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Thermodynamic model of lead oxide activity in PbO–CaO–SiO₂–FeO–Fe₂O₃ slag system

Jin-liang WANG^{1,2}, Xiao-chun WEN¹, Chuan-fu ZHANG²

1. School of Metallurgy and Chemical Engineering,

Jiangxi University of Science and Technology, Ganzhou 341000, China;

2. School of Metallurgy and Environment, Central South University, Changsha 410083, China

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Abstract: According to the ion and molecule coexistence theory, a thermodynamic model of lead oxide activity in PbO–CaO–SiO₂–FeO–Fe₂O₃ slag system was established at the temperature of 1273–1733 K. The activities of PbO in slag were calculated, and their equal activity curves were plotted. The influences of slag basicity Q, iron oxide rate R and temperature T on activity N_{PbO} and activity coefficient γ_{PbO} were also investigated. Results show that the calculated values of γ_{PbO} are in good agreement with the reported experimental data, showing that the model can wholly embody the slag structural characteristics. N_{PbO} departures positively from Raoult values, and increases with increasing PbO content in slag but changes little with T. γ_{PbO} increases with increasing Q, and goes through the maximum with increasing R for basic slag (Q>0.3). Results can be applied to the thermodynamic research and operational optimization of modern lead smelting technologies.

Key words: ion and molecule coexistence theory; thermodynamic model; lead oxide; activity

1 Introduction

Nowadays, some novel technologies, such as QSL, Kivcet and Ausmelt/Isamelt, are replacing conventional lead-making methods [1-3]. The activity of lead oxide is an important parameter that can be widely applied to lowering lead content in slag as well as to optimizing operational parameters of lead smelting process. Several articles have been published on the phase equilibria in lead smelting slags [4-6]; however, only limited data on activity of PbO in CaO–SiO₂–FeO–Fe₂O₃ slags have been reported [7].

The ion and molecule coexistence theory (IMCT) [8,9] has been developed to express the reaction ability of components in a slag by the defined mass action concentration N_i according to the mass action law, like the traditionally applied activity a_i of component *i*. The IMCT has been successfully used to predict sulfur, phosphorus or oxygen distribution at slag-metal interface [10–13], and has been verified as an efficient

method to calculate the activities of structural units in various slags [14–17].

In the present work, a thermodynamic model of lead oxide activity in PbO–CaO–SiO₂–FeO–Fe₂O₃ slag system was established according to the IMCT and verified by reported data [7]. The effects of slag composition and temperature on activity and activity coefficient of PbO were investigated, and the equal activity curves of PbO were plotted.

2 Establishment of PbO-CaO-SiO₂-FeO-Fe₂O₃ activity model

2.1 Slag structural units

According to the basic hypotheses of the IMCT [9], the main assumptions in the developed thermodynamic model for calculating the activity (mass action concentration) of PbO in PbO–CaO–SiO₂–FeO–Fe₂O₃ slag can be simply summarized as follows.

1) Structural units in the studied slag are assumed to be composed of simple ions, such as Pb^{2+} , Fe^{2+} , Ca^{2+} and

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Corresponding author: Jin-liang WANG; Tel: +86-797-8312337; E-mail: simwjl@163.com DOI: 10.1016/S1003-6326(15)63768-2 O^{2-} , simple molecules SiO₂ and Fe₂O₃, and complex molecules as silicates and ferrates. Every cation and anion can be generated from the basic components and exist in the form of ion-pairs as (Pb²⁺+O²⁻), (Fe²⁺+O²⁻) and (Ca²⁺+O²⁻).

2) The ion-pairs, simple molecules and complex molecules are under chemically dynamic equilibrium, by taking $(Ca^{2+}+O^{2-})$ and Fe_2O_3 to form $CaFe_2O_4$ as an example as $(Ca^{2+}+O^{2-})+Fe_2O_3=CaFe_2O_4$, and the chemical reactions of forming complex molecules obey the mass action law.

