Phase Relations, Activities and Minor Element Distribution in Cu-Fe-S and Cu-Fe-S-As Systems Saturated with Carbon at 1473 K

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As a fundamental study to develop a new process for eliminating detrimental arsenic, recovering precious elements from the arsenic-rich matte produced from the copper concentrate, and treating the occasionally generated speiss in nonferrous smelting processes, the phase relations in the Cu-Fe-S and Cu-Fe-S-As systems saturated with carbon and the distribution of some minor elements between the phases in the miscibility gap, where three equilibrated phases of iron-rich alloy, copper-rich alloy and matte coexist, were investigated at 1473 K by using a quenching method.

The experimental results were discussed on the basis of activity coefficient of arsenic in the matte phase at different matte grades. By utilizing the obtained data, material balance calculations concerning to the treatment of arsenic-rich matte produced in copper smelting by adding the pig-iron was elaborated and also laboratory scale experiments using industrial matte were carried to corroborate the calculations. By using the phase separation, the recovery of valuable copper, silver and gold into the copper-rich alloy and matte phases as well as the elimination of iron and arsenic into the iron-rich alloy phase for discarding as a harmless and smaller deposit might be feasible.

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1. Introduction

The Fe-Cu-S ternary system is fundamental for the copper matte, which is made in the smelting stage as an intermediate product to produce metallic copper from the copper concentrate (ore). The matte, which is produced in oxidative smelting or converting using air or oxygen-enriched air as a blowing gas, is basically a mixture of FeS and Cu2S with varying content of copper, which is called “matte grade”. In the recent practical operations, the matte with 65–70% matte grade (65–70 mass% of Cu) is produced in the smelting stage, followed by the converting stage to make white metal (Cu2S) and finally crude copper (blistet copper). Due to an increasing tendency of the arsenic content in the copper ores, the concentration of this element tends to be high in the produced matte, white metal and blister copper. This causes a serious problem in controlling the quality of the final product (cathode copper). Therefore, its elimination before the electro-refining of crude copper is of great concern in the copper production. In this respect, the phase relations and thermodynamic properties in the Fe-Cu-S-As quaternary system are of very important in discussing the behavior of arsenic in matte smelting and converting. The thermodynamic and phase equilibrium studies in this quaternary system were made by Itagaki et al.,1-3 Jalkanen et al.,3) and Mendoza et al.,4,5) and these data are useful to evaluate the fractional distribution of arsenic among the matte, slag and gas phases in the copper smelting and converting processes.6,7)

On the other hand, the matte phase with deficient sulfur apart from the tie line connecting between FeS and Cu2S in the Fe-Cu-S ternary diagram is often produced in reductive smelting of the copper concentrate like a blast furnace operation using coke as fuel and reducer or in processing the copper concentrate which contains coal in the bulk.8) In the bottom of the smelting furnace, this sulfur-deficient matte often coexists with the iron base alloy which is produced due to a very strong reducing condition. This alloy is generally called “furnace residue” or “speiss” when a considerable amount of arsenic is contained in the alloy. In the extreme case of the reducing condition, the iron base alloy is saturated with carbon. Relating to this alloy, the phase relations, activities and distribution of minor elements in the Fe-Cu-As system saturated with carbon was studied by Voisin et al.9)

It is also of interest in smelting the copper concentrate in a very strongly reducing condition to know the behavior of matte which is made along with the furnace residue or the speiss. In this respect, the phase relations, activities and distribution of minor elements in the Cu-Fe-S-As system saturated with carbon are of great importance in the extreme case of reducing smelting. Additionally, the study of this system will provide the fundamental information on a new process proposed in the author’s laboratory to eliminate arsenic from the arsenic-rich matte produced from the copper concentrate containing significant amount of this element. It is considered in the proposed process that the matte is to be reduced with a given amount of molten pig iron at about 1473 K to produce a molten iron base alloy with a considerable amount of arsenic, but with very few amounts of valuable minor elements such as silver and gold, which can be expected to be discarded as a harmless deposit in the yard.

