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Mathematical model of pyritic smelting process for copper-nickel mineral in oxygen top-blown furnace①

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Abstract: Mathematical model for mass transfer of chemical reactions on the surface of the smelting bath pit in oxygen top-blown smelting furnace was put forward. Additionally, one of two mathematical models for mass transfer of chemical reactions forming copper matte in smelting bath and the other for parameters of smelting process were developed. The verification tests were simultaneously carried out in a pilot scale furnace and the experimental results show that these mathematical models are convincing. Thus, these numerical models are reliable to simulate pyritic smelting process for copper-nickel mineral in oxygen top-blown furnace.

Key words: pyritic process; oxygen top-blown furnace; copper-nickel mineral; mathematical model
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1 INTRODUCTION

The idea of refining copper and nickel with pyritic smelting process in oxygen top-blown furnace has come into being for its achievement in oxygen-converter of steel making process from 1960s. The first pyritic smelting furnace with oxygen top-blown smelting nickel had been put into production at North Nickel Co. of Russian in 1986. Nowadays, this technology has been imported and employed in Jinchuan Nonferrous Metal Co. of China. In the past decades, the utilization of flash smelting furnace in nonferrous-making has got extensive development. MEI et al[1-5] have made great efforts to establish numerical simulation system of reactions process in flash smelting furnace. In this paper, several numerical models on copper-nickel mineral being smelted in oxygen top-blown furnace were developed. Simultaneously, a series of verification tests were carried out. The experimental results show that these numerical models are reliable to simulate pyritic smelting process for copper-nickel mineral in oxygen top-blown furnace.

2 MATHEMATICAL MODELS

2.1 Models for mass transfer of chemical reaction on surface of pit in melting bath

When the copper-nickel mineral are smelted in pyritic smelting furnace with oxygen top-blown, the oxygen has been blown in molten bath with an oxygen jet at pressure of 0.98－1.17 MPa. Because of the oxygen impingement, there is a pit on the top of the melting bath[6-8]. The raw minerals are directly put into the blown oxygen zone of the melting bath. As a result, the redox reactions of sulphide are going on, and the materials are smelted. Both the melting of the materials and the oxidation of the pyrites take place in the slag layer. It is considered that the oxygen diffuses from the surface of the pit to the slag and the pyrites diffuse from the slag to the pit surface[9]. So it may be supposed that the oxygen efficiency can reach 100% in most conditions[10]. The oxidation reactions proceeding on surface of the pit can be represented as

$$\frac{1}{2}O_2(g) = [O]_{saturation} \quad (1)$$

$$FeS(l) + 3[O] \rightarrow FeO(l) + SO_2(g) \quad (2)$$

$$2FeS(l) + 6[O] + 2SiO_2(l) \rightarrow 2FeO\cdot SiO_2(l) + 2SO_2(g) \quad (3)$$

$$3FeS(l) + 10[O] \rightarrow Fe_3O_4(l) + 3SO_2(g) \quad (4)$$

$$Cu_2S(l) + 3[O] \rightarrow Cu_2O(l) + SO_2(g) \quad (5)$$

$$Ni_3S_2(l) + 7[O] \rightarrow 3NiO(l) + 2SO_2(g) \quad (6)$$

From a simplification point of view, it can be assumed that the oxidation reactions proceeding on the surface of pit are simplified as formulas (1), (4), (5) and (6). The matter balance for O, FeS, Cu_2S and Ni_3S_2 on the surface of the pit would be

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expressed as follows:

$$\frac{\partial c_O}{\partial t}=D_O\frac{\partial^2 c_O}{\partial n^2}-\sum_i K_i c_i c_O \quad (7)$$

$$\frac{\partial c_i}{\partial t}=D_i\frac{\partial^2 c_i}{\partial n^2}-k_i c_i c_O \quad (8)$$

