Dissolution of Metals in Slag with Special Reference to Phase Separation Thermodynamics

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ABSTRACT

In the ternary FeS-FeO-AO(SiO_2, B_2O_3 or P_2O_5) system, a homogeneous FeS-FeO melt tends to separate into matte and slag by the addition of acidic oxide. Mutual dissolution of FeS in slag and FeO in matte must be recognized as the most basic principle in copper matte-slag system, and some sulfidic copper accompanies this dissolved FeS into slag. The dissolution of sulfides in slag decreases drastically by the addition of SiO_2, CaO or Al_2O_3, and also decreases by the decreasing FeS content in high grade matte where the oxidic copper dissolution in slag becomes predominant. The copper loss in slag, and the oxygen and sulfur contents in matte are discussed from the viewpoint of phase miscibility or separability.

The oxidic dissolution of metal in slag depends primarily on the kinds of metal and the oxygen potential, but the effects of the slag composition must also be a great concern for metallurgists. Oxidic dissolution of metal X in binary and ternary FeO_n-SiO_2-CaO slags is discussed in relation with the activity behavior of XO which is also affected greatly by the phase separability between the neutral component (such as FeO_n or XO) and strong intermediate compound (such as $2CaO.SiO_2$). The concentrations of XO are usually higher in the binary fayalite and ferrite type slags, and decreases in the ternary slag.

However, the total loss of metal in slag depends also on the amount of slag which is inversely proportional to the iron content of slag approximately. By combining the activity coefficient and FeO_n content, the total loss may be evaluated on ternary FeO_n-SiO_2-CaO diagram, and as general trend, decreases with decreasing SiO_2 content. This trend is just the opposite for sulfidic dissolution loss, and thus, high SiO_2 slag is used for matte smelting, while low SiO_2 slag is adopted in the converting stage.

1. INTRODUCTION

The loss of valuable metals and the removal of detrimental elements in slag are great concern for metallurgists. But there remain many contradictory opinions on the effects of slag compositions and temperature, dissolved species of metals, effect of dissolved sulfur, ratio of chemical dissolution to mechanical entrainment, and so on. One of the reasons for such confusion may be ascribable to the lack of understanding from the standpoint of phase separation in the interpretation of metal loss in slag. As an example, the oxidic dissolution of copper in slag is well accepted by everyone, and is primarily affected by the oxygen potential, but the sulfidic copper dissolution is controversial. As a matter of fact, sulfidic copper dissolution is not affected so much by sulfur or oxygen potential under the conditions of metallurgical interests, but could be attributed to the mutual dissolution or phase separability between sulfide and oxide phases[1,2]. Also, when the FeO-SiO_2-CaO slag is considered, the effect of slag composition on the oxidic metal dissolution such as $CuO_{0.5}$ is deeply related with the phase separability between this metal oxide and $2CaO.SiO_2$.[3,4]

Because the important metallurgical significance of phase separation thermodynamics is not yet well recognized the dissolution of metals in slag is discussed in this paper mainly from the standpoint of phase miscibility or separability. In the first half part of this paper, the possible dissolution of sulfidic copper in the slag-matte system is discussed, followed by the oxidic metal dissolution as described from both thermodynamic and experimental aspects. The computer assisted thermodynamic model calculations help greatly for simulating the related phase separations. The total metal loss in slag is also discussed by combining the metal content of slag with the amount of the slag, and the optimum slag compositions in practice are investigated.

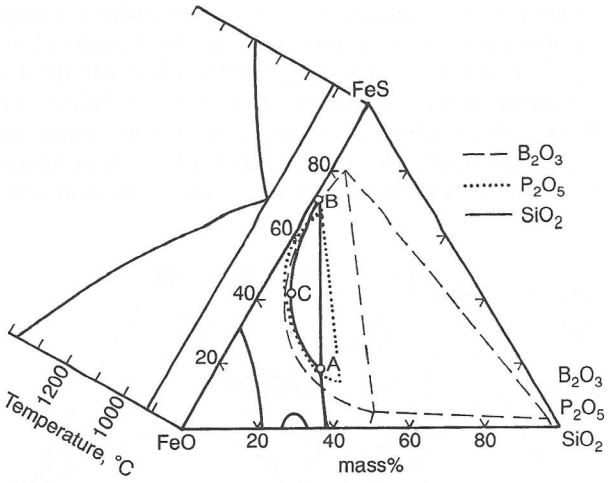

Fig.1. Liquidus isotherms at 1200°C for FeS-FeO-SiO_2 (solid lines), FeS-FeO-B_2O_3(dashed lines) and FeS-FeO-P_2O_5(dotted lines) systems and pseudo-binary diagram for FeS-FeO system.

2. PHASE SEPARATION OF SULFIDE-OXIDE MIXTURE

It is well known that FeS and FeO are most fundamental components of matte and slag. But these form nearly ideal single homogeneous liquid phase with no indication to separate into two liquid phases as shown in Fig.1. The similar miscibilities are observed in many sulfide-oxide systems such as Cu_2S-Cu_2O and MnS-MnO. However, FeS-FeO melt tends to separate into two liquids of matte and slag when an acidic oxide is added. In the FeS-FeO-SiO_2 system[5] in Fig.1, a miscibility gap ACB corresponds to conjugation between matte and slag. The best separation in this ternary is observed at slag A and matte B where the melts are saturated with SiO_2. Similar miscibility gaps are observed when SiO_2 is replaced by other acidic oxides such as B_2O_3 or P_2O_5 as shown in Fig.1[6]. Because of the low melting point of B_2O_3, the liquid region spreads over nearly the whole ternary region at 1100°C.

It is quite natural that an FeS-FeO liquid rich in FeS can dissolve some amount of Cu_2S. The ternary Cu_2S-FeS-FeO_n liquidus diagram[7] is shown in Fig.2(c) together with FeS-FeO_n-SiO_2 diagram (b), and the matte-slag equilibria in quaternary Cu_2S-FeS-FeO_n-SiO_2 system[8] . When the system is saturated with SiO_2, the matte B-Cu_2S conjugates with slag A-E depending on the matte grade, but if SiO_2 is insufficient, more FeO is contained in the equilibrating matte such as C-Cu_2S, or FeS in slag like C-D. The mutual dissolution of matte and slag is decreasing not only with increasing SiO_2, but also with increasing Cu_2S. The white metal Cu_2S represents a clear-cut separation from slag E, D, or FeO_n, regardless of the content of SiO_2. In Fig.2 (a), the liquidus boundary of FeO-SiO_2(or P_2O_5)-CaO system is also illustrated because, as will be described later, we have interests in the effects of lime, ferrite slag and strong calcium silicate compounds on matte-slag equilibria.

