VOLATILIZATION CHARACTERISTICS OF HIGH-LEAD SLAG AND ITS INFLUENCE ON MEASUREMENT OF PHYSICOCHEMICAL PROPERTIES AT HIGH TEMPERATURE

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Abstract

Volatilization causes measurement deviations of physicochemical properties for volatiles-containing slag at high temperature. Hence, investigating the degree of volatilization and identifying the volatilization mechanism and deviation rules are crucial to improve the accuracy of the measured properties. Here, PbO-FeO$_x$-CaO-SiO$_2$-ZnO slag system was selected as a research subject. The volatile characteristics and non-isothermal intrinsic kinetic models of high-temperature volatilization for lead slag were established by thermogravimetric analysis (TGA), and the volatilization mechanism and deviation in the measured properties were determined by analyzing the phase and chemical composition of the residues. In addition, experimental measurements of the melting temperature/ viscosity were compared with theoretically calculated results. The volatilization of PbO decreased the lead-containing phase, but increased the amount of precipitated spinel phase, which led to the deviation in the measured physicochemical properties of the studied slags. The volatilization kinetics for PbO in the slags followed three-dimensional diffusion. The diffusion of PbO gas from PbO-FeO$_x$-CaO-SiO$_2$-ZnO slag was the restrictive step of volatile reaction, and mechanism function was $g(\alpha)=1-(1-\alpha)^{1/3}$. Moreover, during the slag properties measurement at high temperatures, a high heating rate and protective gas can be used to reduce volatilization of lead slag and avoid consequent properties deviation.

Keywords: Lead slag; Measurement deviation; Volatile characteristics; Kinetics

1. Introduction

The physicochemical properties of slag have a notable influence on the determination of smelting temperature, control of chemical reactions during smelting, solidification of the metal, and removal of inclusions. Therefore, it is important to obtain accurate data pertaining to good metallurgical slag performance in pyrometallurgy [1,2]. It is well known that most traditional methods to measure the metallurgical properties of the slags, such as melting point, viscosity, and electrical conductivity, are accomplished over a period of about 2 h at high temperature. The first step of the procedure for measuring the smelting point of slag includes the preparation of the slags which are then pressed into columnar shapes. Then, the sample is placed in a test furnace and heated at a constant rate. The whole melting process of the slags, from the initial melting to hemispherical height, is recorded by a high-temperature camera until the samples are fluidized. Many studies attempted to determine the physicochemical properties of PbO-FeO$_x$-CaO-SiO$_2$-ZnO volatiles-containing slags [3,4]. However, due to long holding time at high temperatures, evaporation of volatile components is inevitable during the measurement of the metallurgical properties [5]. In the past few years, many research groups, including ours, paid particular attention to this phenomenon and carried out a certain amount of research on volatiles-containing slag [6–10]. Osada et al reported an increase in the melting temperature caused by the volatilization of lead slag [6]. Nakada et al also found that volatilization of lead has a notable effect on the slag viscosity [7]. However, the volatilization mechanism and temporal pattern of volatile emission in lead-containing slags at high temperature has not been investigated in adequate detail. In fact, in our

previous measurement work, it was found that the final composition of lead slag was inconsistent with the original designed value, which was mostly caused by the continuous loss of volatile components [10]. In other words, the measured properties of the slag corresponded to a varied slag composition. This inconsistency problem is quite commonly encountered in properties measurement of volatiles-containing slag at high temperatures and it remains unresolved. Therefore, it is of great theoretical and practical application significance to explore the main reason for this inconsistency and the crucial factors influencing the deviation in properties measurement of lead slag at high temperature. Furthermore, the volatilization mechanism will be determined, and the deviation law between the slag composition and its properties will be predicted accordingly.

Based on the above-mentioned understanding and our previous research results, PbO-FeO$_x$-CaO-SiO$_2$-ZnO slag system, with different FeO/SiO$_2$ ratio, CaO/SiO$_2$ ratio, and PbO contents, were chosen as a research system. The volatilization characteristics of lead-containing slag and their influence on the measurement accuracy of melting point, and viscosity at high temperature were determined. The dynamics models of volatilization for lead slags at high temperature were established based on the analysis of the results of Thermogravimetric-Differential Thermal Analysis. The deviation mechanism underlying this poor accuracy of properties measurement for lead slags was determined by X-ray diffraction (XRD) analysis and chemical analysis of the final slags.

2. Experiment
2.1 Material preparation

The slag samples were prepared by complexing synthetic FeO powder with pure chemical reagents such as PbO, ZnO, CaO, and SiO$_2$. The compositions of the slag system used in melting temperature and viscosity experiment are shown in Table 1. FeO

Table 1. Slag compositions /wt%

Number	PbO	ZnO	FeO/SiO$_2$	CaO/SiO$_2$
1	2.7	13.0		
2	20.0	10.0	1.6	0.4
3	40.0	6.0		
4	2.7	13.0		
5	20.0	10.0	1.6	0.6
6	40.0	6.0		
7	2.7	13.0		
8	20.0	10.0	1.8	0.4
9	40.0	6.0		
10	2.7	13.0		
11	20.0	10.0	1.8	0.6
12	40.0	6.0		
13	10.0	13.0		
14	30.0	8.0	1.8	0.6
15	50.0	6.0		

powders were prepared by pyrolysis of ferrous oxalate powder in a GSL-13-8Y tube furnace at 1000 °C for 30 min under high-purity argon protection.