The boundary and initial conditions are:

$$t=0,\ s>0,\ c_O=0,\ c_i=c_{ib}; \quad (9)$$

$$s=0,\ t>0,\ c_O=c_{OS},\ c_i=c_{is}; \quad (10)$$

$$\frac{\partial c_O}{\partial t}=-\frac{J_O}{D_O},\ \frac{\partial c_i}{\partial t}=0,$$
$$s=\infty,\ t\geqslant 0,\ c_O=0,\ c_i=c_{ib}. \quad (11)$$

where

$$c_{ib}=c'_{ib}+\frac{m\cdot P_i\%}{100\cdot(m'+m)\cdot M_1} \quad (12)$$

The overall flux of oxygen absorption on the surface of the pit and oxygen content of the chemical reactions can be calculated with the following formulas:

$$S=J_O\cdot A \quad (13)$$

$$\delta_i\ \frac{D_i\cdot c_{ib}}{\sum_i D_i\cdot c_{ib}} \quad (14)$$

$$A=\frac{4\pi h_0}{3r^2}\left[\left(r^2+\frac{r^4}{4h_0^2}\right)^{3/2}-\frac{r^6}{8h_0^3}\right] \quad (15)$$

According to the above mathematical models, the changes of mass component due to the redox reactions proceeding on the surface of the pit are as follows:

$$d(m_{FeS})/dt=-(3/10)\delta_{FeS}\cdot S\cdot M_{FeS} \quad (16)$$

$$d(m_{Cu_2S})/dt=-(1/3)\delta_{Cu_2S}\cdot S\cdot M_{Cu_2S} \quad (17)$$

$$d(m_{Ni_3S_2})/dt=-(1/7)\delta_{Ni_3S_2}\cdot S\cdot M_{Ni_3S_2} \quad (18)$$

$$d(m_{Fe_3O_4})/dt=-(1/10)\delta_{FeS}\cdot S\cdot M_{Fe_3O_4} \quad (19)$$

$$d(m_{Cu_2O})/dt=(1/3)\delta_{Cu_2S}\cdot S\cdot M_{Cu_2O} \quad (20)$$

$$d(m_{NiO})/dt=(3/7)\delta_{Ni_3S_2}\cdot S\cdot M_{NiO} \quad (21)$$

2.2 Models for mass transfer of chemical reaction forming copper matte in smelting bath

In the smelting bath, the redox reactions of sulphide took place not only on the surface of the pit, but also in the interior of the slag layer with the ferroferric oxide. Inside the smelting bath, the reactions are represented as follows:

$$FeS(l)+Fe_3O_4(l)\rightarrow 10FeO(l)+SO_2(g) \quad (22)$$

$$FeS(g)+3Fe_3O_4(l)+5SiO_2(l)\rightarrow 5(2FeO\cdot SiO_2)(l)+SO_2(g) \quad (23)$$

$$Cu_2O(l)+FeS(l)\rightarrow Cu_2S(l)+FeO(l) \quad (24)$$

$$9NiO(l)+7FeS(l)\rightarrow 3Ni_3S_2(l)+7FeO(l)+SO_2(g) \quad (25)$$

For simplification also, it is assumed that the reactions forming copper matter in smelting bath can be predigested as reactions (23), (24) and (25). And then, the reaction area can be computed with the following formula:

$$A'=\pi\cdot[R^2-r^2] \quad (26)$$

According to the above supposition, the mass content changes of various matters due to the reactions in smelting bath can be deduced as

$$d(m_{Fe_3O_4})/dt=-A'D\rho(c_{Fe_3O_4,s}-c_{Fe_3O_4,b})\cdot M_{Fe_3O_4} \quad (27)$$

$$d(m_{Cu_2O})/dt=-A'D\rho(c_{Cu_2O_4S,s}-c_{Cu_2S,b})\cdot M_{Cu_2O} \quad (28)$$

$$d(m_{NiO})/dt=-3A'D\rho(c_{Ni_3S_2,s}-c_{Ni_3S_2,b})\cdot M_{NiO} \quad (29)$$

$$d(m_{FeS})/dt=-A'D\rho M_{FeS}(1/3)[(c_{Fe_3O_4,s}-c_{Fe_3O_4,b})+(c_{Cu_2S,s}-c_{Cu_2S,b})+(7/3)(c_{Ni_3S_2,s}-c_{Ni_3S_2,b})] \quad (30)$$

$$d(m_{Cu_2S})/dt=A'D\rho(c_{Cu_2S,s}-c_{Cu_2S,b})\cdot M_{CuS} \quad (31)$$

$$d(m_{Ni_3S_2})/dt=A'D\rho(c_{Ni_3S_2,s}-c_{Ni_3S_2,b})\cdot M_{Ni_3S_2} \quad (32)$$

$$d(m_{FeO})/dt=A'D\rho M_{FeO}[(10/3)(c_{Fe_3O_4,s}-c_{Fe_3O_4,b})+(c_{Cu_2S,s}-c_{Cu_2S,b})+(7/3)(c_{Ni_3S_2,s}-c_{Ni_3S_2,b})] \quad (33)$$

