Calculation of equilibrium in the system «metal – slag» during steelmaking in electric arc furnace

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Abstract

A method for simultaneous solution of equations of material balance of the process and mathematical description of the equilibrium with the definition of active ingredients of slag as the phase with itinerant electrons is developed. To find solutions in the method of iterations there tested steepest descent algorithms and random search steps. The proposed approach provides a preliminary assessment of the results of the process steps with the process model, which will allow the staff of electric arc furnace to make right decisions. The use of modern computer technology to support management decision-making process eliminates the computational constraints and performs the

calculation of process parameters with the help of developed model.
Keywords: ELECTRIC ARC FURNACE, PROCESSES, EQUILIBRIUM, METAL, SLAG, DATA, MODELING, METHOD, CALCULATION

Introduction

The process of steelmaking in arc steel-smelting furnace is carried out after loading of iron-bearing burden material and slag-forming components according to the following stages: melting of the charge, holding of oxidation and reduction periods, refining operations and correction of composition of molten metal before tapping [1 - 3]. In each of these stages furnaces pass appropriate metallurgical processes, in which the conditions of equilibrium in the system “metal – slag” are created [4].

Problem statement

The most important component of computer decision support systems for process control subsystem is the calculation of chemical equilibrium and material balance, which is designed to select the type and determine the mass of the components loaded into the furnace during certain stages of the process [5]. Applied in practice methods for calculating the composition of metal and slag are based on experimentally determined coefficients “burn” or “assimilation” of slag-forming, deoxidizing and alloying materials [6 - 8]. This approach allows to determine the mass of reagents approximately, that results in undue overuse of materials and increase in duration of the process due to the need of further adjust of metal composition in furnace bath [9].

The article aim formulation

The aim of the study is to develop mathematical description of the equilibrium in the system “metal - slag” in the process of steelmaking in electric arc steelmaking furnaces based on certain activities of the components of the slag.

Mathematical description of the equilibrium system

In the given below method of joint solution of equations of material balance of a process and mathematical description of equilibrium there applied method for determining the activity of slag components as phase with collectivized electrons.

It is known that in oxides as well as in the metals, electrons of all atoms forming phase, make a single quantum-mechanical system [4], which can be characterized by the chemical potential of electrons. In the simplest implementation of the method of calculating the activity of slag components as a phase with collectivized electrons, partial entropy of mixing H^M_i is assumed as zero [10]. Herein the expression for the chemical potential $\mu_{(i)}$ of element i in the slag is of the form:

$$\mu_{(i)} = \mu^o_{(i)} + RT \ln x_{(i)}\psi_i + \mu^e \nu_i,$$

where $x_{(i)}$ - the concentration of the element i in the slag in atomic proportions;

μ^e - chemical potential of the electrons in the slag phase;

ν_i - degree of oxidation of the element i in the slag: $\nu_{Ca}=2$, $\nu_O=-2$, $\nu_{Mn}=2$ etc;

RT - universal gas constant and temperature multiplication.

The activity coefficient γ_i

$$\gamma_i = \psi_i e^{\frac{\mu^e \nu_i}{RT}}.$$

Ψ_i is calculated by the formula

$$\psi_i = \left(\sum_{j=1}^{k} x_i \cdot e^{\frac{-\varepsilon_{ij}}{RT}} \right)^{-1}$$

where - $\varepsilon_{ij}=½ (k_i^{½} - k_j^{½})^2$ energy swapping of atoms i and j;

k_i, k_j - energy parameters of elements i and j [10].

These formulas allow us to express the chemical potential of component i as a function of the composition of phase with the collectivized electrons and then on the basis of conditions of chemical equilibrium $\mu_{(i)}=\mu_{[i]}$, taking the expression for the metal $\mu_{[i]}=\mu^o_{[i]}$+RT In $a_{[i]}$, to obtain the expression for the constant

$$K^{1/\nu_i} = \left(\frac{a^*_{(i)}}{a_{[i]}} \right)^{1/\nu_i} e^{\frac{\mu}{RT}},$$

where $a^*_{(i)} = x_{(i)} \psi$;

$[i]$ or (i) - element i in metal $[i]$ or slag (i).

