

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Distribution of Precious Metals During the Reducing Pyrometallurgical Processes of Complex Copper Materials

Leandro A. Voisin

*University of Chile, Department of Mining Engineering
Chile*

1. Introduction

The name precious metal, PM, is given to gold, silver, and the six platinum group metals, PGM, platinum, palladium, rhodium, iridium, osmium and ruthenium. These metals have a long history and close relationship with mankind, and they have exerted considerable influence on the development of society because of their special characteristic and specific properties required mainly for technology under an increasing tendency of their prices.

The variety of processes used in the recovery and refining of precious metals can be classified into two major process categories which are based on the differences in the raw material sources, in this way, we can mentioned the primary category related to those concentrates obtained from mined platinum bearing copper-nickel sulfide ores and the secondary category related to raw material sources such as recycled industrial products, spent catalyst, electronic scrap, spent electrolytes, and jewellery scrap.

The recovery method chosen for precious metals depends on the physical form of the source, its precious metal content, and the nature of the other elements present into the source. Among the primary category sources, precious metals are mainly presented as minor elements associated with base metal sulphide concentrates such as copper, lead and nickel, including arsenates, tellurides or antimonates, in fact, it is a common operational practice to use gold and silver siliceous ores as slag-forming fluxing agent in pyrometallurgy processes.

When base metals are produced by pyrometallurgical processes from primary category source ores, precious metals resulted to be concentrated into the electrolytic refining anode slimes, this situation is mainly because they have a heavy specific gravity and a general stronger affinity to metal-sulphide or metal phases than that to oxide phases or slag. According to this, an important primary source of precious metals corresponds to that derived from anodes slimes, a by-product of primary copper and/or nickel electro refining stage.

In recent times, the smelting of copper concentrates with higher content of impurities such as arsenic and antimony has increased and, unfortunately, their concentrations tend to be high in the intermediate products such as matte, white metal and blister copper. This causes a serious problem in controlling the quality of the final product cathode copper and also on

the distribution of their associated precious metals during the overall process. Therefore, under these conditions, the distribution of precious metals and the elimination of impurities before the electro-refining of crude copper are of great concern in the copper production.

This chapter provides essential thermodynamic information, which predicts the distribution of precious elements during the pyrometallurgical treatment, under reducing conditions, of complex copper materials rich in impurities of arsenic and antimony at 1473K which is a common temperature for copper smelting processes. The thermodynamic studies involved in this chapter are related, for example, with the smelting of high impurities-copper sulphide concentrates or with the pyrometallurgical treatment of copper scrap, smelting dust or other kind of materials containing copper as base component, high content of impurities and precious metals as minor elements.

2. Thermodynamic concepts

In the conventional pyrometallurgical process for the production of metallic copper from copper sulfides, the terms related to the melted condensed phases as slag, matte, blister and anodic copper are well known, however, when the concentrations of impurities such as arsenic and/or antimony are high and under reducing conditions, an additional condensed phase called speiss usually appears in the process. Thus, before continuing with the main topic it is important to clarify some thermodynamic terms.

2.1 Formation of speiss in the processing of ores and treatment of secondaries

The speiss phase is basically composed of arsenides and antimonides of iron, copper, nickel and cobalt. Its formation occasionally occurs during treatment of intermediate products of non-ferrous reducing smelters such as sludge, flue dust and dross with high arsenic or antimony concentration in addition to metal bullion, matte and slag phases. A Simplified flowsheet of copper smelter showing the main elimination route of arsenic and antimony from smelting system is shown in Figs. 1. Speiss is considered to have more metallic properties than matte, its density being higher than matte and lower than the metal phase (Fuwa & Otani, 1980) and forms a separated phase between metal and matte in the furnace.

During the practical non-ferrous smelting operations, speiss formation is usually avoided by maintaining the arsenic and antimony contents in the feed materials to low concentration levels. High arsenic and antimony sources are usually blended with other feed materials to maintain low levels of arsenic and antimony in the blended charge, which prevents speiss formation in the main process stream.

Arsenic and antimony contained in the charge are removed to some degree in the slag phase during smelting, while a major portion is volatilized to the flue dust due to the high vapour pressures of sulfidic, oxidic and metallic species of these elements (Hulgren et al., 1973). Arsenic and antimony dissolved in the main process stream are usually eliminated in subsequent processing steps. Sometimes, according to the process, arsenic and antimony form metal compounds with the other base metals components and removed as dross from the system. In addition to arsenic and antimony removed in the flue dust and dross, base metal values such as copper, iron, lead, cobalt and nickel as well as precious metals such as platinum, gold and silver are also distributed in these intermediate products.

The reduction smelting process utilizing an electric furnace is commonly used for recovering these metal values. During treatment of these intermediate products a slag phase, matte phase and metallic bullion phase are formed. When the concentration of arsenic or antimony is significantly high, an additional speiss phase is also equilibrated with slag, matte and metallic bullion phases.

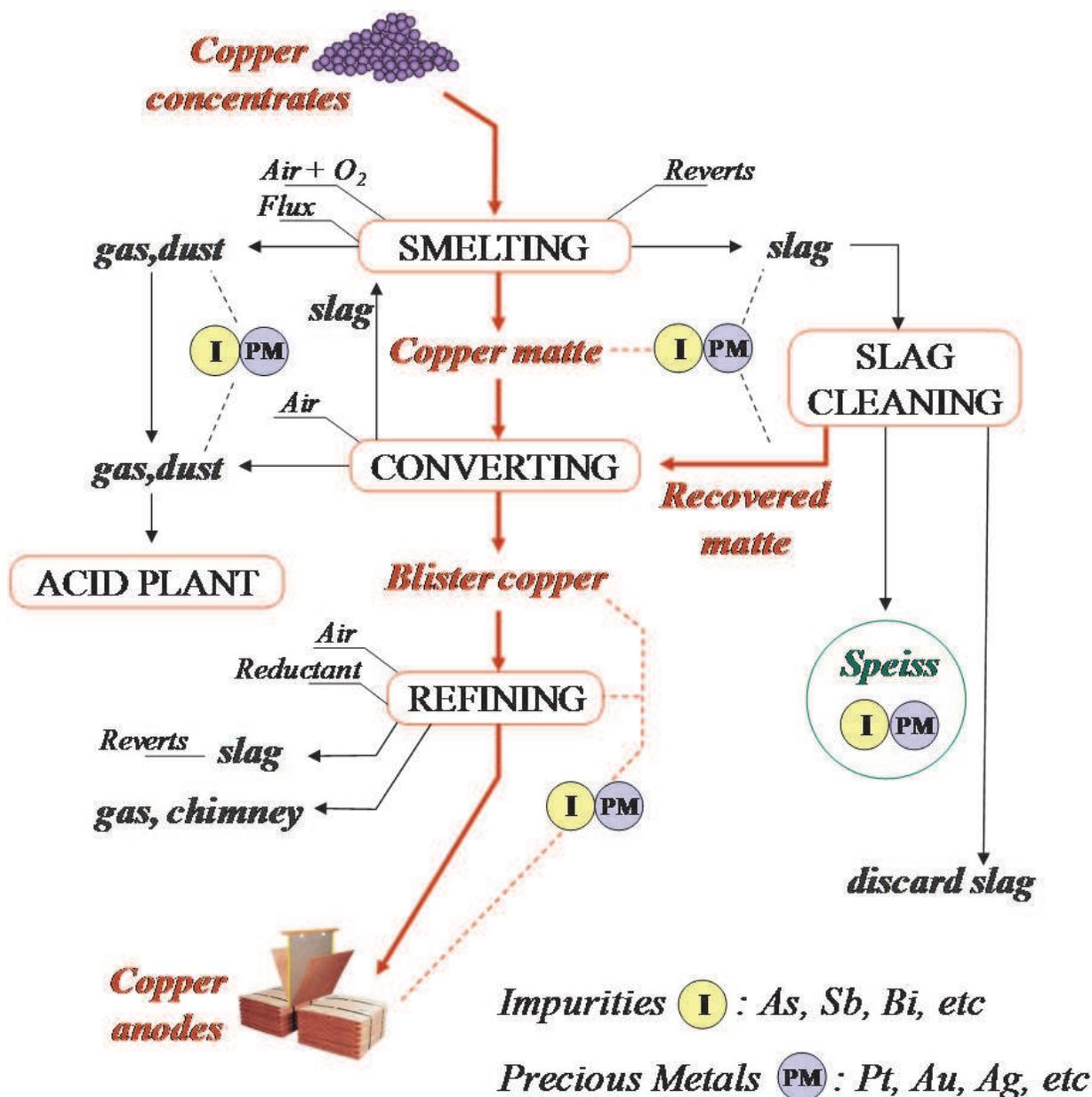


Fig. 1. Simplified copper smelter flowsheet showing the main distributions routes of detrimental impurities and precious metals from the smelting system

All the results presented in this chapter were experimentally obtained. The quenching method combined with the metallographic observation and chemical analyses using combustion-infrared spectrometry for carbon, electron probe micro analysis (EPMA) and inductively coupled plasma spectrometry (ICP) was used to determine the phase relations and the distribution of the precious metals.

2.2 Distribution ratio of precious metals between melted phases

The distribution ratio of a precious metal, X, between two condensed immiscible phases, A_1 and A_2 in a thermodynamic system, $L_X^{A_1/A_2}$, is defined as follows.

$$L_X^{A_1/A_2} = [\text{mass \% X}]_{A_1} / \langle \text{mass \% X} \rangle_{A_2} \quad (1)$$

where $[]_{A_1}$ and $\langle \rangle_{A_2}$ indicate the A_1 and the A_2 phase, respectively. Assuming that the denominator of the equation corresponds to the heavier phase of the system, if there were three condensed phases in equilibrium in the system, and then we will have two distribution ratios, both with a common numerator that will correspond to the less dense phase in the system. By the definition, the element X will be concentrated in the heavier phase when the value of distribution ratio is less than unity.

3. Precious metals behaviour in the Cu-Fe-As/Sb-C systems

Sulfide ores containing bituminous coal reserves sometimes constitute a feed for copper smelting (Parviainen & Fugleberg, 1980; Dobrzanski & Kozminski, 2003). The presence of coal in a shaft furnace makes iron excessively dissolved in the melt. In a ladle adjacent to the furnace, an iron base alloy containing a considerable amount of arsenic solidifies and accumulates as a furnace residue, which is generally called "speiss". Several other metals such as copper, cobalt, nickel, silver, gold and platinum are dissolved in the residue and the recovery of these valuable metals has offered a challenging subject.

In recent years, the content of impurities of arsenic and antimony in the sulfide concentrates of non-ferrous metals tends to rise. This results in the formation of matte, slag and flue dust or dross with a considerably high content of these impurities in the nonferrous smelting processes. The speiss may be also made when these intermediate products are treated in a strongly reducing condition where the metallic iron is formed. Therefore, the behaviour of arsenic, antimony and precious metals in the speiss is of importance for treating the sulfide concentrates and by-products with the high content of impurities.