2.3 Mathematical models for parameters of converting process

2.3.1 Models for mass ingredient of converting process in smelting bath

According to above mathematical models, the models for mass ingredient of converting process in slag layer are shown as

$$d(m_{Fe_3O_4})/dt=-A'D\rho M_{Fe_3O_4}[(c_{Fe_3O_4,s}-c_{Fe_3O_4,b})+(1/10)\delta_{FeS}\cdot S] \quad (34)$$

$$d(m_{Cu_2O})/dt=-A'D\rho M_{Cu_2O}[(c_{Cu_2S,s}-c_{Cu_2S,b})+(1/3)\delta_{Cu_2S}\cdot S] \quad (35)$$

$$d(m_{NiO})/dt=-3A'D\rho M_{NiO}[(c_{Ni_3S_2,s}-c_{Ni_3S_2,b})M_{NiO}+(3/7)\delta_{Ni_3S_2}\cdot S] \quad (36)$$

$$d(m_{FeS})/dt=-A'D\rho M_{FeS}[(1/3)(c_{Fe_3O_4,s}-c_{Fe_3O_4,b})+(c_{Cu_2S,s}-c_{Cu_2S,b})+(7/3)(c_{Ni_3S_2,s}-c_{Ni_3S_2,b})-(3/10)\delta_{FeS}\cdot S] \quad (37)$$

$$d(m_{Cu_2S})/dt=A'D\rho M_{Cu_2S}[(c_{Cu_2S,s}-c_{Cu_2S,b})-(1/3)\delta_{Cu_2S}\cdot S] \quad (38)$$

$$d(m_{Ni_3S_2})/dt=A'D\rho M_{Ni_3S_2}[(c_{Ni_3S_2,s}-c_{Ni_3S_2,b})-(1/7)\delta_{Ni_3S_2}\cdot S] \quad (39)$$

$$d(m_{FeO})/dt=A'D\rho M_{FeO}[(10/3)(c_{Fe_3O_4,s}-c_{Fe_3O_4,b})+(c_{Cu_2S,s}-c_{Cu_2S,b})+(7/3)(c_{Ni_3S_2,s}-c_{Ni_3S_2,b})] \quad (40)$$

2.3.2 Model for temperature on surface of pit

According to heating balance, the model for temperature on the surface of the pit is obtained as

follows:

$$T_s=\frac{[Q_l+(k_z T_z+k_q T_q)A]}{(k_z+k_q)A} \quad (41)$$

2.3.3 Model for temperature of smelting bath

According to the heating balance again, the model for temperature of smelting bath is expressed as follows:

$$\frac{dT_z}{dt}=\frac{Q_l+Q_m+Q_f+Q_s}{(m'+m)\cdot c_z+m_q\cdot c_q} \quad (42)$$

3 COMPARISON BETWEEN NUMERICAL SIMULATION AND RESULTS OF VERIFICATION TESTS

3.1 Experimental

The mineral samples are fine copper-nickel mineral provided by Jinchuan Nonferrous Metal Co, China. And its characterization data are shown in Table 1.

Table 1 Characterisation data for mineral sample (mass fraction, %)

Cu	Ni	Fe	S	Others
67.38	4.40	3.62	21.24	3.36

The experimental tests were carried out in a pilot scale oxygen top-blown furnace that was designed by the authors of this paper. For the sake of approaching the operating conditions in practical production process, we set the experimental conditions after referring to the operating conditions of Jinchuan Co. The main experimental conditions are listed as follows. The rate of mineral fed was 7.5 $t\cdot h^{-1}$, and the quartz was put into the molten bath at the rate of 290 $kg\cdot h^{-1}$. The oxygen and heavy oil were consumed at the rates of 867 $m^3\cdot h^{-1}$ and 204 $kg\cdot h^{-1}$ respectively.