These hypotheses imply the relation between the mole number of basic components and the defined mass action concentration of each structural unit in slag, and connect the defined mass action concentrations of basic components and complex molecules with the chemical reaction equilibrium constant.

According to the IMCT, it can be reasonably obtained that there are four simple ions as Pb^{2+} , Fe^{2+} , Ca^{2+} and O^{2-} , two simple molecules as SiO_2 and Fe_2O_3 in $PbO-CaO-SiO_2-FeO-Fe_2O_3$ slag. Meanwhile, according to phase diagrams of $CaO-SiO_2$, $FeO-SiO_2$, $FeO-Fe_2O_3$, SiO_2-PbO , $CaO-FeO-Fe_2O_3$ and $CaO-FeO-SiO_2$, 13 kinds of complex molecules can be possibly formed in $PbO-CaO-SiO_2-FeO-Fe_2O_3$ slag in the temperature range from 1273 to 1733 K. The structural units are listed in Table 1.

Table 1 Structural units of PbO–CaO–SiO₂–FeO–Fe₂O₃ slag system

Phase diagram	Simple molecules and ions	Complex compounds	Ref.
CaO-SiO ₂	Ca^{2+}, O^{2-}, SiO_2	CaSiO ₃ , Ca ₂ SiO ₄ , Ca ₃ SiO ₅ , 3CaO·2SiO ₂ (1523 K $<$ T \leq 1737 K); CaSiO ₃ , Ca ₂ SiO ₄ , 3CaO·2SiO ₂ (T \leq 1523 K)	[18]
FeO-SiO ₂	Fe ²⁺ , O ²⁻ , SiO ₂	Fe ₂ SiO ₄	[18]
FeO-Fe ₂ O ₃	$Fe^{2^+}, O^{2^-}, Fe_2O_3$	Fe ₃ O ₄	[18]
SiO ₂ –PbO	$Pb^{2+}, O^{2-},$ SiO ₂	PbSiO ₃ , Pb ₂ SiO ₄ , Pb ₄ SiO ₆	[4]
CaO-FeO-Fe ₂ O ₃	$Ca^{2+}, Fe^{2+}, O^{2-}, Fe_2O_3$	Ca ₂ Fe ₂ O ₅ , CaFe ₂ O ₄ , CaFe ₃ O ₅ , Fe ₃ O ₄	[18]
CaO-FeO-SiO ₂	$Ca^{2+}, Fe^{2+}, O^{2-}, SiO_2$	$\begin{array}{c} Ca_3SiO_5, Ca_2SiO_4,\\ Fe_2SiO_4, \ 3CaO\cdot 2SiO_2,\\ CaSiO_3, \ CaFeSiO_4 \end{array}$	[18]

2.2 Chemical reactions between units

The mole numbers of five components in 100 g $PbO-CaO-SiO_2-FeO-Fe_2O_3$ slag are assigned as

 $b_1 = x_{CaO}^0$, $b_2 = x_{FeO}^0$, $b_3 = x_{PbO}^0$, $a_1 = x_{SiO_2}^0$ and $a_2 = x_{Fe_2O_3}^0$ to represent the chemical composition of the slag. The defined equilibrium mole number x_i and mass action concentration (activity) N_i of all structural units in PbO–CaO–SiO₂–FeO–Fe₂O₃ slag are listed in Table 2.

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Unit	Activity	Mole number
(Ca ²⁺ +O ²⁻)	N_1	x_1
$(Fe^{2+}+O^{2-})$	N_2	<i>x</i> ₂
$(Pb^{2+}+O^{2-})$	N_3	x_3
SiO ₂	N_4	x_4
Fe ₂ O ₃	N_5	x_5
Fe ₃ O ₄	N_6	x_6
CaFe ₂ O ₄	N_7	x_7
CaFe ₃ O ₅	N_8	x_8
$Ca_2Fe_2O_5$	N_9	x_9
PbSiO ₃	N_{10}	x_{10}
Pb ₂ SiO ₄	N_{11}	x_{11}
Pb ₄ SiO ₆	N ₁₂	<i>x</i> ₁₂
CaSiO ₃	N_{13}	<i>x</i> ₁₃
Ca ₂ SiO ₄	N_{14}	x_{14}
$3CaO \cdot 2SiO_2$	N_{15}	<i>x</i> ₁₅
CaFeSiO ₄	N_{16}	x_{16}
Fe ₂ SiO ₄	N_{17}	<i>x</i> ₁₇
Ca ₃ SiO ₅	N_{18}	x_{18}