The Cu-Fe-As and the Cu-Fe-Sb ternary systems are a base for the speiss phase related to the production of copper and the treatment of by-products. According to a literature, the Cu-Fe system saturated with carbon (Chang et al., 1979) makes a miscibility gap at considerably low temperatures of less than 1500K, which is composed of the liquid copper phase with very small contents of iron and carbon, and the liquid Fe-C alloy with about 7 mass % copper. This phase separation will be useful for developing a new recovery process to treat the Cu-Fe-As/Sb base speiss, in which the less valuable iron is to be removed into the iron-rich phase, while the valuable copper and other precious metals are enriched in the copper-rich phase.

Information on the phase relations and the distribution of precious metals of silver and platinum in the miscibility gap of the Cu-Fe-As and Cu-Fe-Sb systems saturated with carbon were investigated by the author at 1473 K (Voisin et al., 2004, 2005) by a quenching method.

3.1 Phase relations in the miscibility gap of the Cu-Fe-As-C and Cu-Fe-Sb-C systems

The phase relations for the mass % ratio of Cu/Fe of 1/1 are illustrated in Fig. 2 (a) and 2 (b), respectively, in the N_C and N_{Sb} or N_{As} .

When antimony is added to the Fe-Cu binary system saturated with carbon, antimony and copper form speiss phase, while carbon and iron form an iron-rich phase. As shown in Fig. 2(a), antimony is distributed almost completely in the speiss phase and dissolves very few in the iron-rich phase, while carbon presents an opposite distribution. This behaviour of antimony can be explained from the fact that the activity of antimony shows a more negative deviation from Raoult's law in the Cu-Sb system than in the Fe-Sb system.

On the other hand, when arsenic is added to the Fe-Cu binary system saturated with carbon, arsenic and copper form preferably speiss phase, while carbon and iron form an iron-rich phase, which also contains arsenic with smaller grade. As shown in Fig. 2(b), arsenic is distributed mostly in the speiss phase and dissolves to less extent in the iron-rich phase, while carbon is distributed almost completely in the iron-rich phase and decreases with increasing arsenic content in the same phase. This behaviour of arsenic can be explained from the fact that the activity of arsenic shows a more negative deviation from Raoult's law in the Cu-As system than in the Fe-As system.

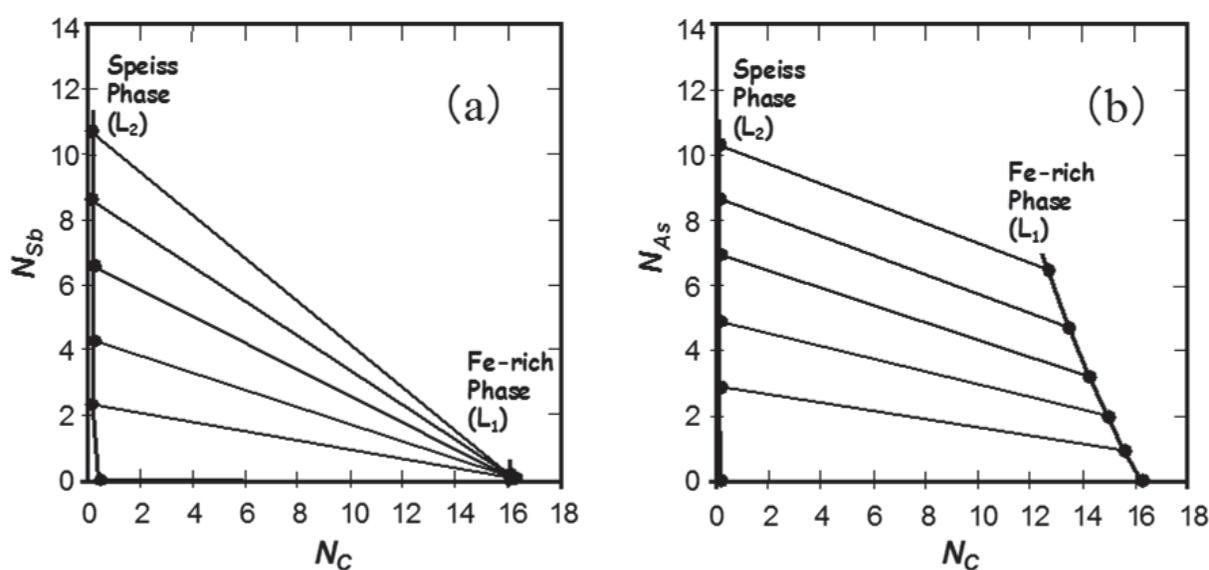


Fig. 2. (a) Relation Between N_{Sb} and N_C in Fe-rich and Speiss Phases in the Cu-Fe-Sb System Saturated with Carbon at 1473K, mass% Fe/Cu = 1; (b) Relation Between N_{As} and N_C in Fe-rich and Speiss Phases in the Cu-Fe-As System Saturated with Carbon at 1473K, mass% Fe/Cu = 1

To represent the whole systems would require quaternary diagrams, however, since the solubility of carbon in liquid copper at the experimental temperature is quite low, the compositions may be expressed with the adjusted calculation result on the pseudo-ternary diagrams in which iron and carbon are regarded as one constituent. The phase relations in the Cu-(Fe+C)-Sb and Cu-(Fe+C)-As pseudo ternary diagrams are illustrated in Figs. 3 and 4, respectively.

It is noticed in Fig. 3 that there is a miscibility gap designated by $(L_1 + L_2)$ over a wide range of concentrations, and that the solubility of copper in the Fe-rich phase L_1 and the solubility of iron in the speiss phase L_2 are quite small. The miscibility gap reported in the Cu-Fe-Sb system at 1423 K (Lee & Itagaki, 1986) is shown with the dotted lines in the figure and the result obtained in the present study is very close to their result in shape though with the mutual solubility increased in the whole range studied.

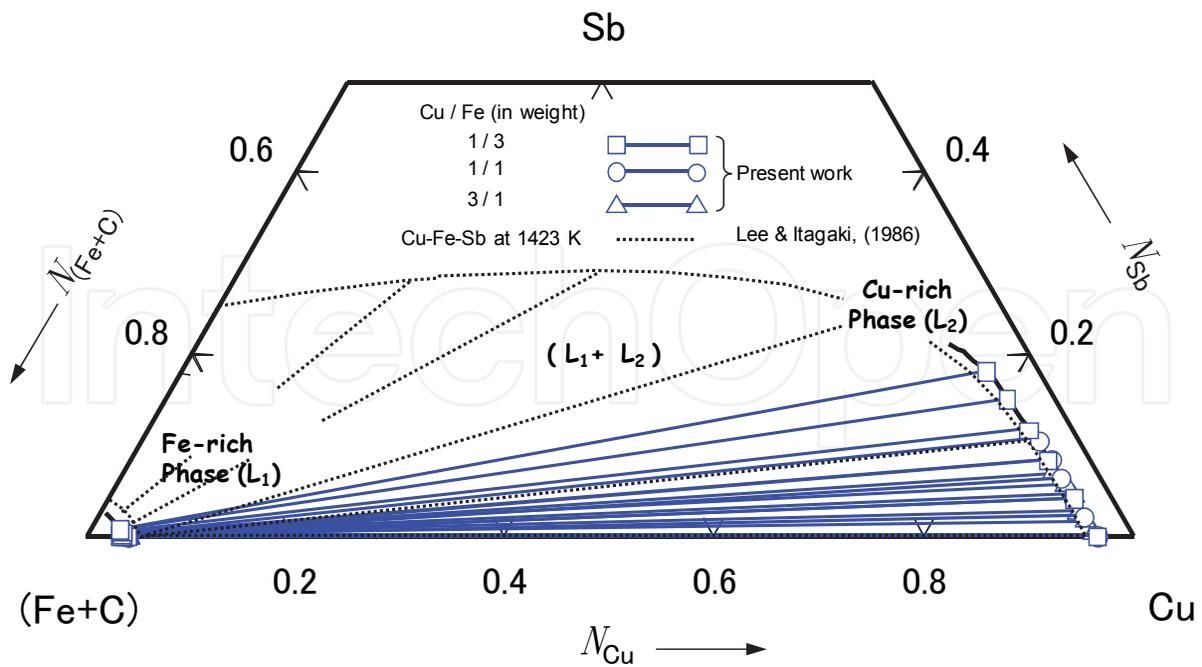


Fig. 3. Phase Relations in the Cu-(Fe+C)-Sb Pseudo Ternary System at 1473 K

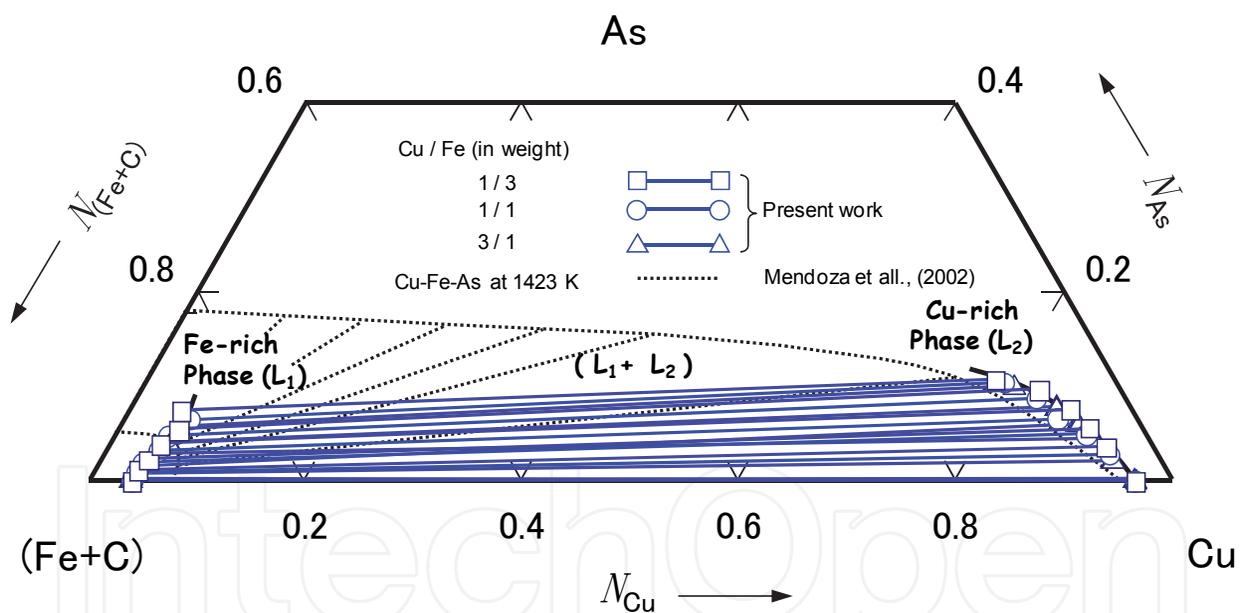


Fig. 4. Phase Relations in the Cu-(Fe+C)-As Pseudo Ternary System at 1473 K

In the Cu-(Fe+C) pseudo binary system the obtained mutual solubility of $N_{\text{Fe}} = 0.036$ in the speiss phase L_2 and of $N_{\text{Cu}} = 0.039$ in the iron-rich phase L_1 differ considerably from the reported values (Massalski, 1990) of $N_{\text{Fe}} = 0.06$ and of $N_{\text{Cu}} = 0.09$ and also from the reported values in the system without carbon (Lee & Itagaki, 1986) of $N_{\text{Fe}} = 0.05$ and of $N_{\text{Cu}} = 0.08$ respectively in the Cu-Fe binary system. This behaviour can be explained by the presence of carbon in the system.

