

Phase Relations, Precious Elements Distribution, and Activities in the Cu-Fe-Pb-As System Saturated with Carbon at 1473 K (1200 °C)

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In order to develop a new pyrometallurgical process for the elimination of detrimental arsenic and the recovery of precious elements, such as, silver, gold, and platinum from arsenic-rich copper-lead scraps, the phase relations in the Cu-Fe-Pb-As system saturated with carbon and the distribution of precious elements between the condensed phases generated during the equilibrium at high temperature were investigated. The investigation was carried out by performing a series of laboratory scale experiments using an electrical furnace at 1473 K (1200 °C), followed by the quenching of molten samples taken on the final stage. The samples obtained from the experiments were analyzed using electron probe X-ray micro analysis, inductively couple plasma, and carbon infrared spectrometry techniques. The results were discussed on the basis of the activity coefficient of arsenic, interaction parameters of minor components, and distribution parameters for precious metals in the three equilibrated alloy phases of lead-rich, copper-rich, and iron-rich that coexists in the corresponding miscibility gap. The present results suggest that the recovery of valuable silver and gold into the copper-rich alloy and lead-rich alloy phases and the elimination of arsenic and iron into the iron-rich alloy phase might be feasible.

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I. INTRODUCTION

DURING the primary lead smelting process in the blast furnace or at the decopperizing stage in an electric furnace, a copper/lead speiss is generated under a strongly reductive smelting operation as a final by-product, which contains considerable amounts of lead and impurities such as arsenic. This speiss is usually sent to copper smelting companies for metal recovery since primary lead smelting plants do not process this product.^[1] The copper/lead speiss contains between 40 to 60 wt pct Cu and 15 to 25 wt pct Pb, depending on various factors such as the lead smelting process and composition of the raw base material.^[2]

The recovery of valuable elements and the stabilization of the heavy metals contained are the major concern in the treatment of speiss. Previous research work has been carried out on the phase relations, activities, and minor element distribution at 1473 K (1200 °C), for the Fe-Pb-As^[3] and Fe-Cu-As^[4,5] systems saturated with carbon. The addition of carbon into these systems allows to decrease the melting point of γ Fe from 1811 K (1538 °C) toward its carbon saturation, ($N_C = 0.171$) until 1426 K (1153 °C).^[6] The high content of lead and copper and the interactions to each other in this type of

reductive materials play an important role on the recovery of the metals. For this reason, it is necessary to study the Cu-Fe-Pb-As system saturated with carbon, considering lead, copper, and iron as major components in order to clarify its behavior.

The present research study not only provides information regarding the phase relations, activities, and distribution of precious elements in the Cu-Fe-Pb-As system saturated with carbon at 1473 K (1200 °C), but also provides the fundamental information on a new proposed process at laboratory scale to eliminate arsenic from the arsenic-rich copper/lead speiss generated during the primary lead smelting in the blast furnace or from the by-product produced during the decopperizing stage in the electric furnace.

The present results revealed that three condensed and immiscible phases of lead-rich, copper-rich, and iron-rich coexist during the equilibrium at 1473 K (1200 °C) and using its separation, arsenic might be concentrated and eliminated into the less valuable iron-rich alloy phase, while precious metals of silver, gold, and platinum can be recovered into the valuable copper-rich and lead-rich alloy phases. The iron-rich alloy phase is expected to be discarded as a stable harmless waste.

II. EXPERIMENTAL METHOD AND PROCEDURE

In order to determine the phase relations and the distribution of the precious elements, a quenching method was used, combined with the metallographic method, combustion-infrared spectrometry for carbon

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(CIS), electron probe X-ray micro analysis (EPMA) and inductively coupled plasma spectrometry (ICP).

A. Phase Relations in the Cu-Fe-Pb and Cu-Fe-Pb-As System Saturated with Carbon

Three different wt pct ratios of iron to lead to copper, $R = M_{Fe}/M_{Pb}/M_{Cu}$, of 3/4/1, 1/2/1, and 1/4/3 were considered. For each of these three wt pct ratios, five levels of arsenic of 2, 4, 6, 8, and 10 wt pct, were investigated. The charged material consisted on a 10 g sample prepared by proportionally mixing Fe_2As (melting point: 1203 K (930 °C)^[7]) and/or Cu_3As (melting point: 1100 K (827 °C)^[7]) with the other elements in order to achieve the desired charge composition. Both arsenates were previously synthesized by a thermal treatment with iron or copper and arsenic (99.99 pct purity) in a vacuum-sealed quartz ampoule and later analyzed using EPMA and ICP techniques.

Since carbon has a very week affinity for copper, lead, and arsenic, the initial charge points for all the experiments can be projected as shown in Figure 1, which corresponds to the pseudo-quaternary system Cu-(Fe+C)-Pb-As. For each test, the sample together with a graphite rod was charged into an MgO crucible and then vacuum sealed in a quartz ampoule of 9 cm length and 2.6 cm internal diameter, ID. The ampoule was heated and kept at 1473 K (1200 °C) for 21.6 ks to establish the equilibrium between the three phases. Finally, the sample was quenched into water.