Starting from the homogeneous sulfide-oxide mixture, similar phase separations into two liquids, matte and slag, are illustrated in the experimental results reproduced in Fig.3[8]. In Fig.3(a), Cu_2S was gradually added into the homogeneous liquid consisting of 30%FeS, 65%FeO and 5%SiO_2. The resulting phase separation between matte and slag are drawn with the solid and dashed lines, respectively. Similarly, Fig.3(b) shows that the single liquid phase consisting of 10%Cu_2S, 30%FeS and 60%FeO separates into matte and slag along the increasing addition of SiO_2. Thus, better phase separation is expected by the addition of SiO_2 and/or Cu_2S. But due to the miscible nature between FeS and FeO, a considerable amount of FeO and a minute amount of SiO_2 are contained in matte, while in the slag, some Cu_2S accompanies the dissolved FeS. This is the basic principle of sulfidic copper dissolution in slag.

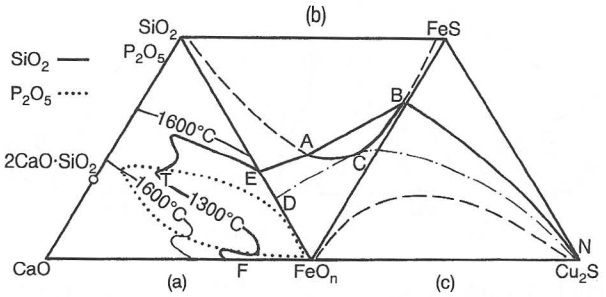

Fig.2. Liquidus diagrams for ternary FeO_n-CaO-SiO_2 or P_2O_5 (a), FeS-FeO_n-SiO_2 (b) and Cu_2S-FeS-FeO_n (c) systems with reference to phase separabilities.

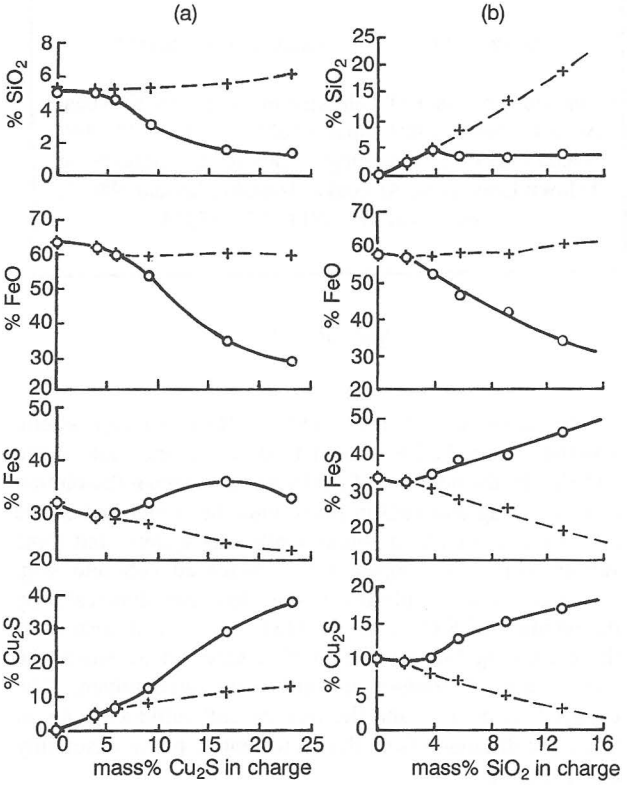

Fig.3. Phase separation between matte (solid lines) and slag (dotted lines) along the addition of Cu_2S (a) or SiO_2 (b) into single homogeneous liquid phase.

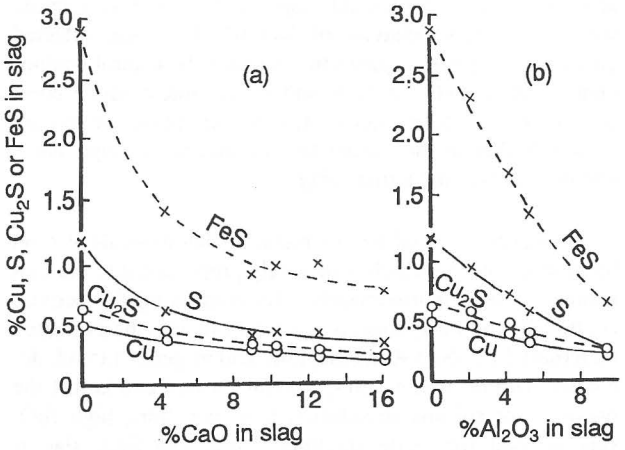

Fig.4. Dissolution of matte constituents in slag plotted against CaO or Al_2O_3 content in FeO-SiO_2-CaO (a) or FeO-SiO_2-Al_2O_3 (b) slag saturated with silica. (1200°C, 57%Cu in matte).

Undoubtedly, much clearer separation is observed in practical matte-slag system not only because of high silica and high copper contents, but also of the coexistence of minor constituents such as CaO and Al_2O_3. Fig.4[9,10] shows the dissolution of matte constituents in silica-saturated slag with different CaO(a) or Al_2O_3(b) content. It is clear that a comparatively small amount of CaO or Al_2O_3 addition in the FeO-SiO_2 slag results in a considerable decrease in the dissolved sulfides. It should be kept in mind that these minor constituents amount at least 5% of the total, or sometimes more than 10-15% in practical slag. These decrease the dissolution of copper and sulfur considerably in comparison with the plain fayalite slag.

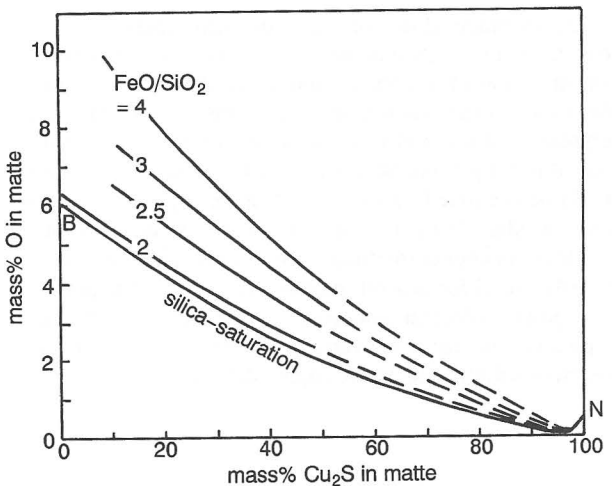

Fig.5. Effect of matte grade on the oxygen content in matte equilibrating with FeO-SiO_2 slag at various FeO/SiO_2 ratio. BN corresponds to silica saturation.