The total equilibrium mole number $\sum x$ can be expressed as

$$\sum x = 2x_1 + 2x_2 + 2x_3 + \sum_{i=4}^{18} x_i \tag{1}$$

According to the IMCT, the mass action concentration (activity) of ion couples in the form of ion-pairs, i.e. $(Pb^{2+}+O^{2-})$, $(Fe^{2+}+O^{2-})$ and $(Ca^{2+}+O^{2-})$, should be represented as

$$CaO = Ca^{2+} + O^{2-}$$

$$N_{1} = N_{Ca^{2+}} + N_{O^{2-}} = \frac{2x_{1}}{\sum x},$$

$$x_{1} = 0.5N_{1}\sum x$$
(2)

 $FeO = Fe^{2+} + O^{2-}$

$$N_{2} = N_{\text{Fe}^{2+}} + N_{\text{O}^{2-}} = \frac{2x_{2}}{\sum x},$$

$$x_{2} = 0.5N_{2}\sum x$$
(3)

 $PbO = Pb^{2+} + O^{2-}$

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$$N_{3} = N_{Pb^{2+}} + N_{O^{2-}} = \frac{2x_{3}}{\sum x},$$

$$x_{3} = 0.5N_{3}\sum x$$
(4)

Meanwhile, the activity of other independent structural units can be calculated by

$$\begin{cases} N_i = \frac{x_i}{\sum x}, \ (i = 4, 5, \dots, 18) \\ x_i = N_i \sum x, \ (i = 4, 5, \dots, 18) \end{cases}$$
(5)

The chemical equations between the units of the PbO–CaO–SiO₂–FeO–Fe₂O₃ slag system are shown as follows:

$$(Fe^{2+} + O^{2-}) + Fe_2O_3 = Fe_3O_4$$

$$\Delta G^{\Theta} = -45845.5 + 10.634T \quad (298 - 1870 \text{ K}),$$

$$K_1 = \frac{N_6}{N_2N_5}, \quad N_6 = K_1N_2N_5 \quad (6)$$

$$(Ca^{2+} + O^{2-}) + Fe_2O_3 = CaFe_2O_4$$

$$\Delta G^{\Theta} = -99218.15 - 152.83T \lg T + 526.62T (973 - 1489 K),$$

$$\Delta G^{\Theta} = 51672.20 - 83.46T \lg T + 205.21T (1216 - 1733 K),$$

$$K_2 = \frac{N_7}{N_1N_5}, N_7 = K_2N_1N_5$$
(7)

$$(Ca^{2+} + O^{2-}) + (Fe^{2+} + O^{2-}) + Fe_2O_3 = CaFe_3O_5$$

$$\Delta G^{\Theta} = -14653.8 - 27.2142T (973 - 1733 \text{ K}),$$

$$K_3 = \frac{N_8}{N_1 N_2 N_5}, N_8 = K_3 N_1 N_2 N_5$$
(8)

$$2(Ca^{2+} + O^{2-}) + Fe_2O_3 = Ca_2Fe_2O_5$$
$$\Delta G^{\Theta} = -53172.4 - 2.5121T (973 - 1723 \text{ K}),$$

$$K_4 = \frac{N_9}{N_1^2 N_5}, \ N_9 = K_4 N_1^2 N_5 \tag{9}$$

$$(Pb^{2+} + O^{2-}) + SiO_2 = PbSiO_3$$

$$\Delta G^{2} = -25120.8 + 1.256I (9/3 - 1/73 \text{ K}),$$

$$K_{5} = \frac{N_{10}}{N_{3}N_{4}}, N_{10} = K_{5}N_{3}N_{4}$$
(10)