The solidified sample was cut with a diamond cutting blade and examined using metallographic analysis and EPMA to confirm the existence of the three clearly separated immiscible phases, and representative sub-samples were extracted from each of the phases. The sub-samples were analyzed by CIS for carbon and ICP for copper, iron, lead, arsenic, and precious metals. The schematic diagram of the experimental apparatus is shown in Figure 2.

B. Distribution of Precious Elements in the Miscibility Gap of Cu-Fe-Pb-As-C System

Silver, gold, and platinum were investigated as precious elements in the region where the equilibrated

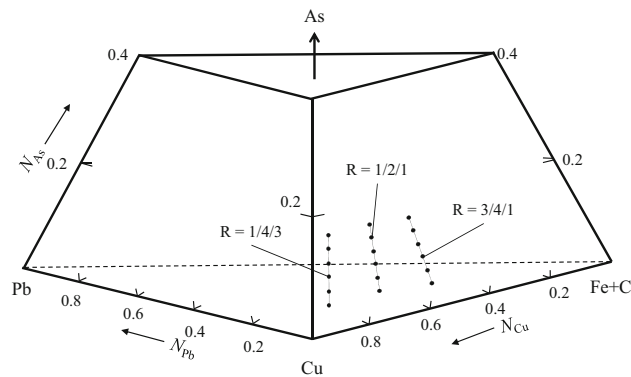


Fig. 1—Initial charge composition in the Cu-(Fe+C)-Pb-As pseudo-quaternary system.

lead-rich, copper-rich, and iron-rich alloy phases coexist in the Cu-Fe-Pb-As-C system at 1473 K (1200 °C). Wt pct ratios of iron to lead to copper, R was kept at 1/2/1, and the content of arsenic was varied from 0 to 10 wt pct, with an increasing step of 2 wt pct. The weight composition for each precious element was 1 wt pct of the total charge. The experimental procedure was the same as the phase relation test described previously.

III. RESULTS

The results of the equilibrium compositions for all the three alloy phases and for the three different wt pct ratios initially charged are listed in Table I. The present results are in agreement with those obtained by other researchers^[3,4] who have reported that the solubility of carbon in the copper-rich alloy and the lead-rich alloy is very small. For this reason, the composition diagram for the Cu-Fe-Pb-As-C system can be simplified to a pseudo-quaternary diagram in which iron and carbon are regarded as one constituent.

A. Phase Relations in the Cu-Fe-Pb-As-C System at 1473 K (1200 °C)

The phase relations for the pseudo-quaternary Cu-(Fe+C)-Pb-As system at 1473 K (1200 °C) are shown in Figure 3, where the immiscible regions have been projected for each of six levels of arsenic. On direct inspection of the results, it is clear that the immiscible zone widens when arsenic is added to the system, and it can be considered rather large when arsenic is present. As the arsenic content increases, the miscibility gap has a tendency to shrink.

The relation of N_{As} against N_C between the iron-rich, copper-rich, and lead-rich alloy phases in the Cu-Fe-Pb-As system saturated with carbon at 1473 K (1200 °C) is

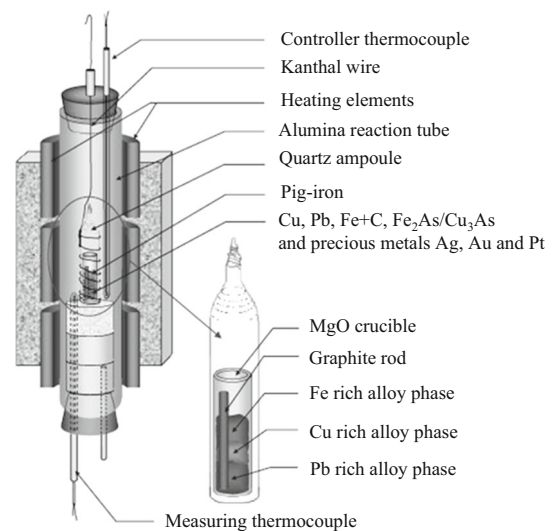


Fig. 2—Schematic diagram of the experimental apparatus.

Table I. Phase Equilibrium Compositions of the Copper-Rich Alloy, Lead-Rich Alloy, and Iron-Rich Alloy Phases in the Cu-Fe-Pb-As System Saturated with Carbon at 1473 K (1200 °C)