All the raw materials were pre-dried at 120 °C for 2 h and then blended according to the targeted compositions in an agate ball mill.

2.2 Experiment

The melting temperature of the prepared slags was measured through the hemispherical method by using an RDS-05 automatic slag melting speed tester under N$_2$ gas, with a heating rate of 15 °C/min. The whole slag melting process was recorded by camera, and the temperature at which hemisphere reached half height of the initial columnar sample was considered as the melting temperature. The viscosity curve of the slag during cooling was measured by the rotating column method [11] using RTW-10 thermophysical property measuring equipment under N$_2$ protective gas at 1350 °C to 1000 °C.

Then, No. 11 sample was selected for the measurement of the weight loss using France Setaram Instrumentation Evo Labsys evo TG-DTA/DSC 1750 synchronous thermal analyzer. The initial mass of all the experimental samples was 12.37 mg (± 1.66 mg), a flow rate of 50 ml/min argon was used as the protective gas, and the lead slags were heated from room temperature to 1450 °C at heating rates of 10 °C/min, 20 °C/min, 30 °C/min, and 40 °C/min, respectively . Synchronous records of mass loss curve was obtained as a TG curve.

Thermogravimetric analysis (TGA) conditions at different temperatures were simulated to analyze the phase and composition of slag after the weight loss. The lead slags were heated in a ZPT90/16A tubular resistance furnace at the rate of 10 °C/min to 1450 °C. Next, the samples were cooled down and quenched at 1100 °C, 1000 °C, and 900 °C, respectively. The German Bruker D8 Advance A25 Powder XRD was used to analyze phase composition of the samples quenched at different temperatures. Composition changes of the slag after weight loss were also studied by chemical elements analysis.

2.3 Thermal analysis kinetics
2.3.1 Mechanism function of volatilization reaction

The volatilization of the components in the PbO-FeO$_x$-CaO-SiO$_2$-ZnO lead slag is a complex reaction that corresponds to non-isothermal, heterogeneous reaction kinetics. The heating rate $\beta = dT/dt$ (K/min) is a constant, which is usually used to study non-isothermal kinetics. According to the non-isothermal kinetic theory, the equation of thermal analysis kinetics [12] can be expressed as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot e^{-\frac{E}{RT}} \cdot f(\alpha) \qquad (1)$$

Here, α is the degree conversion; A is the apparent pre-exponential factor; E is the apparent activation energy, and R is the general gas constant (8.314 J•mol^{-1}•K^{-1}). The kinetic equation of the integral form is obtained by separating the variables of α and T in Eq. (1) and then integrating the variables:

$$g(\alpha) = \int_0^T \frac{A}{\beta} exp\left(-\frac{E}{RT}\right) d \qquad (2)$$

Eq. (1) and Eq. (2) are two of most basic formulas for studying the non-isothermal and heterogeneous reaction kinetics. After determining f(α) and g(α) functions of the reaction system, the parameters of the reaction system, such as the energy E, A, $f(\alpha)$, and $g(\alpha)$, can be calculated.

2.3.2 Calculation of activation energy

The isoconversional method for studying kinetics can provide relatively reliable activation energy E in mold-free methods. In this study, the activation energy E was calculated by combining three methods.

The basic formula of the Coats–Redfern (hereinafter called C-R) method is expressed by Eq. (3).

$$ln\left[\frac{g(\alpha)}{T^2}\right] = ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \qquad (3)$$

The apparent activation energy E and A were obtained from the slope -E/R and intercept $AR/\beta E$ of the graph of $ln[g(\alpha)/T^2]$ with respect to $1/T$ by using the 41 common kinds of kinetic model function [13].

The basic formula [14] of Flynn–Wall–Ozawa method (hereinafter called FWO) can be derived by adding the Doyle's temperature approximation integral into Eq.(2) to obtain Eq.(4).

$$ln\beta = ln\left[\frac{AE}{Rg(\alpha)}\right] - 5.3305 - 1.052\left(\frac{E}{RT}\right) \qquad (4)$$

From the Eq. (4), g(α) is always a constant when the conversion rate α is a constant. The apparent activation energy E is derived from the slope of the regression line (-1.052E/R) of the $ln\beta$ with respect to $1/T$, which is plotted and fitted linearly at four different heating rates.

The basic formula [15] of Kissinger–Akahira–Sunose method (hereinafter called KAS) can be derived by adding the C-R's temperature approximation integral into Eq.(2) to obtain Eq. (5).

$$ln\frac{\beta}{T^2} = ln\left[\frac{AR}{Eg(\alpha)}\right] - \left(\frac{E}{RT}\right) \qquad (5)$$

Similar to the FWO method, the apparent activation energy E is obtained from the slope of the regression line (E/R) of the $ln(\beta/T^2)$ with respect to $1/T$ curve , which is plotted and fitted linearly by using the least squares method.