$$2(Pb^{2+} + O^{2-}) + SiO_2 = Pb_2SiO_4$$

$$\Delta G^{\Theta} = -33494.4 - 6.699T (1158 - 1773 \text{ K}),$$

$$K_6 = \frac{N_{11}}{N_3^2 N_4}, \ N_{11} = K_6 N_3^2 N_4 \tag{11}$$

$$4(Pb^{2+} + O^{2-}) + SiO_2 = Pb_4SiO_6$$

$$\Delta G^{\Theta} = -67118 - 615.932T + 99.079T\ln T - 0.049649T^2(1158 - 1773 \text{ K}),$$

$$K_7 = \frac{N_{12}}{N_3^4 N_4}, \ N_{12} = K_7 N_3^4 N_4 \tag{12}$$

$$(Ca2+ + O2-) + SiO2 = CaSiO3$$

$$\Delta G^{\Theta} = -36425.2 - 30.5636T (298 - 1813 \text{ K}),$$

$$K_8 = \frac{N_{13}}{N_1 N_4}, N_{13} = K_8 N_1 N_4$$
(13)

$$2(Ca^{2+} + O^{2-}) + SiO_2 = Ca_2SiO_4$$

$$\Delta G^{\Theta} = -118905 - 11.3044T (298 - 2403 K),$$

$$K_9 = \frac{N_{14}}{N_1^2 N_4}, N_{14} = K_9 N_1^2 N_4$$
(14)

$$3(\text{Ca}^{2+} + \text{O}^{2-}) + 2\text{SiO}_{2} = 3\text{CaO} \cdot 2\text{SiO}_{2}$$
$$\Delta G^{\Theta} = -236972.9 + 9.6296T (298 - 1773 \text{ K}),$$
$$K_{10} = \frac{N_{15}}{N_{1}^{3}N_{4}^{2}}, N_{15} = K_{10}N_{1}^{3}N_{4}^{2}$$
(15)

$$(\operatorname{Ca}^{2+} + \operatorname{O}^{2-}) + (\operatorname{Fe}^{2+} + \operatorname{O}^{2-}) + \operatorname{SiO}_2 = \operatorname{CaFeSiO}_4$$

$$\Delta G^{\Theta} = -72996.8 - 29.3169T (973 - 1643 \text{ K}),$$

$$K_{11} = \frac{N_{16}}{N_1 N_2 N_4}, N_{16} = K_{11} N_1 N_2 N_4$$
(16)

$$2(Fe^{2+} + O^{2-}) + SiO_2 = Fe_2SiO_4$$

$$\Delta G^{\Theta} = -32260 + 15.27T \quad (25 - 1500 \text{ °C}),$$

$$K_{12} = \frac{N_{17}}{N_2^2 N_4}, \quad N_{17} = K_{12}N_2^2 N_4 \quad (17)$$

$$3(Ca^{2+} + O^{2-}) + SiO_2 = Ca_3SiO_5$$

$$\Delta G^{\Theta} = -118905 - 7.179T \ (25 - 1500 \,^{\circ}C),$$

$$K_{13} = \frac{N_{18}}{N_1^3 N_4}, \ N_{18} = K_{13}N_1^3 N_4$$
(18)

The equilibrium constants K_i ($i = 1, 2, \dots, 13$) in Eqs. (6)–(18) can be calculated by ΔG^{Θ} of each reaction obtained from Ref. [19].

2.3 Activity calculation model

According to the conservation law of mass, the following equations can be deduced.

