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Thermodynamic Factors Affecting The Matte–Slag System

Mutalibkhonov S.S.[1]

[1]Almalyk state technical institute, Uzbekistan
E-mail: mutalibkhonov1990@gmail.com

Abstract *— The matte–slag system plays a crucial role in copper smelting processes by controlling phase equilibria, metal distribution, and thermodynamic stability within the Cu–Fe–S–O–SiO_2 system. This study analyzes the thermodynamic factors affecting phase interactions in copper smelting furnaces, including temperature, oxygen potential, sulfur potential, and phase composition. The behavior of matte, slag, metal, and gas phases was evaluated using Gibbs phase rule principles and phase equilibrium concepts. The results indicate that variations in sulfur–oxygen potential significantly influence the stability of sulfide and oxide phases, thereby affecting copper and iron distribution between matte and slag. The non-ideal behavior of slag melts and activity coefficient*

s were found to be essential parameters governing phase transformations and metallurgical performance. The developed thermodynamic approach provides a theoretical basis for understanding physicochemical processes occurring during copper smelting and contributes to the optimization of furnace operation, metal recovery, slag quality, and overall process efficiency in modern pyrometallurgical technologies.

Keywords*:* Copper smelting; matte–slag system; thermodynamics; phase equilibrium; sulfur–oxygen potential; Gibbs free energy; copper slag; pyrometallurgy; Activity coefficient; Cu–Fe–S–O–SiO_2 system.

1. INTRODUCTION

Copper Smelter of the Almalyk Mining and Metallurgical Complex (AMMC JSC), one of the largest copper producers in Central Asia, generates substantial quantities of copper smelting slag as a by-product of pyrometallurgical operations. These slags are predominantly composed of fayalite (Fe_2SiO_4), magnetite (Fe_3O_4), silica-based phases, and residual sulfide and metallic particles. The physicochemical behavior of the matte–slag system directly affects copper recovery, iron distribution, slag viscosity, and metal losses during smelting [1].

Understanding the thermodynamic factors governing the matte–slag equilibrium is therefore essential for improving process efficiency and reducing valuable metal losses to slag. In industrial conditions, the stability of sulfide and oxide phases is controlled primarily by temperature, sulfur potential, and oxygen potential. Variations in these parameters influence the formation of matte, slag, metallic phases, and gas products, ultimately determining the performance of smelting furnaces [2].

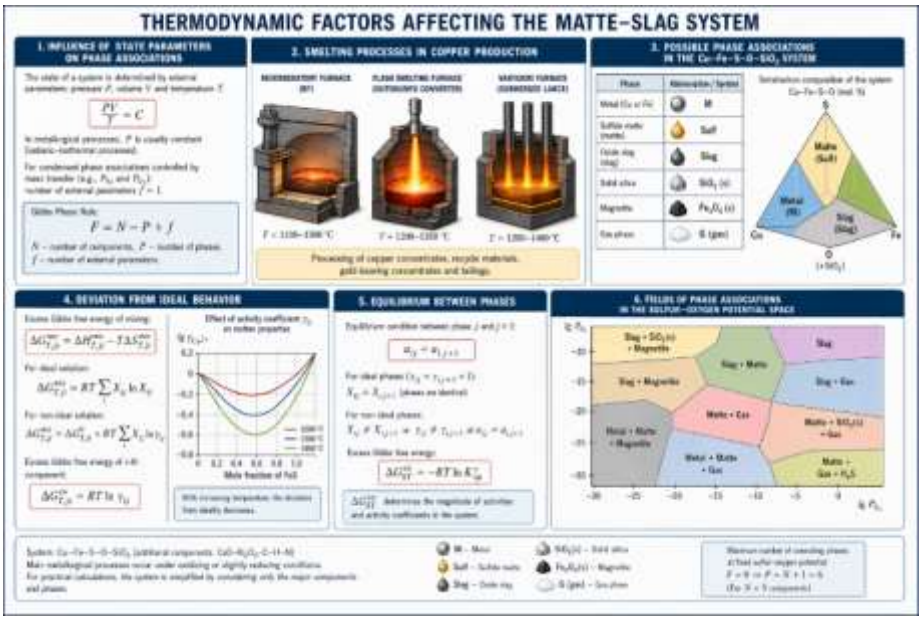

Figure 1. Thermodynamic factors to the matte-slag system

Given the increasing interest in slag valorization, iron recovery, and sustainable metallurgical processing, a detailed thermodynamic assessment of the Cu–Fe–S–O–SiO_2 system is required [3]. Therefore, this study investigates the thermodynamic factors affecting the matte–slag system and evaluates their influence on phase equilibria, metal distribution, and process performance under conditions relevant to copper smelting slags generated at AMMC. At the pyrometallurgical stage of the copper production technological chain, three smelting furnaces — Vanyukov, Inco Flash smelting and Reverberatory to convert solid dry sulfide charge into liquid matte at high temperatures, processing copper concentrates, circular materials, gold-bearing fluxes, dust and cakes [4].

