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Modelling of copper matte smelting process with improved equilibrium constant method

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Abstract: An initialization-improved equilibrium constant method was used for modelling the copper matte smelting process with flash technology. Initial molar amounts of species were calculated by distributing the amounts of given elements. The species containing the largest amount of one element was chosen to be the corresponding thermodynamic component. The equilibrium values were derived via the Newton−Raphson method and converted to industrial forecast values using the mechanical entrainment equations. The results indicate that the calculated equilibrium value for copper concentration in the slag is 0.32 wt.%, while the industrial forecast value is 1.03 wt.%, with the industrial value being 1.13 wt.%. The present model required only 31 outer loops to derive the approximate solution close to the equilibrium value. The iterative path during the computation is considerably reduced and the risk of non-convergence during the computation is decreased.

Key words: initialization; molar Gibbs energy; thermodynamic component; iteration; equilibrium value; mechanical entrainment

1 Introduction

The global demand for copper has continued to increase with the developing economy [1,2]. However, the grade of available copper concentrate is gradually decreasing [3]. Moreover, secondary resources such as waste electrical and electronic equipment [4,5] are used as copper-bearing resources, which contain hazardous minor elements, such as zinc, arsenic and lead that can enter the reactor in the feed mixture, and generate large quantities of hazardous waste [6−8]. Copper matte smelting is carried out at elevated temperatures and closed reactors, making it difficult to obtain real-time distribution data for hazardous elements in products like copper slag [9], copper matte [10], or exhaust gases [11]. Hence, the phase transition and distribution behavior of each species is evaluated via theoretical calculations.

Copper matte smelting involves a complex, heterogeneous, multicomponent system, with heat and mass transfer often acting as limiting factors in process dynamics, and the degree of advancement governed by thermodynamics within intensive processing reactors. Thermodynamic models are highly suitable for modeling the copper matte smelting process. Establishing a thermodynamic model

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for the copper matte smelting process is primarily based on the Gibbs energy minimization [12,13] or equilibrium constant [14] methods. Both these methods are presumed to be in thermodynamic equilibrium and considered equivalent in thermodynamics. GOTO [15] used the equilibrium constant method to develop a thermodynamic model, whereas ERIKSSON and HACK [16] used the Gibbs energy minimization method for the copper matte smelting process. TAN and ZHANG [17] and WANG et al [18] further incorporated the impurity elements present in the copper concentrate into the thermodynamic models based on the equilibrium constant and Gibbs energy minimization methods, respectively. However, their reports were silent on the selection of the thermodynamic components. Moreover, in systems with significant differences in composition, the use of simplified activity coefficient models, such as the dilute solution approach that is not obeying the Gibbs−Duhem equation, poses a high risk of non-convergence during the solving process. Modeling the copper matte smelting process with the classical equilibrium constant method necessitates the imposition of numerous additional mathematical constraints [17], thereby inevitably complicating the modeling task.

The general principle of selection and derivation of the thermodynamic components was presented by BRINKLEY [19] and KANDINER and BRINKLEY [20], according to which, the array of selectable thermodynamic component combinations increases considerably with the increase in the number of elements and components within the system. However, not all combinations prove to be viable for the given chemical system owing to constraints posed by thermodynamic data and boundary conditions. Therefore, the selection of appropriate thermodynamic components implies an improvement in the convergence of the iterative calculation. Further, the initial molar amount should be reasonably close to the equilibrium composition to minimize the loop iteration, thereby reducing the risk of non-convergence and enhancing the computational efficiency. Using the C−H−N−O gas phase system, HEALD [21] reported an initialization-improved Gibbs energy minimization method in which each species was assigned an initial value close to the equilibrium composition, and appropriate thermodynamic components were captured. Only a small number of iterative calculations were required to reach equilibrium, greatly reducing the risk of non-convergence in the model solution. SHIMPO et al [22] employed the same initialization method to improve the classical equilibrium constant method and calculated the equilibrium composition of the C−S−O gas phase system. However, the situation is much more complex for pyrometallurgy, as the reaction system is heterogeneous and the activity coefficients are no longer constants. Currently, there is still a gap in applying this initialization method to thermodynamic models of metallurgical processes [17,18,23−25].

Therefore, in this study, HEALD's initialization method [21] was extended to modeling the equilibrium constant method for the copper matte smelting process. The equilibrium values were converted into industrial forecast values using mechanical entrainment equations. The industrial forecast values were compared with the industrial values to verify the validity of the present model. The initial molar amounts for a majority of species closely approximate their equilibrium values. The number of iterations required to reach equilibrium was considerably low in this model, highlighting the advantages of the improved initialization.

2 Classical equilibrium constant method

In the equilibrium constant method [19,20], it is usually assumed that the entire system is in equilibrium.

Many combinations of chemical reactions among chemical species are possible. If the number of different elements in the system is N_a and that of chemical species is N_c, and then the number of independent reactions is expressed as $N_b=N_c-N_a$, therefore, the N_c-N_a reactions which produce N_c-N_a derived constituents out of the N_a thermodynamic components can be represented in terms of matrices as

$$\boldsymbol{V}_{j,i}\boldsymbol{A}_{i,k}=\boldsymbol{B}_{j,k} \quad (i\in[1,N_a], j\in[1,N_b], j\in[1,N_a]) \tag{1}$$

where $\boldsymbol{A}_{i,k}$ and $\boldsymbol{B}_{j,k}$ respectively are the elemental matrices of thermodynamic components and derived constituents; $\boldsymbol{V}_{j,i}$ is the matrix of chemical reaction coefficients; i, j and k are the numbers of thermodynamic component, derived constituent, and element, respectively.