1) For the mole number of CaO

$$b_{1} = x_{1} + x_{7} + x_{8} + 2x_{9} + x_{13} + 2x_{14} + 3x_{15} + x_{16} + 3x_{18} = (0.5N_{1} + N_{7} + N_{8} + 2N_{9} + N_{13} + 2N_{14} + 3N_{15} + N_{16} + 3N_{18}) \cdot \sum x = (0.5N_{1} + K_{2}N_{1}N_{5} + K_{3}N_{1}N_{2}N_{5} + 2K_{4}N_{1}^{2}N_{5} + K_{8}N_{1}N_{4} + 2K_{9}N_{1}^{2}N_{4} + 3K_{10}N_{1}^{3}N_{4}^{2} + K_{11}N_{1}N_{2}N_{4} + 3K_{13}N_{1}^{3}N_{4}) \cdot \sum x$$
(19)

2) For the mole number of FeO

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$$b_{2} = x_{2} + x_{6} + x_{8} + x_{16} + 2x_{17} =$$

$$(0.5N_{2} + N_{6} + N_{8} + N_{16} + 2N_{17}) \cdot \sum x =$$

$$(0.5N_{2} + K_{1}N_{2}N_{5} + K_{3}N_{1}N_{2}N_{5} +$$

$$K_{11}N_{1}N_{2}N_{4} + 2K_{12}N_{2}^{2}N_{4}) \cdot \sum x \qquad (20)$$

3) For the mole number of PbO

$$b_{3} = x_{3} + x_{10} + 2x_{11} + 4x_{12} =$$

$$(0.5N_{3} + N_{10} + 2N_{11} + 4N_{12}) \cdot \sum x =$$

$$(0.5N_{3} + K_{5}N_{3}N_{4} + 2K_{6}N_{3}^{2}N_{4} +$$

$$4K_{7}N_{3}^{4}N_{4}) \cdot \sum x \qquad (21)$$

4) For the mole number of SiO₂

$$a_{1} = x_{4} + x_{10} + x_{11} + x_{12} + x_{13} + x_{14} + 2x_{15} + x_{16} + x_{17} + x_{18} = (N_{4} + N_{10} + N_{11} + N_{12} + N_{13} + N_{14} + 2N_{15} + N_{16} + N_{17} + N_{18}) \cdot \sum x = (N_{4} + K_{5}N_{3}N_{4} + K_{6}N_{3}^{2}N_{4} + K_{7}N_{3}^{4}N_{4} + K_{8}N_{1}N_{4} + K_{9}N_{1}^{2}N_{4} + 2K_{10}N_{1}^{3}N_{4}^{2} + K_{11}N_{1}N_{2}N_{4} + K_{12}N_{2}^{2}N_{4} + K_{13}N_{1}^{3}N_{4}) \cdot \sum x$$
(22)
5) For the mole number of Fe₃O₃

5) For the mole number of Fe_2O_3

$$a_{2} = x_{5} + x_{6} + x_{7} + x_{8} + x_{9} =$$

$$(N_{5} + N_{6} + N_{7} + N_{8} + N_{9}) \cdot \sum x =$$

$$(N_{5} + K_{1}N_{2}N_{5} + K_{2}N_{1}N_{5} + K_{3}N_{1}N_{2}N_{5} +$$

$$K_{4}N_{1}^{2}N_{5}) \cdot \sum x$$
(23)

6) For the sum of all activities

$$\sum_{i=1}^{18} N_i = N_1 + N_2 + N_3 + N_4 + N_5 + K_1 N_2 N_5 + K_2 N_1 N_5 + K_3 N_1 N_2 N_5 + K_4 N_1^2 N_5 + K_5 N_3 N_4 + K_6 N_3^2 N_4 + K_7 N_3^4 N_4 + K_8 N_1 N_4 + K_9 N_1^2 N_4 + K_{10} N_1^3 N_4^2 + K_{11} N_1 N_2 N_4 + K_{12} N_2^2 N_4 + K_{13} N_1^3 N_4 = 1$$
(24)