Wt pct in Charge Fe/Pb/Cu (R)	Wt pct in Cu-Rich Phase					Wt pct in Pb-Rich Phase					Wt pct in Fe-Rich Phase				
	Fe	Pb	As	Cu	C	Fe	Pb	As	Cu	C	Fe	Pb	As	Cu	C
3/4/1	0.49	80.2	—	19.2	0.02	0.24	81.6	—	18.1	0.04	89.5	2.60	—	4.02	3.93
	1.49	42.4	2.29	53.2	0.66	0	89.7	0.03	10.3	0.02	82.9	4.02	4.27	5.57	3.24
	2.94	22.7	5.02	68.8	0.55	0	91.5	0.05	8.40	0.02	82.7	2.54	6.66	5.16	2.95
	5.29	19.3	6.86	68.0	0.47	0	93.6	0.11	6.31	0.01	77.1	0.42	12.7	7.31	2.40
	3.77	18.1	7.93	69.8	0.37	0	93.5	0.13	6.33	0.02	71.6	1.28	16.0	9.25	1.85
	6.26	15.0	10.4	68.2	0.26	0	93.3	0.15	6.53	0.03	65.9	1.00	19.3	12.26	1.43
1/2/1	1.02	55.1	—	43.9	0.02	0.09	82.2	—	17.7	0.03	91.1	0.97	—	4.06	3.87
	1.04	32.2	2.46	64.2	0.15	0	89.7	0.03	10.3	0.03	82.1	3.59	3.90	7.22	3.25
	2.08	25.7	5.19	66.9	0.09	0	92.4	0.06	7.52	0.02	78.4	1.95	8.15	8.31	3.19
	2.64	18.6	8.62	70.1	0.05	0	94.9	0.10	4.89	0.02	77.9	0.49	11.8	6.81	3.06
	3.80	12.8	12.06	71.3	0.04	0	95.8	0.15	4.03	0.02	71.7	0.58	15.8	9.30	2.62
	4.82	4.32	16.06	74.8	0.04	0	96.2	0.22	3.58	0.01	66.7	2.13	18.9	9.91	2.27
1/4/3	1.16	49.3	—	49.6	0.02	0.14	88.1	—	11.7	0.02	92.2	0.11	—	3.59	4.14
	2.12	34.6	2.58	60.7	0.03	0.14	89.9	0.08	9.79	0.02	79.9	3.67	3.89	9.45	3.14
	2.94	27.0	6.27	63.7	0.02	0.13	91.5	0.09	8.27	0.02	78.6	2.47	6.53	9.25	3.17
	4.40	19.9	9.17	66.6	0.02	0.12	93.9	0.10	5.84	0.02	76.4	1.13	10.2	9.01	3.30
	4.31	16.1	11.9	67.7	0.02	0.14	94.1	0.15	5.58	0.02	76.8	0.19	14.1	5.79	3.18
	5.71	10.4	15.8	68.1	0.01	0.12	96.3	0.19	3.39	0.02	67.5	1.79	18.5	9.90	2.33

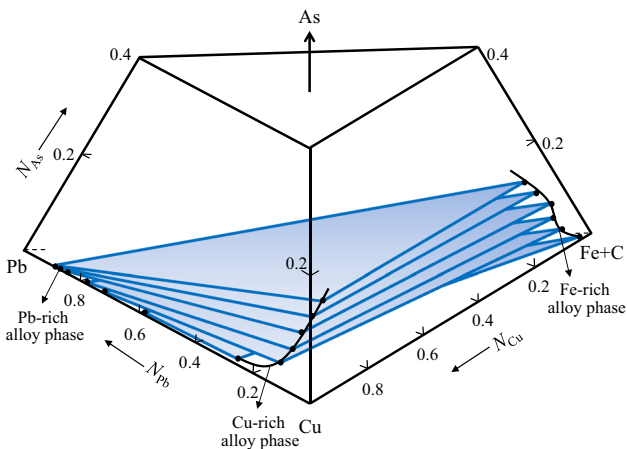


Fig. 3—Phase relations in the Cu-(Fe+C)-Pb-As pseudo-quaternary system at 1473 K (1200 °C), $R = 1/2/1$.

shown in Figure 4. When arsenic is added to the Cu-Fe-Pb system saturated with carbon, it is preferentially enriched in the copper-rich and the iron-rich alloy phases in almost the same magnitude. The copper-rich alloy phase contains relatively small content of iron and negligible carbon, while the lead-rich alloy phase has very low concentrations of both iron and carbon. The iron-rich alloy phase contains high concentrations of carbon and iron.

It can be noted that with the increase of arsenic in the charge, the copper content in the copper-rich alloy phase increases while the lead content decreases. The opposite effect occurs in the lead-rich alloy phase, while in the iron-rich alloy phase iron decreases, copper increases and lead is almost negligible. As can be seen from the data provided in Table I, the carbon concentration in the iron-rich alloy phase decreases from about 4.2, at

carbon saturation, to 1.4 wt pct, while remains lower than 0.7 wt pct and almost imperceptible in the copper-rich alloy and lead-rich alloy phases, respectively, as the arsenic content increases in the charge.