The equilibrium constants K_j for each independent reaction are given as

$$K_j = \exp\left[\frac{-1}{RT}\left(\Delta G_j^{\Theta} - \sum_i V_{j,i}\Delta G_i^{\Theta}\right)\right] \quad (2)$$

where ΔG_i^{Θ} and ΔG_j^{Θ} are the standard Gibbs energy of formation of the ith thermodynamic component and the jth derived constituent, respectively; R and T are the molar gas constant and equilibrium temperature, respectively.

The interrelationship between the molar amounts of thermodynamic components and derived constituents in equilibrium state is given as

$$Y_j = \left(\frac{Z_{m(j)}}{\gamma_j}\right) K_j \prod_i \left(\frac{\gamma_i X_i}{Z_{m(i)}}\right)^{V_{j,i}} \quad (3)$$

where X_i and γ_i denote the molar amount and activity coefficient of the ith thermodynamic component, respectively; Y_j and γ_j denote the molar amount and activity coefficient of the jth derived constituent, respectively; $Z_{m(i)}$ and $Z_{m(j)}$ denote the molar amount of the phases containing the ith thermodynamic component and the jth derived constituent, respectively.

The total molar amount of the mth phase is denoted by Z_m, which is expressed in terms of X_i and Y_j as

$$Z_m = \sum_{i(m)} X_i + \sum_{j(m)} Y_j \ \ (m \in [1, N_p]) \quad (4)$$

where $i(m)$ means that the summation must be performed only when the ith thermodynamic component belongs to the mth phase, and similarly, $j(m)$ indicates that the summation must be performed only when the jth derived constituent belongs to the mth phase.

As a closed system is considered, the total amount of each element is fixed, and so Eq. (5) must be satisfied.

$$Q_k = \sum_i A_{i,k} X_i + \sum_j B_{j,k} Y_j \quad (5)$$

where Q_k is the total molar amount of the kth element in the system.

If the total number of phases is denoted by N_p, the sum of the quantities of Eqs. (3)−(5) is N_c+N_p, which is equal to that of the unknowns X_i, Y_j, and Z_m. By solving these equations, the molar amount of each component at equilibrium can be obtained.

3 Initialization and solving procedure

3.1 Thermodynamic data and boundary conditions

The parameters required for equilibrium calculations are temperature, pressure, molar amount of each element, standard Gibbs energy of formation, and activity coefficients for each species. Similar to the classical equilibrium constant method in the copper matte smelting process [17,24], 58 chemical species contained in the system at equilibrium were assumed as follows: (1) Gas phase: O_2, N_2, CO, CO_2, H_2, H_2O, S_2, SO, SO_2, Pb, PbO, PbS, Zn, ZnS, As_2, AsS, AsO, Sb, SbS, SbO, Bi, BiS, BiO, SnO, and SnS; (2) Slag phase: FeO, FeS, Fe_3O_4, SiO_2, Cu_2S, Cu_2O, CaO, Al_2O_3, MgO, PbO, ZnO, $AsO_{1.5}$, $SbO_{1.5}$, $BiO_{1.5}$, NiO, CoO, and SnO; (3) Matte phase: Cu, Cu_2S, FeS, FeO, Fe_3O_4, Pb, PbS, ZnS, As, Sb, Bi, $NiS_{0.67}$, CoS, SnS, Au, and $AgS_{0.5}$.

In this study, single pure substances such as silica and magnetite, common in copper matte smelting, are regarded as slag components.

To facilitate a direct comparison, in this study, thermodynamic data and boundary conditions that align with the classical equilibrium constant method model employed by TAN and ZHANG [17] were used. The composition of the feed mixture is listed in Table 1. The compositions of the air and industrial oxygen used are listed in Table 2. The operation parameters used for simulation calculation are shown in Table 3. Activity coefficients and standard Gibbs energy for each species are presented in Tables 4 and 5, respectively. All gas species are

Table 1 Composition of feed mixture (wt.%)

Cu	Fe	S	SiO_2	Pb	Zn	As
21.07	26.34	28.36	12.24	0.13	0.33	0.12
Sb	Bi	Ni	Co	Sn	Au	Ag
0.09	0.04	0.01	0.01	0.001	0.0007	0.0077
CaO	Al_2O_3	MgO	C*	H*	O	N
1.00	1.00	0.93	86.70	12.72	−	−

* C and H belong to heavy oil and remaining elements belong to copper concentrate

Table 2 Composition of air and industrial oxygen (vol.%)

Item	N_2	O_2	CO_2	H_2O
Air	79.42	20.5	0.03	−
Industrial oxygen	0.5	99	−	0.5

Table 3 Operation parameters

Mass of feed mixture/g	Mass of heavy oil/g	Volume of air/m^3	Volume of industrial oxygen/m^3	Temperature/K	Oxygen utilization coefficient
60	0.78	0.041	0.004	1483	0.99