The physical properties of these alloys in smelting furnaces (VF, FF and RF) directly affect the main parameters of metallurgical processes. The physical properties of the melt (F) are functions of the composition of the investigated phase and external parameters that determine the state of the system, usually P,T.

2. MATERIALS AND METHODS

A thermodynamic analysis of the matte–slag system was carried out within the Cu–Fe–S–O–SiO_2 system framework. The study considered the interactions among metallic, sulfide, oxide, and gaseous phases commonly encountered during copper smelting operations. The equilibrium behavior of the system was evaluated using Gibbs phase rule principles and classical solution thermodynamics [5].

The effects of temperature, sulfur potential ($lgPS_2$), oxygen potential ($lgPO_2$), and phase composition on phase stability were analyzed. Both ideal and non-ideal solution models were considered to assess deviations from equilibrium behavior. The activities and activity coefficients of individual components were used to describe the thermodynamic state of matte and slag melts.

The phase associations existing under different sulfur–oxygen potential conditions were identified, and their equilibrium relationships were evaluated through chemical potential equality criteria. Thermodynamic factors affecting matte–slag interactions, including excess Gibbs free energy, phase stability, and melt composition, were systematically examined. The obtained results were interpreted to determine the influence of external and internal thermodynamic parameters on copper smelting performance, metal distribution, and slag formation mechanisms [6].

3. RESULTS

The thermodynamic analysis revealed that the matte–slag system is strongly influenced by temperature and sulfur–oxygen potential. Variations in $lgPS_2$ and $lgPO_2$ significantly altered the stability regions of sulfide, oxide, and metallic phases within the Cu–Fe–S–O–SiO_2 system. Under increasing sulfur potential, the stability of copper and iron sulfides increased, promoting matte formation, whereas increasing oxygen potential favored the formation of oxide phases such as FeO, Fe_3O_4, and silica-rich slag [7].

The results indicate that matte, slag, metal, and gas phases can coexist in equilibrium depending on process conditions. Non-ideal behavior of slag melts was found to play a critical role in determining phase compositions and component distributions. Activity coefficients and excess Gibbs free energy contributed significantly to deviations from ideal solution behavior, affecting phase boundaries and equilibrium conditions [8].

Furthermore, the analysis demonstrated that thermodynamic parameters directly influence copper losses to slag, iron oxidation behavior, and slag composition. Control of sulfur–oxygen potential enables optimization of phase equilibria, leading to improved copper recovery and more stable furnace operation. These findings highlight the importance of thermodynamic modeling for understanding complex phase interactions and enhancing the efficiency of modern copper smelting processes.

The equilibrium in the phase association participating in the given system and the associated phase equilibrium within it have been considered within the framework of the traditional approach until now. In this approach, the state of the system is determined by state parameters [9].

The state parameters that determine the external impact on the system are pressure, volume, and temperature (P, V, T). Since these parameters are related by the PV/T = C equation, only two are considered, usually P and T, which characterizes the isobaric-isothermal nature of the processes occurring in the phase association. The Gibbs phase rule F = n-m+f is applied in this case at f = 2, depending on the number of external state parameters [10].

If the phase association is considered as an association of condensed phases, the state of which is determined by mass exchange parameters, for example, lgPS2 and lgRO2, the pressure can be ignored. In this case, f = 1 [1]. However, other external influences can also affect the phase association, which can be conventionally taken as state parameters. In this case, f > 2. If any additional factor acts on the phase association, either its number of degrees of freedom increases by one, or an additional phase appears within its composition. In thermodynamics, phase refers to a homogeneous mixture or solution of components bounded by a separation surface with other phases [1][11]. Any j-th phase, except for mass, is characterized by the set of components {Xij}, where Xij = 1. A phase that obeys the laws of non-ideal solutions is also characterized by {aij} or {γij}.