Hence, the phase relations, the activity of arsenic and the distribution ratios of such minor elements as silver, gold and platinum in the Fe-Cu-S and Fe-Cu-S-As systems saturated with carbon at 1473 K were investigated in this study.

2. Experimental Method and Procedure

The quenching method combined with the metallographic method, combustion-infrared spectrometry for carbon, electron probe micro analysis (EPMA) and inductively coupled plasma spectrometry (ICP) were used to determine the phase relations and the distribution of the minor elements.
2.1 Phase relations in the Fe-Cu-S and Fe-Cu-S-As systems saturated with carbon

The phase relations in the Fe-S-As-C and Fe-Cu-S-As-C systems were determined at 1473 K as explained later in this work. The compositions of iron, copper and sulfur in the starting samples were fixed at the points shown in Fig. 1 while the content of arsenic in the samples was varied by the addition of Fe$_2$As.

Two experimental zones were investigated, zone I, where the iron-rich alloy and matte phases are in equilibrium and zone II, where a further copper-rich alloy is equilibrated with the iron-rich alloy and matte phases.

First, in experimental zone I, the four initial experiments without the presence of arsenic were carried out to obtain, for one side, the corresponding equilibrated compositions of the matte and iron-rich alloy phases, and for the other side, enough starting material in the experiments with the presence of arsenic. About 25 g of sample was prepared by proportionally mixing FeS, Cu$_2$S and pig iron according to the required charge composition in the Cu-Fe-S system saturated with carbon. FeS and Cu$_2$S were previously synthesized with iron or copper and sulfur (99.99% purity) by using a thermal treatment. The sample was charged in a graphite crucible and then it was heated and kept at 1473 K under an argon atmosphere for 1.8 ks to establish the equilibrium between the two phases, and then it was cooled outside the furnace. For each obtained tie line, four levels of arsenic with 3, 6, 9 and 12 mass percent were evaluated. A 5 g sample prepared by proportionally mixing Fe$_2$As and the previously obtained matte and iron-rich alloy phases, together with a graphite rod, was charged in a MgO crucible, and then vacuum sealed in a quartz ampoule of 0.09 m length and 0.026 m ID. The ampoule was heated and kept at 1473 K for 21.6 ks to establish the equilibrium between the two phases, and then it was quenched into water. The schematic diagram of experimental apparatus is shown in Fig. 2. The solidified sample was examined by the metallographic analysis and EPMA to confirm the presence of two clearly separated immiscible phases. Once this was confirmed, the two phases were separated with a blade and representative samples were taken for each phase and later analyzed for their components.

For experimental zone II where three equilibrated phases coexist, an 8 g sample was prepared with different ratios between Fe$_2$As, Cu$_2$S, Cu and pig iron. The experimental procedure was identical to that previously described.

2.2 Distribution of minor elements in miscibility gap of Fe-Cu-S-As-C system

Silver, gold and platinum were investigated as minor elements in the region where the equilibrated matte, copper-rich alloy and iron-rich alloy equilibrated phases coexist in the Cu-Fe-S-As-C system at 1473 K. The mass% ratio of the total charge, $M_{Cu}/M_{Fe}/M_{S}$, was kept at 27.6/62.9/9.5, and the content of arsenic was varied from 0 to 12 mass percent, while the weight composition was 1 mass percent for each minor element. The experimental procedure was identical to that described in 2.1.

3. Results

The equilibrium compositions on the tie lines of zones I and II in the Cu-Fe-S-As-C system saturated with carbon at 1473 K are listed in Tables 1 and 2, respectively. Since the solubility of carbon in the copper-rich alloy and matte phases is very small, the composition diagram for the quaternary system may be simplified to the pseudo-ternary diagram in which iron and carbon are regarded as one constituent. The phase relations in the Cu-(Fe+C)-S pseudo ternary system at 1473 K are shown in Fig. 1, together with those in the Cu-Fe-S ternary system at 1473 K in the region where copper-rich alloy and matte phases coexist, which were determined by Mendoza et al.\textsuperscript{4,5} The phase relations in the Cu-Fe-C ternary system at 1473 K obtained by Voisin et al.\textsuperscript{9} were also plotted in the same figure. The composition diagram of Cu-Fe-S-C quaternary system at 1473 K is shown in Fig. 3.