Table 4 Activity coefficient of each species

Species	Phase	Activity coefficient	Ref.
Cu	mt	14	[18,29]
Cu_2S	mt	1	[18,29]
FeS	mt	$0.925/(N_{Cu_2S}+1)$	[18,29]
FeO	mt	$\exp[5.1+6.2\ln N_{Cu_2S}+6.41(\ln N_{Cu_2S})^2+2.8(\ln N_{Cu_2S})^3]$	[17,29]
Fe_3O_4	mt	$\exp[4.96+9.9\ln N_{Cu_2S}+7.43(\ln N_{Cu_2S})^2+2.55(\ln N_{Cu_2S})^3]$	[17,29]
Pb	mt	23	[18,29]
PbS	mt	$\exp\{-2.761+2441/T-(0.815-3610/T)\cdot(80-[Cu]_{mt})/100\}$	[18,27]
ZnS	mt	$\exp\{-2.054+6917/T-(1.522-1032/T)\cdot(80-[Cu]_{mt})/100\}$	[18,27]
As	mt	$8.087-0.128[Cu]_{mt}+0.014[Cu]_{mt}\cdot\lg[Cu]_{mt}$	[18,28]
Sb	mt	$-0.1423+0.3547[Cu]_{mt}-0.18[Cu]_{mt}\cdot\lg[Cu]_{mt}$	[17,28]
Bi	mt	$10^{1900/T-0.464}$	[18,28]
$NiS_{0.67}$	mt	$\exp(1377/T)$	[17,26]
CoS	mt	0.4	[24,30]
SnS	mt	$10^{-2100/T-0.068}$	[24,31]
Au	mt	$10^{-3310/T+3.15}$	[24,32]
$AgS_{0.5}$	mt	$10^{-425/T-0.074+0.09N_{FeS}}$	[24,32]
Cu_2S	sl	$\exp(2.46+6.22N_{Cu_2S})$	[17,29]
Cu_2O	sl	$57.14N_{Cu_2O}$	[17,29]
FeO	sl	$1.42N_{FeO}-0.044$	[17,29]
FeS	sl	70	[18,29]
Fe_3O_4	sl	$0.69+56.8N_{Fe_3O_4}+5.45N_{SiO_2}$	[18,29]
PbO	sl	$\exp(-3926/T)$	[24,29]
ZnO	sl	$\exp(287/T)$	[15,17]
$AsO_{1.5}$	sl	$3.828\left[\exp(1523/T)\right]\cdot(P_{O_2})^{0.158}$	[18,33]
$SbO_{1.5}$	sl	$\exp(1055.66/T)$	[18,33]
$BiO_{1.5}$	sl	$\exp(-1055.66/T)$	[18,33]
NiO	sl	$10^{3050/T-1.31}$	[17,34]
CoO	sl	0.91	[17,35]
SnO	sl	$10^{8800/T-5.7}$	[17,36]
SiO_2	sl	2.1	[17,29]

mt: Matte; sl: Slag; The activity coefficients of CaO, MgO and Al_2O_3 in the slag are considered to be 1

Table 5 Standard Gibbs energy formation ($\Delta G^{\ominus}=A+B\cdot T\cdot\lg T+C\cdot T$)

Species	State	Temperature/K	*A*	*B*	*C*	Ref.
CO	g	298−2500	−111712.80	0	−87.65	[37]
CO_2	g	298−2000	−394132.80	0	−0.84	[37]
H_2O	g	298−2500	−246437.60	0	54.81	[37]
SO_2	g	298−2000	−362208.90	0	72.38	[37]
SO	g	298−2000	−64433.60	0	−5.86	[37]
Pb	g	1323−1573	193907.50	18.84	−158.49	[29]
PbO	g	1323−1573	59747.52	53.01	−240.12	[29]
PbS	g	1323−1573	73805.76	0	−56.11	[29]
ZnS	g	1453−1653	−105424.30	0	82.01	[15,17]
AsS	g	1473−1673	43262.56	0	1.38	[38]
AsO	g	1473−1673	−29246.16	0	−13.35	[38]
Sb	g	1473−1673	237734.90	0	−102.76	[38]
SbS	g	1473−1673	100667.00	0	−52.97	[38]
SbO	g	1473−1673	169284.60	0	−56.78	[38]
Bi	g	1473−1673	193175.30	0	−101.00	[38]
BiS	g	1473−1673	87864.00	0	−55.65	[38]
BiO	g	1473−1673	100081.30	0	−56.15	[38]
SnO	g	1423−1623	−19664.80	0	−48.45	[36]
SnS	g	505−1973	25900	0	−49.37	[39]
Cu_2S	l	1323−1573	–141000.80	0	37.28	[29]
FeS	l	1323−1573	−117612.20	0	33.64	[29]
FeO	l	1323−1573	−229659.80	0	44.14	[29]
Fe_3O_4	s	1323−1573	−1091480.00	0	302.25	[29]
PbS	l	1323−1573	−11838.80	0	51.04	[29]
ZnS	s	1453−1653	−373045.40	0	198.74	[15,17]
As	l	1473−1673	−69705.44	0	57.07	[38]
$NiS_{0.67}$	l	1453−1653	−110512.00	0	54.39	[17,40]
CoS	l	1400−1600	−116859.10	0	47.20	[30]
SnS	l	1453−1653	−36398.40	0	59.91	[17,31]
$AgS_{0.5}$	l	1400−1500	−50124.32	0	21.54	[32]
Cu_2O	l	1323−1573	−127235.0	0	46.86	[29]
PbO	l	1323−1573	−195099.90	0	77.70	[29]
ZnO	s	1453−1653	−460825.80	0	198.11	[15,17]
$AsO_{1.5}$	l	1473−1673	−400325.10	0	172.46	[33,38]
$SbO_{1.5}$	l	1473−1673	−332167.80	0	100.63	[33,38]
$BiO_{1.5}$	l	1473−1673	−225559.40	0	82.22	[33,38]
NiO	s	1423−1623	−234617.80	0	85.60	[36]
CoO	s	1400−1600	−234391.90	0	70.96	[30]
SnO	l	1423−1623	−262295.00	0	86.57	[36]