A solution (melt) of i-components is characterized by an excess Gibbs free energy of mixing.

$$\Delta G_{Tji}^{sm} = \Delta H_{Tji}^{sm} - \Delta S_{Tji}^{sm}$$

For an ideal solution consisting of i-components (j-phase),

$$\Delta G_{Tji}^{sm} = \sum X_{ji} \ln X_{ij}$$

For a non-ideal solution

$$\Delta G_{Tji}^{sm} = \Delta G_{Tj}^{0} + \sum X_{ji} \ln \gamma_{ij}$$

An ideal solution as the standard state (γij=1). Then for a non-ideal solution, the deviations from ideality are determined by the excess Gibbs free energy for the i-th component (〖ΔG〗 _Tji^(exc.sm)). For the case f=2 (only P and T are taken into account as state parameters), the Gibbs free energy excess of the phase coincides with the free energy excess of the mixing, i.e. $\Delta G_{Tji}^{exc.sm} = \Delta G_{Tji}^{sm}$.
For an ideal solution

$$\Delta G_{Tji}^{excess} = \Delta G_{Tji}^{excess} = 0.$$

Since

$$\Delta G_{Tji}^{excess} = \Delta G_{Tji}^{excess} = RT\ln\gamma_{ij} \quad (\gamma_{ij} = 1).$$

The existence of equilibrium phase association implies the presence of several phases that are in equilibrium with each other. The equilibrium of two phases implies the equality of chemical potentials in them for each i-th component, and consequently, the equality of activities for each i-th component [12]. The equilibrium condition for the j-th and j+1th phases is aij = aij+1. If both phases are perfect, then it follows that under

$$\gamma_{ij} = \gamma_{ij+1} = 1,\ X_{ij} = X_{ij+1}.$$

Under conditions of identity for j and j+1 phases and, consequently, complete equality of concentrations in two condensed phases at f=2, these phases are identical or considered as a single phase, even if divided into several parts. The above is true only when the j and j+1 phases are in the same state. If there are two phases in equilibrium that obey ideal laws, then their aggregate states are different, but in this case, it is necessary to consider the heat of transition from one aggregate state to another as a state parameter and f=3, if the degree of transition of one phase to another is considered as a degree of freedom. From this, it follows that two ideal phases with the same set of components in the same state cannot exist in equilibrium [13].
To identify phases that are in the same aggregate state and are not ideal (establishing that these phases are not one phase), it is required that the condition for at least one i be met. Xij ≠ Xij+1. under equilibrium conditions, or γij ≠ γij+1 when aij= aij+1
The condition γij= 1 (ideality condition) can be fulfilled only for one of the phases,
participating in equilibrium in the phase association [14].
Accounting for deviations from ideality can be carried out in two ways. Let the reaction S be possible in the j-th phase:

$\Delta G_T^o = -RT\ln K_{sp}^c$ (for the ideal phase of the Kc-constant for concentration),

$\Delta G_{ST}^o = -RT\ln K_{sp}^a = -RT\ln K_{sp}^c K\gamma_{sp}$. (where Kγ- the activity complex for the S-reaction LS),

The value — R T ln Kγ s p — corresponds to some value of ΔGST, which determines the deviation from ideality. This value is called the excess Gibbs free energy (ΔG_ST^ex) for the S-reaction in the j-phase, which determines the activity values and activity coefficients [2]. The ideal phase in this case is considered standard. In this case, the formula is valid.

$$\Delta G_{ST} = \Delta G_{ST}^{o} + \Delta G_{ST}^{excess} = -RT\ln K_{ST}^{c} \text{ or } \Delta G_{ST}^{excess} = -RT\ln K\gamma,$$
$$\Delta G_{ST}^{0excess} = \Delta G_{S}^{excess} + T\Delta S_{ST}^{excess}.$$

With a sufficiently high degree of reliability, it can be considered that the technological processes of copper production occur in phase associations within the Cu-Fe-S-O-SiO_2 system, which can be supplemented with CaO-Al_2O_3-C-H-N [15].
Meltings containing Mg, Na, K, P, Cr, Ti, As, Si, and other elements participate in the real technological process. The complete quantitative accounting of all elements and compounds is currently a practically insoluble task due to the lack of necessary thermodynamic data. Therefore, it is necessary to introduce separate simplifications and consider only the main components. During the physicochemical analysis of the presented system, it is considered that the physicochemical processes occur under oxidative or weakly reducing conditions. In this case, the dissociation of SiO_2, CaO, Al_2O_3, and their reduction or sulfidization can be neglected. Subsequently, when presenting certain issues, this restriction may be removed.

The main components of the system under consideration are: metals, their sulfides, and oxides, which form independent phases. Components include Cu, Cu_2S, Cu_2O, Fe, FeS, FeO, Fe_3O_4, Fe_2O_3, SiO_2, Si, CaO, $A1_2O_3$, C, CO, H2, H_2O, S, SO_2, SO, H_2S,

N_2, O_2. Research has shown that in this system, under conditions corresponding to melting for matte, the following phases can take place: metal, sulfide alloy (matte), oxide alloy (slag), and gas phase [16].