3.1 Phase relations in the Cu-Fe-S-C quaternary system

Three different zones were observed in the Cu-Fe-S system.
Zone I is delimited by points a, b, c and d where the iron-rich alloy and matte phases are in equilibrium. Zone II is delimited by points c, d and e where a further copper-rich alloy is equilibrated with the iron-rich alloy and matte phases. Zone III is delimited by points c, e, f and g where the copper-rich alloy and matte phases are in equilibrium.

In the first zone, the slope of the tie lines shifts to the iron side since the presence of carbon in the system makes the iron fusible at the experimental temperature. In Zone II, a large miscibility gap is observed. The obtained matte composition with a copper content (matte grade) of 63 mass percent and also the sulfur content in the liquid copper-rich alloy are in a good agreement with those reported by Mendoza et al. 4,5) though the solubility of iron in the copper-rich alloy is larger than the reported value. In zone III, the obtained solubility limits of sulfur for the copper-rich alloy and matte phases in saturated with carbon at 1473 K, as shown in Figs. 1 and 3.

### Table 1 Phase equilibrium compositions of the iron-rich alloy and matte phases in the Cu-Fe-S-As system saturated with carbon at 1473 K (zone I).

<table>
<thead>
<tr>
<th>mass% in charge</th>
<th>mass% in iron-rich alloy phase (L₂)</th>
<th>mass% in matte phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Fe</td>
<td>S</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>94.84</td>
<td>1.45</td>
<td>0.00</td>
</tr>
<tr>
<td>90.47</td>
<td>2.27</td>
<td>4.24</td>
</tr>
<tr>
<td>86.57</td>
<td>2.92</td>
<td>8.13</td>
</tr>
<tr>
<td>80.84</td>
<td>5.43</td>
<td>11.85</td>
</tr>
<tr>
<td>77.23</td>
<td>7.12</td>
<td>14.35</td>
</tr>
</tbody>
</table>

### Table 2 Phase equilibrium compositions of the copper-rich alloy, iron-rich alloy and matte phases in the Cu-Fe-S-As system saturated with carbon at 1473 K (zone II).

<table>
<thead>
<tr>
<th>mass% in copper-rich alloy phase (L₁)</th>
<th>mass% in iron-rich alloy phase (L₂)</th>
<th>mass% in matte phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>S</td>
<td>As</td>
</tr>
<tr>
<td>94.06</td>
<td>1.22</td>
<td>0.00</td>
</tr>
<tr>
<td>89.55</td>
<td>1.60</td>
<td>4.39</td>
</tr>
<tr>
<td>84.95</td>
<td>2.03</td>
<td>8.82</td>
</tr>
<tr>
<td>80.85</td>
<td>2.69</td>
<td>12.59</td>
</tr>
<tr>
<td>76.00</td>
<td>3.49</td>
<td>16.91</td>
</tr>
</tbody>
</table>

mass% Cu/%Fe/%S in charge = 27.6/62.9/9.5
the Cu-S-C system are in a good agreement with the reported
data because the content of carbon in both phases is very
small. Furthermore, the data obtained for the Cu-Fe-C system
at 1473 K by the Voisin et al.\textsuperscript{9)} were also plotted in Figs. 1
and 3 and the results are in a good projection toward the
obtained points e and d in the copper-rich and iron-rich
alloys, respectively, in the Cu-Fe-S system saturated with
carbon.