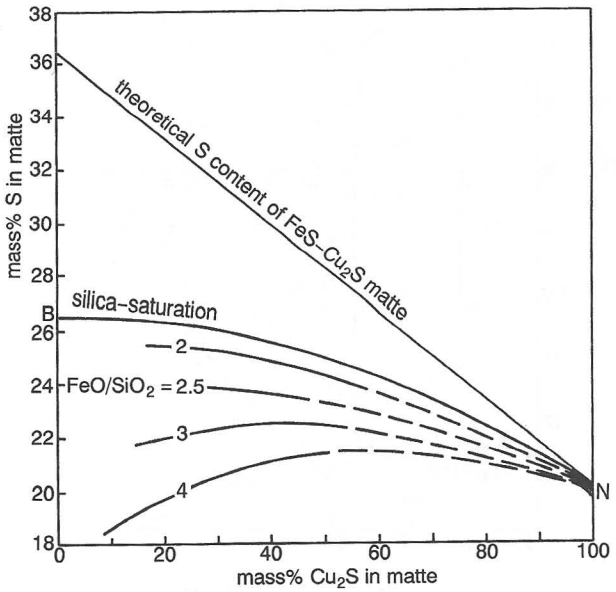

Fig.6. Sulfur contents in matte under same condition with Fig.5. Topmost straight line represents sulfur content in plain Cu_2S-FeS containing no FeO.

On the other hand, dissolution of FeO_n in matte is not seriously affected by the minor constituents, but is determined mainly by the matte grade(FeS in matte) and the activity of FeO_n (SiO_2 content of slag). The oxygen and sulfur contents of matte equilibrating with FeO-SiO_2 slag were determined experimentally[11], and summarized as shown in Figs.5 and 6. Decreasing SiO_2, or increasing basicity, results in increasing mutual solubility between matte and slag. Because of the increasing FeO in matte, the oxygen content of matte increases, while sulfur in matte decreases. The oxygen contents of matte in practice were found approximately on the line BN. It is clear from Fig.6 that the sulfur deficiency in matte compared with the stoichiometric Cu_2S-FeS melt is ascribable to the dissolution of FeO_n in matte.

As discussed above, the phase separation of sulfide-oxide mixture is caused primarily by the addition of SiO_2 to form silicate slag, but it will also be interesting to discuss the replacement of SiO_2 by CaO to form the ferrite slag. As shown some results in Fig.7[2], it was confirmed that the mutual dissolution between ferrite slag and matte is much larger than the case of silicate slag, and low grade matte is miscible with ferrite slag to form a homogeneous melt[12]. From the standpoint of melt structure, the FeS-FeO-CaO- Cu_2S forms covalent bonding, but with the addition of SiO_2, the ionic bonding is gradually becoming predominant. Accordingly, when thermodynamic discussions are carried out on the standpoint of molecular association, the existence of $CuS_{0.5}$ in slag must be accepted as well as $CuO_{0.5}$. It is clear that these molecules are not real species in molten slag, but the molecular expression is directly related with the phase diagram and thermodynamic data, and is more convenient for general discussion on the system including matte, silicate and ferrite slags.

3. DISSOLUTION OF COPPER AND SULFUR IN SLAG

Fig.7[1,2,12] shows the summary of the experimental results done in our laboratory on the dissolution of copper and sulfur in slags equilibrating with matte. The contents of Cu and S in silica-saturated plain FeO_n-SiO_2 slag under oxidative smelting conditions are illustrated with curves I. On the sulfur-oxygen potential diagram for Cu-Fe-S-O-SiO_2 system shown in Fig.8[10,13], curves I were obtained at around AB under a given SO_2 stream. Similar data but under reductive smelting condition with metal saturation corresponding to qrC' in Fig.8 are shown by curves II. Curves II are slightly lower than curves I probably due to the lower FeS content in matte as a consequence of the metal dissolution in matte. This means that the dissolutions of copper and sulfur in slag are not significantly affected by the oxygen and sulfur potentials when matte grade is below 70% where the oxygen potential does not change so much. From Fig.8, the p_{O2} at matte smelting temperature may be in the order of 10^{-8}-10^{-9} in oxidative smelting of curves I, and 10^{-11}-10^{-12} in reductive smelting of curves II. When slag constituents are considered on the basis of molecular association, most sulfur dissolved in slag exists as FeS.

The sinuous shape of the copper contents in curves I and II with peaks at around 30% Cu in matte may be understood as follows: The dissolution of $CuS_{0.5}$ in slag tends to increase with increasing $CuS_{0.5}$ in matte, but at the same time tends to decrease with decreasing FeS in slag. The shape of curve III represents the expected sulfidic copper loss. Drastic increases in the dissolved copper of curves I and II are observed after 70% Cu in matte where the oxygen potential increases suddenly and the oxidic copper dissolution becomes more predominant. Because the mutual dissolution between ferrite slag and matte is much higher than in the case of silicate slag, copper and sulfur contents of ferrite slag are also higher as shown by curve IV. The dissolved copper likewise shows a drastic sinuous form[10].

The results of curves I and II were obtained for plain fayalite type slag. The effects of CaO addition on copper and sulfur contents in silica saturated slag are illustrated by curves V and VI. As already shown in Fig.4, considerable reductions in both copper and sulfur dissolution are expected by the addition of CaO or Al_2O_3, but it will be noticed that the peaks similar to curves I and II disappear in curve V by the addition of only 3% CaO. As described above, the slags in practice are not plain FeO_n-SiO_2 slag, but contain a substantial amount of minor oxides of up to around 10% or so. Accordingly, the chemical dissolutions of copper and sulfur in practical smelting slags will be rather near to curve VI. Because the data of curve VI were determined under metal saturation at low oxygen potential, the copper content in practical slag equilibrating with more than 70%Cu matte will be higher than VI, probably like VI'.

