte charging are repeated several

Table II. Thermodynamic Data Used in the Computer Model

	Reaction	Free Energy, ΔG_T° (cal/mole)	Equilibrium Constant, 1573 K	Reference
1	$2\,\mathrm{Ni}(s) + \tfrac{1}{2}\,\mathrm{S_2}(g) = \mathrm{Ni_2S}(l)$	$-28{,}090 + 6.17\,T$	$K_1 = 3.596 \times 10^2$	Appendix
2	$2\,\mathrm{Cu}(l) + \tfrac{1}{2}\,\mathrm{S_2}(g) = \mathrm{Cu_2S}(l)$	$-35{,}160 + 10.05\,T$	$K_2 = 4.900 \times 10^2$	1
3	$\mathrm{Fe}(\gamma) + \tfrac{1}{2}\,\mathrm{S_2}(g) = \mathrm{FeS}(l)$	$-24{,}250 + 5.50\,T$	$K_3 = 1.474 \times 10^2$	21
4	$\mathrm{Fe}(\gamma) + \tfrac{1}{2}\,\mathrm{O_2}(g) = \mathrm{FeO}(l)$	$-54{,}890 + 10.55\,T$	–	1
5	$3\,\mathrm{Fe}(\gamma) + 2\,\mathrm{O_2}(g) = \mathrm{Fe_3O_4}(s)$	$-260{,}870 + 72.24\,T$	–	1
6	$\mathrm{Cu}(l) + \tfrac{1}{4}\,\mathrm{O_2}(g) = \mathrm{CuO_{0.5}}(l)$	$-17{,}490 + 7.21\,T$	$K_6 = 7.158$	1
7	$\mathrm{Ni}(s) + \tfrac{1}{2}\,\mathrm{O_2}(g) = \mathrm{NiO}(s)$	$-58{,}450 + 23.55\,T$	$K_7 = 9.459 \times 10^2$	7
8	$\tfrac{1}{2}\,\mathrm{S_2}(g) + \mathrm{O_2}(g) = \mathrm{SO_2}(g)$	$-86{,}620 + 17.31\,T$	$K_8 = 1.805 \times 10^8$	7
9	$3\,\mathrm{Fe_3O_4}(s) + \mathrm{FeS}(l) = 10\,\mathrm{FeO}(l) + \mathrm{SO_2}(g)$	$171{,}340 - 99.41\,T$	$K_9 = 8.301 \times 10^{-3}$	*
10	$\mathrm{Fe}(\gamma) + \mathrm{Fe_3O_4}(s) = 4\,\mathrm{FeO}(l)$	$41{,}310 - 30.04\,T$	$K_{10} = 6.702$	†

*Combination of reactions (3), (4) and (8).

†Combination of reactions (4) and (5).

more times. Slags from the earlier skimming tend to contain less nickel and cooper, while slag losses are higher toward the end of converting. The iron content, temperature and magnetite activity, therefore, vary with time in a complicated, discontinuous manner. Consequently, reported slag losses can be associated only difficultly with the five above-defined parameters. Assuming some additional data, however, the nickel and copper losses reported for commercial converter slags[5,6] may be compared with the present computer model in Table V. The value for p_{SO_2} was assumed as 0.15 atm in the case of Falconbridge air converting practice and 0.20 atm in the case of Copper Cliff oxygen-enriched blowing (25 pct O_2). The reported and calculated metal losses are in an excellent agreement despite the various assumptions incorporated in the computer model. This may be interpreted as indicating that most of the metal values present in slag are a result of chemical dissolution rather than physical entrainment of matte particles.