3. Results and discussions
3.1 Analysis of slag weight loss

Fig. 1 (a) and (b) show the TG-DTG results of lead slags at different heating rates. It can be seen from the figure that the weight loss processes of the tested PbO-FeO$_x$-CaO-SiO$_2$-ZnO lead slag are consistent at different heating rates. (1) When the temperature is in the range of 100 °C to 460 °C, the weight loss of the high-lead-content slags increases obviously with the increase of temperature, which indicates that the moisture and crystallization water in the different slag samples lead to the change in the slag quality. (2) When the temperature is about 460 °C to 700 °C, because of carbonate dissociation, the lead slag undergoes a slight weight loss. (3) When the temperature is around 700 °C to 1450 °C, the high-lead slags weight lose rapidly.

The process of high-temperature volatilization and weight loss of components is the focus of this study. Therefore, the volatilization and weight loss at temperatures below 700 °C is not studied in detail. In addition, the heating rate has a great influence on the temperature range and rate of slag weight loss, as shown in Fig. 1. Moreover, the increase of heating rate leads to TG and DTG curves offset to higher-temperature region. This is because the higher heating rates of samples lead to shorter reaction time, and the heat transfer resistance and thermal hysteresis are increased at the same time within the same temperature range. The low heating rate can provide more instantaneous thermal energy for the system, and the system may need a long time to balance the temperature between the purge gas and the furnace or sample [13].

The reaction of lead-slag in high temperature stage is complicated, not only including volatilization of volatile components, but also concerning interreaction of components with volatiles such as PbO. When heating rate is low, the instantaneous thermal energy is large, and the volatilization is greatly affected by melting effect. Therefore, a smaller peak fluctuation arise on the DTG curve with heating rate of 10 °C/min. With the increase of heating rate, the instantaneous heat energy gradually decreases, so the weight loss curve gradually moves to the high temperature zone, and the melting reaction has a greater impact on the volatilization reaction. So the

DTG curve of heating rate 20 °C/ min has a larger peak fluctuation.

As the heating rate increases to 30 °C/min, the weight loss curve continues to move to the high temperature zone, and the lead slag is partially melted reaction before a large amount of volatilization, at which time the volatilization effect dominates, so there is only one typical peak of volatilization in DTG curve. When the heating rate is as high as 40 °C/min, PbO is largely volatilized before it reacts with other components, the volatilization effect of lead slag is very obvious. Thus, there is also only one typical peak of volatilization in DTG curve. The reaction characteristic values for liquid high-lead slags are shown in Table 2.

Table 2. *Reaction characteristic values for liquid high-lead slags at different heating rates*

Heating rates/ °C /min	Starting volatilization temperature T_0/ °C	End volatilization temperature Te/ °C	Weight loss rate /%
10	766.10	1111.75	19.48
20	780.09	1155.71	19.45
30	811.87	1091.07	18.33
40	729.12	1339.33	20.40

3.2 Volatilization kinetics and mechanism

The FWO and KAS method are used to calculate the apparent activation energy E of the lead-containing slag system. The value of $g(\alpha)$ is fixed when the conversion rate α value (α from 0.1 to 0.9) remains constant at different heating rates β. In the analysis process of the FWO method, the curves of $ln\beta$ with respect to $1/T$ are fitted linearly at different heating rates as shown in Fig. 2(a). The apparent E can be calculated from the slope of the regression line for each conversion rate α, as shown in Table 3. And in the analysis process of the FWO method, the curves of $ln(\beta/T^2)$ with respect to $1/T$ are fitted linearly as shown in Fig. 2(b). The apparent E is obtained from the slope of the regression line (E/R) as shown in Table 3.

From Table 3, the average activation energy E obtained by the KAS and FWO method are 205.35 kJ/mol and 210.54 kJ/mol, respectively. The activation energy obtained by these two methods has a slight difference, which may be due to the difference in the temperature integral approximation defined by the two methods. In order to improve the accuracy of the activation energy obtained, first, the average value of the results using the above two methods is calculated, i.e., 207.94 kJ/mol, then, the dynamic model and its parameters of lead slag were obtained by the C-R.
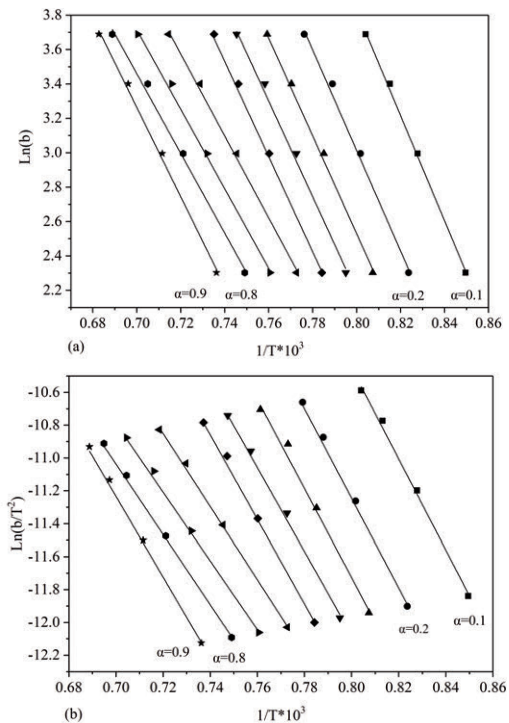

Figure 1. *TG-DTG curves of lead slag with FeO/SiO₂ = 1.8, CaO/SiO₂ = 0.6, PbO = 20% with different heating rates (a) —TG curves; (b) —DTG curves*