As for practical smelting slag, the sulfur and copper contents are not so high, and one need not consider the peaks of copper as shown in curves I and II. Undoubtedly copper in slag exists as cuprous ion, and copper dissolution may be interpreted as a result of association of cuprous ion and sulfur ion. It is not proven, but complex ion species such as CuS^- might be presumed. However, when we explain the copper loss in slag from the standpoint of phase separation equilibria in copper smelting, simple ionic theory is not necessarily useful for general interpretation. From the practical standpoint, molecular association is preferable. In this case, copper loss in slag is conveniently explained by the combination of sulfidic and oxidic copper dissolutions.

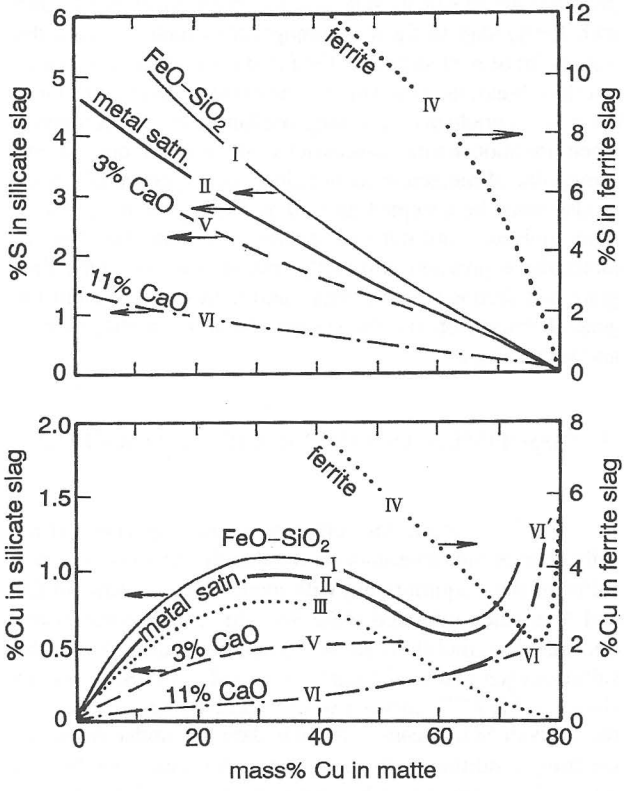

Fig.7. Copper and sulfur contents in silicate and ferrite slags plotted against equilibrating matte grade. Silicate slags are saturated with silica. Copper or sulfur content in slag obtained under the condition :
I : plain FeO-SiO_2 slag under oxidative matte smelting,
II : same in reductive matte smelting (metal saturation),
III : presumed sulfidic copper contents in I and II,
IV : equilibrating slag is calcium ferrite slag,
V : FeO-SiO_2 -3%CaO slag with metal saturation,
VI : FeO-SiO_2-11% CaO slag with metal saturation,
VI' : presumed copper content in VI under SO_2.

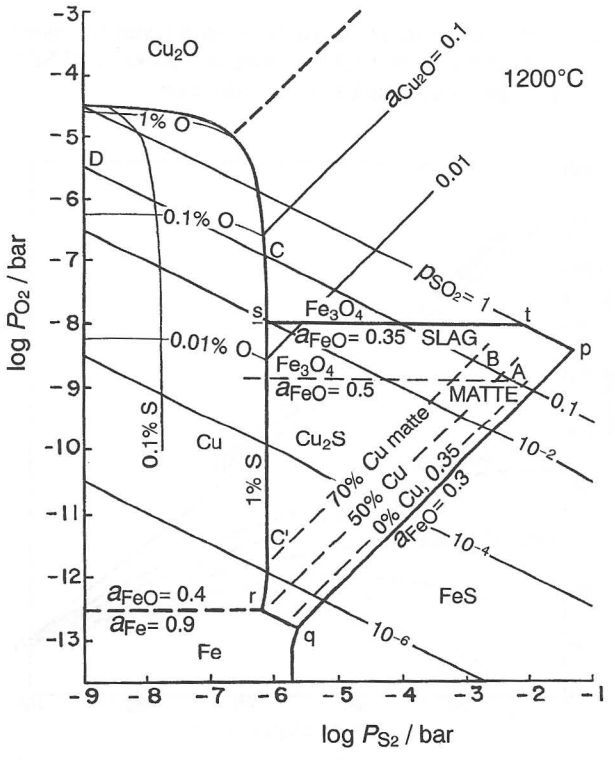

Fig.8. Sulfur-oxygen potential diagram for Cu-Fe-S-O-SiO_2 system at 1200°C.

4. COMPARISONS WITH OTHER LABORATORY DATA ON MATTE-SLAG EQUILIBRIA

Although there are not so many reliable data for direct measurements of matte-slag equilibria, there are many valuable data for simple systems, such as molten silicates, molten sulfides, or metal-slag systems. It is not our purpose to discuss these basic systems in the present paper, but one should be very careful to apply these basic data to the matte-slag equilibria. For example, the data obtained in liquid copper-slag system are valuable to discuss the copper loss in slag, but to apply them on matte smelting, it must be taken into account that the activity of Cu is in the order of $0.0x$ at the area of AB in Fig.8[10], and the quantitative evaluation of the interaction between dissolved copper and sulfur is not so easy. The precise data for Cu-Fe-S-O system were given by Kaiser and Elliott[14-16] and well reviewed by Gaskell et al.[17], but because of their experimental conditions, their data were given in many cases under too low SO_2 pressure and too high FeO activity(more than 0.5) to discuss matte smelting directly. In Fig.8, solid Fe_3O_4 separation lines are given at a_{FeO}=0.35(approximately silica saturation) and also at 0.5. Because of the higher FeO activity, they reported a higher oxygen(FeO_n) and lower sulfur contents in their matte in comparison with those obtained in silica saturated matte-slag equilibria as illustrated in Figs.5 and 6.

As suggested from Fig.8, copper smelting proceeds under limited conditions, and variations in p_{O_2}, p_{S_2}, p_{SO_2}, a_{FeO} (SiO_2 content) and a_{FeS} (matte grade) are intimately interrelated and difficult to change or designate independently. Recently, Simenov et al.[18,19] discussed copper smelting and derived sulfur and copper contents of slag under a fixed value of p_{S_2} equal to 10^{-2} or 10^{-3}. They combined this with p_{O_2} at around 10^{-10} which is too low for matte smelting under coexistence of substantial SO_2. As shown in Fig.8, oxidative matte smelting proceeds along the SO_2 isobar at around AB where p_{S_2} is really 10^{-2}-10^{-3} but is not a fixed value, and decreases even slightly with increasing matte grade and also with slightly increasing oxygen potential at 10^{-8}-10^{-9} under a fixed SO_2. When oxygen potential is reduced in the settling slag under coexistence of some matte, sulfur potential must also be decreasing.