Table III. Summary of Calculated Values for the Example in the Text

Given	Calculated
$T = 1300°C$ Cu/Ni = 0.45 pct Fe = 1.0 $p_{SO_2} = 0.15$ atm $a_{Fe_3O_4} = 1.0$	pct Ni(matte) = 53.6, pct Cu(matte) = 24.1, pct S(matte) = 21.3 $N_{FeS} = 0.027, N_{Ni_2S} = 0.687, N_{Cu_2S} = 0.286$ $a_{FeS} = 0.027, a_{Ni_2S} = 0.472, a_{Cu_2S} = 0.082$ $p_{S_2} = 2.74 \times 10^{-4}, p_{O_2} = 5.02 \times 10^{-8}$ $a_{Fe} = 1.10 \times 10^{-2}, a_{Ni} = 0.282, a_{Cu} = 0.100$ $a_{NiO} = 5.97 \times 10^{-2}, a_{CuO_{0.5}} = 1.07 \times 10^{-2}, a_{FeO} = 0.522$ pct Ni(slag) = 1.90, pct Cu(slag) = 0.39

In the case of Falconbridge converting, the calculated activity of FeO is 0.42, which corresponds to 27 pct SiO_2 using the data of Korakas[14] (Fig. 4). The calculated value of a_{FeO} for Copper Cliff converting is 0.38, which corresponds to 29 pct SiO_2. Since the converter slags normally contain other constituents such as Al_2O_3 and CaO, which may be considered more or less as neutral diluent species, the actual silica content should be somewhat lower than the calculated contents. In this sense, the silica content for the Copper Cliff converter slag is in a good agreement, whereas the silica content of the Falconbridge converter slags is apparently too high. In Falconbridge converting practice the converter slag is purposely solidified by adding excessive silica toward the end of converting when the iron content of matte becomes 2 to 3 pct. This special practice may account for the reported high silica content.

Nickel-copper bessemer matte can be produced continuously from concentrate[22] or low grade matte, and the system may be controlled to any desired conditions in terms of the five parameters. The nickel and copper losses in such a steady-state process can be assessed by means of the computer model as a function of the five parameters.

The computer program was run to investigate continuous converting conditions for Falconbridge concentrate (*i.e.*, Cu/Ni = 0.45). Among the five parameters which define the nickel and copper losses, the iron content of the matte, or a_{FeS}, has the largest effect on metal losses. The metal losses are plotted as functions of the iron content in Figs. 6 and 7. The magnetite activity of 0.7 corresponds to 18 to 20 pct Fe_3O_4 at 1200°C and 22 to 24 pct Fe_3O_4 at 1300°C, according to Korakas.[14]