On the other hand, it is noted in Fig. 4 that the Cu-(Fe+C)-As pseudo ternary also exhibits a miscibility gap over a wide range of concentrations, nevertheless, the mutual solubility of

iron in the speiss phase and of copper in the iron-rich phase increase with increasing arsenic content. This behaviour can be explained from the fact that the activity of iron as well as copper decreases with increasing activity of arsenic.

The miscibility gap reported in the Cu-Fe-As system (Mendoza et al., 2002) is shown with the dotted lines in the figure and the obtained tendency in the present study is close to their result though the solubility of iron is increased in the whole composition of speiss investigated, which extends above 12 at% As. This behaviour can be also explained by the presence of carbon in the system.

3.2 Distribution of silver and platinum in the miscibility gap of the Cu-Fe-As-C and Cu-Fe-Sb-C systems

Adjusting the equation (1) to the corresponding systems, we will have:

$$L_X^{Fe/Sp} = [\text{mass \% X}]_{Fe} / \langle \text{mass \% X} \rangle_{Sp} \quad (2)$$

where $[]_{Fe}$ and $\langle \rangle_{Sp}$ are the iron-rich and speiss phases, respectively. Then, when the value of the distribution coefficient is larger than unity, the concentration of the element in the iron-rich phase is higher than that in the speiss phase.

Fig. 5 shows the distribution coefficients of silver and platinum in relation to the antimony content in the charge in the Cu-Fe-Sb ternary system saturated with carbon at 1473 K (Voisin et al., 2005). It is clearly demonstrated that the distribution coefficient of platinum is slightly larger than unity, thus it dissolves more easily in the iron-rich phase while silver dissolves mostly in the speiss phase.

On the other hand, Fig. 6 shows the distribution coefficient of silver and platinum in relation to the arsenic content in the charge in the Cu-Fe-As ternary system saturated with carbon at 1473 K (Voisin et al., 2004). The distribution coefficient of platinum is almost constant at about 0.8 against the arsenic content. It is noted that silver dissolves mostly in the speiss phase, though its distribution coefficient increasing with increasing arsenic in the charge. The distribution of a precious metal between two phases would mainly depend on the affinity between the precious minor element and component elements of the two phases.

As the activity coefficient of antimony (Hino & Toguri, 1987) and arsenic (Hino & Toguri, 1986), are very small in the speiss, a large amount of these elements are concentrated into the speiss. From this fact, antimony and arsenic in nonferrous ores can be concentrated and fixed into the speiss and then be changed to a harmless substance which can be discarded safely. In this case, dissolution of metals in the speiss has to be minimized. On the contrary, there is a way to recover valuable metals from the speiss containing those metals as much as possible. For such metallurgical use of the speiss, it is necessary to know various properties of the speiss.

Since, in the Cu-Fe-Sb system saturated with carbon, platinum distributed in an iron-rich phase containing very few amounts of antimony together with copper around 4.5% in weight, these metals can be recovered by sulphuric leaching. In the Cu-Fe-As system saturated with carbon, arsenic could be concentrated and fixed into the iron-rich phase, and later on to be discarded. In case that cobalt and nickel are not of interest in the process. On

the other hand, for both systems the speiss phase of copper, which contains platinum and the entirety of silver, should be treated later on.

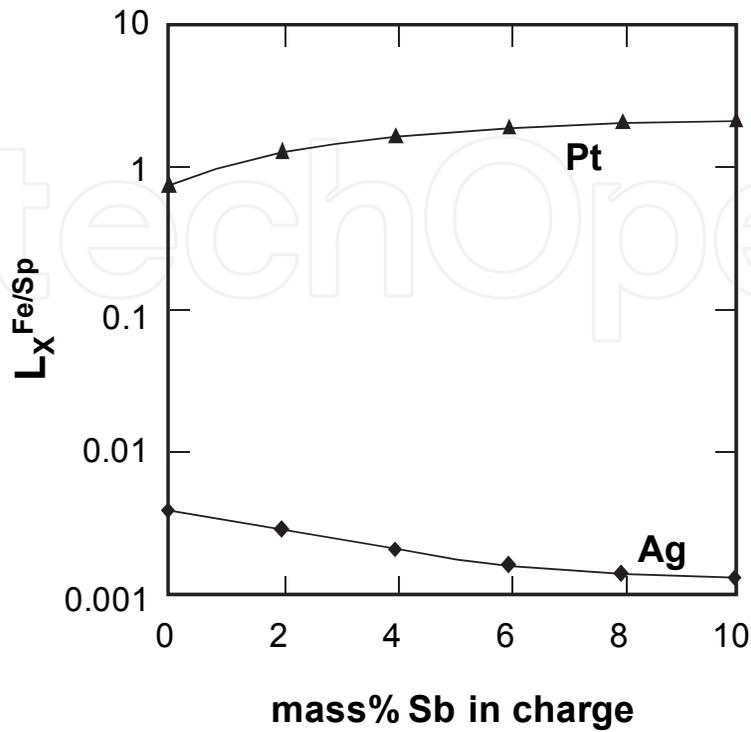


Fig. 5. Distribution Coefficient of Precious Metals in Relation to Mass% Antimony in the Charge in the Cu-Fe-Sb System Saturated with Carbon at 1473K.

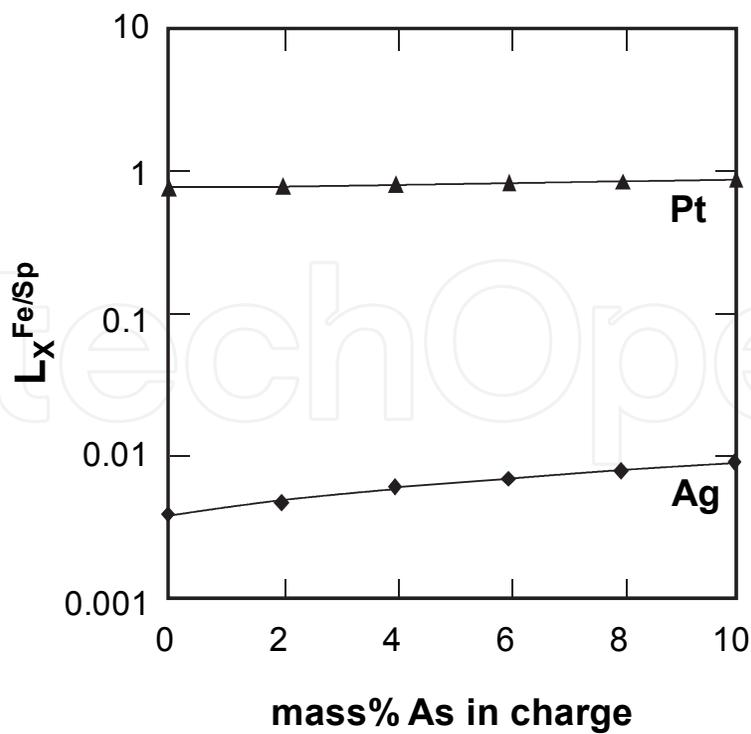


Fig. 6. Distribution Coefficient of Precious Metals in Relation to Mass% Arsenic in the Charge in the Cu-Fe-As System Saturated with Carbon at 1473K.

4. Precious metals behaviour in the Cu-Fe-C-S-As/Sb systems

In the previous section, we studied the behaviour of some precious metals in the Cu-Fe-C-As/Sb systems, which is useful to recover them from high impurities-iron-copper sources like scraps or flue dust by the addition of carbon or to understand their distribution during the formation of speiss in reductive smelting of the copper concentrate.

During the latter process like a blast furnace operation using coke as fuel and reducer or in processing the copper concentrate which contains coal in the bulk (Dobrzanski & Kozminski, 2003), also a matte phase with deficient sulfur apart from the tie line connecting between FeS and Cu₂S in the Cu-Fe-S ternary diagram is often produced in equilibrium with the speiss.

Then, it is also of interest in smelting the copper concentrate in a very strongly reducing condition to know the behaviour of precious metals between the matte and the furnace residue or the speiss. In this respect, the phase relations and distribution of precious metals in the Cu-Fe-S-As-C (Voisin & Itagaki, 2006) and Cu-Fe-S-Sb-C (Voisin et al., 2008) systems are of great importance in the extreme case of reducing smelting. Additionally, the study of those systems will provide the fundamental information on a new process proposed by the author to eliminate arsenic and antimony from the impurities-rich matte produced from the copper concentrate containing significant amount of those elements.

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 (speiss) with a considerable amount of impurities (arsenic or antimony), but with very few amounts of precious metals such as silver and gold, which can be expected to be discarded as a harmless deposit in the yard. Hence, the phase relations and the distribution ratios of such precious metals as silver, gold and platinum in the Cu-Fe-S and Cu-Fe-S-As/Sb systems saturated with carbon at 1473 K are presented in this section.

4.1 Phase relations in the Cu-Fe-S-C system

Three different zones were observed in the Cu-Fe-S system saturated with carbon at 1473 K, as shown in Fig. 7. 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 % and also the sulfur content in the liquid copper-rich alloy are in a good agreement with those reported in the Cu-Fe-S system at the same temperature (Mendoza et al., 2002a, 2002b) 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 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 (Voisin et al. 2004) showed in the previous section 3, were also plotted in Fig. 7 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. The Fig. 8 shows the results in the corresponding quaternary system.