Species with standard Gibbs energy of 0 in matte smelting are not listed

considered ideal gases at elevated temperatures, with their activity coefficients equal to 1. Activity coefficients for individual species in both the slag and matte are derived through experiments, which are mainly carried out under conditions associated with those of medium to high-grade copper matte [26−28]. Although extrapolation can be employed to some extent, its scope is restricted to copper matte grade exceeding 40 wt.%.

3.2 Initialization process

Chemical equilibrium may be regarded as a competition for negative Gibbs energy. According to HEALD [21], the molar Gibbs energy $g_{at}=G^{\Theta}/m_k$ predicts the equilibrium concentration of element k-containing species in homogeneous systems, where G^{Θ} and m_k are the standard Gibbs energy of each species and the coefficient of element k, respectively. The smaller the g_{at} value, the larger the equilibrium concentration of that species. Species with the most negative molar Gibbs at the reaction temperature and pressure will be the ones present in the greatest abundance at equilibrium. Initial molar amounts of species for the iterative calculations are calculated by distributing the amounts of the given elements.

3.2.1 Assignment of initial molar amount

Equation (6) is used to calculate the ratio of the standard Gibbs energy of formation to the number of atoms for each species.

$$g_{at}(n)=\frac{\Delta G_n^{\Theta}}{\sum_{k=1}^{N_a} AB_{nk}},\ n\in[1,N_c] \tag{6}$$

where AB_{nk} is the atom number of the nth species.

The molar amount Q_k of the elements is preferentially allocated to the compound with the smallest $g_{at}(n)$ until all compounds are allocated, and subsequently, the remaining molar amount of each element is allocated to the simple substance.

The minimum value of the ratio of the molar amount Q_k of element k to the number of element k in species i, Q_k/AB_{ik}, was taken as the initial molar amount of this species.

3.2.2 Selection of thermodynamic components

The species containing more element k were regarded as the thermodynamic components, and the remaining species were denoted as the derived constituents. The chemical reaction system was close to the thermodynamic equilibrium using this approach.

The molar amount of each element in each species was calculated according to the initial molar amount of each species. The species with the largest molar amount of element k was selected as the corresponding thermodynamic component, and subsequent thermodynamic components were selected from the remaining species using a similar approach until 21 thermodynamic components corresponding to the elements were selected. The selected thermodynamic components are listed as follows: (1) Gas phase: N_2, CO, CO_2, H_2, SO_2, and BiS; (2) Slag phase: ZnO, $AsO_{1.5}$, $SbO_{1.5}$, CoO, SnO, SiO_2, CaO, Al_2O_3, and MgO; (3) Matte phase: Cu_2S, FeS, PbS, $NiS_{0.67}$, Au, and $AgS_{0.5}$.

The remaining 37 species are derived constituents, as listed in Table S1 of the Supplementary Material (SM).

The element matrices $\boldsymbol{A}_{i,k}$ and $\boldsymbol{B}_{j,k}$ were obtained according to the selected thermodynamic components and derived constituents, respectively, as shown in Tables S2 and S3 of SM.

The chemical reaction coefficient matrix $\boldsymbol{V}_{j,i}$ and the independent reactions producing 37 derived constituents individually were deduced using Eq. (1). $\boldsymbol{V}_{j,i}$ and the chemical equations are given in Tables S4 and S5 of SM, respectively.

3.3 Newton–Raphson method

The simultaneous mathematical solution of Eqs. (3)–(5) is difficult, therefore, the Newton-Raphson method was applied to obtaining their approximate solutions, which yielded values close to those of true solutions. The solving process of the model was divided into five stages.

Stage 1: Calculation of iterative initial values

The equilibrium constant K_j of each independent reaction, the sum of the molar amounts of each phase Z_m, the activity coefficient of each species γ, and the molar amounts of derived constituents Y_j^* are calculated.

Stage 2: Calculation of error

The residual function F_k is obtained by substituting X_i and Y_j^* into the element conservation Eq. (5) as given in Eq. (7).

$$F_k=\sum_i A_{i,k}X_i+\sum_j B_{j,k}Y_j^*-Q_k \tag{7}$$

When Eq. (8) holds, where the order of ε is 10^{-7}, then the elements in the system can be considered to be conserved and the calculations can

skip to Stage 5.

$$\sum_k |F_k| < \varepsilon \tag{8}$$

However, the iterative initial values X_i and Y_j^* cannot converge Eq. (8) and Stage 3 must be performed.