3.2 Phase relations in the Cu-Fe-S-As-C system

The phase relations in the Fe-S-As system saturated with
carbon at 1473 K are shown in Fig. 4(a) in relation to the
mole fractions of sulfur ($N_{S}$) and arsenic ($N_{As}$) in both phases.
When arsenic is added to the Fe-S system saturated with
carbon, it is preferentially enriched in the iron-rich alloy with
almost the entirety of carbon, while sulfur forms the matte
phase with a smaller amount of arsenic and iron when
compared with that in the iron-rich alloy. The sulfur content
decreases in the matte phase, while increases in the iron-rich
alloy with increasing content of arsenic in the charge and also
the slope of the tie lines, which connect the two equilibrated
phases, increases.

Furthermore, as listed in Table 1, with increasing arsenic
amount in the charge, the content of carbon in the iron-rich
alloy decreases, while increases in the matte phase. It is
important to note that the content of carbon in the matte phase
is much smaller than that in the iron-rich alloy. The obtained
compositions in this work for the Fe-S-C ternary system are
in a good agreement with those reported by Nagasaka et al.,\textsuperscript{10)} which are shown together in Fig. 4(a).

The phase relations in the Fe-Cu-S-As system saturated
with carbon at 1473 K obtained from the different starting tie
lines in zone I, where the matte grades are 17.5, 35.5 and
48 mass\% of Cu, are shown in Figs. 4(b), (c) and (d),
respectively, in relation to the mole fractions of sulfur ($N_{S}$)
and arsenic ($N_{As}$) in both phases. The corresponding
compositions are listed in Table 1. As in the Fe-S-As-C
system, arsenic is preferentially enriched in the iron-rich
alloy together with carbon, while sulfur and copper in the
matte phase with smaller amounts of arsenic and iron when
compared with those in the iron-rich alloy phase. The sulfur
content decreases in the matte phase, while increases in the
iron-rich alloy phase and the slope of the tie lines increases
with increasing arsenic content in the charge. While, the
carbon content decreases in both phases. With increasing
matte grade, the sulfur and carbon contents decrease in both
phases.

The phase relations in the Cu-Fe-S-As-C system for zone
II are shown in Figs. 4(e) and (f) for the iron-rich alloy and
matte phases and for the copper-rich alloy and matte phases,
respectively, in relation to the mole fractions of sulfur ($N_{S}$)
and arsenic ($N_{As}$). While, the corresponding compositions are
listed in Table 2.

When arsenic is added to the Cu-Fe-S-C system in zone II,
it is preferentially enriched in the metallic copper-rich and
iron-rich alloys with a small amount of sulfur, while sulfur,
copper and iron form the matte phase with a smaller amount of arsenic when compared with that in the metallic phases.

With increasing arsenic content in the charge, the sulfur content decreases in the matte phase and increases in the metallic phases. Furthermore, as listed in Table 2, with increasing arsenic content, the carbon content in the iron-rich alloy decreases, while that in the copper-rich alloy and matte phases increases and decreases, respectively, though they are negligibly small. The copper content in the copper-rich alloy phase decreases with increasing arsenic content, while the iron content increases. On the contrary, the copper content in the iron-rich alloy phase increases with increasing arsenic content while the iron content decreases.

3.3 Distribution of minor elements in miscibility gap of Cu-Fe-As-C system

The distribution ratio of a minor element \( X \) between the matte and copper-rich alloy or iron-rich alloy phases in the Cu-Fe-S-As-C system saturated with carbon, \( L_{Xm/L} \), is defined by

\[
L_{Xm/L} = \frac{[\text{mass\% } X]_m}{[\text{mass\% } X]_L},
\]

where \([ X]_m\) and \([ X]_L\) indicate the matte and the iron-rich alloy or copper-rich alloy phases, respectively. By the definition, the element \( X \) will be concentrated in the alloy phase when the value of distribution ratio is less than unity. Hence, a larger value of \( L_{Xm/L} \) corresponding to the iron-rich alloy phase and a smaller one corresponding to the copper-rich alloy phase are preferable when a process for treating the by-products containing arsenic is considered, in which the valuable elements will be recovered into the copper-rich alloy phase, while the less valuable iron eliminated into the iron-rich alloy phase.