B. Distribution of Precious Elements in Miscibility Gap of Cu-Fe-Pb-As-C System at 1473 K (1200 °C)

The distribution ratio of a precious element X between the iron-rich or copper-rich, and the lead-rich alloy phase in the Cu-Fe-S-As system saturated with carbon, $L_X^{L/Pb}$, is defined by

$$L_X^{L/Pb} = \frac{\{\text{wt pct X}\}_L}{[\text{wt pct X}]_{Pb}}, \quad [1]$$

where $\{\}_L$ and $[_]_{Pb}$ indicate the iron-rich or copper-rich, and the lead-rich alloy phases, respectively. By the definition, the precious element X will be concentrated in the lead alloy phase when the value of distribution ratio is less than unity. Hence, a larger value of $L_X^{L/Pb}$ corresponding to the copper-rich alloy phase and a smaller one corresponding to the iron-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 and lead-rich alloy phases, while the less valuable iron eliminated through the iron-rich alloy phase with low contents of precious elements.

The distribution ratios of silver, gold, and platinum as precious elements between the iron-rich or the copper-rich and the lead-rich alloy in relation to the arsenic content in the charge for the Cu-Fe-Pb-As system saturated with carbon at 1473 K (1200 °C), considering $R = 1/2/1$, are shown in Figures 5 and 6, respectively.

With the increasing content of arsenic in the charge, the distribution ratios of platinum, $L_{pt}^{Fe/Pb}$ and $L_{pt}^{Cu/Pb}$,

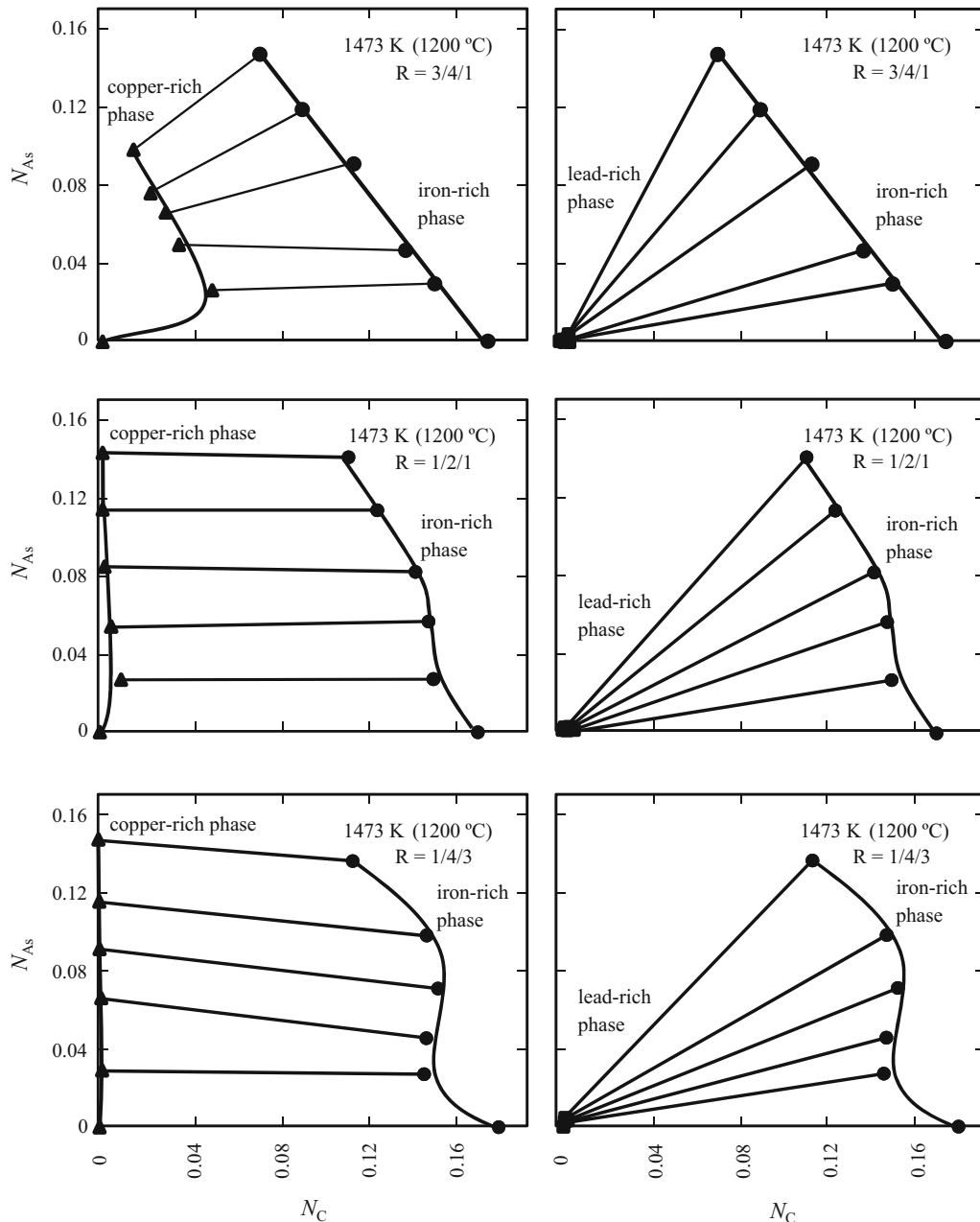


Fig. 4—Relation between N_{As} and N_C between the iron-rich, copper-rich, and lead-rich alloy phases in the Cu-Fe-Pb-As system saturated with carbon at 1473 K (1200 °C), $R =$ wt pct in charge of Fe/Pb/Cu.

increase from 12 to 18 and from 3 to 20, respectively, while the distribution ratios of gold, $L_{Au}^{Fe/Pb}$ and $L_{Au}^{Cu/Pb}$ decrease strongly from 1 to 0.2 and from 21 to 3, respectively, up to 2 wt pct arsenic in charge where the values remain rather constant..