Stage 3: Iteration

The Newton–Raphson method is used to obtain a new set of X_i, which is close to the true solutions, as shown in the calculations using Eq. (9).

$$\begin{bmatrix} \Delta \ln X_1 \\ \vdots \\ \Delta \ln X_i \\ \vdots \\ \Delta \ln X_{N_a} \end{bmatrix} = \begin{bmatrix} X_1 \dfrac{\partial F_1}{\partial X_1} & \cdots & X_{N_a} \dfrac{\partial F_1}{\partial X_{N_a}} \\ \vdots & \vdots & \vdots \\ \cdots & X_i \dfrac{\partial F_k}{\partial X_i} & \cdots \\ \vdots & \vdots & \vdots \\ X_1 \dfrac{\partial F_{N_a}}{\partial X_1} & \cdots & X_{N_a} \dfrac{\partial F_{N_a}}{\partial X_{N_a}} \end{bmatrix}^{-1} \begin{bmatrix} -F_1 \\ \vdots \\ -F_k \\ \vdots \\ -F_{N_a} \end{bmatrix} \tag{9}$$

Equation (10) shows the secant method, which is used to calculate $\dfrac{\partial F_k}{\partial X_i}$ to simplify the calculation process.

$$\frac{\partial F_k}{\partial X_i} = \frac{F_k\left(X_i + \Delta X_i\right) - F_k\left(X_i\right)}{\Delta X_i} \tag{10}$$

where $\Delta X_i = X_i/10^r$ and $r \in [1, 10]$. $\Delta \ln X_i$ can be solved by substituting the value of $\dfrac{\partial F_k}{\partial X_i}$ into the Newton–Raphson matrix.

Stage 4: Update of each variable

The new molar amounts of thermodynamic components $X_i^* = X_i \exp\left(\Delta \ln X_i\right)$ and the derived constituents Y_j^*, along with the new sum of the molar amounts of each phase Z_m^* are calculated. Since Z_m variation is small during the iterative calculation, if Eq. (11) is true, then $Z_m = Z_m^*$, otherwise, the value of Z_m remained unaltered.

$$\sum_{N_P} \left| Z_m - Z_m^* \right| < l \tag{11}$$

where $l \in [2, 5]$.

By the procedure described so far, a new set of X_i^* and Z_m^* is obtained, which is then returned to Stage 1 to get another new set of Y_j^* and the same calculations are reiterated until Eq. (8) is satisfied. The last set of X_i^*, Y_j^*, and Z_m^* are used for the calculations in the Stage 5.

Stage 5: Adjudication for convergence

At each end of Stage 4, a new set of activity coefficient of each species γ^* is calculated based on the last set of X_i^* and Y_j^*, which in turn is used to calculate $\overline{Y_j}$. The adjudication for convergence is examined using Eq. (12).

$$\sum \left| \overline{Y_j} - Y_j^* \right| < \delta \tag{12}$$

where δ is the value of adjudication for convergence, and it is considered to be in the order of 10^{-3}. When Eq. (12) is satisfied, the system is considered to be in equilibrium, and the algorithm is terminated with the outputs X_i^*, Y_j^*, γ^* and Z_m^*; the result is outputs obtained, otherwise Stages 1–5 are repeated using $X_i = X_i^*$, $Y_j = Y_j^*$, and $\gamma = \gamma^*$. The calculation process as described above is outlined in Fig. S1 of SM.

3.4 Thermodynamic equilibrium calculation results

Table 6 provides a comparative analysis of the initial molar amounts and equilibrium values of each species, most of which are of the same order of magnitude. Following the initialization improvement, the equilibrium calculation process comprises only 31 outer loops. This computational workload is even less than 10% of that utilized by the classical equilibrium constant method employed by TAN and ZHANG [17]. Undoubtedly, the reduction in the number of iterations lowers the risk of non-convergence during the solving process. This demonstrates the superior performance and reliability of the initialization method in this study.

4 Conversion to industrial forecast values

The copper matte smelting process operates in a steady state with the charging materials continuously charged, the melt semi-continuously tapped, and the off-gas continuously discharged from the reactor [41]. One important issue to note is

Table 6 Initial molar amounts and equilibrium values for each species (mol)