The distribution ratios of silver, gold and platinum in the Cu-Fe-As-C system obtained by the authors in a previous study\(^9\) are also shown in Fig. 6 with broken lines. It is noteworthy in Fig. 6 that, in terms of the magnitude and the dependency against the arsenic content in the copper-rich alloy phase, \( L_{Agm/L} \) presents values of less than 1, while \( L_{Ptm/L} \) and \( L_{Ptm/L} \) very small values around 0.001 in the whole range of arsenic content.

As shown in Fig. 5, the distribution ratios of silver and platinum are shown in Fig. 6 for the Cu-Fe-S-As-C system together with those obtained by the authors in the Cu-Fe-As-C system\(^9\) in relation to \( N_{As} \) in the matte in the Cu-Fe-S-As-C system saturated with carbon at 1473 K.

As shown in Fig. 6, the distribution ratios of silver and platinum in the Cu-Fe-As-C system obtained by the authors in a previous study\(^9\) are also shown in Fig. 6 with broken lines. It is noteworthy in Fig. 6 that, in terms of the magnitude and the dependency against the arsenic content in the copper-rich alloy phase, \( L_{Agm/L} \) is larger than 10 while \( L_{Ptm/L} \) close to unity in the whole range of arsenic content. The distribution ratios of silver and platinum in the Cu-Fe-As-C system obtained by the authors in a previous study\(^9\) are also shown in Fig. 6 with broken lines. It is noteworthy in Fig. 6 that, in terms of the magnitude and the dependency against the arsenic content in the copper-rich alloy phase, \( L_{Agm/L} \) is almost constant at about 12 while \( L_{Ptm/L} \) abruptly decreases and \( L_{Ptm/L} \) increases against the arsenic content in the matte.

![Fig. 5 Distribution ratios of silver, gold and platinum minor elements in relation to \( N_{As} \) in the matte in the Cu-Fe-As-C system saturated with carbon at 1473 K.](image)

![Fig. 6 Distribution ratios of silver and platinum between the copper-rich alloy (L_1) and iron-rich alloy (L_2) alloy phases in relation to \( N_{As} \) in the copper-rich alloy phase in the Cu-Fe-S-As-C system saturated with carbon at 1473 K.](image)
4. Discussion

4.1 Activity coefficient of arsenic in three phases region of Cu-Fe-S-As-C system

The thermodynamic properties of arsenic in the Cu-Fe-S-As system saturated with carbon are of major concern for the phase relations in this system as well as the treatment of arsenic in the arsenic-rich matte produced from the copper concentrate containing a significant amount of this element. Since this value investigated system was barely different from that indicated with about 1.5 times higher in magnitude. This discrepancy may be ascribed to the appearance of an iron-rich alloy in the matte.

Once γAs in the iron-rich alloy phase on the tie lines, which connect the iron-rich alloy and matte phases in the Cu-Fe-S-As-C system, was derived from eq. (7), in relation to the arsenic content in the matte. The activity coefficient of arsenic in the iron-rich alloy phase in Cu-Fe-S-As-C systems was determined.

4.2 Activity coefficient of arsenic in matte phase in equilibrium with iron-rich alloy phase in Cu-Fe-S-As-C systems

It was assumed that the activity coefficient of arsenic in the Cu-Fe-S-As-C systems with Fe as a solvent and Cu, C, S and As as solutes might be expressed by eq. (6), which is valid when the higher order terms in Taylor’s series expansion can be neglected. Although the mole fraction of carbon in the present iron-rich alloy phase is considerably high at about 0.16, the application of eq. (6) to the present system was made, assuming that ln γAs changes proportionally to NC up to the saturation point of carbon.