To exclude μ let us divide this expression into similar recorded for any other component (j) of the slag:

$$K_{i/j} = \frac{K^{1/\nu_i}}{K^{1/\nu_j}} = \left(\frac{a^*_{(i)}}{a_{[i]}} \right)^{1/\nu_i} \left(\frac{a_{[j]}}{a_{(j)}} \right)^{1/\nu_j}$$

This expression is equivalent to the law of mass action for the reaction:

$$\frac{1}{\nu_i}[i] + \frac{1}{\nu_j}(j) = \frac{1}{\nu_i}(i) + \frac{1}{\nu_j}[j].$$

As an example, for the equilibrium reaction of manganese in metal with its oxides in slag

$$[Mn] + (Fe) = (Mn) + [Fe].$$

For this reaction, the equilibrium constant equals to the equilibrium constant of the exchange reaction, written in the normal format via oxides, i.e. $K_{Fe/Mn} = K_{FeO/MnO}$

$$[Mn] + (FeO) = (MnO) + [Fe],$$

For the described variant of calculation, let us assume the temperature of process 1873K, when

$K_{FeO/MnO} = 2{,}865$ [11].

In the smelt iron activity $a_{[Fe]} = 1$, so we will obtain

$$[Mn] = a_{(Mn)} /(a_{(Fe)} K_{FeO/MnO}),$$

Table 1 shows the results of calculation of components activities of the slag as phase with collectivized electrons with energy parameters of elements. Initial data for calculation are the slag composition and temperature [12].

Table 1. Example of calculation of equilibrium compositions according to the slag activity as a phase with collectivized electrons

Slag Composition, %								Calculation formulas
(CaO)	(SiO_2)	(FeO)	(Fe_2O_3)	(MgO)	(P_2O_5)	(MnO)	(Cr_2O_3)	
36,11	33,04	6,41	1,26	14,97	1,37	6,33	0,1	The composition of the slag is set
The number of moles of oxides per 100 g of slag								
$m_{(CaO)}$	$m_{(SiO_2)}$	$m_{(FeO)}$	$m_{(Fe_2O_3)}$	$m_{(MgO)}$	$m_{(P_2O_5)}$	$m_{(MnO)}$	$m_{(Cr_2O_3)}$	
0,645	0,551	0,0890	0,0079	0,374	0,0096	0,089	0,0007	$m_{(i)} = (i)/M_i$
The number of moles elements per 100 g of slag								
$n_{(Ca)}$	$n_{(Si)}$	$n_{(Fe)}$	$n_{(Mg)}$	$n_{(P)}$	$n_{(Mn)}$	$n_{(Cr)}$	$n_{(O)}$	$n_{(Ca)} = m_{(CaO)}$
0,645	0,551	0,105	0,374	0,019	0,089	0,001	2,415	S $n_{(i)}$ = 4,199
Numbers of atomic masses of elements in 100 g of slag								
$x_{(Ca)}$	$x_{(Si)}$	$x_{(Fe)}$	$x_{(Mg)}$	$x_{(P)}$	$x_{(Mn)}$	$x_{(Cr)}$	$x_{(O)}$	
0,154	0,131	0,025	0,089	0,005	0,021	0,000	0,575	$x_{(i)} = n_{(i)}/$ S
The energy parameters of elements, kJ								
104,6	171,5	334,7	146,4	205,0	251,0	251,0	1255,0	k_i
0	4,114	32,541	1,753	8,366	15,767	15,767	317,484	e $_{Ca-i}=½ (k_i^{½} - k_{Ca}^{½})^2$
1	0,768	0,124	0,894	0,584	0,363	0,363	0	$A_{Ca-i}=\exp(-\varepsilon_{Ca-i}/RT)$
4,114	0	13,515	0,496	0,747	3,773	3,773	249,318	e $_{Si-i}=½ (k_i^{½} - k_{Si}^{½})^2$
0,768	1	0,420	0,969	0,953	0,785	0,785	0	$A_{Si-i}= \exp(-\varepsilon_{Si-i}/RT)$
32,541	13,515	0	19,190	7,908	3,006	3,006	146,739	$\varepsilon_{Fe-i}=½ (k_i^{½} - k_{Fe}^{½})^2$
0,124	0,420	1	0,292	0,602	0,824	0,824	0	$A_{Fe-i}= \exp(-\varepsilon_{Fe-i}/RT)$
1,753	0,496	19,190	0	2,460	7,006	7,006	272,060	e $_{Mg-i}=½ (k_i^{½} - k_{Mg}^{½})^2$
0,894	0,969	0,292	1	0,854	0,638	0,638	0	$A_{Mg-i}=\exp(-\varepsilon_{Mg-i}/RT)$
8,366	0,747	7,908	2,460	0	1,163	1,163	222,777	e $_{P-i}=½ (k_i^{½} - k_P^{½})^2$
0,584	0,953	0,602	0,854	1	0,928	0,928	0	$A_{P-i}= \exp(-\varepsilon_{P-i}/RT)$
15,767	3,773	3,006	7,006	1,163	0	0	191,747	e $_{Mn-i}=½ (k_i^{½} - k_{Mn}^{½})^2$
0,363	0,785	0,824	0,638	0,928	1	1	0	$A_{Mn-i}=\exp(-\varepsilon_{Mn-i}/RT)$
15,767	3,773	3,006	7,006	1,163	0	0	191,747	e $_{Cr-i}=½ (k_i^{½} - k_{Cr}^{½})^2$
0,363	0,785	0,824	0,638	0,928	1	1	0	$A_{Cr-i}=\exp(-\varepsilon_{Cr-i}/RT)$
317,48	249,31	146,73	272,06	222,78	191,75	191,75	0	e $_{O-i}=½ (k_i^{½} - k_O^{½})^2$
0	0	0	0	0	0	0	1	$A_{O-i}=\exp(-\varepsilon_{O-i}/RT)$
0,347	0,367	0,146	0,378	0,330	0,262	0,262	0,575	S $x_{(i)}A_{j-}$
2,878	2,724	6,871	2,643	3,026	3,818	3,818	1,739	y $_i$=(S $x_{(i)}A_{j-i})^{-1}$