Table IV. An Example of the Computer Printout

```
ACTIVITY OF CUO.5 AND NIO IN NICKEL MATTE-SLAG EQUILIBRIA

WT%CU/WT%NI(IN MATTE)  =  0.450

TEMP  NI%MT CU%MT  FE%MT AMAG PSO2 AFEO  ACUO.5  ANIO  FE/SIL CU%SLG NI%SLG  ACU     ANI     AFE        PS2        PO2

1200: 52.73 23.73  2.000 0.70 0.15 0.346 0.0043 0.0345  1.23  0.155  0.940  0.0507  0.1538  0.748E-02  0.815E-03  0.443E-08
1200. 53.59 24.11  1.000 0.70 0.15 0.323 0.0061 0.0534 -0.00  0.217  1.392  0.0640  0.1940  0.569E-02  0.360E-03  0.667E-08
1200. 54.02 24.31  0.500 0.70 0.15 0.302 0.0084 0.0817 -0.00  0.300  1.797  0.0797  0.2417  0.432E-02  0.158E-03  0.101E-07

1200. 52.73 23.73  2.000 1.00 0.15 0.385 0.0046 0.0370  1.63  0.164  0.846  0.0526  0.1594  0.803E-02  0.707E-03  0.476E-08
1200. 53.59 24.11  1.000 1.00 0.15 0.359 0.0064 0.0573  1.41  0.229  1.342  0.0663  0.2010  0.611E-02  0.312E-03  0.716E-08
1200. 54.02 24.31  0.500 1.00 0.15 0.336 0.0088 0.0878  1.20  0.317  1.832  0.0826  0.2505  0.464E-02  0.137E-03  0.108E-07


1200. 52.73 23.73  2.000 0.70 0.25 0.329 0.0042 0.0363  1.12  0.152  1.026  0.0458  0.1389  0.610E-02  0.123E-02  0.602E-08
1200. 53.59 24.11  1.000 0.70 0.25 0.307 0.0059 0.0562 -0.00  0.212  1.480  0.0577  0.1751  0.464E-02  0.541E-03  0.906E-08
1200. 54.02 24.31  0.500 0.70 0.25 0.287 0.0081 0.0860 -0.00  0.292  1.828  0.0720  0.2182  0.353E-02  0.237E-03  0.137E-07

1200. 52.73 23.73  2.000 1.00 0.25 0.366 0.0045 0.0390  1.46  0.160  0.952  0.0475  0.1439  0.655E-02  0.106E-02  0.646E-08
1200. 53.59 24.11  1.000 1.00 0.25 0.342 0.0062 0.0603  1.25  0.223  1.451  0.0598  0.1815  0.498E-02  0.469E-03  0.973E-08
1200. 54.02 24.31  0.500 1.00 0.25 0.319 0.0086 0.0924 -0.00  0.309  1.863  0.0746  0.2261  0.379E-02  0.206E-03  0.147E-07



1300. 52.73 23.73  2.000 0.70 0.15 0.502 0.0073 0.0359  3.55  0.262  1.156  0.0768  0.2156  0.135E-01  0.716E-03  0.310E-07
1300. 53.59 24.11  1.000 0.70 0.15 0.469 0.0102 0.0556  3.27  0.366  1.772  0.0968  0.2719  0.103E-01  0.316E-03  0.467E-07
1300. 54.02 24.31  0.500 0.70 0.15 0.438 0.0141 0.0851  3.00  0.505  2.676  0.1206  0.3387  0.781E-02  0.139E-03  0.706E-07

1300. 52.73 23.73  2.000 1.00 0.15 0.558 0.0077 0.0386  0.00  0.276  1.240  0.0795  0.2234  0.145E-01  0.621E-03  0.333E-07
1300. 53.59 24.11  1.000 1.00 0.15 0.522 0.0107 0.0597  0.00  0.386  1.900  0.1003  0.2817  0.110E-01  0.274E-03  0.502E-07
1300. 54.02 24.31  0.500 1.00 0.15 0.487 0.0148 0.0914  3.87  0.533  2.866  0.1250  0.3510  0.839E-02  0.120E-03  0.758E-07


1300. 52.73 23.73  2.000 0.70 0.25 0.477 0.0071 0.0378  3.34  0.255  1.215  0.0693  0.1946  0.110E-01  0.108E-02  0.422E-07
1300. 53.59 24.11  1.000 0.70 0.25 0.445 0.0099 0.0585  3.07  0.357  1.862  0.0874  0.2455  0.839E-02  0.476E-03  0.635E-07
1300. 54.02 24.31  0.500 0.70 0.25 0.416 0.0137 0.0896  2.81  0.492  2.811  0.1089  0.3058  0.637E-02  0.208E-03  0.959E-07

1300. 52.73 23.73  2.000 1.00 0.25 0.531 0.0075 0.0406  0.00  0.269  1.303  0.0718  0.2017  0.118E-01  0.934E-03  0.453E-07
1300. 53.59 24.11  1.000 1.00 0.25 0.496 0.0105 0.0628  3.96  0.376  1.996  0.0906  0.2544  0.901E-02  0.412E-03  0.682E-07
1300. 54.02 24.31  0.500 1.00 0.25 0.463 0.0145 0.0962  3.63  0.520  3.009  0.1128  0.3169  0.684E-02  0.181E-03  0.103E-06
```

Table V. Comparison Between the Reported and Calculated Metal Losses to Slag

Smelter	Computer Input Data		Slag Loss	
	Reported	Assumed	Reported	Calculated
Falconbridge[5]	1260-70°C Cu/Ni = 0.45 pct Fe = 1.0 (32 pct SiO_2)	1270°C p_{SO_2} = 0.15 atm $a_{Fe_3O_4}$ = 0.7	1.19 pct Ni 0.64 pct Cu 1.83 pct (Ni + Cu)	1.49 pct Ni 0.32 pct Cu 1.81 pct (Ni + Cu)
Copper Cliff[6]	Cu/Ni = 0.65 pct Fe = 0.5 (25 pct SiO_2)	1270°C p_{SO_2} = 0.20 atm $a_{Fe_3O_4}$ = 0.7	2.3 pct (Ni + Cu)	2.13 pct Ni 0.55 pct Cu 2.68 pct (Ni + Cu)