The following equations can be obtained when $\sum x$ in Eqs. (20)–(23) was eliminated using Eq. (19):

$$b_{2}(0.5N_{1} + K_{2}N_{1}N_{5} + K_{3}N_{1}N_{2}N_{5} + 2K_{4}N_{1}^{2}N_{5} + K_{8}N_{1}N_{4} + 2K_{9}N_{1}^{2}N_{4} + 3K_{10}N_{1}^{3}N_{4}^{2} + K_{11}N_{1}N_{2}N_{4} + 3K_{13}N_{1}^{3}N_{4}) - b_{1}(0.5N_{2} + K_{1}N_{2}N_{5} + K_{3}N_{1}N_{2}N_{5} + K_{11}N_{1}N_{2}N_{4} + 2K_{12}N_{2}^{2}N_{4}) = 0$$
(25)

$$\begin{split} b_3(0.5N_1 + K_2N_1N_5 + K_3N_1N_2N_5 + 2K_4N_1^2N_5 + \\ K_8N_1N_4 + 2K_9N_1^2N_4 + 3K_{10}N_1^3N_4^2 + \\ K_{11}N_1N_2N_4 + 3K_{13}N_1^3N_4) - \\ b_1(0.5N_3 + K_5N_3N_4 + 2K_6N_3^2N_4 +) \end{split}$$

$$4K_{7}N_{3}^{4}N_{4}) = 0$$
(26)

$$a_{1}(0.5N_{1} + K_{2}N_{1}N_{5} + K_{3}N_{1}N_{2}N_{5} + 2K_{4}N_{1}^{2}N_{5} + K_{8}N_{1}N_{4} + 2K_{9}N_{1}^{2}N_{4} + 3K_{10}N_{1}^{3}N_{4}^{2} + K_{11}N_{1}N_{2}N_{4} + 3K_{13}N_{1}^{3}N_{4}) - b_{1}(N_{4} + K_{5}N_{3}N_{4} + K_{6}N_{3}^{2}N_{4} + K_{7}N_{3}^{4}N_{4} + K_{8}N_{1}N_{4} + K_{9}N_{1}^{2}N_{4} + 2K_{10}N_{1}^{3}N_{4}^{2} + K_{11}N_{1}N_{2}N_{4} + K_{12}N_{2}^{2}N_{4} + K_{13}N_{1}^{3}N_{4}) = 0$$
(27)

$$a_{2}(0.5N_{1} + K_{2}N_{1}N_{5} + K_{3}N_{1}N_{2}N_{5} + 2K_{4}N_{1}^{2}N_{5} + K_{8}N_{1}N_{4} + 2K_{9}N_{1}^{2}N_{4} + 3K_{10}N_{1}^{3}N_{4}^{2} + K_{11}N_{1}N_{2}N_{4} + 3K_{13}N_{1}^{3}N_{4}) - b_{1}(N_{5} + K_{1}N_{2}N_{5} + K_{2}N_{1}N_{5} + K_{3}N_{1}N_{2}N_{5} + K_{4}N_{1}^{2}N_{5}) = 0$$
(28)

By transforming Eq. (24), the following equation can be obtained:

$$N_{1} + N_{2} + N_{3} + N_{4} + N_{5} + K_{1}N_{2}N_{5} + K_{2}N_{1}N_{5} + K_{3}N_{1}N_{2}N_{5} + K_{4}N_{1}^{2}N_{5} + K_{5}N_{3}N_{4} + K_{6}N_{3}^{2}N_{4} + K_{7}N_{3}^{4}N_{4} + K_{8}N_{1}N_{4} + K_{9}N_{1}^{2}N_{4} + K_{10}N_{1}^{3}N_{4}^{2} + K_{11}N_{1}N_{2}N_{4} + K_{12}N_{2}^{2}N_{4} + K_{13}N_{1}^{3}N_{4} - 1 = 0$$
(29)

Equations (25)–(29) are the activity models for the PbO–CaO–SiO₂–FeO–Fe₂O₃ slag system.

3 Calculation flowchart

The activity model is a set of higher order equations and its calculation process is a typical solving process of nonlinear equations. The calculation flowchart of the activity model is shown in Fig. 1.



Fig. 1 Calculation flowchart of activity model

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For the calculation process, the temperature *T* and the compositions $(b_1, b_2, b_3, a_1 \text{ and } a_2)$ of the PbO–CaO– SiO₂–FeO–Fe₂O₃ slag system were inputted at the beginning. The equilibrium constants of each chemical reaction K_i ($i = 1, 2, \dots, 13$) then can be calculated. After being linearized, the higher order equations of the activity model were transformed to linear equations about activities N_i ($i = 1, 2, \dots, 5$), which can be solved by the Newton iterative method. To control the iteration process, a precision parameter ε was adopted.