Species	Initial	Equilibrium	Species	Initial	Equilibrium
O_2(g)	4.32357×10^{-9}	4.24297×10^{-9}	Fe_3O_4(mt)	1.03135×10^{-2}	8.84289×10^{-2}
N_2(g)	1.45456×10^{0}	1.45456×10^{0}	Pb(mt)	1.56239×10^{-6}	5.76282×10^{-9}
CO(g)	4.27960×10^{-3}	3.33363×10^{-3}	PbS(mt)	2.63944×10^{-4}	1.38079×10^{-6}
CO_2(g)	5.25720×10^{-2}	5.32955×10^{-2}	ZnS(mt)	1.34978×10^{-4}	1.77581×10^{-4}
H_2(g)	1.55858×10^{-3}	1.99322×10^{-2}	As(mt)	2.00918×10^{-4}	0.00000×10^{0}
H_2O(g)	4.85534×10^{-2}	3.01798×10^{-2}	Sb(mt)	1.66579×10^{-4}	1.64597×10^{-6}
S_2(g)	1.33600×10^{-2}	7.17803×10^{-2}	Bi(mt)	1.63266×10^{-5}	2.88051×10^{-8}
SO_2(g)	3.42292×10^{-1}	2.86473×10^{-1}	$NiS_{0.67}$(mt)	9.14969×10^{-5}	5.99463×10^{-6}
SO(g)	2.86095×10^{-3}	1.31135×10^{-3}	CoS(mt)	8.20302×10^{-5}	5.97024×10^{-6}
Pb(g)	8.58848×10^{-6}	0.00000×10^{0}	SnS(mt)	7.26606×10^{-6}	3.70794×10^{-8}
PbO(g)	8.69968×10^{-7}	2.20750×10^{-5}	Au(mt)	2.00799×10^{-6}	2.00799×10^{-6}
PbS(g)	7.21665×10^{-5}	8.63686×10^{-8}	$AgS_{0.5}$(mt)	4.28174×10^{-5}	4.01392×10^{-5}
Zn(g)	3.45918×10^{-4}	7.41143×10^{-7}	Cu_2S(sl)	4.40850×10^{-4}	5.83275×10^{-3}
ZnS(g)	7.75576×10^{-6}	1.11077×10^{-5}	Cu_2O(sl)	4.85494×10^{-4}	8.50336×10^{-6}
As_2(g)	1.93859×10^{-4}	1.17594×10^{-7}	FeO(sl)	1.48976×10^{-1}	6.49228×10^{-5}
AsS(g)	4.08037×10^{-5}	3.52482×10^{-6}	FeS(sl)	9.21494×10^{-4}	2.54011×10^{-7}
AsO(g)	4.88850×10^{-5}	5.63521×10^{-5}	Fe_3O_4(sl)	1.38203×10^{-2}	5.53123×10^{-3}
Sb(g)	3.16412×10^{-6}	0.00000×10^{0}	PbO(sl)	2.93351×10^{-5}	3.52918×10^{-4}
SbS(g)	4.45209×10^{-5}	2.65746×10^{-5}	ZnO(sl)	2.53980×10^{-3}	2.83902×10^{-3}
SbO(g)	1.53337×10^{-10}	1.27181×10^{-7}	$AsO_{1.5}$(sl)	2.82700×10^{-4}	9.00913×10^{-4}
Bi(g)	3.56477×10^{-5}	0.00000×10^{0}	$SbO_{1.5}$(sl)	2.38938×10^{-4}	4.24854×10^{-4}
BiS(g)	6.51167×10^{-5}	6.90181×10^{-6}	$BiO_{1.5}$(sl)	5.97373×10^{-7}	1.10341×10^{-4}
BiO(g)	1.46047×10^{-8}	4.31708×10^{-7}	NiO(sl)	1.07351×10^{-5}	9.58374×10^{-5}
SnO(g)	5.38549×10^{-8}	5.92796×10^{-7}	CoO(sl)	1.97858×10^{-5}	9.54474×10^{-5}
SnS(g)	2.62632×10^{-6}	2.31931×10^{-9}	SnO(sl)	1.63266×10^{-7}	9.47715×10^{-6}
Cu(mt)	9.90828×10^{-4}	7.61356×10^{-4}	SiO_2(sl)	1.22267×10^{-1}	1.22267×10^{-1}
Cu_2S(mt)	9.80495×10^{-2}	9.32493×10^{-2}	CaO(sl)	1.06990×10^{-2}	1.06990×10^{-2}
FeS(mt)	5.86000×10^{-2}	4.06092×10^{-6}	Al_2O_3(sl)	5.88466×10^{-3}	5.88466×10^{-3}
FeO(mt)	2.08820×10^{-3}	1.03793×10^{-3}	MgO(sl)	1.38427×10^{-2}	1.38427×10^{-2}

that, due to non-equilibrium factors, the composition of matte and slag tapped from an operating flash furnace may deviate from equilibrium values. Considering that reliable sampling is difficult under industrial conditions, investigation of equilibrium or non-equilibrium problems in an operating flash furnace is impractical. Hence, the rationality and necessity of transitioning to industrial practice could be further demonstrated by inferring the non-equilibrium properties of industrial practice using the previously published reports.

4.1 Non-equilibrium factors in industrial practice

Firstly, thermodynamic equilibrium between the phases is not established in the flash smelting furnace. Depending upon the mass and heat transfer conditions of the materials in the reaction shaft and differences in the specific rates of different mass transfer processes, the phases leaving the reaction shaft might be in a completely different thermodynamic state. KEMORI et al [42] measured oxygen pressures in the reaction shaft of the Toyo flash smelting furnace of Sumitomo Metal Mining

Co., in Japan. SOLNORDAL et al [43] used computational fluid dynamics (CFD) modeling to simulate the flow and reactions in the reaction shaft of the Olympic Dam flash smelting furnace. Their findings confirmed that the temperature and gas composition in the reaction shaft of the flash smelting furnace were not uniform. TASKINEN et al [44] measured the temperature in the settler of an industrial copper flash smelting furnace. The result exhibited a significant temperature gradient across the slag-matte interface. Additionally, KEMORI et al [42] reported considerably lower SO_2 pressure in the bulk of the off-gas than that just above the slag layer. Therefore, during the copper matte flash smelting, the oxidation and slagging reactions proceed via different thermodynamic states, and a thermodynamic equilibrium could not be established between the phases leaving the flash smelting furnace.