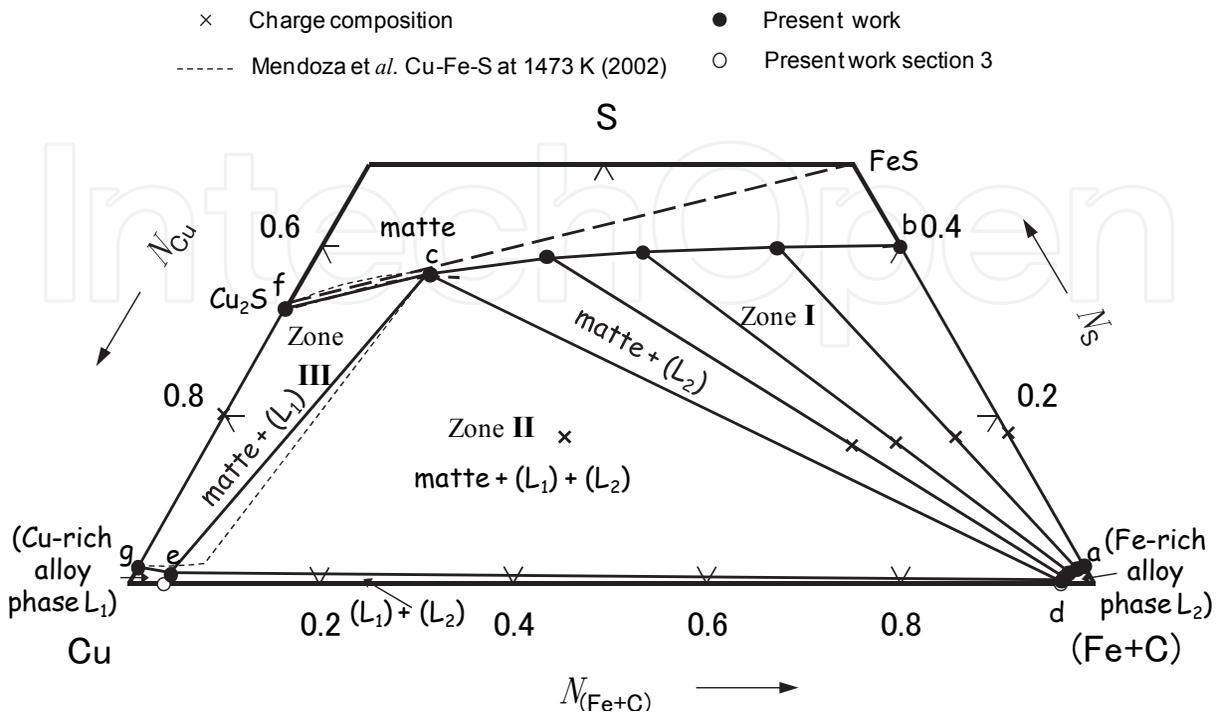


Fig. 7. Phase relations in the Cu-(Fe+C)-S pseudo ternary system at 1473 K

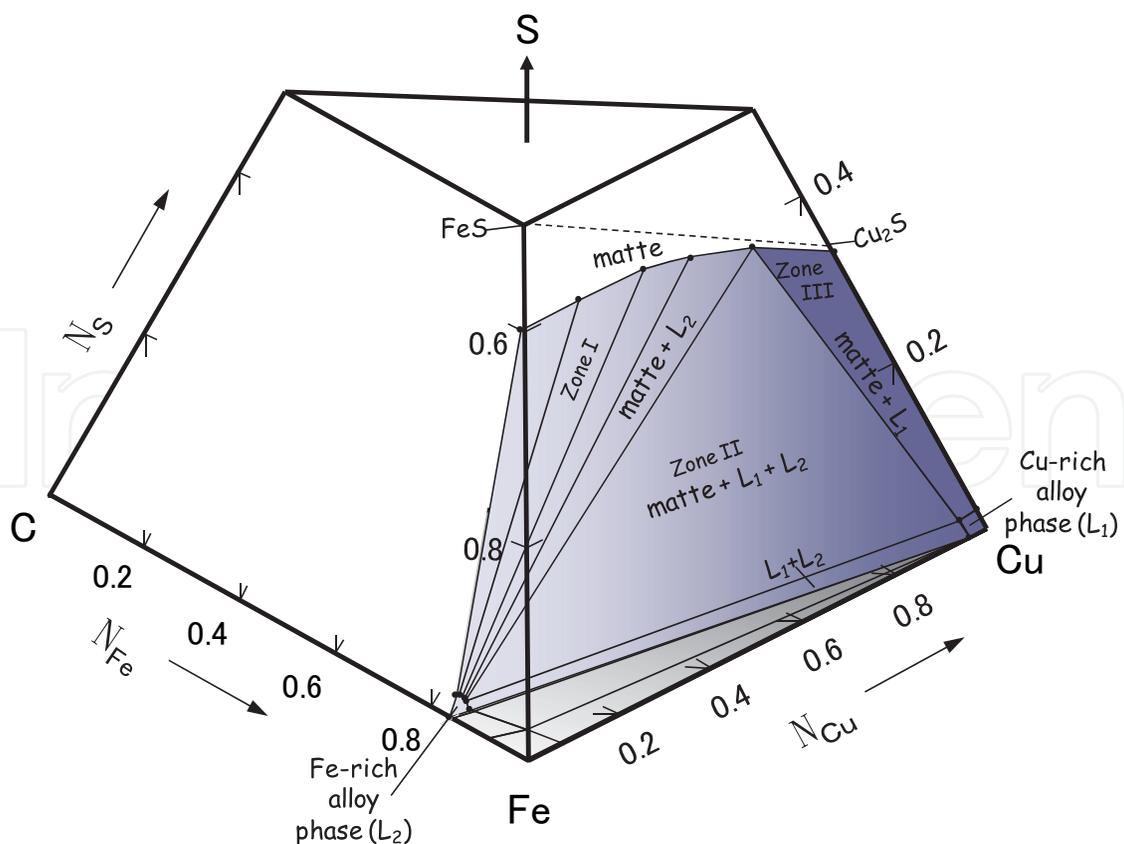


Fig. 8. Phase relations in the Cu-Fe-S-C quaternary system at 1473 K

Since the distribution of precious metals was studied under the presence of impurities of arsenic and antimony into the zone II forming a matte phase in equilibrium with two speiss phases, it is important to clarify the behavior of those impurities in Cu-Fe-S-C system previous to show that for precious metals between the three equilibrated phases.

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

The phase relations in the Cu-Fe-S-As-C system for zone II are shown in Figs. 9-a and -b 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}). The corresponding compositions are listed in Table 1.

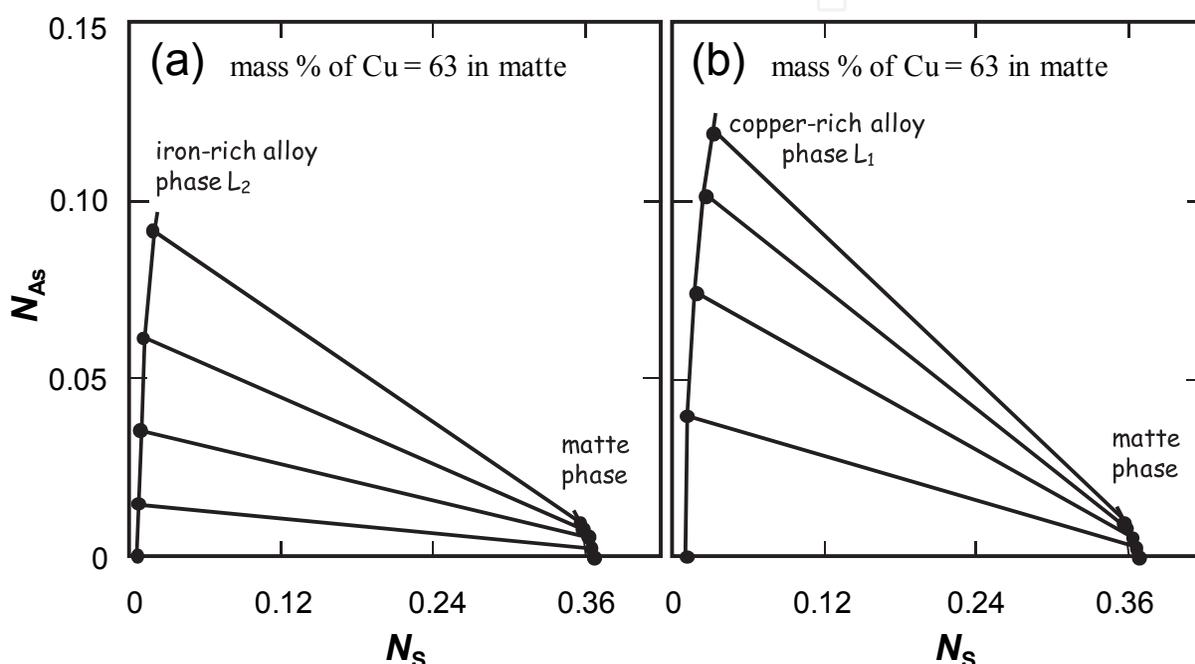


Fig. 9. Relation between N_{As} and N_S in the iron-rich or copper rich alloy and matte phases in the Cu-Fe-S-As systems saturated with carbon at 1473 K (zone II)

mass% in copper-rich alloy phase (L_1)					mass% in iron-rich alloy phase (L_2)					mass% in matte phase				
Fe	S	As	Cu	C	Fe	S	As	Cu	C	Fe	S	As	Cu	C
3.41	0.58	0	95.99	0.021	91.59	0.38	0	4.07	3.96	13.85	23.16	0	62.95	0.047
5.51	0.64	4.69	89.14	0.027	88.88	0.45	2.22	4.90	3.55	14.61	23.00	0.37	61.96	0.044
8.11	0.98	8.80	82.08	0.032	85.58	0.56	5.23	5.31	3.33	14.92	22.84	0.82	61.39	0.034
11.91	1.38	12.06	74.61	0.039	81.39	0.68	8.85	6.38	2.70	15.54	22.43	1.20	60.80	0.027
16.56	1.71	14.27	67.42	0.042	71.58	1.12	12.62	12.77	1.92	16.57	22.29	1.40	59.73	0.016

mass%Cu / %Fe / %S in charge = 27.6 / 62.9 / 9.5

Table 1. Phase equilibrium composition 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)

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 1, 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.

4.3 Phase relations in the Cu-Fe-S-Sb-C system

The phase relations in the Cu-Fe-S-Sb-C system for zone II are shown in Figs. 10-a and -b 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_{Sb}). The corresponding compositions are listed in Table 2.

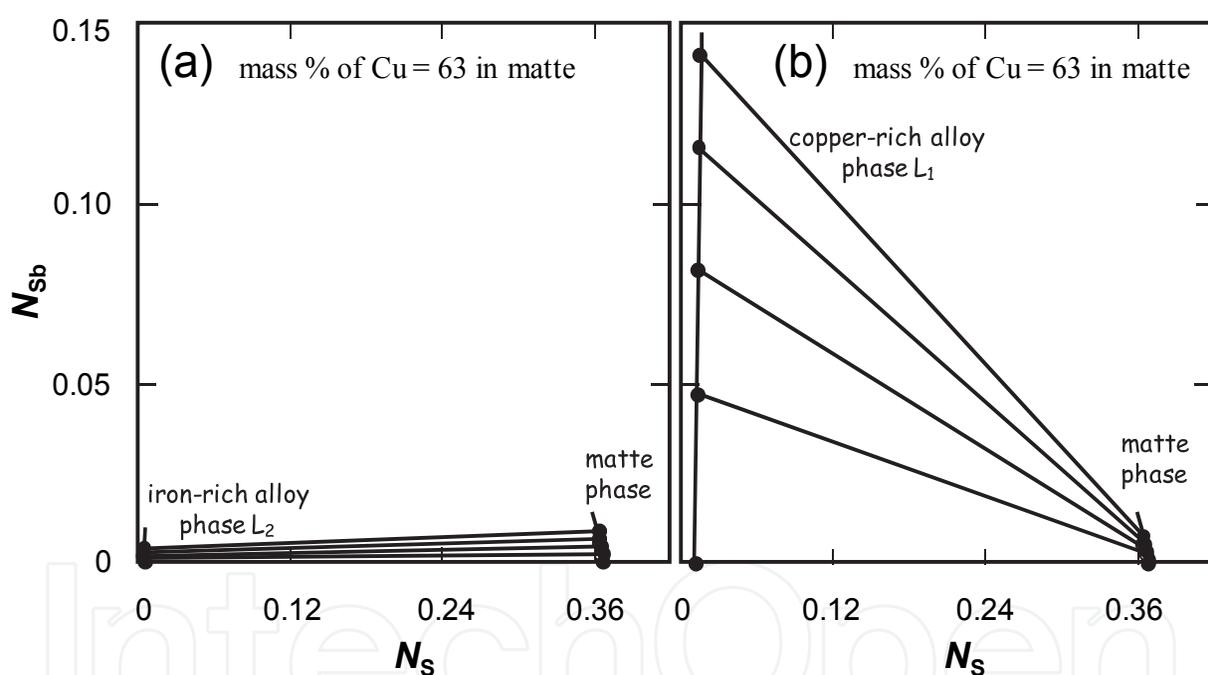


Fig. 10. Relation between N_{Sb} and N_S in the iron-rich or copper rich alloy and matte phases in the Cu-Fe-S-Sb systems saturated with carbon at 1473 K (zone II)

When antimony is added to the Cu-Fe-S-C system in zone II, it is preferentially enriched in the copper-rich alloy with a small amount of sulfur, while the most sulfur, copper and iron form the matte phase with a smaller amount of antimony when compared with that in the copper-rich alloy phase. The iron-rich alloy phase contains very few antimony even less than the matte phase and almost the entirety of carbon and a copper content between 2.7 and 4 mass %.