In this work, an activity calculation program was developed using Delphi 7.0 based on the activity model above. ε was set to be 1×10^{-4} , because the activities can be regarded as the desired values when all of them changed less than 1×10^{-4} in the iteration process.

4 Results and discussion

The PbO activity N_{PbO} and the PbO activity coefficient γ_{PbO} ($\gamma_{PbO}=N_{PbO}/f_{PbO}$, f_{PbO} is the mole fraction of PbO in slag) were calculated for slags with different compositions at different temperatures (*T*).

The slag basicity (Q) and the iron oxide rate (R), defined by Eqs. (30) and (31), are introduced to simplify the description of the slag composition.

$$Q = w(CaO) / [w(CaO) + w(SiO_2)]$$
(30)

$$R = w(FeO_x) / [w(FeO_x) + w(CaO) + w(SiO_2)]$$
(31)

4.1 Effect of slag composition on activity and activity coefficient of PbO in slag

Figure 2 shows the model calculated values of the activity coefficient of PbO (γ_{PbO}) in PbO–CaO–SiO₂– FeO–Fe₂O₃ slag with different *Q* at 1573 K when the mass ratio of FeO to Fe₂O₃ is 5.0:1 and the mass fraction of PbO in slag is 1%. The corresponding measured data by KUDO et al [7] are also shown in Fig. 2.



Fig. 2 Comparison of calculated values and measured data of PbO activity coefficient in slag

As shown in Fig. 2, the model calculated values of γ_{PbO} are in good agreement with the measured data, showing that the activity calculation model can reflect the structural characteristics of the PbO–CaO–SiO₂– FeO–Fe₂O₃ slag system.

It can also be seen from Fig. 2 that γ_{PbO} in the slag, varying from 0.5 to 2.5 depending on the slag composition, increases with increasing Q. At a fixed R, the higher the Q value is, the higher the γ_{PbO} is. The effect of Q on the activity coefficient is stronger for R=0.31 than for R=0.60, because the slag with R=0.31 is less diluted with iron oxide than the slag with R=0.60. This means that CaO can reduce the solubility of PbO in the slag system, but SiO₂ can improve it. Therefore, in order to reduce the lead content in smelting slag, slags with high CaO content are usually adopted in modern lead smelting process.

Figure 3 shows the effect of *R* on the PbO activity coefficient γ_{PbO} at 1573 K when the mass ratio of FeO to Fe₂O₃ is 5.0:1, the mass fraction of PbO is 15%, and *Q* is equal to 0.1, 0.3 and 0.5.



Fig. 3 Effect of R on PbO activity coefficient at 1573 K

As shown in Fig. 3, in acidic slag with Q values less than 0.3, γ_{PbO} increases with increasing R, owing to a dilution of the acid component of silica by iron oxide. The activity coefficient in basic slag, with Q value over 0.3, goes through the maximum with increasing R. Slag with Q value of 0.5 has the maximum γ_{PbO} at R=0.3-0.4. The acid-base reaction may give a good explanation for the relation between the activity coefficient of PbO or lead solubility in slag and the slag composition. For modern lead smelting adopting basic slag, the iron oxide rate (R) is vital to decrease the lead content in the final smelting slag.

Figure 4 shows the relationship between PbO activity N_{PbO} and PbO mole fraction f_{PbO} in PbO–CaO–SiO₂–FeO–Fe₂O₃ slag at 1573 K when the mass ratio of FeO to Fe₂O₃ is 5.0:1 and Q is equal to 0.4.



Fig. 4 Effect of mole fraction of PbO in slag on PbO activity at Q=0.4 and T=1573 K

As shown in Fig. 4, N_{PbO} departures positively from Raoult values regardless of *R* values. The Raoult deviation increases first and then decreases with increasing f_{PbO} , and reaches the maximum at $f_{PbO}=0.4$ when *R*=0.8, but at $f_{PbO}=0.6$ when *R*=0.2.