Another non-equilibrium problem is the difference in the rates of sulfide oxidation and slag-forming reactions. The flash smelting furnace can be functionally divided into three separate zones (reaction shaft, settler, and uptake shaft) that interact with each other quite modestly, where the chemical reactions are exceptionally localized [45]. In the reaction shaft of the flash furnace, the concentrate particles are diffusely dispersed in the oxygen-enriched process air. The oxidation of sulfides primarily proceeded in the reaction shaft owing to its extremely fast reaction rate [46,47]. The formation process of slag and matte is completed on the top layer of the settler bath surface below the reaction shaft [44,47], limited by the contact area between matte and flux in the reaction shaft. It is the kinetics of different processes which determine how closely the phases leaving the flash smelting furnace are equilibrated with each other. FAGERLUND and JALKANEN [48] confirmed the differences in the average oxidation degree of slag and matte in the settler. MA and LIAN [49] reported magnetite precipitation owing to the poor slag formation in the flash smelting furnace of Zijin Copper Co., in China. Clearly, the kinetic prerequisites for further equilibration in the flash smelting furnace are very limited.

4.2 Consideration for mechanical entrainment

Non-equilibrium factors significantly influence the distribution of various species between matte and slag. Deviations between industrial and equilibrium values may be closely related to these and displayed as physically suspended slag or matte. The mechanical entrainment equation proposed by NAGAMORI and MACKEY [50] was used in this model to complete the conversion from the equilibrium to the industrial value as given in Eqs. (13) and (14).

$$[\mathrm{M}]_{\mathrm{mt}}^{\mathrm{ap}} = \{[\mathrm{M}]_{\mathrm{mt}} \times (100 - S_{\mathrm{mt}}^{\mathrm{sl}}) + [\mathrm{M}]_{\mathrm{sl}} \times S_{\mathrm{sl}}^{\mathrm{mt}}\} / 100 \tag{13}$$

$$[\mathrm{M}]_{\mathrm{sl}}^{\mathrm{ap}} = [\mathrm{M}]_{\mathrm{sl}} (100 - S_{\mathrm{mt}}^{\mathrm{sl}}) + [\mathrm{M}]_{\mathrm{mt}} \times S_{\mathrm{mt}}^{\mathrm{sl}}\} / 100 \tag{14}$$

where $S_{\mathrm{mt}}^{\mathrm{sl}}$ and $S_{\mathrm{sl}}^{\mathrm{mt}}$ denote the mass fraction of suspended matte in slag and the suspended slag in matte, respectively; $[\mathrm{M}]_{\mathrm{mt}}$ and $[\mathrm{M}]_{\mathrm{sl}}$ denote the mass fraction of element M in matte and slag at chemical equilibrium, respectively; $[\mathrm{M}]_{\mathrm{mt}}^{\mathrm{ap}}$ and $[\mathrm{M}]_{\mathrm{sl}}^{\mathrm{ap}}$ denote the apparent mass fraction of M in the matte and slag phases containing mechanical suspension, respectively. The suspension indices (Table 7) in this study that align with TAN and ZHANG [17], derived from estimates in the pilot furnace conducted by JALKANEN et al [51].

Table 7 Suspension indices of flash furnace [51] (wt.%)

Copper content in matte	$S_{\mathrm{sl}}^{\mathrm{mt}}$	$S_{\mathrm{mt}}^{\mathrm{sl}}$
50	2	1
65	3	1.5
75	3	2
80	3	2.5

5 Model validation

The Eqs. (1)−(14) were combined to form a thermodynamic model of the copper matte flash smelting process. As a model, the most crucial aspect is ensuring that calculation results align well with industrial values. Additionally, the initialization-improved used in this study aim to reduce the computational effort required for equilibrium calculations while maintaining accuracy at a level not inferior to the classical equilibrium constant method. These are the key concerns for engineers.

The industrial forecast values are presented in Table 8, along with the industrial and equilibrium calculated values. Compared to the equilibrium values, the industrial forecast values are closer to the industrial values. Furthermore, the operational parameters by TAN and ZHANG [17] were used in the present study, and the comparison of the model output results are compiled in Table 9. The output

Table 8 Content comparison of equilibrium value with industrial data (wt.%)

Phase	Item	Cu	S	Fe	SiO_2	Pb	Zn	As	Sb	Bi
Matte	Industrial	51.94	22.63	−	0.24	0.24	0.35	0.10	0.083	0.061
	Equilibrium	53.90	21.57	20.99	0	0.23	0.32	0.06	0.088	0.013
	Forecast	52.25	21.03	22.25	0.63	0.23	0.36	0.06	0.087	0.014
Slag	Industrial	1.13	0.57	39.08	32.94	0.037	0.46	0.12	0.11	<0.005
	Equilibrium	0.32	0.18	43.12	31.06	0.026	0.41	0.08	0.12	<0.005
	Forecast	1.03	0.40	45.23	30.94	0.028	0.41	0.09	0.12	<0.005

Table 9 Content comparison of this work and published data (wt.%)

Phase	Item	Cu	S	Fe	SiO_2	Pb	Zn	As	Sb	Bi
Matte	Forecast	52.25	21.03	22.25	0.63	0.23	0.36	0.06	0.087	0.014
	Ref. [17]	51.47	20.97	22.65	0.64	0.23	0.36	0.06	0.086	0.014
Slag	Forecast	1.03	0.40	45.23	30.94	0.028	0.41	0.09	0.12	<0.005
	Ref. [17]	0.90	0.40	45.15	31.43	0.027	0.41	0.09	0.12	<0.005

data of this model agree with the previously reported data. The copper content in copper matte and slag forecasted in this study is close to the industrial value.

The industrial value of Fe concentration in the slag is marginally lower than the calculated value, primarily because the activity coefficient of FeO in the slag used in this study is that of FeO in the ternary system of $FeO–Fe_3O_4–SiO_2$. According to KEMORI et al [52], the addition of CaO in the $FeO–FeO_{1.5}–SiO_2$ system increasesed the activity coefficient of FeO.