Evaluations of dissolved copper in slag based on sulfidic and oxidic copper were reported by Sehnalek and Imris[20], Nagamori[21], Takeda[22] and also by the present authors[1,2] previously. Recently, similar ideas were discussed extensively by Nagamori[23] for many metals by use of the Flood-Forland-Grjotheim structure model, and were also adopted by Takeda and Roghani[24] to evaluate silver dissolution in slag. Shimpo et al.[25] and Nagamori confirmed the sinuous behavior of copper contents of plain fayalite slag in accordance with curves I and II in Fig.7. However, Davey and Willis[26], Gaskell et al.[17], Matousek[27] and Simenov et al.[19] do not accept the justification of the sulfidic-oxidic concept because of the lack of thermodynamic or structural background, and also sometimes because of their misinterpretation of the data given by Nagamori[21]. As previously described, the sulfidic-oxidic concept will be meaningless from the standpoint of ionic slag chemistry, but practically this concept is useful from the standpoint of molecular association. The sulfidic dissolution is reasonably understood based on not only chemical reaction thermodynamics but also on phase separation thermodynamics. Mutual dissolution between matte and slag must be always kept in mind when the concentrations of copper and sulfur in slag, or sulfur and oxygen in matte are discussed.

5. SIMULATION OF TERNARY PHASE SEPARATION

Some of the important examples of ternary phase separability or miscibility relating to matte-slag equilibria are already shown in Fig.2. The thermodynamic simulations of the ternary phase separation appearing in metallurgical systems were demonstrated previously[4,28] by use of binary regular solution data. Three ternary miscibility gaps derived in a similar manner are illustrated in Fig.9 where Cu_2S in Fig.2 is replaced by CaO because we have interests in ferrite slag and the shape of the miscibility gap in Cu_2S-FeS-FeO_n ternary is similar to those in Figs.9 (b) and (c). The value of binary α function defined by Eq.1 must be a fixed value in a regular solution, and is assumed as shown on each binary in Fig.9. The ternary miscibility gaps were derived from these α values by use of THERMOCALC[29].

$$\alpha = \ln \gamma_i / (1 - N_i)^2 \qquad (1)$$

$$a_i = \gamma_i \cdot N_i = (\gamma_i \cdot \%i) / (M_i \cdot n_T) \qquad (2)$$

where a_i and γ_i are activity and activity coefficient of component i, N is mole fraction, M_i is molar weight, and n_T is total mole number of 100 g of the phase. When α is more than 2, the activities deviate greatly in positive and the system has a miscibility gap as shown in Figs.9 (b) and (c), while large negative value of α suggests strong negative deviation to form intermediate compound as shown in (a).

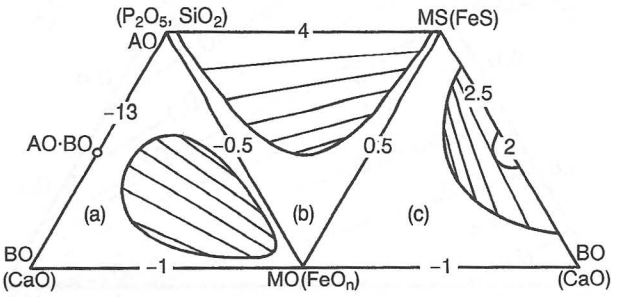

Fig.9. Assessments of ternary phase separability based on values of binary α function. Immiscibility between :
(a) : neutral oxide and strong intermediate compound,
(b) : silicate slag and matte,
(c) : ferrite slag and matte.

Fig.9(b) corresponds to (sulfide)-(iron oxide)-(acidic oxide), MS-MO-AO ternary such as Fig.1, and the miscibility gap represents the matte-slag equilibria. Fig.9(c) suggests the higher miscibility between matte and ferrite slag than in the case of silicate slag (b), due to the much higher miscibility of MS-BO binary than MS-AO binary in (b). Thus, as shown in Fig.7, dissolutions of copper and sulfur are much higher in ferrite slag than in silicate slag.

Fig.9(a) is oxide slag system consisting of acidic, basic and neutral oxides. Highly miscible ternary is expected from the negative values of α for all three binaries, but it should be noticed that rejective trend is existing between the neutral oxide and the intermediate compound AO.BO. As an extreme case, a large miscibility gap is observed as shown in Fig.9(a) or the FeO_n-P_2O_5-CaO system in Fig.2(a). The important metallurgical significance of such phase separability has been widely explained[4]. In the present paper, the phase separation will be discussed in relation to the oxidic metal loss in slag. The effect of such phase separability on the activity behavior in common metallurgical slag is simulated with the aid of THERMOCALC.

In Fig.9(a), if the α value in AO-BO binary is increased, the area of the ternary miscibility gap will decrease gradually until it disappears at a value beyond -10. The FeO_n-SiO_2-CaO system which is one of the most common ternary metallurgical slags corresponds to this case, and as shown in Fig.2(a), there is no miscibility gap observed, but the rejecting tendency between FeO_n and calcium silicate compound is suggested from the shape of the isotherm of the $2CaO.SiO_2$ liquidus.

As a model calculation, the activity behavior is illustrated in Figs.10 and 11 for the ternary MO-AO-BO slag assuming that $\alpha_{AO\text{-}BO} = -9$, $\alpha_{BO\text{-}MO} = 1$ and $\alpha_{MO\text{-}AO} = -1.2$. The iso-activity curves of AO and BO are illustrated in Fig.10, suggesting acceptable normal trends although the curves are reflecting the large negative deviation in AO-BO binary. However, the shapes of iso-activity curves of MO represent strong convexities near the tie line connecting MO and AO.BO as shown with solid curves in Fig.11. Similar behavior was confirmed in the iso-activity curves of FeO in the FeO-SiO_2-CaO system[4]. These are caused by the rejecting tendency or phase separability between neutral component and strong intermediate compound.