4.2 Effect of temperature on activity coefficient of PbO in slag

Figure 5 shows the effect of temperature *T* on the PbO activity coefficient γ_{PbO} at 1373 K and 1573 K when the mass ratio of FeO to Fe₂O₃ is 5.0:1, the mass fraction of PbO is 15%, and *Q* is equal to 0.1 and 0.5.



Fig. 5 Effect of temperature on activity coefficient of PbO at Q=0.1 and 0.5

As shown in Fig. 5, the activity coefficients change little with temperature. Accordingly, the effect of temperature on the activity coefficient of PbO is not significant within the temperature range from 1373 K to 1573 K at Q=0.1 and Q=0.5.

4.3 Equal activity curves

Figures 6 and 7 show the equal activity curves of

PbO in PbO–CaO–SiO₂–FeO–Fe₂O₃ slag at Q=0.5 and FeO/Fe₂O₃ mass ratio of 5.0:1, which is the popular slag composition of modern lead smelting, at 1423 K and 1523 K respectively. For these ternary diagrams, CaO and SiO₂ were bound as one coordinate point, named CaO+SiO₂, and FeO+Fe₂O₃ was regarded as another coordinate point, named FeO_x.



Fig. 6 Equal activity curves of PbO in PbO–CaO–SiO₂–FeO– Fe₂O₃ slag at 1423 K



Fig. 7 Equal activity curves of PbO in PbO–CaO–SiO₂–FeO– Fe₂O₃ slag at 1523 K

As shown in Figs. 6 and 7, the equal activity curves are almost parallel. PbO activity increases with increasing PbO content in slag, but the activity curves near the PbO–CaO+SiO₂ line vary larger with the changing PbO content in slag than that near the PbO–FeO_x line for the reason that PbO can combine with SiO₂ more strongly than with FeO or Fe₂O₃.

5 Conclusions

1) Calculated values of the activity model are in good agreement with the reported experimental data,

showing that the thermodynamic model can reflect the structural characteristics of the PbO–CaO–SiO₂–FeO– Fe_2O_3 slag system.

2) N_{PbO} departures positively from the Raoult values regardless of *R* values, and increases with increasing PbO content in slag but changes little with *T*.

3) γ_{PbO} varies from 0.5 to 2.5 depending on the slag composition and increases with increasing Q value. CaO can reduce the solubility of PbO in the slag system, but SiO₂ can improve it.

4) γ_{PbO} in basic slag with *Q* values over 0.3 goes through the maximum with increasing *R* value. Slag with *Q* value of 0.5 has the maximum γ_{PbO} at *R*=0.3–0.4.

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PbO-CaO-SiO₂-FeO-Fe₂O₃ 渣系氧化铅活度热力学模型

汪金良^{1,2},温小椿¹,张传福²

1. 江西理工大学 冶金与化学工程学院, 赣州 341000; 2. 中南大学 冶金与环境学院, 长沙 410083

摘 要:基于炉渣结构分子和离子共存理论,建立 1273~1733 K 下的 PbO-CaO-SiO₂-FeO-Fe₂O₃渣系氧化铅活度 热力学模型,计算 PbO 活度并绘制等活度曲线,考察炉渣碱度 Q、氧化铁比率 R 和温度 T 对活度 N_{PbO} 和活度系 数 γ_{PbO} 的影响。结果表明,活度系数 γ_{PbO} 的模型计算值与文献测定值吻合程度高,说明该模型能较好地反映该渣 系结构本质; N_{PbO}呈拉乌尔正偏差,且随渣中 PbO 含量的升高而增大,但受温度的影响不明显; γ_{PbO} 随 Q 的升 高而增大;对于 Q>0.3 的碱性渣, γ_{PbO} 随 R 的升高而出现极大值。该研究结果可用于现代炼铅工艺的热力学研究 和操作优化。

关键词:分子和离子共存理论;热力学模型;氧化铅;活度