At the same time, we utilize the above-founded models to calculate the various parameters at different smelting stages.

3.2 Results and discussion

The comparison between the results of the numerical simulation and the verification tests about the temperature vs time of the slag layer and on surface of the pit are shown in Fig. 1.

As indicated in Fig. 1, the temperatures on the surface of the pit are higher than those inside the smelting bath. From the simulation curves and the experimental results, it is clear that there are very small deviations between the simulation and experiment results. In other words, the numerical models are substantially reliable.

The simulation values and experimental results of the concentrations of FeO, SiO_2, Cu_2S and FeS in slag versus smelting time are reported in Figs. 2 - 5, respectively.

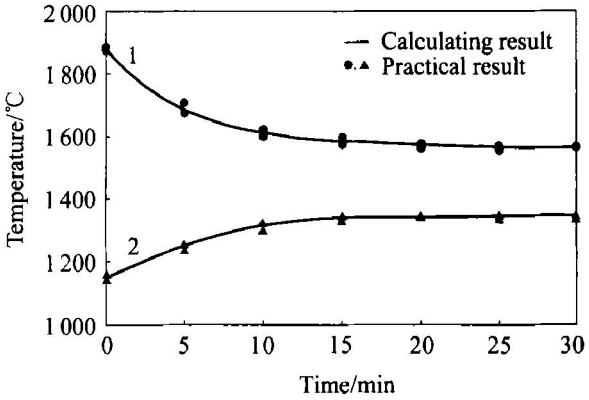

Fig. 1 Temperature of smelting bath and surface of pit vs time
1—Temperature on surface of pit;
2—Temperature in smelting bath

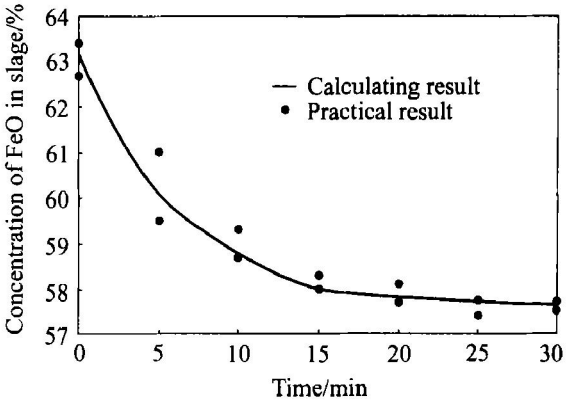

Fig. 2 Concentration of FeO in slag vs time

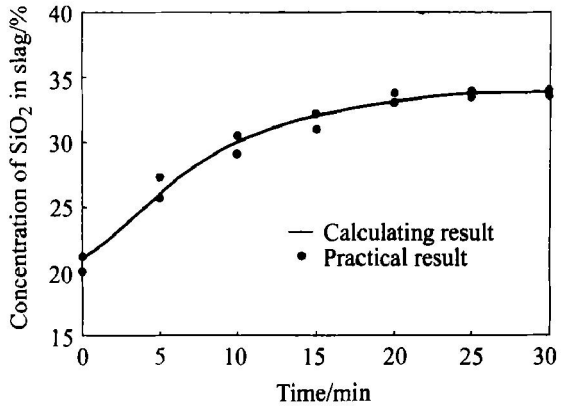

Fig. 3 Concentration of SiO_2 in slag vs time

Fig. 2 shows good agreement between experimental and numerical values of FeO fraction in slag layer during smelting process. As indicated in Fig. 2, the numerical results are within the two values of experimental determination. The agreement is expected since the numerical simulation is conducted under practical operating conditions. But, as we all know, the practical smelting process always has unpredictable factors. Thus, the dis-