In Fig.11, the derived iso-activity coefficient curves are also illustrated with dashed lines, suggesting also strong convexities with opposite direction from solid lines. On this simple regular solution model, it is clear that when $\alpha_{BO\text{-}MO} = \alpha_{MO\text{-}AO}$, the curves in Fig.11 must be symmetric at the axis connecting between MO and AO.BO. Asymmetric curves are the result of the difference in these two α values, and an extreme case is shown in Fig.12 where $\alpha_{BO\text{-}MO} = 2$ and $\alpha_{MO\text{-}AO} = -5$.

6. SLAG COMPOSITION TO MINIMIZE METAL OXIDE CONTENT

It should be noticed that most nonferrous metal oxides XO dissolved in slag are also neutral components, and may be considered to exist by replacing FeO. Accordingly, as a

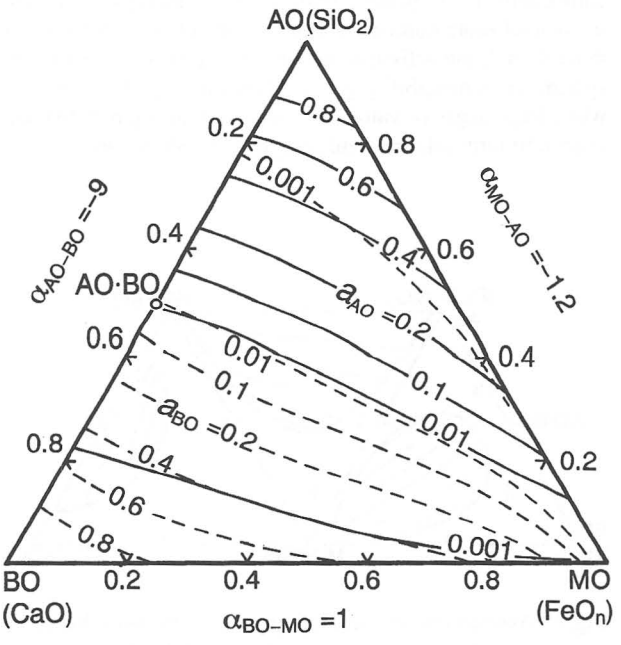

Fig.10. Iso-activity lines of acidic AO and basic BO in homogeneous liquid ternary derived from binary α values of -9, 1 and -1.2.

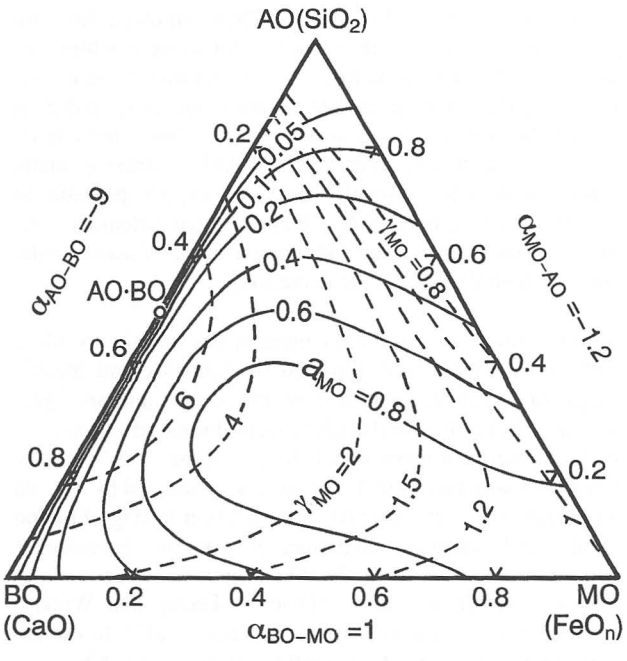

Fig.11. Contours of activity (solid lines) and activity coefficient (dashed lines) of neutral MO in the same ternary with Fig.10.

general trend, the activity behavior of nonferrous metal oxide XO in slag will be similar to those in Fig.11. It is well known that under a given condition, the metal oxide content in slag is inversely proportional to its activity coefficient as shown by Eq.(2). Thus, to decrease oxidic metal dissolution loss, the slag composition having higher γ_{XO} is preferable.

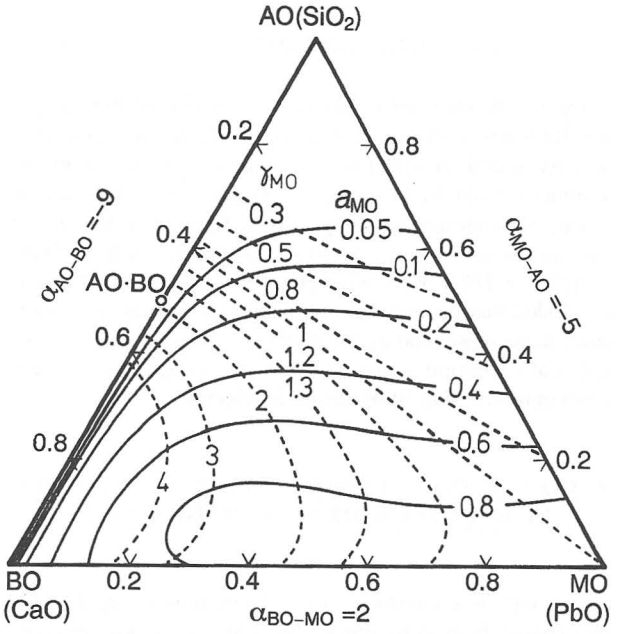

Fig.12. Contours of activity (solid lines) and activity coefficient (dashed lines) of basic MO derived from binary α values of -9, 2 and -5.

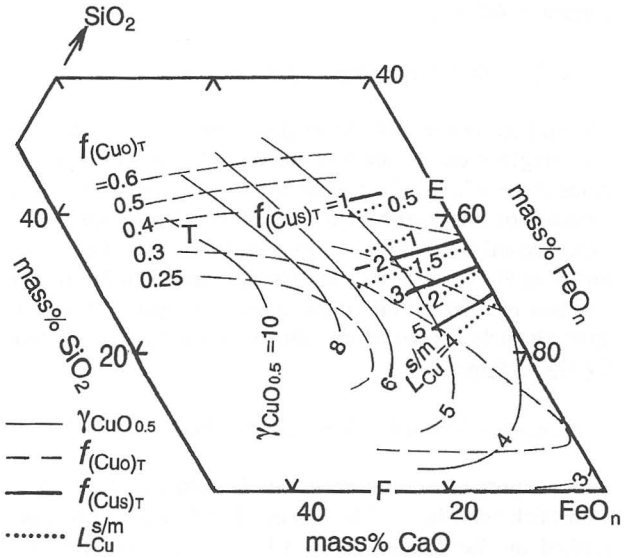

Fig.13. Contours for activity coefficient $\gamma_{CuO_{0.5}}$ (solid lines), total oxidic dissolution $f(Cu_O)_T$ (dashed lines), distribution ratio of sulfidic copper between slag and matte $L_{Cu}^{s/m}$ (dotted lines), and total sulfidic dissolution $f(Cu_S)_T$ (thick solid lines).