Figure 2. *Fitting results of activation energy calculated for lead slag with FeO/SiO₂ = 1.8, CaO/SiO₂ = 0.6, and PbO = 20%; (a)—FWO method; (b)—KAS method*

Table 3. *Apparent activation energy calculated by the FWO and KAS for lead slag with FeO/SiO$_2$ = 1.8, CaO/SiO$_2$ = 0.6, and PbO = 20%*

α	KAS		FWO	
	Ea (kJ·mol^{-1})	R^2	Ea (kJ·mol^{-1})	R^2
0.1	230.43	0.998	241.53	0.999
0.2	226.73	0.9968	230.99	0.997
0.3	225.11	0.9978	224.57	0.996
0.4	212.01	0.9958	219.79	0.996
0.5	213.83	0.994	218.67	0.996
0.6	184.93	0.999	188.29	0.998
0.7	173.62	0.999	182.66	0.993
0.8	177.68	0.998	183.10	0.997
0.9	203.79	0.994	205.26	0.982
average	205.35	-	210.54	-

The heating rate is considered as one of the main factors in thermal analysis [16]. In order to avoid the loss of the reaction signal delay of intermediate product caused by high heating rate. Therefore, the heating rate of 10 °C/min was selected to calculate the kinetic parameters in C-R method study. The average activation energy values obtained from the FWO and KAS methods (as shown in Table 3) were compared with the kinetic parameters calculated by 41 common mechanism functions [16,17] using the C-R method. It was found that the activation energies obtained from FWO and KAS methods were close to the activation energy of the mechanism function number

29 calculated by C-R method, and the correlation coefficient R^2 = 0.96 (as shown in Table 4). Therefore, function number 29 in Table 4 is determined to be the most probable mechanism for the volatilization reaction system of lead slags. Its mechanism function integral in the form of *g(α)* is expressed as follows:

$$g(\alpha) = 1 - (1-\alpha)^{1/3} \tag{6}$$

The activation energy is 209.51 kJ/mol, the apparent pre-exponential factor is 6.61×10^{-4} S^{-1}, the reaction mechanism follows the mechanism function R3 of the three-dimensional phase boundary to advance the spherical contraction, and the reaction order n is 1/3. This result is some extent different from that of 20% PbO-containing slag with FeO/SiO$_2$=1.6 and CaO/SiO$_2$=0.6 [18], which can be contributed to high energy demand for nucleation process of ferric lead oxides.

The activation energy changes with the conversion rate, as shown in Fig. 3. Clearly, the activation energy decreases as the reaction progresses, and then increases again, which indicates that the volatile reaction for lead slag is extremely complex. Once the reaction occurs, the system does not require too much energy to propel it. At this time, the particle of lead slag has a large kinetic energy and can easily move away from the original position and migrate (i.e., diffuse); therefore, the volatile reaction is rapid, and simultaneously, a large amount of PbO vapor is

Table 4. *Kinetic parameters of the common mechanism function calculated by the C-R method*

Function number	Activation energy E/kJ·mol^{-1}	Apparent pre-exponential Factor A/S^{-1}	R^2	Function number	Activation energy E/kJ·mol^{-1}	Apparent pre-exponential Factor A/S^{-1}	R^2
1	413.95	2.78×10^5	0.938	21	-	-	-
2	433.46	1.20×10^6	0.952	22	16.85	2.98×10^{-12}	0.575
3	81.68	4.11×10^{-9}	0.923	23	35.76	3.49×10^{-11}	0.782
4	446.33	2.46×10^6	0.960	24	73.58	2.19×10^{-9}	0.877
5	84.82	4.89×10^{-9}	0.937	25	187.04	1.57×10^{-4}	0.924
6	84.82	4.89×10^{-9}	0.937	26	300.49	7.13	0.934
7	441.74	6.61×10^5	0.958	27	413.94	2.78×10^5	0.938
8	394.67	3.58×10^3	0.925	28	212.84	7.21×10^{-4}	0.964
9	520.17	3.50×10^9	0.982	29	209.51	6.61×10^{-4}	0.960
10	26.00	1.23×10^{-11}	0.871	30	209.51	1.98×10^{-3}	0.960
11	47.96	1.74×10^{-10}	0.932	31	203.23	4.89×10^{-4}	0.952
12	65.65	1.23×10^{-9}	0.945	32	203.23	9.79×10^{-4}	0.952
13	91.88	1.96×10^{-8}	0.959	33	163.23	2.08×10^{-5}	0.867
14	135.79	1.70×10^{-6}	0.967	34	146.34	4.42×10^{-6}	0.816
15	157.75	1.51×10^{-5}	0.970	35	133.46	1.31×10^{-6}	0.772
16	223.63	9.65×10^{-3}	0.974	36	51.31	9.61×10^{-10}	0.314
17	355.37	3.11×10^3	0.977	37	278.22	4.16	0.965
18	487.12	8.62×10^8	0.978	38	5.72	$8.03E \times 10^{-13}$	0.023
19	750.62	5.45×10^{19}	0.979	39, 40	-	-	-
20	1014.12	3.02×10^{30}	0.980	41	142.49	4.75×10^{-5}	0.465