With increasing antimony content in the charge, the sulfur content decreases in the matte and iron-rich alloy phases and increases in the copper-alloy rich phase. Furthermore, as

listed in Table 2, with increasing antimony content, the carbon content in the iron-rich alloy is almost constant at about 4 mass % while that slightly decreases in the copper-rich alloy and matte phases though they are negligibly small. The copper content decreases, while the iron content increases with increasing antimony content in the alloy phases.

mass% in copper-rich alloy phase (L ₁)					mass% in iron-rich alloy phase (L ₂)					mass% in matte phase				
Fe	S	Sb	Cu	C	Fe	S	Sb	Cu	C	Fe	S	Sb	Cu	C
3.41	0.58	0	95.99	0.021	91.59	0.38	0	4.07	3.96	13.85	23.16	0	62.95	0.047
3.50	0.59	8.98	86.90	0.020	91.76	0.31	0.33	3.65	3.95	14.90	23.26	0.52	61.37	0.045
3.84	0.61	15.06	80.47	0.017	91.84	0.30	0.52	3.38	3.96	15.62	22.93	1.07	60.34	0.038
4.06	0.62	20.61	74.69	0.016	92.12	0.31	0.74	2.88	3.96	18.46	22.85	1.55	57.10	0.036
5.42	0.66	24.66	69.25	0.015	92.01	0.32	1.05	2.67	3.96	20.37	22.80	2.10	54.70	0.033

mass %Cu / %Fe / %S in charge = 27.6 / 62.9 / 9.5

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

4.4 Distribution of silver, gold and platinum in the miscibility gap of the Cu-Fe-S-As-C and Cu-Fe-S-Sb-C systems

Adjusting the equation (1) to the distribution ratio of a precious metal X between the matte and copper-rich alloy or iron-rich alloy phases in the Cu-Fe-S-As or in the Cu-Fe-S-Sb system saturated with carbon, $L_X^{m/L}$, is defined by

$$L_X^{m/L} = [\text{mass \% X}]_m / <\text{mass \% X}>L \quad (3)$$

where []_m and < >_L indicate the matte and the iron-rich alloy or copper-rich alloy phases, respectively. By 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 $L_X^{m/L}$ 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 or antimony is considered, in which the precious metals 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 between the matte and copper-rich alloy (L₁) or iron-rich alloy (L₂) phases are shown in Fig. 11 in relation to the arsenic content while in Fig. 12 in relation to the antimony content in the matte for the Cu-Fe-S-As and Cu-Fe-S-Sb system saturated with carbon, respectively.

As shown in Fig. 11, the distribution ratios of silver, gold and platinum between the matte and copper-rich alloy (L₁) phases increase with increasing content of arsenic in the matte phase. It is noted that the distribution ratio at a given arsenic content in the matte decreases in the order of silver, platinum and gold. L_{Ag}^{m/L_1} presents values of less than 1, while L_{Au}^{m/L_1} and L_{Pt}^{m/L_1} very small values around 0.001 in the whole range of arsenic content.

It is shown in the same figure that the distribution ratio between the matte and iron-rich alloy (L₂) phases at a given arsenic content in the matte decreases in the order of silver, gold and platinum. L_{Ag}^{m/L_2} is almost constant at about 12 while L_{Au}^{m/L_2} abruptly decreases and L_{Pt}^{m/L_2} increases against the arsenic content in the matte.

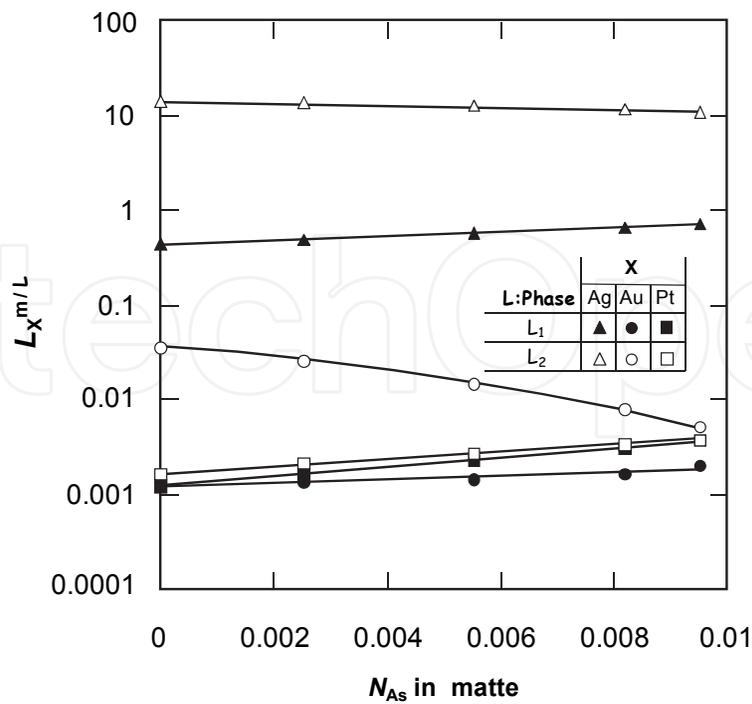


Fig. 11. Distribution ratios of silver, gold and platinum in relation to N_{As} in the matte in the Cu-Fe-S-As system saturated with carbon at 1473 K.

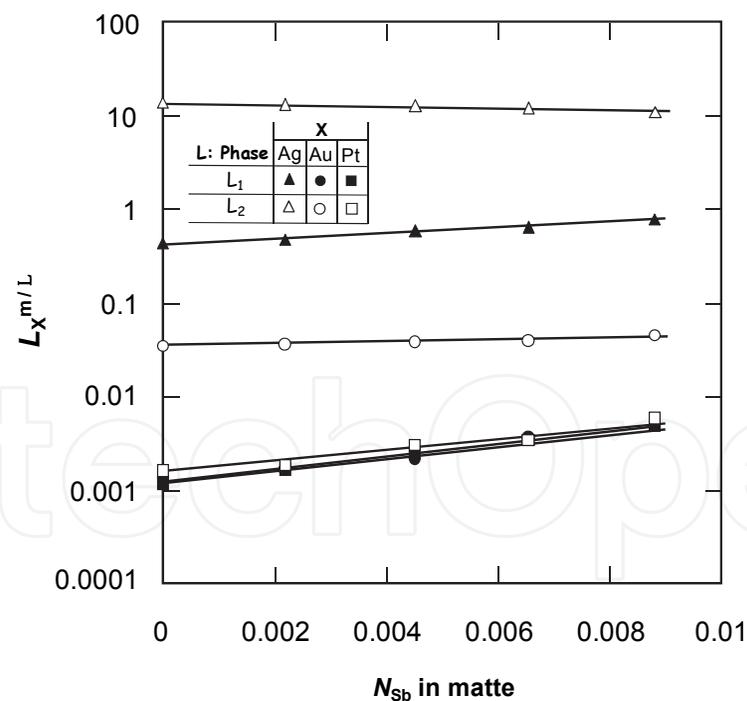


Fig. 12. Distribution ratios of silver, gold and platinum in relation to N_{Sb} in the matte in the Cu-Fe-S-Sb system saturated with carbon at 1473 K.

On the other hand, as shown in Fig. 12, the distribution ratios of those precious metals between the matte and copper-rich alloy (L_1) phases increase with increasing content of antimony in the matte phase. It is noted that the distribution ratio at a given antimony

content in the matte decreases in the order of silver, platinum and gold. L_{Ag}^{m/L_1} presents values of less than 1, while L_{Au}^{m/L_1} and L_{Pt}^{m/L_1} very small values between 0.01 and 0.001 in the whole range of antimony content.

It is shown in the same figure that the distribution ratio between the matte and iron-rich alloy (L_2) phases at given antimony content in the matte decreases in the order of silver, gold and platinum. L_{Ag}^{m/L_2} and L_{Au}^{m/L_2} are almost constant at about 12 and 0.04, respectively, while L_{Pt}^{m/L_2} increases from 0.0015 to 0.007 against the antimony content in the matte.

Finally, we can determine the distribution ratio of silver and platinum between two metallic-rich alloy phases in the zone II where they are also in equilibrium with matte in the Cu-Fe-S-As or in the Cu-Fe-S-Sb system saturated with carbon and compare them to the results obtained in section 3 for those precious metals where there is not presence of sulfur and there are only two metallic-rich alloy phases in equilibrium. According to this, we need to adjust the equation (1) as follow:

$$L_X^{L_1/L_2} = [\text{mass \% X}]_{L_1} / <\text{mass \% X}>_{L_2} \quad (4)$$

where $[]_{L_1}$ and $< >_{L_2}$ indicate the copper-rich alloy and the iron-rich alloy phase, respectively. The distribution ratios of silver and platinum are shown in Figs. 13 and 14 for the Cu-Fe-S-As-C and Cu-Fe-S-Sb-C systems in relation to the arsenic and antimony content in the copper-rich alloy phase, respectively, the results are shown together with those obtained in section 3 in the corresponding system without the presence of sulfur.