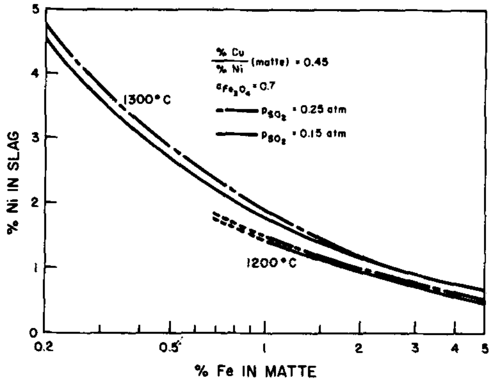

Fig. 6—Solubility of nickel in slag as a function of the iron content of matte.

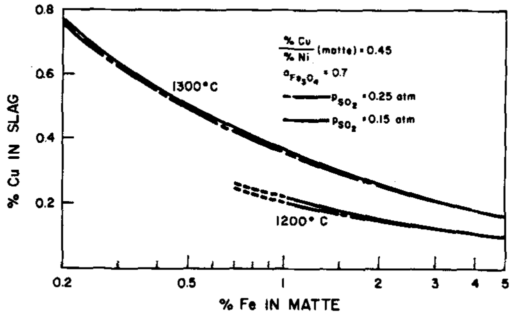

Fig. 7—Solubility of copper in slag as a function of the iron content of matte.

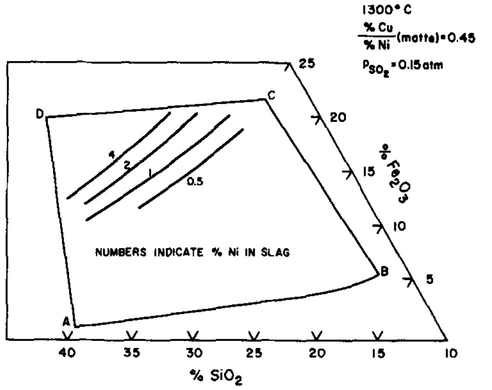

Fig. 8—Solubility of nickel in fayalite slag, based on the solubility limits and the activities of FeO and Fe_3O_4 of Korakas.[14]

When the iron content of the matte decreases to below about 1 pct at 1200°C, the slag becomes saturated with silica, and therefore the iron content cannot be lowered any further and still retain a homogeneous slag.

Setting a tentative criterion of 0.5 pct Ni for a discardable slag, continuous converting must be carried out at a temperature of 1200°C with an iron content in the matte of 5 pct. If a matte containing 5 pct Fe is not acceptable for hydrochloric acid leaching[23] or other processes, the matte can be oxidized further only if a slag cleaning step is incorporated.

When the iron content of the matte is considerably higher than about 5 pct, the sulfidic loss becomes noticeably high and the actual slag losses, especially copper, would be larger than the computer prediction. For this reason, only slag losses for mattes containing less than 5 pct Fe are given in Figs. 6 and 7. The sulfidic loss of nickel, however, may not be as large as copper.

The effects of the silica and magnetite contents of the slag on the Ni and Cu losses are shown in Figs. 8 and 9, respectively. Although the silica content of slag is often discussed in regard to metal losses, it is evident from Figs. 8 and 9 that the effect of silica can correctly be defined only when the activity of magnetite is specified, as well as three more parameters. In other words, an increase in the silica content of the slag, accompanied by a change in four other variables, can result in either an increase or decrease of the metal loss, depending upon the magnetite content, and so forth. A similar specification is also required in discussing the effect of the other factors. For example, it is not correct to state, without specifying four more parameters, that the activity of magnetite increases the metal losses. The metal losses are affected only slightly by magnetite activity when the iron content in matte is rather high, as shown in Fig. 10. In conventional converting, however, a decrease in the iron content of the matte is accompanied by an increase in the magnetite activity, because the total amount of iron in the matte-slag system is conserved. In contrast, an independent control of the iron content of the matte, and the magnetite activity, may be exercised more easily in continuous converting. The effect of oxygen-enriched blowing is shown in Fig. 11. It is of interest to note that the copper loss decreases with oxygen enrichment, while the nickel loss increases under the same condition. The effect of the Cu/Ni ratio is shown in Fig. 12.