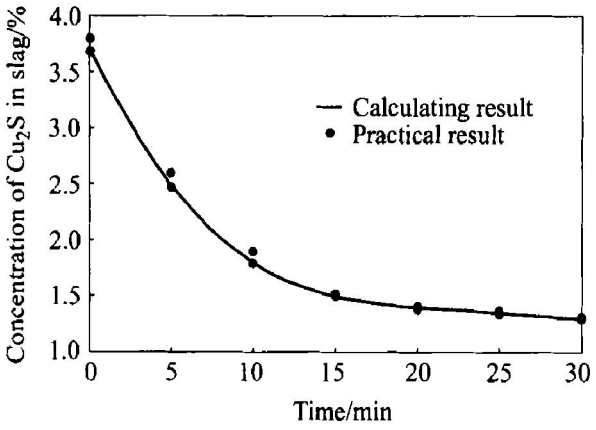

Fig. 4 Concentration of Cu_2S in slag vs time

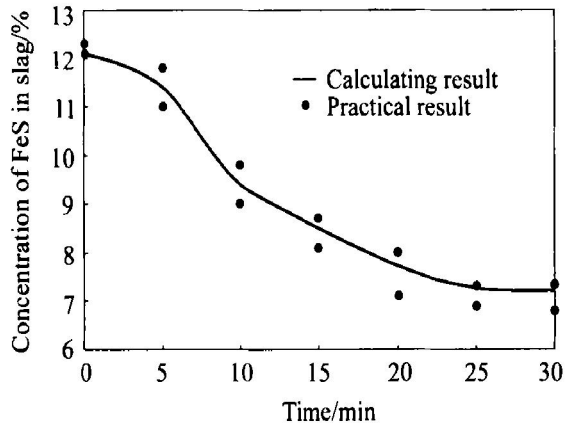

Fig. 5 Concentration of FeS in slag vs time

crepancy between the experimental and numerical data is inevitable.

Figs. 3 – 5 also suggest that there are only small deviations between the calculation values and the practical results of the SiO_2, Cu_2S, FeS contents in slag. Although discrepancy exists, the maximum difference between the experimental and numerical values is less than seven percent. So these numerical models are convincing to simulate the smelting behaviors of copper-nickel mineral in oxygen top-blown furnace. It is supposed that the models founded in this paper can be used to predict the smelting process and outcome of copper-nickel mineral in top-blown furnace.

4 CONCLUSIONS

A series of mathematical models of pyritic smelting process for copper-nickel mineral in oxygen top-blown furnace were put forward. In order to testify the reliability of these models, the verification tests were performed in a pilot scale furnace. As a result, the experimental results kept in good agreement with those of the mathematical simulation. It is evident that these numerical models are reliable to simulate the pyritic smelting process for copper-nickel mineral in oxygen top-blown furnace.

NOMENCLATURE

A —boundary area of pit, m^2;

A' —boundary area of reaction in slag, m^2;

c_i —molar concentration of i, kg/kmol;

c_O —concentration of [O], kmol/kg;

c_z, c_q —specific heat of slag and gas, kJ/(kg·K);

c_{ib} —concentration of i in slag, kmol/kg;

c_{os}, c_{is} —concentration of oxygen and i on surface of pit, kmol/kg;

$c_{ib'}$ – concentration of i in slag before Δt, kmol/kg;

D —diffusion coefficient of the matter in slag, m/s;

D_O, D_i —diffusion coefficients of oxygen and i, m/s;

h_0 —maximum depth of pit, m;

i —FeS, Cu_2S, Ni_3S_2;

J_O —molar flux of oxygen, kmol/(m^2·s);

k_i —reaction coefficient, kg/(kmol·s);

M_i —molar mass of i, kg/kmol;

s —perpendicular distance on surface of pit, m;

P_i —percentage of i in mineral, %;

Q_f —rate for releasing heat of forming copper matte in slag bath, kJ/s;

Q_l —heat transfer rate from surface of pit to slag, kJ/s;

Q_m —rate of releasing heat of oxidation reaction, kJ/s;

Q_s —rate of loss heat, kJ/s;

R —radius of smelting bath, m;

r —radius of pit, m;

S —overall molar flux of absorbed oxygen on surface of pit, kmol/s;

t —time, s;

T_q, T_z, T_s —temperature of gas, slag and surface of pit, K;

m —mass of matter input at Δt, kg;

m_i —mass of i in slag, kg;

m_q —mass of gas, kg;

m' —mass of overall matter in slag before Δt, kg;

k_z, k_q —heat transfer coefficients of slag and gas, kJ/(m^2·S·K);

δ —distributive coefficient of i;

ρ—density of slag, kg/m^3;

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