produced. Here, the reaction mechanism is three-dimensional diffusion, and the diffusion of PbO is the key restrictive factor of the reaction. When the conversion rate was between 0.8 and 0.9, the activation energy of the lead slag system suddenly increased. This could be attributed to the weight loss and the continuous volatilization reaction at 1450 °C, as shown in the thermogravimetric curve of the sample in Fig.1. The PbO volatilization reaction may be a multi-step reaction. When the conversion rate is 0.9, higher energy is needed to facilitate the reaction to proceed to the next stage.
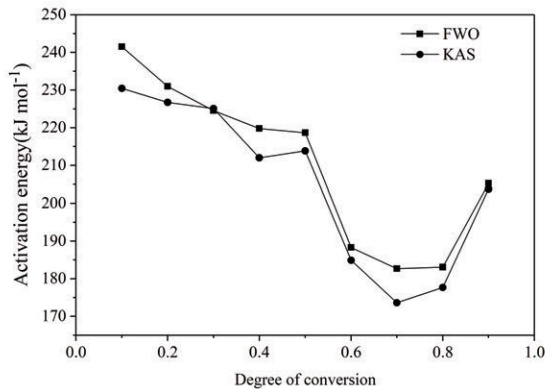
Figure 3. Relation between the activation energy and conversion rate of lead slag with FeO/SiO_2=1.8, CaO/SiO_2=0.6, and PbO=20%, heating rate of 10 °C/min

3.3 Analysis of measured property deviation

To further explore the volatilization mechanism of the PbO-FeO_x-CaO-SiO_2-ZnO lead slag system, high temperature properties, such as melting temperature and viscosity were measured, and XRD and chemical element analyses of the final slag were also carried out.

3.3.1 Melting temperature deviation

The melting temperatures measured by the hemispherical method were compared to the theoretical melting temperature calculated by FactSage software [19], and the measured melting temperatures of the tested PbO-FeO_x-CaO-SiO_2-ZnO slags were always higher than the theoretical values (as shown in Fig. 4).

When the FeO/SiO_2 ratio and CaO/SiO_2 ratio of slags were fixed at 1.6 and 0.4 respectively, the difference between the theoretical melting temperature and the actual values was in the range of 110 °C to 193.14 °C. When the CaO/SiO_2 ratio was fixed at 0.6, it was in the range of 32 °C to 36.48 °C. Further, for samples with FeO/SiO_2 ratio fixed at 1.8 and CaO/SiO_2 ratio fixed at 0.4 and 0.6, it was in the range of 35.5 °C to 158.06 °C and 3 °C to 43.13 °C, respectively.
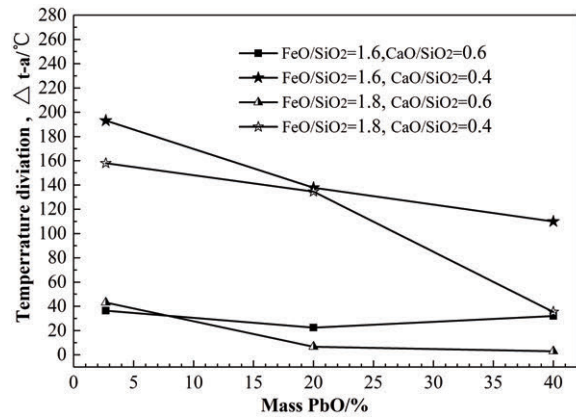

Figure 4. Melting point deviation curve for tested slags with different PbO contents, FeO/SiO_2 and CaO/SiO_2 ratio

3.3.2 Viscosity deviation

The measured and theoretical viscosity values calculated by FactSage software in the range of 1100 to 1350 °C, with different PbO contents in slags for FeO/SiO_2 =1.8, CaO/SiO_2 = 0.6 , are compared in Fig. 5.

It can be concluded from Fig. 5 that the experimental values of viscosity are higher than the theoretical values, and the slag viscosity obtained in both cases increases with the decrease of PbO content in the lead slags. The viscosity values obtained by theoretical calculations and experimental measurement differ significantly, and the difference is between 0.009 and 0.727 Pa•s.

3.3.3 Deviation analysis of property measurement

Chemical element analysis results of the tested slags before and after high temperature volatilization
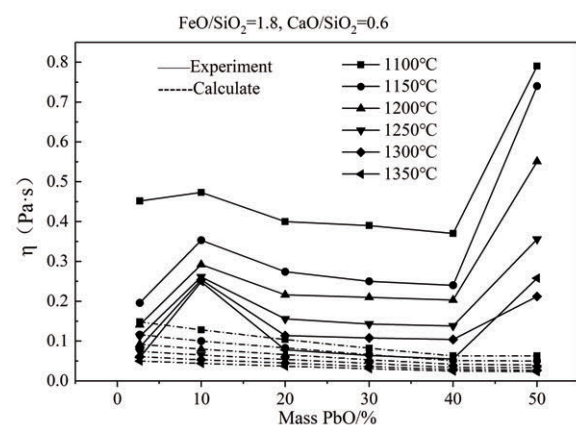

Figure 5. Viscosity deviation for tested lead slags with different PbO contents

are shown in Table 5. It can be seen that the total volatilization rate of Pb content is up to 16.83% when the slag samples are heated from room temperature to 1450°C with a heating rate of 10°C/min, which is consistent with the weight loss results of TG-DTG analyses. In fact, in the high-temperatures measurement of melting temperature and viscosity of $PbO-FeO_x-CaO-SiO_2-ZnO$ lead slag, volatilization of lead compounds leads to an inconsistency with the final measured slag properties and the actual slag compositions. The actual slag compositions differ from the original value due to volatilization of Pb-containing and Zn-containing compounds. In other words, the measured properties of the slag correspond to a varied slag composition.