\[
\ln \gamma_{As} = \ln \gamma_{As}^{o} + \varepsilon_{As}^{As} N_{As} + \varepsilon_{As}^{Cu} N_{Cu} + \varepsilon_{As}^{C} N_{C} + \varepsilon_{As}^{S} N_{S}
\]

where \( \gamma_{As}^{o} \) is the limiting activity coefficient. \( N_{As}, N_{Cu}, N_{C} \) and \( N_{S} \), and \( \varepsilon_{As}^{As}, \varepsilon_{As}^{Cu}, \varepsilon_{As}^{C} \) and \( \varepsilon_{As}^{S} \) are mole fractions and interaction parameters of As, Cu, C and S, respectively. First, \( \varepsilon_{As}^{As}, \varepsilon_{As}^{Cu} \) and \( \varepsilon_{As}^{C} \) were fixed using the reported values of \( \gamma_{As} \) in the Fe-As binary as well as \( \varepsilon_{As}^{C} \) and \( \varepsilon_{As}^{Cu} \) which were determined by Voisin et al.9,12) in the corresponding investigation, respectively. Then, \( \varepsilon_{As}^{S} \) in eq. (6) was derived by combining \( \gamma_{As} \) in the iron-rich alloy phase, previously calculated in 4.1. The result is given in eq. (7), with \( \varepsilon_{As}^{S} = 23.3 \).

\[
\ln \gamma_{As} = -6 + 13N_{As} + 7.3N_{Cu} + 9.7N_{C} + 23.3N_{S}
\]
arsenic (the standard state of activity is pure liquid arsenic) in the matte phase, in the region where the iron-rich alloy and matte phases coexist in the Cu-Fe-S-As system saturated with carbon at 1473 K are shown in Fig. 8, in relation to the mole fraction of arsenic in the matte phase. It is noted in Fig. 8 that \( \log \gamma_{\text{As}} \) increases proportionally with \( N_{\text{As}} \), and that, at a given \( N_{\text{As}} \), \( \gamma_{\text{As}} \) in the matte without copper (matte grade is zero) is the smallest.

4.3 Material balances in a proposed process for eliminating arsenic from arsenic-rich matte produced in copper smelting

Based on the present experimental results, the material balances were evaluated for the new process proposed by the authors. Furthermore, laboratory experiments using industrial copper mattes doped with Fe\(_2\)As were carried out to compare with the results of mass balance calculations.

It was supposed in the calculation that a given amount of copper matte with 70 mass% of Cu, which contains 0.5 mass% of As and silver, gold and platinum with each 0.01 mass percent is treated by adding pig-iron at 1473 K. The calculation was made by varying values of \( \alpha = \frac{\text{amount of added pig-iron}}{\text{amount of initial copper matte}} \), up to 0.5. In the calculation, the loss of arsenic and sulfur by volatilization was neglected because the summation of equilibrium partial pressures of predominant As and As\(_2\) for arsenic and the partial pressure of S\(_2\) for sulfur gas species over the corresponding alloys and matte at 1473 K are very small at less than 10 and 2 Pa, respectively.\(^9,13\)

According to the results obtained in the present experiments, copper-rich and iron-rich alloys together with a matte with about 63 mass% of Cu are in equilibrium when \( \alpha \) is over 0.065. The fractional distribution of copper, iron and arsenic as major components among the matte, iron rich alloy and copper rich alloy phases is shown on the left axis, while mass% of these elements in the treated matte on the right axis, in relation to \( \alpha \) in Fig. 9. While those of silver, gold and platinum as precious minor elements are shown in Fig. 10.

Since carbon and sulfur are mostly distributed in the iron-rich alloy and matte phases, respectively, their results are not shown in Figs. 9 and 10.
For the major components, as shown in Fig. 9, with increasing value of $\alpha$ from 0.1 to 0.5, the fractional distribution of copper decreases from 15 to 11.9%, increases from 0.24 to 2.81% and is almost constant at about 85% in the copper-rich alloy, iron-rich alloy and matte phases, respectively. The matte grade (mass% of Cu) in the treated matte is constant at about 63 mass percent. For iron, the fractional distribution decreases from 2.5 to 0.6% and from 76.9 to 24.3% in the copper-rich alloy and matte phases, respectively, while increases from 20.6 to 75.1% in the iron-rich alloy phase. For arsenic, the fractional distribution decreases from 60.1 to 28.1% and from 32.4 to 19.2% in the copper rich alloy and matte phases, respectively, while increases from 7.5 to 52.7% in the iron-rich alloy phase. The content of arsenic in the treated matte at $\alpha$ of 0.1 is 0.18 mass%.