6 Conclusions

(1) An initial molar amount was assigned to each species in the copper matte smelting system according to the initialization method. The one with the highest molar amount among all species containing element K was chosen as the thermodynamic component. 58 species in the copper matte flash smelting system were divided into 21 thermodynamic components and 37 derivative species. The equilibrium values were derived via the Newton−Raphson method. The initial molar amounts and equilibrium values of most species are of the same order of magnitude.

(2) A comprehensive review of the non-equilibrium factors in the copper matte flash smelting process was conducted, followed by the utilization of mechanical entrainment equations to convert equilibrium values into industrial forecast values. The results indicate that the equilibrium calculation value for copper concentration in the slag is 0.32 wt.%, while the industrial forecast value is 1.03 wt.%, with the industrial value being 1.13 wt.%. This clearly demonstrates the rationale and necessity of considering non-equilibrium factors.

(3) Approximate solutions close to the equilibrium values can be derived by performing 31 outer loops, which is remarkably less than that of the classical equilibrium constant method. The iterative path during the computation is considerably reduced and the risk of non-convergence during the computation is decreased. This initialization-improved equilibrium constant method exhibits superior performance and reliability.

Nomenclatures

N_a: Number of thermodynamic component

N_b: Number of derived constituent

N_c: Number of chemical species

i: Index of thermodynamic component

j: Index of derived constituent

k: Index of chemical element

$\boldsymbol{A}_{i,k}$: Elemental matrix of thermodynamic components

$\boldsymbol{B}_{j,k}$: Elemental matrix of derived constituents

$\boldsymbol{V}_{j,i}$: Matrix of chemical reaction coefficients

ΔG_i^{Θ}: Standard Gibbs energy of formation of the ith thermodynamic component

ΔG_j^{Θ}: Standard Gibbs energy of formation of the jth derived constituent
R: Molar gas constant
T: Equilibrium temperature
K_j: Equilibrium constants of the jth independent reaction
γ_i: Activity coefficient of the ith thermodynamic component
γ_j: Activity coefficient of the jth derived constituent
X_i: Molar amount of the ith thermodynamic component
Y_j: Molar amount of the jth derived constituent
N_p: Number of phase
m: Index of phase
Z_m: Total molar amount of the mth phase
$Z_{m(i)}$: Molar amount of the mth phase containing the ith thermodynamic component
$Z_{m(j)}$: Molar amount of the mth phases containing the jth derived constituent
$i(m)$: Summation is possible only when the ith thermodynamic component belongs to the mth phase
$j(m)$: Summation is possible only when the jth derived constituent belongs to the mth phase
Q_k: Total molar amount of the kth element
N_{Cu_2S}: Molar fraction of Cu_2S in copper matte
$[Cu]_{mt}$: Copper matte grade
N_{FeS}: Molar fraction of FeS in copper matte
N_{Cu_2O}: Molar fraction of Cu_2O in slag
N_{FeO}: Molar fraction of FeO in slag
$N_{Fe_3O_4}$: Molar fraction of Fe_3O_4 in slag
N_{SiO_2}: Molar fraction of SiO_2 in slag
P_{O_2}: Partial pressure of O_2 in gas
$[M]_{mt}$: Mass fraction of element M in matte
$[M]_{sl}$: Mass fraction of element M in slag
$[M]_{mt}^{ap}$: Apparent mass fraction of M in matte
$[M]_{sl}^{ap}$: Apparent mass fraction of M in slag
S_{mt}^{sl}: Mass fraction of suspended matte in slag
S_{sl}^{mt}: Mass fraction of suspended slag in matte

CRediT authorship contribution statement

Hui-chuan REN: Methodology, Investigation, Formal analysis, Writing − Original draft; **Xiao-bo MIN:** Resources, Funding acquisition; **Yong KE:** Formal analysis, Data curation, Project administration; **Long-gong XIA:** Writing − Review & editing; **Yun-yan WANG:** Formal analysis, Data curation; **Cong PENG:** Validation, Supervision, Project administration; **Yun LI:** Validation, Supervision; **Wan-lan WU:** Data curation, Validation, Supervision; **Jie FU:** Data curation, Validation, Supervision; **Xi-long WU:** Data curation, Validation; **Chuan-fu ZHANG:** Validation, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Materials

Supplementary Materials in this paper can be found at: https://tnmsc.csu.edu.cn/download/21-p4281-2024-0604-Supplementary_Materials.pdf.

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用改进的平衡常数法模拟铜锍熔炼过程

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摘 要：采用初始化改进的平衡常数法模拟铜锍闪速熔炼过程。基于分配给定元素的物质的量计算各物种的初始量，并选择含某一元素量最大的物种作为相应的热力学组分。利用 Newton−Raphson 法确定平衡值，并通过机械夹带方程将其转换为工业预测值。结果显示，渣中铜的平衡浓度计算值为 0.32%(质量分数)，而工业预测值为 1.03%，实际工业值为 1.13%。该模型仅需 31 次外循环就可以得出接近平衡值的近似解，大大减少了计算过程中的迭代路径，降低了计算过程中不收敛的风险。

关键词：初始化；摩尔吉布斯能量；热力学组分；迭代次数；平衡值；机械夹带

(Edited by Xiang-qun LI)