Activity of slag components								
$a_{(Ca)}$	$a_{(Si)}$	$a_{(Fe)}$	$a_{(Mg)}$	$a_{(P)}$	$a_{(Mn)}$	$a_{(Cr)}$	$a_{(O)}$	
0,442	0,357	0,171	0,236	0,014	0,081	0,001	1,000	$a_i=\Psi_i x_{(i)}$
Metal composition, %								
[Ca]	[Si]	[Fe]	[Mg]	[P]	[Mn]	[Cr]	[O]	
0	0,0084	99,741	9,4E-08	0,0755	0,1650	0,0105	0,0394	Equilibrium calculation

The numbers of atomic masses of slag components are determined from

$$n_{(Ca)} = m_{(CaO)},$$

$$n_{(Si)} = m_{(SiO_2)},$$

$$n_{(Fe)} = m_{(FeO)} + 2\, m_{(Fe_2O_3)},$$

$$n_{(Mg)} = m_{(MgO)},$$

$$n_{(P)} = 2\, m_{(P_2O_5)},$$

$$n_{(Mn)} = m_{(MnO)},$$

$$n_{(Cr)} = 2\, m_{(Cr_2O_3)},$$

$$n_{(O)} = m_{(CaO)} + 2\, m_{(SiO_2)} + m_{(FeO)} +$$

$$+ 3\, m_{(Fe_2O_3)} + + m_{(MgO)} + 5\, m_{(P_2O_5)} +$$

$$+ m_{(MnO)} + 3\, m_{(Cr_2O_3)}.$$

After calculation of activities of all slag components, determination of molten metal composition which is in equilibrium with the slag is defined. In this example, the values of equilibrium constants [7 - 11] at the temperature of 1873 K for reactions are used:

$$[Si] + 2(FeO) = (SiO_2) + 2[Fe],$$

$$K_{FeO/SiO2} = 1445 \;\; [7];$$

$$[Si] = a_{(Si)} /(a^2_{(Fe)} K_{FeO/SiO2});$$

$$[Mg] + (FeO) = (MgO) + [Fe],$$

$$K_{FeO/MgO} = 1{,}4\; 10^7 \;\; [11];$$

$$[Mg] = a_{(Mg)} /(a_{(Fe)} K_{FeO/MgO});$$

$$2[Cr] + 3(FeO) = (Cr_2O_3) + 3[Fe],$$

$$K_{FeO/Cr2O3} = 0{,}0129 \;\; [8];$$

$$[Cr] = (a^2_{(Cr)} /(a^2_{(Fe)} K_{FeO/\,Cr2O3}))^{0,5};$$

$$2[P] + 5(FeO) = (P_2O_5) + 5[Fe],$$

$$K_{FeO/P_2O_5} = 229 \;\; [10].$$

During operation of the electric arc furnace automatic control system these equilibrium constants will be calculated as a function of average temperature of metal in the furnace.

The oxygen content in the metal is defined by the equilibrium of the reaction at T = 1873 K [11]:

$$[Fe] + [O] = (FeO),$$

$$K_{[O]/(FeO)} = 4{,}351;$$

$$[O] = a_{(Fe)} / K_{[O]/(FeO)};$$

$$[P] = (a^2_{(P)} /(a^2_{(Fe)} K_{FeO/\,P2O5}))^{0,5}.$$

Thus, as follows from the above mentioned dependencies, at known composition of the slag, equilibrium impurity content of [Si], [Mn], [Mg], [Cr], [P] in metal can be calculated. These components are distributed in the form of elements and oxides between metal and slag.

The aim of calculation of material balance is the determination of such composition of the slag, in which the condition of overall balance in each of the elements of the system "metal – slag" will be fulfilled

$$Y = \sum_{k=1}^{n} \left(x_k^0 - x_k^r\right)^2 \le \xi,$$

where x_k^0 - total weight of *k*-element loaded into the furnace;

x_k^r - total weight of *k*-element after equilibrium calculating.

During calculations the content of (FeO) and (Fe_2O_3) in the slag was determined depending on the concentration of carbon in the metal according to the method, which is based on the experimental data [12].

The distribution of sulfur between slag and metal was calculated as described in [12]. The value of imbalance ξ is accepted on the basis of accuracy of chemical analysis - 0,001% [9]. With such accuracy of analysis for 3500 kg of metal charged into the furnace of type EAF - 3M, imbalance should be no more than 0.035 kg.

Multi-sweep procedure

To find solutions there were tried steepest descent methods and random search steps. In case of successful step, motion towards minimum of function *Y* is made in the direction previously selected; if the step is unsuccessful, one should define the new direction of search. In the algorithms *a* and *b* shown in Fig.1, the introduced procedure of back space, if the step is unsuccessful in order to reduce the "search" in the area of solutions.

Solution search process includes:

G - the operator of determination of function gradient Y; Z - operator of definition of random directions; "+" - operator of step in the direction of the gradient or in random direction (or the same direction as the previous step); s - operator of changes of the step size when searching; "-" – back space.

Search for solution is in determination of distribution coefficients

$$L_k = \frac{x_k^s}{x_k},$$

where x_k^s – mass of k^{th} element in the slag.

Algorithm of variables change in the steepest descent method and random search

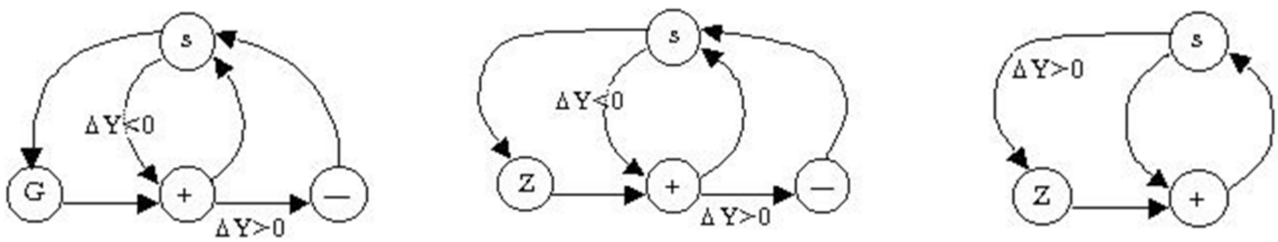
$$L_k^{(i+1)} = L_k^{(i)} + h_i \cdot \frac{g_k}{(\sum_k g_j^2)^{1/2}}.$$

where L_k – are normalized values of variables, $0 < L_k < 1$;

k - index of elements (Si), (Mn), (Mg), (Cr), (P);

h_i - value of the *i*-th step;

g_k - differential derivatives at the steepest descent or random vectors in step method of random search.