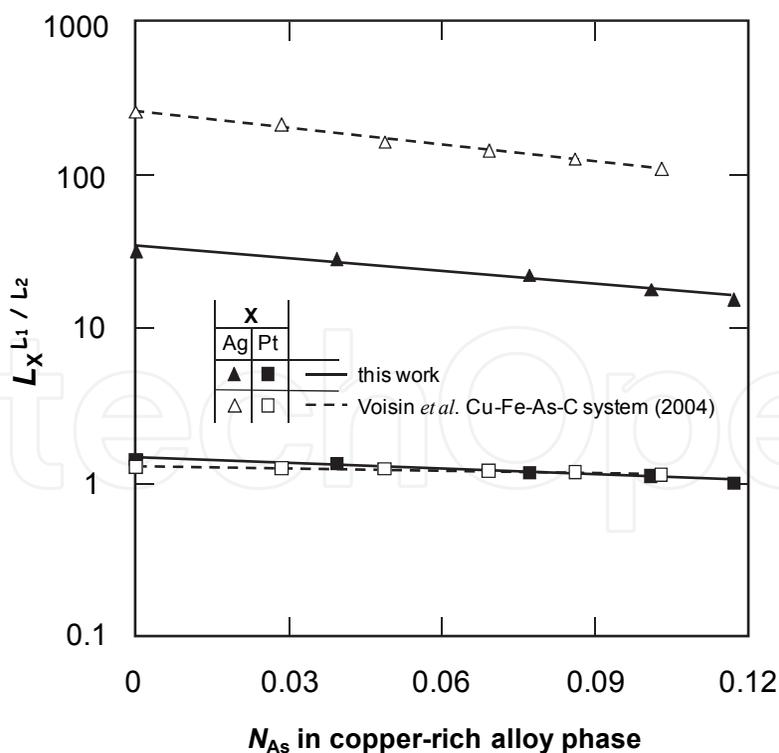


Fig. 13. Distribution ratios of silver and platinum between the copper-rich alloy (L_1) and iron-rich (L_2) alloy phases in relation to N_{As} in the copper-rich alloy phase in the Cu-Fe-S-As system saturated with carbon at 1473 K

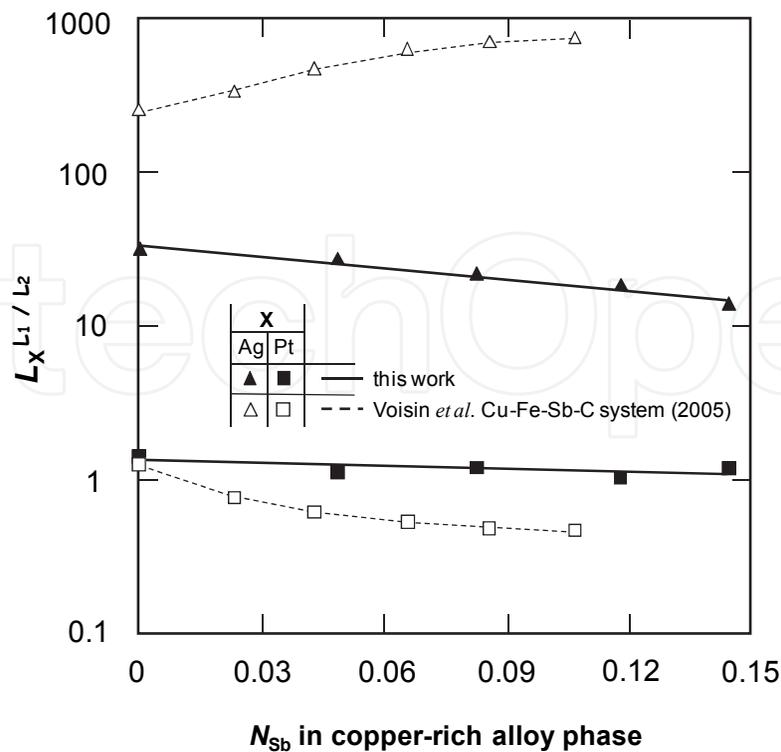


Fig. 14. Distribution ratios of silver and platinum between the copper-rich alloy (L_1) and iron-rich (L_2) alloy phases in relation to N_{Sb} in the copper-rich alloy phase in the Cu-Fe-S-Sb system saturated with carbon at 1473 K

As shown in Figs. 13 and 14, the distribution ratios of silver and platinum between the copper-rich alloy (L_1) and iron-rich alloy (L_2) phases in the Cu-Fe-S-As-C and Cu-Fe-S-Sb-C systems decrease with increasing arsenic and antimony content, respectively, in the copper-rich alloy phase. $L_{Ag}^{L_1/L_2}$ is larger than 10 while $L_{Pt}^{L_1/L_2}$ close to unity in the whole range of impurity content.

The distribution ratios of silver and platinum in the Cu-Fe-As-C and Cu-Fe-Sb-C systems obtained in section 3 are also shown in the corresponding Figs. 13 and 14, respectively, with broken lines. In Fig. 13, it is noteworthy that, in terms of the magnitude and the dependency against the arsenic content in the copper-rich alloy phase, $L_{Pt}^{L_1/L_2}$ is very similar while $L_{Ag}^{L_1/L_2}$ is about 10 times larger than that for the Cu-Fe-S-As-C system. On the other hand, in Fig. 14, $L_{Ag}^{L_1/L_2}$ presents an increasing trend and it is about 10 times larger and $L_{Pt}^{L_1/L_2}$ is similar but decreases more drastically than those for the Cu-Fe-S-Sb-C system.

5. Treatment of complex copper matte by reducing condition

Based on the experimental results showed in this chapter, the material balances were evaluated for the treatment of complex copper matte according to the proposed process by the author.

It was supposed in the calculation that 100 kg of copper matte with a matte grade of 70% Cu containing arsenic and antimony with 0.5 mass % for each one, and precious metals of silver, gold and platinum with each 0.01 mass % is treated at 1473 K by adding different

amounts of pig-iron at 1473 K (iron saturated with about 4.3 mass % of carbon) of 10, 20, 30, 40 and 50 kg. Then, these values were converted to the dimensionless ones of $\alpha = 0.1, 0.2, 0.3, 0.4$ and 0.5 with $\alpha = (\text{amount of added pig-iron}) / (\text{amount of initial copper matte (100 kg)})$. According to the results obtained by the author, metallic copper-rich and iron-rich alloys together with a sulfide matte phase containing about 63 % of copper are in equilibrium in these conditions.

In the calculation, the loss of arsenic, antimony and sulfur by volatilization was neglected because the summation of equilibrium partial pressures of predominant As and As_2 for arsenic, Sb, Sb_2 and Sb_4 for antimony and S_2 for sulfur gas species over the corresponding alloys and matte at 1473 K are very small at less 10 (Voisin et al., 2004), 0.1 (Voisin et al., 2005) and 2 Pa (Zekeri et al., 2000), respectively. The schematic diagram with the corresponding charge compositions is shown in Fig. 15, while the compositions of iron, copper and sulfur for the different levels of α are represented in the Cu-(Fe+C)-S pseudo ternary system and shown in Fig. 16.

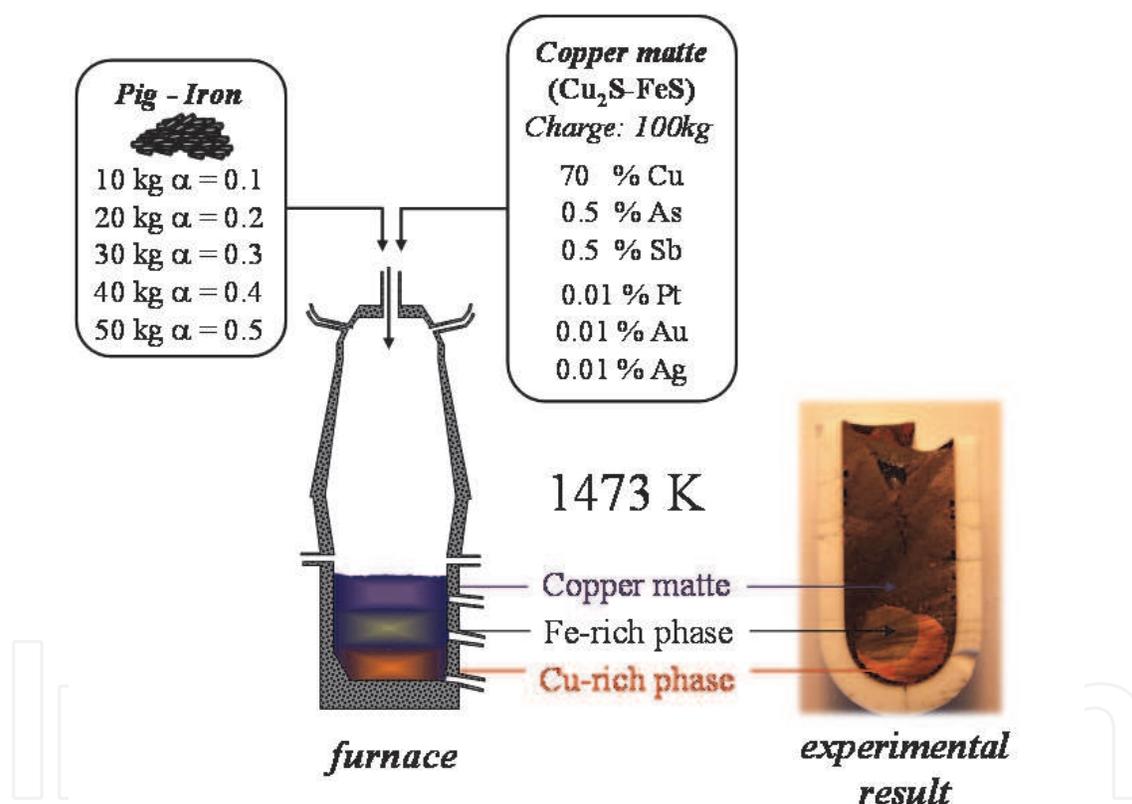


Fig. 15. Schematic diagram with the corresponding charge compositions for the treatment of complex copper matte at 1473 K

The calculated results are listed in Tables 3, 4 and 5 representing the fractional distribution (%) of all the elements for the copper-rich alloy, iron-rich alloy and matte phases, respectively. Furthermore, the fractional distribution, between the three phases and the mass % in the treated matte phase are shown against α in Figs. 17, 18 and 19 for copper, arsenic and antimony as impurities and silver, gold and platinum as precious metals, respectively. Since carbon and sulfur are mostly distributed in the iron-rich alloy and matte phases, respectively, their results are not shown in those figures.

According with the calculation, 0.065 correspond to the minimum value of α where the three phases start appearing when the pig-iron is added to the charged matte. This means that at least 6.5 kg of pig-iron must be added to the system for treating 100 kg of matte. It is indicated in Tables 3, 4 and 5 that the amount of copper-rich alloy phase decreases from 11.6 to 9.2 kg, the amount of iron-rich alloy phase increases from 3.8 to 45.7 kg and the amount of matte phase is almost constant at about 94.5 kg with increasing value α , respectively.