Finally, the distribution ratio of silver, $L_{Ag}^{Fe/Pb}$ is almost constant around 0.1 and independent of the content of arsenic in charge, while $L_{Ag}^{Cu/Pb}$ keeps the unity up to 4 wt pct arsenic in charge, where it then starts to decrease reaching a value of 0.2 at 10 wt pct arsenic in charge. The results show that for any given arsenic content, the distribution ratio decreases in the order of platinum, gold, and silver.

IV. DISCUSSION

A. Activity Coefficient of Arsenic in the Three-Phase Region of the Cu-Fe-Pb-As-C System

It is important to study the thermodynamic properties of arsenic in the miscibility gap where three phases of copper-rich, iron-rich, and lead-rich alloys are at equilibrium in the Cu-Fe-Pb-As system saturated with carbon at 1473 K (1200 °C), because this will provide useful information for the treatment of arsenic in arsenic-rich copper-lead speiss produced as a by-product during the decopperizing stage of primary lead refining. In this work, γ_{As}^0 and ϵ_{As}^{As} were calculated considering

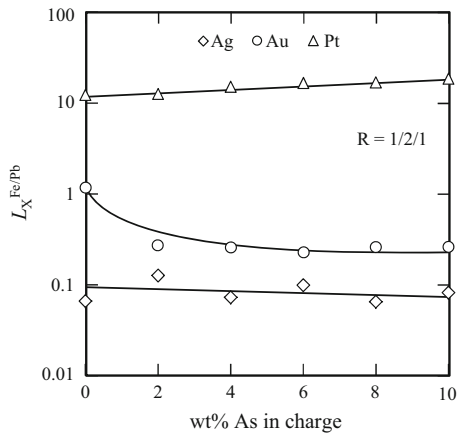


Fig. 5—Distribution ratios of precious elements between the iron-rich and lead-rich alloy phases in relation to the arsenic content in the Cu-Fe-Pb-As system saturated with carbon at 1473 K (1200 °C).

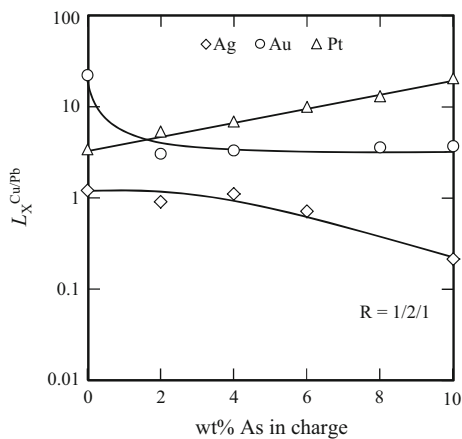


Fig. 6—Distribution ratios of precious elements between the copper-rich and lead-rich alloy phases in relation to the arsenic content in the Cu-Fe-Pb-As system saturated with carbon at 1473 K (1200 °C).

iron, lead, and copper as solvent and arsenic as solute, using activity data previously reported by other authors in the Fe-As,^[8,18] Pb-As,^[9,10] Cu-As^[11] binary systems, respectively. Then, on the basis of the present data for the miscibility gap, and those obtained in the Fe-Pb-As^[3] and Fe-Cu-As^[4] systems saturated with carbon at 1473 K (1200 °C), the Raoultian activity coefficients of arsenic in the three alloy phases in the Cu-Fe-Pb-As system saturated with carbon at 1473 K (1200 °C) were derived as follows.

Equations [2] and [3] are established in the equilibrium condition because of the same standard state for two liquid phases, where γ_{As} and N_{As} are the Raoultian activity coefficient and the mole fraction of arsenic, and $\langle \rangle$, $[]$, and $\{ \}$ denote the lead-rich, iron-rich, and copper-rich alloy phases, respectively.

$$\langle a_{As} \rangle = \langle \gamma_{As} \rangle \langle N_{As} \rangle = [\gamma_{As}] [N_{As}] [a_{As}] \quad \text{and} \quad [2]$$

$$[a_{As}] = [\gamma_{As}] [N_{As}] = \{ \gamma_{As} \} \{ N_{As} \} = \{ a_{As} \}. \quad [3]$$

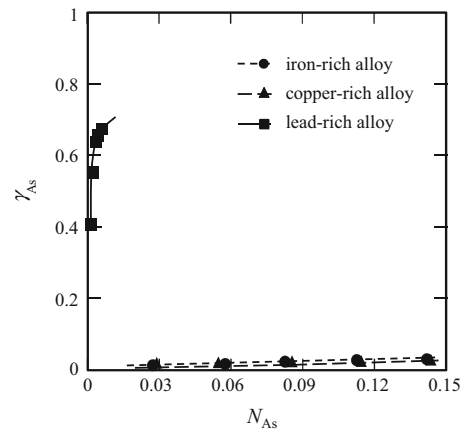


Fig. 7—Activity coefficient of arsenic at the phase boundary in the miscibility gap of Cu-Fe-Pb-As system saturated with carbon at 1473 K (1200 °C) (standard state, pure liquid As).

The concentrations of carbon and iron in the lead-rich alloy phase in the Cu-Fe-Pb-As-C system are very small and for this reason it is possible to simplify this phase to the Cu-Pb-As ternary system. In the same way, since the concentration of carbon in the copper-rich alloy phase and that of lead in the iron-rich alloy phase are also very low, it can be simplified to the Cu-Fe-Pb-As and the Cu-Fe-As-C quaternary systems, respectively. Hence, $[\gamma_{As}]$ in Eq. [2] is obtained by combining the reported activity data in the Cu-Fe-As-C^[4] quaternary system and the present data for the miscibility gap line in the iron-rich alloy phase. Subsequently, γ_{As} in the lead-rich alloy and copper-rich alloy phases can be derived from Eq. [2] and Eq. [3], respectively, in relation to their respective arsenic contents.

The Raoultian activity coefficients of arsenic (the standard state of activity is pure liquid arsenic) in the three coexisting phases in the miscibility gap of Cu-Fe-Pb-As system saturated with carbon at 1473 K (1200 °C) in relation to the mole fraction of arsenic considering $R = 1/2/1$ is shown in Figure 7.

It should be noted that the activity coefficients in the copper-rich and iron-rich alloy phases presented similar and considerably small values of approximately 0.04, which suggests that arsenic in these alloy phases has a strong negative deviation from Raoult's law and consequently a strong affinity for their corresponding main elements of copper and iron, respectively. Regarding the activity coefficients in the lead-rich alloy, the results show higher values, above 0.4, that approaches a value of 0.7 with the increasing arsenic content, which suggests that arsenic in this alloy phase has a slightly negative deviation from Raoult's law.

The activity coefficient values of arsenic for the iron-rich alloy are very small of <0.03 , which agree well with the activity data found for the Fe-Pb-As system saturated with carbon previously reported by Voisin *et al.*^[3] As for the lead-rich alloy phase, the relatively lower values, between 0.4 and 0.7, may be ascribed to the effect of copper contained in this phase with amounts between 3 and 10 wt pct.

B. Interaction Parameters of Cu-Fe-Pb-As-C System

The activity coefficient of arsenic, $\langle \gamma_{As} \rangle$, in the lead-rich alloy phase of the Cu-Fe-Pb-As-C system at 1473 K (1200 °C) can be expressed by Eq. [4], by considering lead as a solvent and assuming only arsenic and copper as solutes, since in this case the phase contains negligible amounts of carbon and iron, simplifying the system into the ternary Cu-Pb-As. This expression is valid when the higher order terms in Taylor's series expansion can be neglected:

$$\ln \langle \gamma_{As} \rangle = \ln \gamma_{As}^0 + \varepsilon_{As}^{As} N_{As} + \varepsilon_{As}^{Cu} N_{Cu}, \quad [4]$$

where γ_{As}^0 is the limiting activity coefficient in the Pb-As binary system. N_{As} , N_{Cu} , and ε_{As}^{As} , ε_{As}^{Cu} are mole fractions and interaction parameters of arsenic and copper, respectively. First, γ_{As}^0 and ε_{As}^{As} were fixed using the reported values in the Pb-As binary system^[9] for N_{As} between 0.01 and 0.09, and extrapolating them to a temperature of 1473 K (1200 °C) assuming a regular solution behavior. Then, ε_{As}^{Cu} in Eq. [4] was derived by combining $\langle \gamma_{As} \rangle$ for the lead-rich alloy phase determined in this study in the Cu-Fe-Pb-As-C system shown in Figure 7. The average value for ε_{As}^{Cu} , by applying the Taylor's series expansion, is -3.84 with a standard deviation of 1.08. The result combining all the reported data and the derived parameters is shown in Eq. [5]:

$$\ln \langle \gamma_{As} \rangle = 0.105 - 1.19 N_{As} - 3.84 N_{Cu}. \quad [5]$$

In order to estimate the new interaction parameter ε_{As}^{Pb} in the iron-rich alloy phase, the same method of the Taylor's series expansion was used by considering iron as a solvent and arsenic, lead, copper, and carbon as solutes. The derived expression is shown in Eq. [6]:

$$\ln \{ \gamma_{As} \} = \ln \gamma_{As}^0 + \varepsilon_{As}^{As} N_{As} + \varepsilon_{As}^{Pb} N_{Pb} + \varepsilon_{As}^{Cu} N_{Cu} + \varepsilon_{As}^C N_C, \quad [6]$$

where γ_{As}^0 is the limiting activity coefficient in the Fe-As binary system. N_{As} , N_{Pb} , N_{Cu} , N_C , and ε_{As}^{As} , ε_{As}^{Pb} , ε_{As}^{Cu} , ε_{As}^C are mole fractions and interaction parameters of arsenic, lead, copper, and carbon, respectively. First, γ_{As}^0 and ε_{As}^{As} were fixed using the reported values in the Fe-As binary system^[8,18] while those of ε_{As}^{Cu} and ε_{As}^C were derived by Voisin *et al.* in the Cu-Fe-As-C^[12] and Fe-Pb-As-C^[3] systems at 1473 K (1200 °C). It is important to mention that, since carbon contents as solutes in the iron solvent are high, the latter parameter was derived using the thermodynamic expression determined by Miki *et al.*^[13,14] which including higher order terms based on the quadratic formalism proposed by Darken^[15] and the relations between first and second order interaction parameters represented by Wagner's formalism^[16].

Finally, ε_{As}^{Pb} in Eq. [6] was derived by combining $\{ \gamma_{As} \}$ for the iron-rich alloy phase determined in this study in the Cu-Fe-Pb-As-C system shown in Figure 7. The average value for ε_{As}^{Pb} is 2.18 with a standard deviation of 0.82. The result combining all the reported data and the derived parameters are shown in Eq. [7]:

$$\ln \{ \gamma_{As} \} = -6 + 13 N_{As} + 2.18 N_{Pb} - 5.7 N_{Cu} + 9.7 N_C. \quad [7]$$

The same method is used to estimate a new interaction parameter, ε_{As}^{Pb} , in the copper-rich alloy phase. The Taylor's series expansion was used by considering this time copper as solvent and assuming only iron, lead, and arsenic as solutes, since the phase contains negligible amounts of carbon, simplifying to the Cu-Fe-Pb-As system. The derived expression is shown in Eq. [8]:

$$\ln \{ \gamma_{As} \} = \ln \gamma_{As}^0 + \varepsilon_{As}^{As} N_{As} + \varepsilon_{As}^{Pb} N_{Pb} + \varepsilon_{As}^{Fe} N_{Fe}, \quad [8]$$

where γ_{As}^0 is the limiting activity coefficient in the Cu-As binary system. N_{As} , N_{Pb} , N_{Fe} , and ε_{As}^{As} , ε_{As}^{Pb} , ε_{As}^{Fe} are mole fractions and interaction parameters of arsenic, lead, and iron, respectively. First, γ_{As}^0 , ε_{As}^{As} were calculated using the reported activity data in the Cu-As^[13] binary system and assuming a regular solution behavior in order to extrapolate the data to a temperature of 1473 K (1200 °C). Then, ε_{As}^{Fe} was calculated using the reported activity coefficient in the Cu-Fe-As-C^[4] system and finally, ε_{As}^{Pb} in Eq. [8] was derived by combining $\{ \gamma_{As} \}$ for the copper-rich alloy phase determined in this study in the Cu-Fe-Pb-As-C system shown in Figure 7. The average value for ε_{As}^{Pb} is 4.81 with a standard deviation of 1.7. The result combining the reported data and the derived parameters are shown in Eq. [9]:

$$\ln \{ \gamma_{As} \} = -4.7 + 10.1 N_{As} + 4.8 N_{Pb} - 8.5 N_{Fe}. \quad [9]$$

C. Material Balance for the Proposed Process

Based on the present experimental results, a mass balance was carried out for the new process proposed. The process consists on adding excess carbon to the Cu-Fe-Pb base speiss in order to make three immiscible liquid alloy phases of lead-rich, copper-rich, and iron-rich, at a relatively low temperature of approximately 1500 K (1227 °C). By this phase separation technique, it is expected to recover valuable metals into the lead-rich and copper-rich alloys, and to eliminate the less valuable iron and arsenic into the iron-rich alloy phase, which may be discarded as a harmless residue.

In the mass balance calculation, it was supposed that 1000 kg of speiss containing copper, iron, lead, and arsenic with 22.5, 22.5, 45, and 9.7 wt pct, respectively, together with 0.1 wt pct of silver, gold, and platinum each, is treated at 1473 K (1200 °C) by adding 7.7 kg of carbon, which is the minimum amount required for its saturation in the melt. The loss of arsenic by volatilization is neglected in the calculation, since the equilibrium partial pressures of arsenic gas species As, As₂, As₃, and As₄ do not exceed 10⁴ Pa^[17] in the region of the miscibility gap in the Cu-Fe-Pb-As-C. The results are listed in Table II representing the weight amount in kg, and their corresponding fractional distribution in percentage and indicated in brackets, of all the elements in each of the three equilibrated phases at 1473 K (1200 °C).

Table II. Material Balance, Weight Amount, and Fractional Distribution of Elements for the Treatment of 1000 kg of Cu-Fe-Pb-As Speiss Under Saturation of Carbon at 1473 K (1200 °C)

Element	Amount in Charge		Amount in kg and [Fractional Distribution in pct]					
	kg	Wt pct	Cu-Rich Alloy Phase		Fe-Rich Alloy Phase		Pb-Rich Alloy Phase	
Cu	225	22.5	178	[79.1]	30.0	[13.3]	17.0	[7.57]
Fe	225	22.5	11.0	[4.89]	214	[95.1]	0.10	[0.04]
Pb	450	45.0	14.8	[3.29]	4.34	[0.96]	431	[95.8]
As	97.0	9.7	37.8	[39.0]	58.3	[60.1]	0.86	[0.89]
C	7.70	—	0.24	[3.14]	7.41	[96.3]	0.04	[0.58]
Ag	1	0.1	0.089	[8.90]	0.046	[4.60]	0.865	[86.5]
Au	1	0.1	0.621	[62.1]	0.057	[5.70]	0.322	[32.2]
Pt	1	0.1	0.426	[42.6]	0.532	[53.2]	0.042	[4.24]
Total	1008	100	243	[24]	315	[31]	450	[45]

Table II shows that almost the whole amount of iron and carbon initially charged, 95 and 96 pct, respectively, will be distributed into the iron-rich alloy phase, while more than 95 pct of lead into the lead-rich alloy phase and approximately 80 pct of copper into the copper-rich alloy phase. For arsenic, its fractional distribution is 39 pct and high at 60 pct in the copper-rich and iron-rich alloy phases, respectively, while it is almost negligible, lower than 1 pct, in the lead-rich alloy phase.

Regarding precious metals, it is noted that almost 87 pct of silver together with more than 30 pct of gold will be distributed into the lead-rich alloy phase; the remaining gold will be distributed into the copper-rich alloy phase with a fractional distribution of about 62 pct. Platinum distributes almost entirely into the copper-rich alloy phase and the iron-rich alloy phase with a fairly similar amount, 43 and 53 pct, respectively.

The results suggest that the recovery of valuable silver and gold from the Cu-Fe-Pb base speiss into the lead and copper-rich alloy phases and the elimination of iron and arsenic into the iron-rich alloy phase might be feasible by the means of phase separation. The proposed process will be on a good level of acceptance if the content of the platinum in the initial charge is small. Also it is important to note that both the lead- and copper-rich alloy phases may be further treated by a pyrometallurgical or hydrometallurgical process in order to extract gold, silver, and the remaining lower arsenic.

V. CONCLUSIONS

As a fundamental study for the treatment of the speiss produced in the smelting and recycling processes of lead, by utilizing the phase separation of Cu-Fe-Pb base speiss in equilibrium with solid carbon, the phase relations in the miscibility gap of the Cu-Fe-Pb-As saturated with carbon were determined at 1473 K (1200 °C). The distributions of precious elements of silver, gold, and platinum between the liquid equilibrated phases in the corresponding miscibility gap of the system were also investigated. The results are summarized as follows.

1. A miscibility gap composed of copper-rich, iron-rich, and lead-rich alloy phases extend over a wide concentration range. Carbon is preferentially distributed in the iron-rich alloy phase, while arsenic is distributed almost entirely in the copper-rich and iron-rich alloy phases.
2. The behavior of precious metals of platinum, gold, and silver were clarified in the Cu-Fe-Pb-As saturated with carbon at 1473 K (1200 °C) and their corresponding distribution ratios between the copper-rich, iron-rich, and lead-rich alloy phases, for up to 10 wt pct of arsenic in the charge, were determined.
3. In the miscibility gap where the three equilibrated phases coexist, platinum shows a strong affinity for the iron-rich and the copper-rich alloy phases that increases with increasing arsenic in charge, gold presents more affinity with copper-rich and lead-rich alloy phases that strongly decreases up to 2 wt pct of arsenic in charge but later it attains a constant value, and silver has a clear strong affinity for the lead-rich alloy phase specially when the content of arsenic in charge is higher than 4 wt pct.
4. Raoultian activity coefficients of arsenic in the iron-rich and the copper-rich alloy phases shows the same tendency, with low values between 0.01 and 0.03, which is consistent with the strong affinity of this impurity for copper and iron as major component of their corresponding phases. On the other hand, the activity coefficients of arsenic in the lead-rich alloy phase are found to be greater than 0.4.
5. Interaction parameter of different elements for arsenic in the lead-rich, iron-rich, and copper-rich alloy phases, which coexist in the equilibrium at 1473 K (1200 °C) in the Cu-Fe-Pb-As-C multicomponent system, were determined by combining experimental results with the use of mathematical formalisms and predictive models for Raoultian activity coefficients.
6. The present results suggest that the recovery of valuable silver and gold into the copper-rich and lead-rich alloy phases as well as the stable elimination of less valuable iron together with an high amount of 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 significant.

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