a) b) c)

Figure 1. Graphics of solutions search methods: a - steepest descent; b - random step search with return to the best result; c - random step search without return to the best result

As an indicator of the effectiveness of methods there accepted ratio of total number of steps N to the number of successful steps of search Nu. As is seen from the results in Fig. 2, with the largest computational costs there occur search for solutions in case of steepest descent method. Random search without return to the best solution proved to be the most effective.

Fig. 3 shows the convergence of the mass balance calculation during searching of solution by steepest descent method. It took more than 600 calls to the sub-program of equilibrium calculation to find the solution.

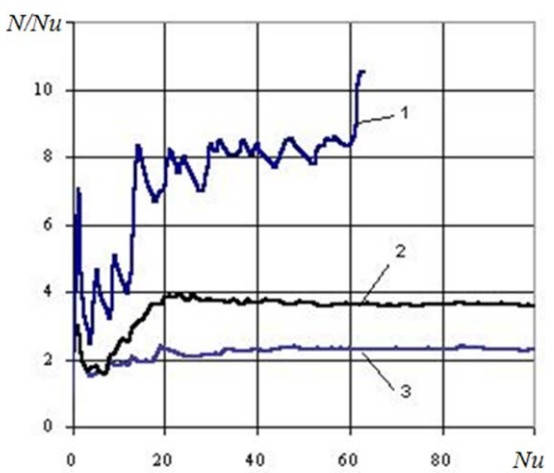


Figure 2. Comparison of methods of search solution: 1 - steepest descent, 2 – step random with return, 3 - step random without return

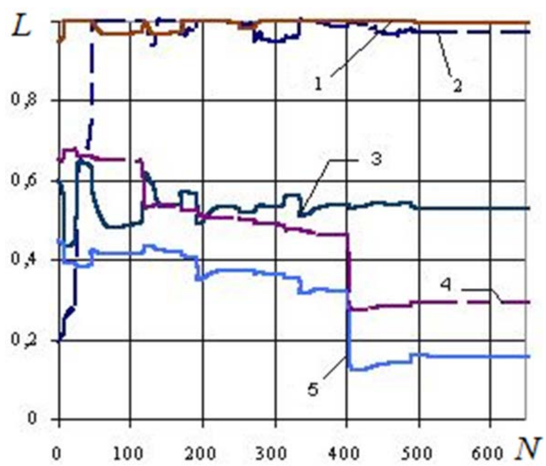


Figure 3. Convergence of calculation of material balance during the search for a solution by the steepest descent: 1 – MgO; 2 – SiO_2; 3 – MnO; 4 – P_2O_5; 5 – Cr_2O_3

Search by steepest descent method takes place in conditions of prolonged "yaw" in the extremum area due to ravine character of the function in the target area. The methods where direction of search is determined randomly are more effective for such functions.

Conclusions

Suggested method of application of a technique for determining the activity of slag components as phase with itinerant electrons for mathematical description of the equilibrium in the system "metal - slag" is the basis for the construction of decision support system for managing of steelmaking process. In the course of melting concentration of impurities in metal is specified by real data of chemical analysis. The feature of suggested approach is the possibility of preliminary evaluation of technical operations with the use of process model that will allow staff to make right and informed decisions.

The use of modern computer technology to support decision-making, as well as in the training systems [13, 14], eliminates the computational constraints and to perform the calculation of process parameters on the basis of analytical relationships [15]. The results obtained can be used to automate the process of building of system and also will be useful in the design of computer simulator for arc steel-making furnace.

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