For simplicity, let us consider the Cu-Fe-S-O-SiO2 system. The region of existence for various phase associations in it can be established within the boundaries of different values of the sulfur-oxygen potential. The total number of components in the system is -5. Phase associations can include metallic phases based on copper or iron; the sulfide-stain phase and the oxide-slag phase. Furthermore, as a result of the heterogenization of oxide alloys within a temperature range corresponding to the temperature range of technological processes, two solid phases can exist: silicon dioxide and magnetite. Given the gas phase, phase associations may include 4 liquid, 2 solid, and 1 gas phases, with a total number of phases of 7.

When the number of components is 5, under the conditions of fixing the sulfur-oxygen potential, the equation for determining the number of degrees of freedom has the form FS=Nk-Nf+1, where FS = NK – NF + 1. The use of the Gibbs equation for the degree of freedom F = n - m + f for f = 1 and not for f = 2 is related to the accepted method of accounting for the influence of external factors. In a system, no more than 6 phases can simultaneously exist in equilibrium, i.e., phase associations with a maximum number of phases are six-phase. A diagram of the existence of various phase associations for the Cu-Fe-S-SiO_2-O_2 system in coordinates constituting the sulfur-oxygen potential was compiled by Yazava [2][3][17].

Thus, in the case where the total number of co-existent phases in the phase association is FC = 0, it increases to 7, i.e., two metallic phases can coexist in the system. This is confirmed by data regarding the presence of stratification in the Cu-Fe-C system. The boundaries of phase existence in the coordinates of the sulfur-oxygen potential for strongly reducing conditions in the presence of carbon have not been studied.

4. DISCUSSION

The obtained thermodynamic analysis demonstrates that the behavior of the matte–slag system is primarily governed by sulfur potential, oxygen potential, and temperature. These parameters collectively determine phase stability, metal distribution, and the physicochemical properties of the molten phases. The results indicate that increasing sulfur potential promotes the stability of sulfide species, particularly Cu_2S and FeS, thereby enhancing matte formation. In contrast, elevated oxygen potential favors the formation of oxide phases such as FeO and Fe_3O_4, leading to increased iron oxidation and greater incorporation of iron into the slag phase.

The calculated phase relationships reveal that the coexistence of matte, slag, metallic, and gaseous phases is highly sensitive to changes in thermodynamic conditions. This observation is consistent with previous studies on copper smelting systems, which reported that even minor variations in oxygen potential can significantly affect copper losses to slag and the overall metal recovery efficiency. Consequently, precise control of oxygen partial pressure remains a critical requirement for optimizing industrial smelting operations.

Another important finding is the strong influence of non-ideal solution behavior on phase equilibria. The activity coefficients of major components differ considerably from unity, indicating substantial deviations from ideality in both matte and slag melts. These deviations alter chemical potentials and shift equilibrium boundaries, making activity-based thermodynamic calculations more reliable than concentration-based approaches for predicting industrial process behavior.

The analysis further suggests that the Fe–Si–O subsystem plays a key role in determining slag characteristics. The formation of fayalite-rich slag contributes to the stability of the oxide phase and influences viscosity, density, and metal settling behavior. Excessive fayalite formation may increase copper entrainment in slag, whereas controlled slag chemistry can improve matte–slag separation and enhance copper recovery.

Overall, the results confirm that thermodynamic modeling provides valuable insight into phase interactions within the Cu–Fe–S–O–SiO_2 system. A comprehensive understanding of sulfur–oxygen potential relationships, phase stability, and non-ideal melt behavior can contribute to improved furnace control, reduced metal losses, enhanced process efficiency, and the development of more sustainable copper smelting technologies.

CONCLUSIONS

The thermodynamic behavior of the matte–slag system is governed by the complex interactions among sulfide, oxide, metallic, and gaseous phases within the Cu–Fe–S–O–SiO_2 system. Analysis of phase equilibria demonstrates that temperature and sulfur–oxygen potential are the principal factors controlling phase stability and metal distribution during copper smelting. The application of Gibbs phase rule and activity-based thermodynamic models provides a reliable framework for describing equilibrium conditions in both ideal and non-ideal melts. The study confirms that deviations from ideality significantly influence phase composition, activity coefficients, and metallurgical performance. Furthermore, the coexistence of matte, slag, metal, and gas phases determines the efficiency of copper recovery and the physicochemical properties of the resulting slag. Understanding these thermodynamic relationships is essential for optimizing smelting operations, reducing metal losses, and improving process sustainability. The obtained results contribute to the development of more efficient copper production technologies and provide a theoretical foundation for future investigations of complex metallurgical melt systems.

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