When the dissolution of XO in FeO_n- SiO_2- CaO slag is considered, it is clear from Figs.11 and 12 that, starting from the fundamental FeO-SiO_2 system, the addition of CaO is very effective to increase the value of γ_{XO} and to decrease the %XO in slag. The optimum composition of slag from this standpoint is located approximately on tie line connecting FeO_n and calcium silicate compounds where strong convexities are observed in the iso-activity coefficient curves.

These theoretically derived predictions derived based on phase separation thermodynamics are well proven by our experimental studies on metal-slag equilibria. Although the experimentally possible regions in the FeO_n-SiO_2-CaO system are limited as shown with liquidus lines in Fig.2(a), binary fayalite (FeO_n-SiO_2) slag E, binary ferrite(FeO_n-CaO) slag F, or ternary slag T were equilibrating with various metals and alloys. The activity coefficients of the metal oxides were derived as well as the dissolved oxidic metal contents.

The detailed discussions were given in previous papers[4,28], and some results are reproduced in Figs.13 and 14. In Fig.13[30] the iso-activity coefficient curves of $CuO_{0.5}$ with solid lines show similar tendencies with those in Fig.10. Similar behavior of the activity coefficients showing the peak in the middle of ternary FeO_n- SiO_2-CaO slag was confirmed also for other neutral oxides such as ZnO, SnO, NiO, as well as FeO. An exception is PbO whose peak is located not on the middle of ternary slag but at near the binary calcium ferrite slag. This phenomenon is reasonably explained by the fact that PbO is not neutral but rather a basic oxide that has strong affinity with SiO_2, while rejecting CaO. The activity behavior in this case is illustrated in Fig.12, and the strong convexities are found just near the binary FeO_n-CaO system.

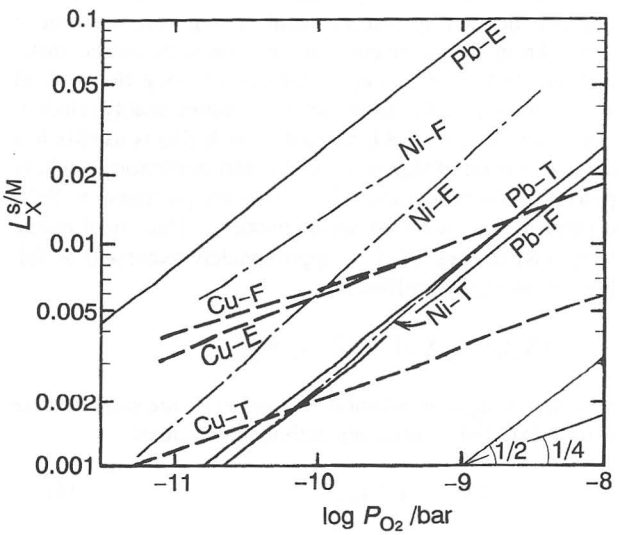

Fig.14. Distribution ratios of copper, nickel and lead between iron oxide slag and liquid metal in relation to oxygen potential at 1300°C. E : plain binary fayalite slag, F : binary calcium ferrite slag, T : ternary slag with CaO/SiO_2= 1.

In Fig.14, the distribution ratios of Cu, Ni and Pb between slag and metal phases, $L_X^{S/M}$ = (%X in slag)/[%X in metal], are plotted against log p_{O_2} for binary fayalite(E), binary ferrite (F) and ternary(T) slags. Reflecting the behavior of activity coefficients, the metal contents in slag T are the lowest. Much higher copper and nickel values are observed in the binary slags E and F. Similar tendencies were confirmed for FeO_n, CoO, ZnO and SnO. Again in the case of basic PbO, the minimum dissolution of lead is observed in ferrite slag F in agreement with the activity behavior of Fig.12. Accordingly, ferrite slag is effective to recover lead in metal, but not convenient for oxidation removal of lead into slag phase.

While this is not directly related with the phase separation thermodynamics, Fig.14 gives another useful information. Because copper is monovalent, the slope of the distribution ratio lines is not as steep in comparison to the divalent metals. Accordingly, in the reductive smelting of mixed oxides of copper, nickel and lead, copper is first reduced into metal at the initial stage. After a while, nickel reduction takes place under nearly constant copper content in slag. Thus, under strong reducing condition, complete removal of copper from slag is more difficult than nickel. Also because copper is monovalent, temperature dependence of copper distribution between metal and slag is not significant, and at higher temperature as in ferro-nickel smelting, reduction of copper will be more difficult than nickel, or even cobalt[31].

7. TOTAL LOSS OF DISSOLVED METAL TAKING ACCOUNT OF SLAG AMOUNT

It is well known in practice that the total metal loss in slag is expressed by percent metal in slag times amount of slag. From above discussions, to minimize oxidic metal content, (%X_O), the slag composition having the peak of γ_{XO} is preferable due to the inverse proportionality relationship. However, the FeO_n content in such slag is usually low and the amount of slag is large. In most nonferrous smelting processes, the slag amount V is inversely prortional to FeO_n content in slag as a first approximation. Thus, total oxidic metal loss in slag, $(X_O)_T$ is approximately expressed as follows by using the coefficient c,

$$(X_O)_T = (\%X_O)V = c\,/[\gamma_{XO} \cdot N_{FeO}] \qquad (3)$$

It is interesting to note that if XO and FeO_n are similar to the neutral oxide MO including activity coefficients,

$$(X_O)_T = c\,/\,a_{MO} \qquad (4)$$

that is, roughly speaking, total oxidic metal loss is inversely proportional to the activity of the metal oxide. Thus, in Fig.11, the iso-activity curves correspond approximately to the contours of the total oxidic metal loss.