For the precious minor elements, as shown in Fig. 10, with increasing value of $\alpha$, the fractional distribution of platinum abruptly decreases and those of silver and gold slightly decrease. On the contrary, the fractional distribution of platinum in the iron-rich alloy phase increases and those of silver and gold decrease. In the matte phase, the fractional distribution of platinum slightly decreases while those of silver and gold are almost constant.

The experimental results using industrial copper matte doped with Fe$_2$As ($Cu = 70$, $Fe = 7.54$, $S = 19.4$, $As = 0.5$, others = 2.56 mass percent) are shown in Table 3. They are in a good agreement with those in the material balance calculations. These results suggest that, the recovery of valuable copper, silver and gold into the copper-rich alloy phase as well as the elimination of less valuable iron together with the detrimental arsenic into the iron-rich alloy phase might be feasible even though the proportion of valuable platinum lost in the iron-rich alloy phase is considerably large. The copper-rich alloy may be further treated in a pyrometallurgical or hydrometallurgical process to extract silver, gold and copper; the iron-rich alloy phase may be harmlessly encapsulated in a small volume and discarded if the content of platinum in the initial charge is small, while the matte phase might be continuously processed in the following converting stage.

### 5. Summary

As a fundamental study for eliminating arsenic from the arsenic-rich matte produced from the copper concentrate containing a significant amount of arsenic and for treating speiss which is a by-product with a considerably high content of arsenic in nonferrous smelting processes, the phase relations in the Cu-Fe-S and Cu-Fe-S-As systems saturated with carbon and the distribution of some minor elements between the phases in the miscibility gap, where three equilibrated phases coexist, were investigated at 1473 K. On the basis of the obtained results, material balance calculations and laboratory experiments using industrial copper matte were made in order to deepen the development of the new proposed process. The results are summarized as follows:

1. The phase relations in the Cu-Fe-S-C quaternary system are similar to those in the Cu-Fe-S ternary system.
2. Arsenic has strong preference to the alloy phases and carbon is distributed almost completely in the iron-rich alloy phase. In the region where iron-rich alloy and matte phases are in equilibrium, arsenic is preferentially distributed in the iron-rich phase. This effect increases when the matte grade is increased in the system.
3. Raoultian activity coefficient of arsenic in the matte phase with a matte grade of 63 mass% of Cu is around 0.08, while log $f_A$ increases proportionally with $N_{Cu}$ in the matte phase in equilibrium with the iron-rich alloy in the Cu-Fe-S-As system saturated with carbon.
4. In the region where the matte (m), copper-rich alloy ($L_1$) and iron-rich alloy ($L_2$) phases coexist, $L_{As}^{m/L_1}$ is less than 1 and $L_{Ag}^{m/L_2}$ larger than 10, $L_{Au}^{m/L_1}$ is around 0.001 and $L_{As}^{m/L_1}$ less than 0.1, while $L_{Pt}^{m/L_2}$ and $L_{Au}^{m/L_2}$ are very similar at about 0.001. These suggest that most gold and a large part of silver will be enriched in the copper-rich phase while platinum in both metal phases.
5. For the treatment of arsenic-rich matte produced in copper smelting by adding the pig-iron, the recovery of valuable copper, silver and gold into the copper-rich alloy phase as well as the elimination of iron and arsenic into the iron-rich alloy phase might be feasible. The elimination of arsenic increases with increasing pig-iron amount in the charge.
6. Since the experimental results obtained in this investigation using industrial mattes agreed very well with those in the material balance calculation, may be an important way to predict the behavior of arsenic-rich matte produced in copper processes when they are treated by using pig iron at 1473 K.

### REFERENCES