Table 5. *Contents of volatile compounds after volatilization in high-lead slag with $FeO/SiO_2=1.8$ and $CaO/SiO_2=0.6$, wt.%*

before volatiliza tion, Pb	after volatiliza tion, Pb	volatiliza tion rate, Pb	before volatiliza tion, Zn	after volatilizat ion, Zn	volatilizat ion rate, Zn
2.70	2.36	7.20	10.44	10.32	1.15
18.57	17.13	7.75	8.03	7.95	1.00
37.13	30.88	16.85	4.82	4.76	1.26

XRD phase analysis of lead slags residues after simulating the volatilization conditions of the heat-weight experiment and melting point measure were carried out. XRD phase patterns for lead slags at 900–1100 °C wherein the ratios FeO/SiO_2 were from 1.6 to 2.0 and CaO/SiO_2 from 0.4 to 0.6 are shown in Fig. 6, Fig.7, and Fig. 8 respectively. XRD results showed that the lead slags began to generate stable zinc-

containing spinel $ZnFe_2O_4$ and melilite $Ca_2ZnSi_2O_7$ phase at about 900°C. This result verifies the similar research results in previous studies found in literature, in which Jiao et al. [20] and Jung et al. [21] agreed that ZnO easily reacted with SiO_2 and Fe_2O_3 to generate inert substances, like Zn_2SiO_4 and $ZnFe_2O_4$. Chemical analysis results (shown in Tab. 5) also prove that inert substances can reduce the volatilization of ZnO in tested lead slag.

The most probable lead-containing phases, such as Pb_3SiO_5, $Pb_2(Zn,Fe)Si_2O_7$ and $Pb_5Si_3O_{11}$ detected in our previous study [10] and Jak Hayes et. al [22] for high-lead slags, cannot be detected in the slag residues after volatilization. It is the high temperature volatilization of Pb-containing compounds that result in this phenomenon. For the same reason, none other than the volatilization of slag components during the melting points measurement at high temperature that lead to large deviations between theoretical and measured melting temperature values, As a result, high-melting-point phases such as Fe_3O_4 and $ZnFe_2O_4$ spinel were observed forming in the slag residues.

There are two reasons for the viscosity deviation besides system error of the measurement method. On the one hand, the volatilization of slag components leads to the change in the phase, which results in high-melting-points compounds $ZnFe_2O_4$, $Ca_2ZnSi_2O_7$, and $(Ca, Fe)SiO_4$ increasing. Therefore, the viscosities are increased consequently. On the other hand, SiO_2 in the slag often exists as tetrahedral $[SiO_4]^{4-}$ silicon oxygen anions because of high temperature, and the excess SiO_2 will produce complicated complex-anions such as $[Si_2O_7]^{6-}$, which will also lead to the increase in the viscosity.

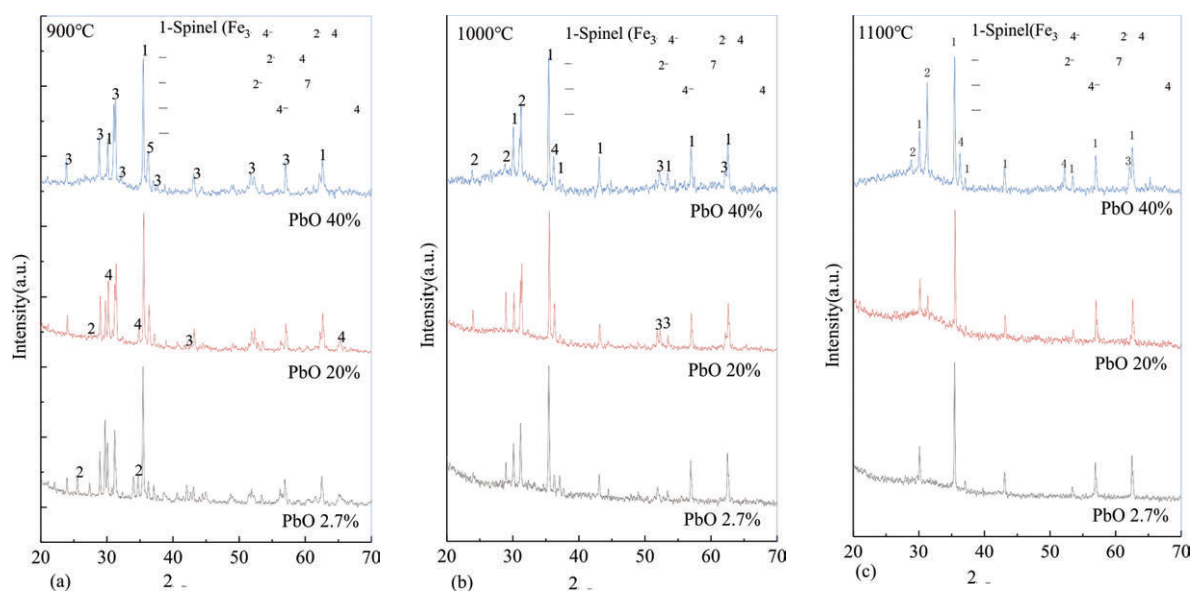In the above comprehensive analysis, the slag

Figure 6. *X-ray diffraction patterns of high-lead slags with $FeO/SiO_2=1.6$, $CaO/SiO_2=0.4$ at different temperature   (a) 900 °C; (b) 1000 °C; (c) 1100 °C*
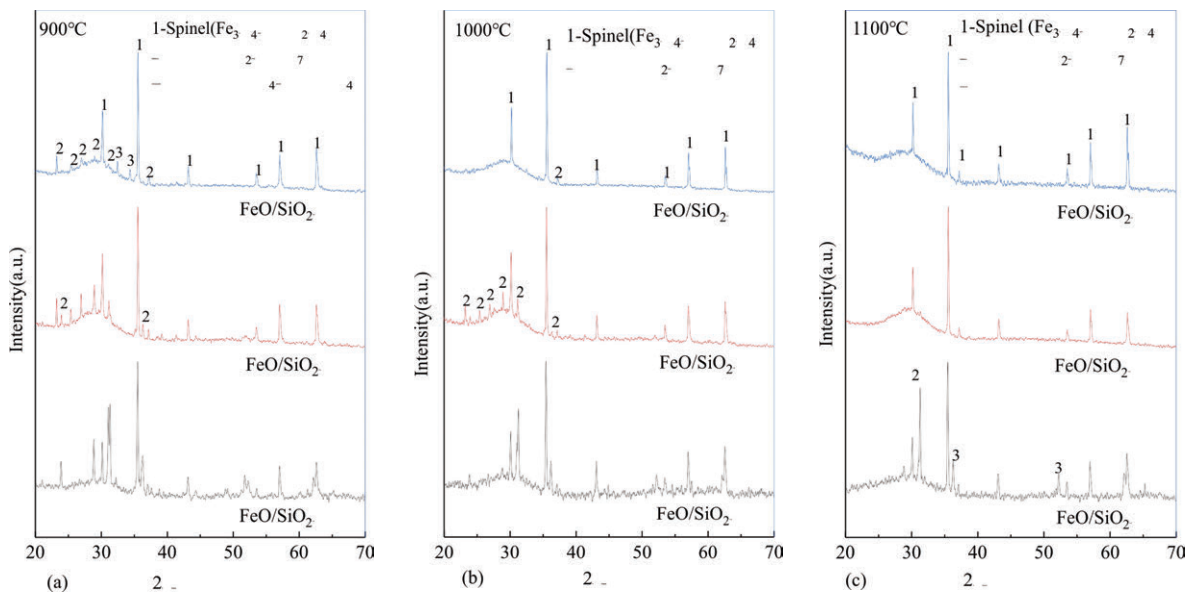
Figure 7. X-ray diffraction patterns of high slags with PbO=40%, CaO/SiO₂=0.4 and different values of FeO/SiO₂ at different temperature   (a) at 900 °C; (b) at 1000 °C; (c) at 1100 °C
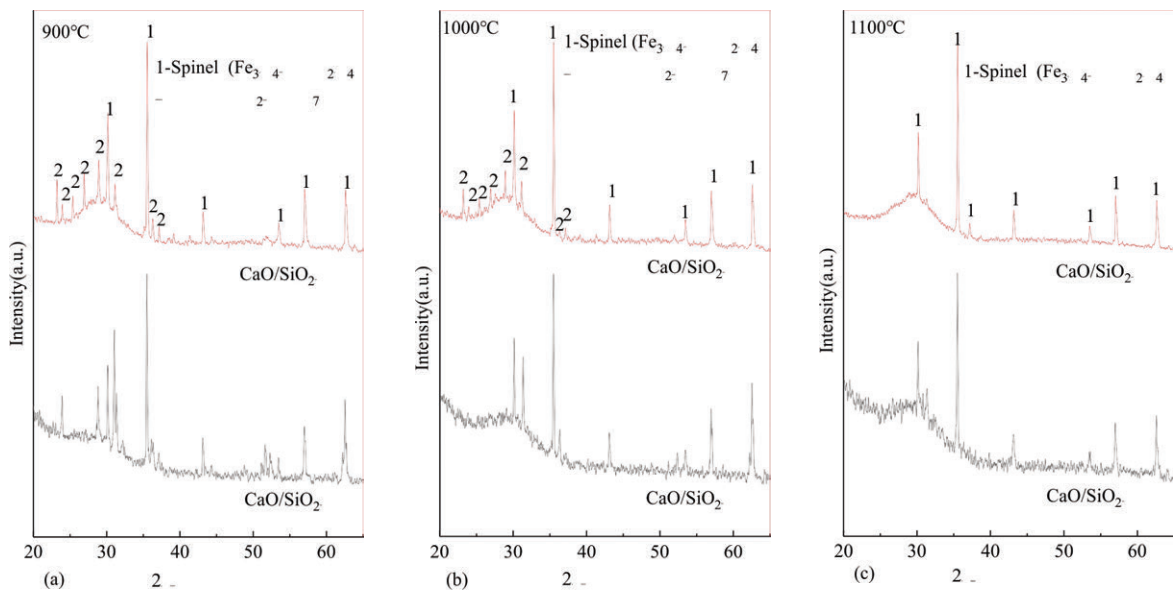

Figure 8. X-ray diffraction patterns of high slags with FeO/SiO₂=1.8, PbO=40% and different values of CaO/SiO₂ at different temperature; (a) at 900 °C; (b) at 1000 °C;(c) at 1100 °C

residues after volatilization mainly contain high-melting-point spinel and melilite phases, whereas with the volatilization of PbO, lead-containing phases such as $Pb_5Si_3O_{11}$ and $Pb_3Ca_2Si_3O_{11}$, and others decrease until the lead-containing silicate cannot be detected, which primarily causes the melting temperature and viscosity properties to deviate from the actual value. The TG-DTG analysis and chemical analysis of the tested lead-slag further prove that the measurement deviation of melting temperature and viscosity at 700–1450 °C was mainly caused by the volatilization of PbO. When the melting point and

viscosity of the lead-slags were measured at high temperature, PbO was highly volatile with the increase of temperature, therefore, which the decrease of lead-containing fusible silicates occurred, but it was followed by the increase of the amount of high-melting-points spinel phase precipitated in the slag residues. Therefore, for purpose of preventing slag composition change incurred by the high-temperature volatilization of the lead slag, protective atmosphere and high heating rate can be adopted to decrease volatility.

4. Conclusions

The volatilization reaction dynamics and volatilization mechanism of PbO-FeO$_x$-CaO-SiO$_2$-ZnO lead-containing slag at high temperature were studied and discussed in this study. The major reason of properties measuring deviation for lead-containing slag are also analyzed. The main research results can be summarized as follows.

(1) There is a great difference between the measured value and theoretical value in the physicochemical properties of lead slag. The property deviation of volatile-lead slags at 700–1450 °C is mainly caused by the volatilization of PbO. Consequently, the lead-containing low-melting-point phase in the slag decreases. Furthermore, the deviation of the physicochemical properties of the slag is caused by the high-melting-point spinel phase.

(2) The volatilization reaction follows the mechanism function R3 of the three-dimensional phase boundary to advance the spherical contraction. Its mechanism function is an integral form of g (α), expressed by $g(\alpha)=1-(1-\alpha)^{1/3}$. The activation energy is 209.51 kJ/mol, the apparent pre-exponential factor is 6.61×10^{-4} s^{-1}, and the reaction series n is 1/3.

(3) When the volatilization reaction occurs, the lead slag system will no longer require much energy to promote the reaction. Each particle in the system has a large kinetic energy and can easily move away from the original position (diffusion), due to which the volatile reaction occurs rapidly, while generating a large amount of PbO vapor. The reaction mechanism is thus three-dimensional diffusion, and the restrictive factor of volatile reaction is the diffusion of PbO gas.

(4) When measuring the actual properties at high temperature, in order to prevent composition change caused by the high-temperature volatilization of the lead slag, the heating rate can be increased, and a protection gas should be used to reduce the volatilization.

For this study, the biggest regret lies in the collection and analysis of the volatiles (especially PbO) from lead-containing slag in thermogravimetric experiment under high temperature due to the lack of necessary devices. Further studies are needed to determine the volatiles in lead-containing slag for measuring their properties at high temperature.

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OSOBINE ISPARAVANJA ŠLJAKE SA VISOKIM SADRŽAJEM OLOVA I NJIHOV UTICAJ NA MERENJE FIZIČKO-HEMIJSKIH OSOBINA NA VISOKIM TEMPERATURAMA

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Apstrakt

Isparavanje dovodi do odstupanja prilikom merenja fizičko-hemijskih osobina šljake koja sadrži volatile. Zbog toga je potrebno ispitati stepen isparavanja i identifikovati mehanizme isparavanja, kao i pravila odstupanja koja su od izuzetne važnosti za poboljšanje preciznosti merenih osobina. U ovom radu je za ispitivanje izabran PbO-FeOx-CaO-SiO₂-ZnO sistem šljake. Termogravimetrijska analiza (TGA) je korišćena za utvrđivanje karakteristika isparavanja i neizotermičkih kinetičkih modela za volatalizaciju kod šljake sa visokim sadržajem olova na visokim temperaturama. Mahanizmi volatalizacije i odstupanja kod utvrđenih osobina su određena analiziranjem faze i hemijskog sastava taloga. Pored toga je izvršeno eksperimentalno izračunavanje temperature topljenja i viskoznosti koje je upoređeno sa rezultatima dobijenim na osnovu teorijskog izračunavanja. Prilikom volatalizacije PbO, faza sa sadržajem olova se smanjila, ali se nataložena spinel faza povećala što je dovelo do odstupanja prilikom izračunavanja fizičko-hemijskih svojstava ispitivane šljake. Kinetika isparavanja PbO u šljaci je propraćena trodimenzionalnom difuzijom. Difuzija PbO u gasnom stanju iz PbO-FeOx-CaO-SiO₂-ZnO je ograničila volatilnu reakciju, a funkcija mehanizma je bila g(α)=1-(1-α)¹ᐟ³. Povrh toga, tokom određivanja osobina šljake na visokim temperaturama, velika brzina zagrevanja i zaštitni gas mogu da se koriste za smanjenje isparavanje šljake na bazi olova i da se izbegnu odstupanja koja nastaju kod osobina.

Ključne reči: *Šljaka sa sadržajem olova; Odstupanja prilikom merenja; Karakteristike isparavanja; Kinetika.*