To evaluate the total metal loss in practice, Eq.(4) is too ideal, and Eq.(3) may be rewritten by the use of the activity coefficient derived from experimental data :

$$(X_O)_T = c'\,/[\gamma_{XO}\,(\%FeO)] \qquad (5)$$

Thus, the following function is available as a measure of the total oxidic metal dissolution in slag. It is easily calculated and illustrated on the ternary FeO_n-SiO_2-CaO system.

$$f(X_O)_T = 100\,/[\gamma_{XO}\,(\%FeO)] \qquad (6)$$

In Fig.13, the contours of $f(Cu_O)_T$ derived from the $\gamma_{CuO_{0.5}}$ are illustrated with the dashed lines. These contours must be very useful in selecting the slag composition with the minimum oxidic loss of metal. To discuss total loss of zinc in zinc blast furnace smelting, similar figure was derived for zinc on the ternary ΣFeO-SiO_2-CaO system[32], where ΣFeO = %FeO + 10%ZnO + 8%Al_2O_3. From these results, it is concluded that decreasing SiO_2 content is of primary importance to decrease total dissolution loss of oxidic metal in slag, and CaO addition is not always but sometimes efficient when optimum slag composition is selected.

8. CONTOURS OF SULFIDIC COPPER DISSOLUTION IN SLAG EQUILIBRATING WITH MATTE

It will be interesting now to know how to regulate the slag composition to minimize the total sulfidic loss in matte smelting slag. Unfortunately, the available systematic laboratory data are limited. Equilibrium experiments between FeO_n-SiO_2-CaO slag and 30%Cu matte were carried out by using an iron crucible[33]. From the obtained data , the distribution ratio of copper between slag and matte is defined in percent as follows:

$$L_{Cu}^{s/m} = 100(\%Cu \text{ in slag}) \,/\, \{\%Cu \text{ in matte}\} \qquad (7)$$

The sulfidic copper will be predominant in slag under this low oxygen pressure and low matte grade. When the matte grade is 30%Cu, $L_{Cu}^{s/m}$ is equal to 3.3 (%Cu in slag). The contours of this distribution ratio obtained from the above experimental conditions are illustrated along the FeO_n-SiO_2 binary in Fig.13 with the dotted lines. Similar to Eq.(6), the function of total sulfidic dissolution of copper, $f(Cu_S)_T$, is approximately expressed as follows by taking into account the slag volume V:

$$f(Cu_S)_T = c''(\%Cu)V = 100(L_{Cu}^{s/m}) \,/\, (\%FeO) \qquad (8)$$

The contours of this function are also illustrated in Fig.13 with thick solid lines. The values of $L_{Cu}^{s/m}$ and $f(Cu_S)_T$ described on the contours in Fig.13 are derived from the slag-30%Cu matte equilibria. It must change depending on the matte grade, but the tendencies of sulfidic loss of copper are estimated from these lines.

Now, it is interesting to note in Fig.13 that the effects of slag compositions on the dissolution loss of copper are quite

different between oxidic and sulfidic dissolutions. As suggested from the contours of $f(Cu_O)_T$ in the common ternary region, total oxidic copper loss decreases as a whole with decreasing SiO_2 content. This tendency is also similar to the oxidic losses of other metals, and the slag with low SiO_2 is preferred in many reductive smelting of oxide as long as the melting point is low enough. Inversely, as shown from the contours illustrated along FeO_n-SiO_2 binary in Fig.13, the sulfidic copper loss decreases with increasing SiO_2 content in slag. Moreover, judging from the degrees of change in $f(Cu_O)_T$ and $f(Cu_S)_T$ caused by a given change in $\%SiO_2$, the effect of SiO_2 content is much larger for sulfidic copper loss than oxidic loss.

In the practical matte smelting , it is usually observed that copper content of slag decreases with increasing SiO_2 content because sulfidic copper is predominant in matte smelting slag. However, as described in section 3, oxidic copper dissolution is becoming predominant when the matte grade goes beyond 70% because of the drastic increase in oxygen potential. Here the slag low in SiO_2 is preferable. Thus, on the basis of long practical experience, copper smelting is divided into two steps, and the high SiO_2 slag is used in matte smelting, while low SiO_2 is preferred as the slag in the converting stage.

There exist various controversial opinions for the effect of CaO on the metal loss in slag. From Fig.13, if we use CaO addition in unsuitable way, the total metal loss could be increasing. When CaO addition starts from plain binary FeO_n-SiO_2 slag, increase in CaO at a fixed FeO content or FeO/SiO_2 ratio will be convenient to decrease total oxidic metal loss, but those routes may not be helpful to reduce sulfidic copper loss in matte smelting. Increasing the SiO_2 content in slag is the most efficient way to decrease the sulfidic copper loss, but it often results in slag with high viscosity and high melting point. To overcome these difficulties, a little CaO addition under an increasing SiO_2 content may result in decreasing the sulfidic copper loss in slag.

9. CONCLUDING REMARKS

Extractive metallurgy consists essentially of two steps; chemical reaction followed by phase separation. There are many excellent papers on chemical reaction thermodynamics to evaluate metallurgical processes, but the lack of understanding from the viewpoint of phase separation thermodynamics sometimes brings about confusion and misunderstanding in the process analysis of extractive metallurgy. Controversial discussion on dissolution of valuable or detrimental elements in slag seems to be a typical example. General principles of oxidic metal dissolution or oxidation removal of impurity metals are well accepted by metallurgists, but when the effect of slag composition is discussed, the viewpoint of phase separability or miscibility is indispensable.

Sulfidic metal dissolution in slag, such as CaS, FeS, MnS, etc., may be also acceptable when we discuss the behavior of sulfur in slag on the standpoint of molecular association. In oxidative copper smelting, the concentrate is first brought into a homogeneous molten phase of Cu_2S-FeS-FeO_n containing small amount of SiO_2, but gradually separate into matte and slag with the increase in SiO_2 content. During this stage, some Cu_2S associates with the dissolved FeS which could amount to at least a few percent in matte smelting slag. Dissolution of these sulfides must be understood on the basis of phase miscibility or separability between matte and slag as well as effect of chemical potentials such as p_{S_2} and p_{O_2}. In copper smelting the sulfidic form is the predominant dissolved copper in slag during matte smelting stage, but at higher matte grade, especially beyond 70%Cu, oxidic copper dissolution becomes predominant along the drastic increase in oxygen potential. It should be noticed that sulfidic copper dissolution can decrease with the increasing SiO_2 content of slag. And not only for copper but also for most common metals, the total oxidic metal dissolution decreases with decreasing SiO_2 content.

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