The above are only limited examples of possible computer predictions, and the computer program can be run for any conditions of interest. By means of the present computer model it is also possible to investigate the behaviors of impurities such as cobalt, lead and zinc, since the distribution of these elements between slag and matte are governed only by the oxygen

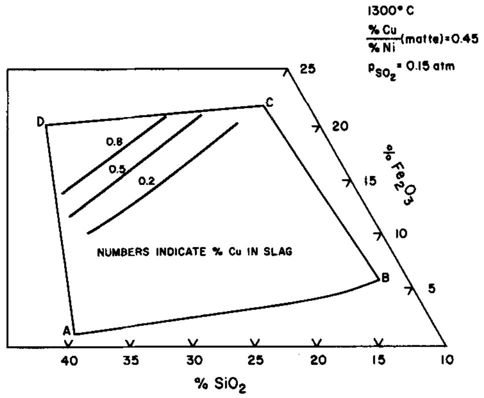

Fig. 9—Solubility of copper in fayalite slag, based on the solubility limits and the activities of FeO and Fe_3O_4 of Korakas.[14]

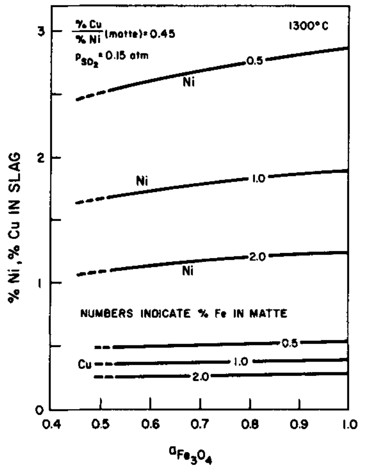

Fig. 10—Effect of magnetite activity on nickel loss to slag.

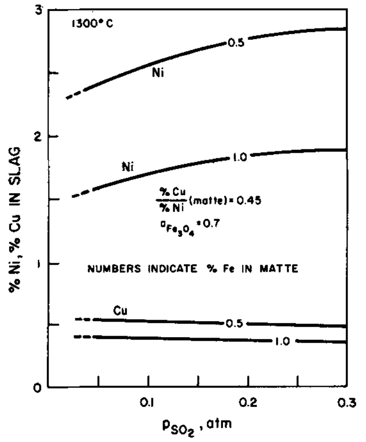

Fig. 11—Effect of SO_2 partial pressure on slag losses of nickel and copper.

and sulfur potentials,[24] which have already been given in the computer program.

When some of the assumptions incorporated in the computer model can be replaced with actual experimental data, the accuracy of the prediction will be improved substantially. The following experimental program may be suggested:

1) Activity measurements in the Ni-Cu-Fe-S matte, especially in the vicinity of the Ni_2S-Cu_2S-FeS pseudoternary. However, this should only follow activity studies in Ni-Cu-S, Ni-Fe-S and Cu-Fe-S mattes. The investigation may be extended to the solubility of oxygen in nickel matte.

2) The effects of Al_2O_3, CaO and other slag constituents on the solubility of nickel in slag, and also the sulfidic dissolution of nickel in slag.

3) The solubility of copper in SiO_2-unsaturated slag, and the effects of Al_2O_3, CaO, ZnO and other constituents.

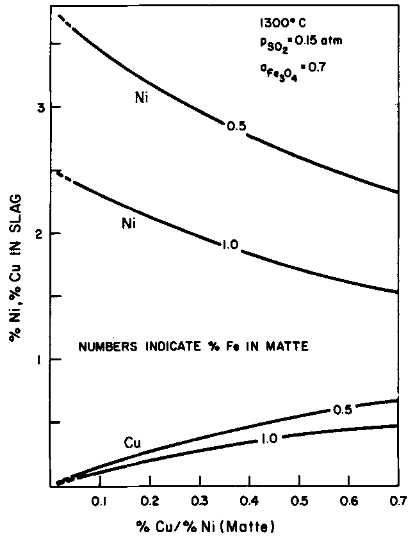

Fig. 12—Effect of copper to nickel ratio on slag losses of nickel and copper.

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