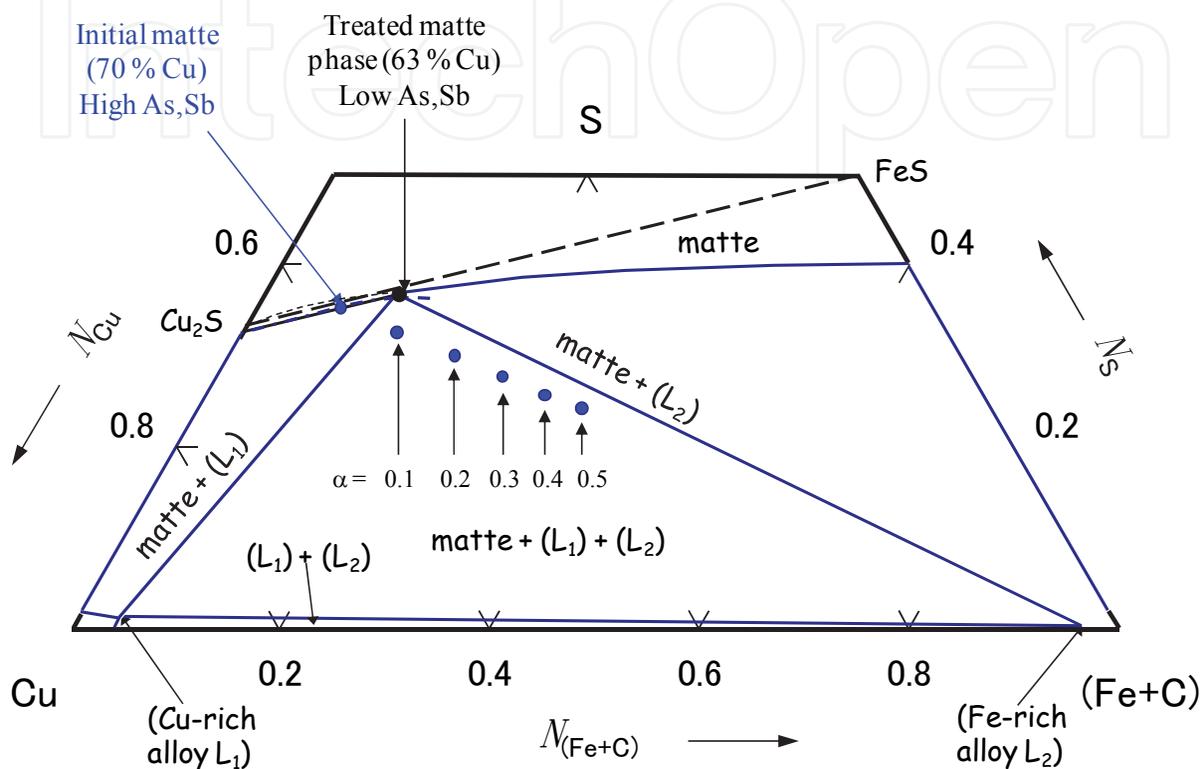


Fig. 16. Phase relations in the Cu-(Fe+C)-S pseudo ternary system at 1473 K

element	fractional distribution (%)				
Cu	15.0	13.6	13.3	12.7	11.9
Fe	2.49	1.44	1.03	0.780	0.604
As	60.1	47.3	39.8	33.3	28.1
Sb	70.0	65.6	62.9	59.9	56.4
C	1.26	0.368	0.220	0.146	0.107
S	0.291	0.265	0.258	0.247	0.232
Ag	20.7	19.1	18.6	18.0	17.0
Au	97.4	93.0	89.3	85.1	81.0
Pt	78.8	48.0	34.9	26.1	20.5
total (kg)	11.6	10.6	10.3	9.8	9.2
pig-iron in charge (kg)	10	20	30	40	50
α	0.1	0.2	0.3	0.4	0.5

Table 3. Material balances for the copper-rich alloy phase in the treatment of 100 kg of complex copper matte at 1473 K

element	fractional distribution (%)				
Cu	0.24	0.89	1.50	2.19	2.81
Fe	20.6	49.6	61.3	70.8	75.1
As	7.50	24.5	35.7	45.6	52.7
Sb	1.18	4.61	7.64	11.1	14.3
C	76.1	92.3	95.3	96.8	97.5
S	0.069	0.259	0.437	0.639	0.820
Ag	0.234	0.890	1.49	2.19	2.81
Au	1.49	5.82	9.53	13.7	17.8
Pt	20.3	51.4	64.6	73.6	79.2
total (kg)	3.83	14.5	24.4	35.6	45.7
pig-iron in charge (kg)	10	20	30	40	50
α	0.1	0.2	0.3	0.4	0.5

Table 4. Material balances for the iron-rich alloy phase in the treatment of 100 kg of complex copper matte at 1473 K

element	fractional distribution (%)				
Cu	84.8	85.5	85.2	85.1	85.2
Fe	76.9	49.0	37.6	28.4	24.3
As	32.4	28.2	24.4	21.2	19.2
Sb	28.8	29.8	29.4	29.0	29.3
C	22.7	7.31	4.49	3.09	2.44
S	99.6	99.5	99.3	99.1	98.9
Ag	79.1	80.0	79.9	79.8	80.2
Au	1.10	1.17	1.16	1.15	1.18
Pt	0.891	0.591	0.437	0.334	0.280
total (kg)	94.3	94.8	95.1	94.4	94.9
pig-iron in charge (kg)	10	20	30	40	50
α	0.1	0.2	0.3	0.4	0.5

Table 5. Material balances for the matte phase in the treatment of 100 kg of complex copper matte at 1473 K

As is shown in Fig. 17, with increasing value of α , 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, and the matte grade (% Cu) of treated matte is about 63 %. For the 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 it increases from 20.6 to 75.1 in the iron-rich alloy phase. The sulfur is almost completely distributed in the matte phase while the carbon in the iron-rich alloy phase.

For the impurities, as is shown in Fig. 18, with increasing value of α , the fractional distribution of arsenic decreases from 60.1 to 28.1%, and from 32.4 to 19.2 % in the copper rich alloy and matte phases, respectively, and increases from 7.5 to 52.7 % in the iron-rich alloy phase. For the antimony, the fractional distribution decreases from 70 to 56.4 %, increases from 1.18 to 14.3 % and is almost constant at about 29 % in the copper-rich alloy, iron-rich alloy and matte phases, respectively. The mass % of arsenic and antimony in the treated matte for the value of α close to 0.1 are 0.18 and 0.15 respectively.

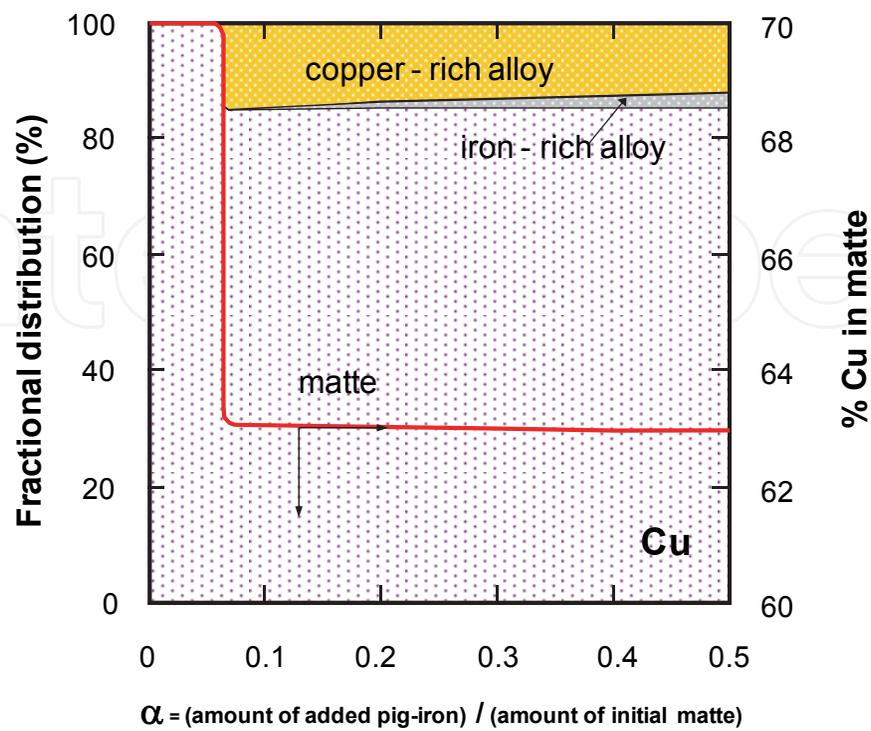


Fig. 17. Fractional distribution of copper and mass % of copper in matte against α during the reducing treatment of complex copper matte at 1473 K

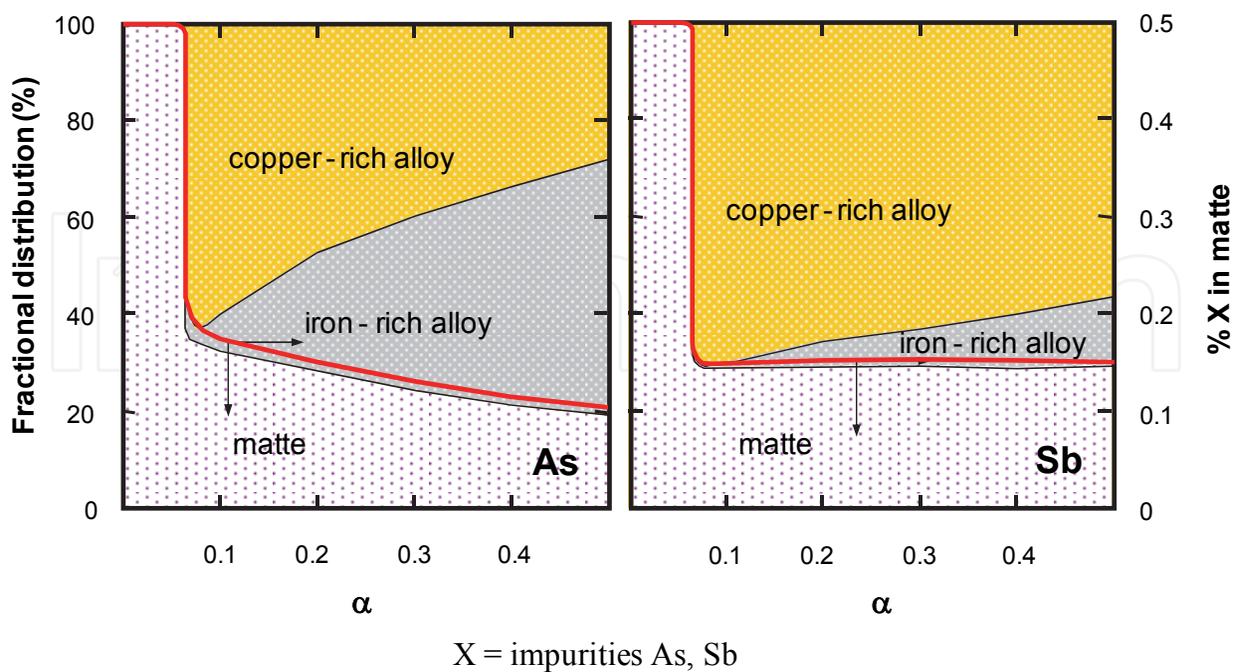


Fig. 18. Fractional distribution of impurities and their mass % in matte against α during the reducing treatment of complex copper matte at 1473 K

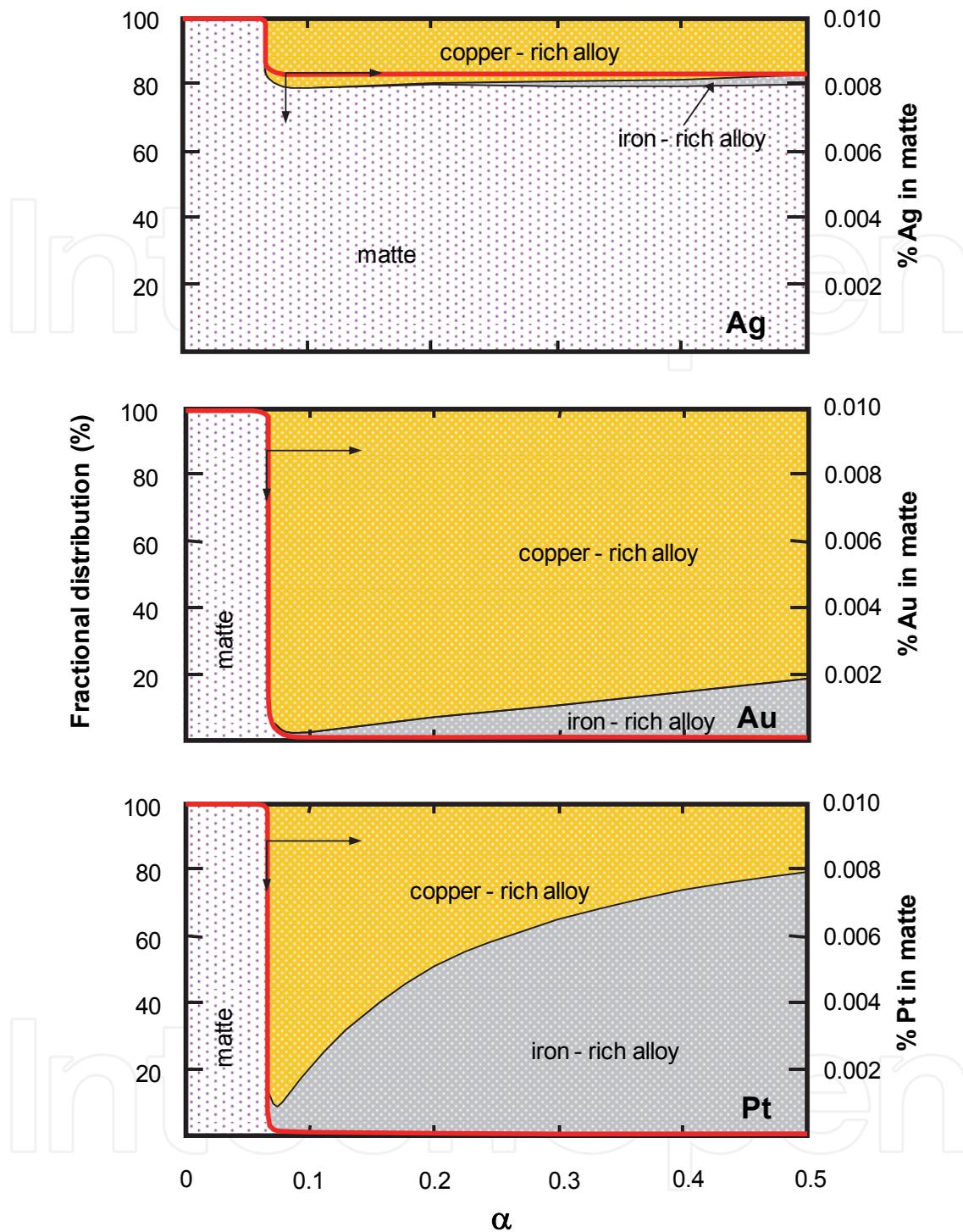


Fig. 19. Fractional distribution of precious metals and their mass % in matte against α during the reducing treatment of complex copper matte at 1473 K

For the precious metals, as is shown in Fig. 19, with increasing value of α , the fractional distribution of platinum abruptly decreases and those of silver and gold slightly decrease in the copper-rich alloy phase and those in the iron-rich alloy phase present an opposite behaviour, while, in the matte phase, the fractional distribution of platinum slightly decreases and those of silver and gold are almost constant.

These results suggest that, when the recovery of precious metals and the elimination of detrimental arsenic and antimony from the copper matte are considered by means of the phase separation, 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 phase is considerably large.

The copper-rich alloy may be further treated in a pyro- or hydro-metallurgical process to extract silver, gold and copper; the iron-rich alloy may be harmlessly 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.

6. Conclusions

The distribution of some precious metals during a proposed reducing pyrometallurgical treatment of complex copper materials such as scrap, flue dust, furnace residue, sulfide matte, concentrates and by-products with high content of impurities was studied in this chapter.

According to section 3, it was clarified that in the Cu-Fe-As and Cu-Fe-Sb systems saturated with carbon at 1473 K, there is a large miscibility gap composed of copper-rich and iron-rich phases, which extends over the wide concentration range where the mutual solubility between them is very small. For impurities, arsenic distributes in both phases while antimony preferentially distributes in copper-rich phase. Carbon almost completely distributes in the iron-rich phase forming a pig-iron-rich alloy.

As for precious metals, most of silver will be enriched in the copper-rich phase while platinum in both phases. Thus for example if the source to be treated contains high amounts of antimony and platinum the latter could be concentrated in the iron-rich phase to be recovered it along with the dissolved copper by a leaching process, or if the source contains high arsenic and silver but low platinum, the impurity could be fixed into the iron-rich phase and subsequently be more safely discarded while silver could be concentrated into a smaller volume of copper-rich phase and be recovered in a subsequent hydro- or pyrometallurgical process.

In section 4, thermodynamic equilibrium in the Cu-Fe-S, Cu-Fe-S-As and Cu-Fe-S-Sb systems saturated with carbon at 1473 K were determined, they present a large miscibility gap, named zone II in this study, where two metallic-rich alloy phases of copper and iron are in equilibrium with a matte phase which contains around 63 mass % of copper. Arsenic has strong preference to the metal alloy phases, while antimony preferentially distributes in the copper-rich alloy phase. Carbon is distributed almost completely in the iron-rich alloy phase.

The zone II in the Cu-Fe-S-As and Cu-Fe-S-Sb systems saturated with carbon at 1473 K represents the thermodynamic basis for studying the treatment of complex copper mattes containing impurities and precious metals. Here, in section 5, the behaviour of silver, gold and platinum between the three equilibrated phases was investigated and also based on the experimental results material balances were evaluated for a proposed process by the author.

For the treated complex copper mattes, the contents of impurities may be considerably decreased. The elimination of arsenic from the matte increases with increasing pig-iron amount in the charge, while that of antimony is almost independent. According to the results by using the equilibrium phase separation, 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.

The copper-rich alloy may be further treated by some hydro- or pyro-metallurgical process to extract silver, gold and copper; the iron-rich alloy may be harmlessly 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.

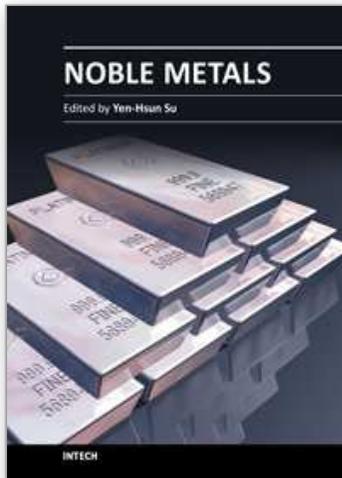
7. References

- Chang, Y. Newmann, J. Mikula, A. & Goldberg, D. (1979). *INCRA Series on the Metallurgy of Copper - Phase Diagrams and Thermodynamic Properties of Ternary Copper - Metal Systems*, International Copper Research Association, Milwaukee, Wisconsin, USA.
- Dobrzanski, J. & Kozminski, W. (2003). *Proceedings of Copper 2003*, Vol. IV, Santiago, Chile, Nov-Dec 2003.
- Fuwa, T. & Otani, M. (1980). *Non ferrous Extractive Metallurgy*, Japan Institute of Metals, Japan.
- Hino, M. & Toguri, J. (1986). Arsenic Activities in Molten Copper and Copper Sulfide Melts. *Met. Trans. B*, Vol 17B, No. 4, (755-761).
- Hino, M. & Toguri, J. (1987). Antimony Activities in Copper Mattes. *Met. Trans. B*, Vol 18B, No. 1, (189-194).
- Hultgren, R. Desai, P. D. Hawkins, D. T. Gleiser, M. Kelley, K. K. & Wagman, D. D. (1973). *Selected Values of the Thermodynamic Properties of the Elements*, ASM, USA.
- Lee, Y. & Itagaki, K. (1986). Distribution Equilibria of Various Slag Systems with Cu-Fe-Sb Ternary Speiss. *J. Min. Mater. Inst. Japan*, 102, (591-595).
- Massalski, T.B. (1990). *Binary Alloy Phase Diagrams* (Second Edition), Vol. 2, ASM International, Materials Park, Ohio.
- Mendoza, D. Hino, M. & Itagaki, K. (2002). Phase Relations and Activity of Antimony in Cu-Fe-S-Sb System at 1473 K. *Mater. Trans. JIM*, 43, No. 5, (1166-1172).
- Mendoza, D. Hino, M. & Itagaki, K. (2002). Distribution Equilibria between Cu-Fe-As Ternary Speiss and Slag Phases. *J. Min. Mater. Process. Inst. Japan*, 118, No. 3.4, (197-201).
- Parviainen, A. & Fugleberg, S. (1980). *Proceedings of Cobalt 80*, CIM, Edmonton, Canada.
- Voisin, L. Henao, H. & Itagaki, K. (2004). Phase Relations and Distribution of Some Minor Elements in Cu-Fe-As System Saturated with Carbon at 1473 K. *Mater. Trans., JIM*, 45, No. 9, (2851-2856).
- Voisin, L. Henao, H. & Itagaki, K. (2005). Phase Relations and Distribution of Some Minor Elements in Cu-Fe-Sb System Saturated with Carbon at 1473 K. *Mater. Trans., JIM*, 46, No. 1, (74-79).
- Voisin, L. & Itagaki, K. (2006). Phase Relations, Activities and Minor Element Distribution in Cu-Fe-S and Cu-Fe-S-As Systems Saturated with Carbon at 1473 K. *Mater. Trans., JIM*, 47, No. 12, (2963-2971).

- Voisin, L. Okura, T. & Itagaki, K. (2008). Phase Relations, Activities and Precious Metal Distribution in the Cu-Fe-S-Sb Systems Saturated with Carbon at 1200 °C. *Mater. Trans., JIM*, 49, No. 6, (1311-1319).
- Zakeri, A, Hino, M. & Itagaki, K. (2000). Silver Activity in Matte and Copper Two Phase Region of Cu-Fe-S System. *J. Min. Mater. Process. Inst. Japan*, 17, (43-60).

IntechOpen

IntechOpen



Noble Metals

Edited by Dr. Yen-Hsun Su

ISBN 978-953-307-898-4

Hard cover, 426 pages

Publisher InTech

Published online 01, February, 2012

Published in print edition February, 2012

This book provides a broad spectrum of insights into the optical principle, resource, fabrication, nanoscience, and nanotechnology of noble metal. It also looks at the advanced implementation of noble metal in the field of nanoscale materials, catalysts and biosystem. This book is ideal not only for scientific researchers but also as a reference for professionals in material science, engineering, nonascience and plasmonics.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Leandro A. Voisin (2012). Distribution of Precious Metals During the Reducing Pyrometallurgical Processes of Complex Copper Materials, Noble Metals, Dr. Yen-Hsun Su (Ed.), ISBN: 978-953-307-898-4, InTech, Available from: <http://www.intechopen.com/books/noble-metals/distribution-of-precious-metals-during-the-reducing-pyrometallurgical-processes-of-complex-copper-ma>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2012 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](#), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen