



Article Effects of CaO, Al₂O₃ and MgO on Kinetics of Lead-Rich Slag Reduction

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Abstract: Lead-rich slag as a green feedstock can be used in a blast furnace or smelting reduction furnace to produce lead metal. It is desirable to understand the reduction mechanisms of lead-rich slag to optimize the reduction operations. The volume of CO/CO_2 gases was continuously measured in the experiments to determine the reduction degree of lead-rich slag by carbon. The effects of CaO, Al₂O₃ and MgO on reaction kinetics of lead-rich slag with carbon were investigated in the temperature range 1073 to 1473 K. The activation energies of the reduction were determined experimentally in the chemically controlled and diffusion-controlled stages, and the reduction mechanism is analyzed using experimental results and thermodynamic calculations. It was found that the activation energies at the chemically controlled and diffusion-controlled stages decrease with increasing optical basicity. CaO and MgO have a similar behavior to accelerate the reduction of the lead-rich slag by carbon. In contrast, Al₂O₃ can increase the activation energies at both chemically controlled and diffusion-controlled stages resulting in a slow reaction.

Keywords: lead-rich slag; kinetics; fluxes; FactSage; reduction mechanisms



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Sinter plant-blast furnace is a traditional route to produce primary lead from the concentrates [1]. Fine lead sulphide concentrates are sintered in a Dwight Lloyd machine to remove the sulphur and form agglomerated oxide sinter lump for the blast furnace. In the sintering process the concentration of SO_2 in the gas is low, creating a difficulty for producing acid. The capture of SO_2 and lead-bearing dust during the sintering process is not efficient as the moving sintering machine results in significant leakage. The productivity of the lump sinter suitable for the blast furnace is low in the sinter plant due to the low physical strength of the sinter, and approximately 30% of sinter needs to return to the sintering process. The sinter lumps fed into the blast furnace are not uniform in the composition and microstructure, and to overcome these disadvantages several lead-smelting technologies have been developed in recent years [1–6]. These smelting technologies, including top submerged lance technology (TSL), bottom-blowing smelting technology (SKS) and sideblowing smelting technology, have a greatly simplified operation with more efficient capture and utilization of SO₂ and lead-bearing dust. The lead-rich slag produced from the smelting process is low in sulphur and high in uniformity. Lead metal is also produced simultaneously in these processes making the smelting furnaces more productive.

The molten lead-rich slag can be casted and sent to a blast furnace or a smelting reduction furnace to produce lead metal. The lead-rich slag has the similar composition and reactions during the reduction process; however, the dense slag has different macrostructure from the sinter due to the different technologies used for their production and it is necessary to study the kinetics and mechanism of the lead-rich slag reduction by carbon. Kinaev et al., [7] studied the reduction kinetics of lead oxide by graphite and coke at high temperatures. The synthetic slags PbO–FeO–Fe₂O₃–CaO–SiO₂ were used for the study and the volume of the product gases was measured to monitor the reaction progress. Due to the limitation of the technique used, only initial 300 s reaction was studied. It was found that the rate-limiting step was the chemical reaction at the gas/slag interface. The composition of the product gas $(CO/CO_2 \text{ ratio})$ was not determined in this study [7]. Upadhya [8] studied reaction kinetics of the PbO-CaO-Al₂O₃-SiO₂ slags by carbon in iron at 1693 K. The reaction rate was determined by the PbO concentration in the reduced slag collected at different times. It was found that the reaction rate for the initial stage reduction was controlled by the chemical reaction and the second stage reduction was best explained by the mass transport control [8]. The study was limited to the slags with up to 6.6 wt% PbO. The composition of the product gases was not determined in this study. However, Upadhya adopted the results of Sommerville and Bullard that the product gas was almost CO because CO_2 was consumed by the excess carbon [8]. All of these studies [7,8] were not directly related to the lead-rich slags that only appeared in recent years. The study on the reduction of synthetic lead-rich slags and industrial lead sinters by CO gas indicated that liquid phase played an important role in the reduction process [9]. Both synthetic lead-rich slags and industrial lead sinters showed similar behaviors during the reduction if they have the same composition. The reduction kinetics of the synthetic lead-rich slag and industrial lead sinter by graphite were compared by Hou et al. [10]. It was found that rapid reduction was associated with the formation of the liquid slag that was a function of composition and temperature. The effect of PbO concentration on the reduction kinetics of lead-rich slags by graphite was studied recently by Xie et al. [11]. They found that a high PbO concentration in the slag is favorable to the reduction. During the production and reduction of lead-rich slag, CaO is usually added as a flux to decrease the liquidus temperature and viscosity of the slag. Al_2O_3 and MgO from the concentrates, carbon-containing materials and refractory are always present in the slag. The effects of CaO, Al₂O₃ and MgO on the reduction kinetics of lead-rich slags remain unclear. Additionally, optical basicity has been associated with the properties of the metallurgical slags with different compositions [12–15]. The concept of optical basicity has been adopted to describe the effects of CaO, Al_2O_3 and MgO on the reduction mechanisms and kinetics of lead-rich slags by graphite. The reduction mechanisms are analyzed by experimental data and FactSage 8.1 software [16]. The remodified shrinking core model is also used to analyze the reduction kinetics of the lead-rich slag by graphite [17–20].

2. Research Methodology

The lead-rich slags used for the reduction experiments were first prepared and characterized. The ground slag samples were then reacted with graphite in a properly sealed system and the volume of the product gas was accurately measured to determine the progress of the reduction reactions. The FactSage software was used to interpret the experimental results from thermodynamic point of view.

3. Preparation of Lead-Rich Slags

Pure PbO, ZnO, Fe₂O₃, CaCO₃, SiO₂, Al₂O₃ and MgO chemicals were used to prepare the lead-rich slags Y1, Y2 and Y3 in an induction furnace in air. A 1000 g pelletized mixture prepared from pure powders was placed in a mullite crucible. The slag and crucible were melted between 1100 to 1150 °C for 60 min by a Heraeus 25 KW induction generator through a graphite susceptor. The temperature of the slag was monitored by an R-type thermocouple (Pt/Pt-13%Rh) that was placed in an alumina sheath. Argon gas with a 5000 mL·min⁻¹ flow rate was used to stir the slag throughout the experiment, and the molten slag was cooled naturally after the induction furnace was turned off. The slowcooled lead-rich slags were mounted, polished and examined using optical and scanning electron microscopy. The compositions of the phases present in the samples were measured by a JEOL 8800 L Electron Probe Microanalyser (EPMA) with Wavelength-Dispersive Spectrometer (WDS). An accelerating voltage of 15 kV and a probe current of 15 nA were applied. The average accuracy of the EPMA measurements is within 1 wt%.

4. Reduction of Lead-Rich Slag by Graphite

The schematic diagram of the experimental system including a vertical tube furnace, gas collection and data record system is shown in Figure 1. The experiments were carried out in a 19 mm ID corundum reaction tube. A platform consisting of a Pt/Pt-13%Rh thermocouple was inserted from the bottom to support a graphite crucible (18 mm OD, 14 mm ID, and 40 mm high) located in the hot zone of the furnace. A water-containing pressure device was developed to capture the gas generated from the reaction and it displaced the same volume of water into a container sitting on a balance. The weight of the water was recorded by a computer and then converted to the gas volume.



Figure 1. Schematic diagram of the experimental system used in this study.

The graphite crucible was raised from the bottom to the hot zone of the reaction tube after 30 min flushing by ultrahigh purity argon. The gas flushing was stopped, and the reaction tube was sealed properly. The argon gas was then turned on carefully to enable the water to stay at point A indicated in Figure 1 and then the argon gas was stopped. The balance was adjusted to zero and the computer was started to record the weight changes. A 5.00 g lead-rich slag (~1 mm diameter size) was added into the graphite crucible from the airtight funnel that was placed on the top of the furnace. The reduction reaction started when the sample touched the graphite crucible at the required temperature. The generated CO/CO₂ gases were captured by the water-containing pressure device and the weight of water was continuously recorded by the computer in 5 s interval. When the experiment finished, up to 400 mL CO/CO₂ gases were generated and displaced approximately 400 g H₂O into a container sitting on a balance. The reduction was stopped when the graphite crucible was lowered rapidly to the bottom-end of the furnace.

5. Thermodynamic Calculations

FactSage 8.1 software was used to predict the compositions of liquid slags, and activities of PbO and ZnO in liquid slags at high temperature [16]. The databases selected were "FactPs" and "Ftoxide". The solution phases selected included "FToxid-SLAGA", "FToxid-SPINA", "FToxid-MeO", "FToxid-cPyrA", "FToxid-PyrA", "FToxid-WOLLA", "FToxid-Bred", "FToxid-bC2SA", "FToxid-aC2SA", "FToxid-Mel", "FToxid-Oliv", "FToxid-Mull", "FToxid-CORU", "FToxid-ZNIT", "FToxid-WILL", "FToxid-PbO" and "FToxid-PCSi".

The optical basicity, the electron-donating power of the oxygen in an oxidic glass, was defined by Duffy [12,13]. The Equation (1) below is usually used to calculate the optical basicity of an oxide slag [14]:

$$\Lambda = \frac{\sum x_1 n_1 \Lambda_1 + x_2 n_2 \Lambda_2 + \cdots}{\sum x_1 n_1 + x_2 n_2 + \cdots}$$
(1)

where Λ is the optical basicity of the slag, $\Lambda_{1,2...}$ is the optical basicity of an individual oxide as shown in Table 1, *x* is the mole fraction of the individual oxide and $n_{1,2...}$ is the number of oxygen atoms associated with the oxide.

Table 1. The optical basicity of individual oxide [13,15].

Oxide	PbO	ZnO	Fe ₂ O ₃	CaO	SiO ₂	Al_2O_3	MgO
Λ	0.95	0.95	0.69	1	0.47	0.68	0.92

6. Results and Discussion

6.1. Characterization of Slags

The target and actual compositions of the lead-rich slags are shown in Table 2. The $ZnO/Fe_2O_3/CaO/SiO_2$ ratios are approximately the same in three samples.

Slag	РЬО	ZnO	Fe ₂ O ₃	CaO	SiO ₂	Al_2O_3	MgO
Y1-planned	52.4	11.5	17.2	6.8	12.1	0.0	0.0
Y1-actual	51.8	11.4	17.0	6.7	11.9	1.3	0.0
Y2-planned	50.5	11.0	16.5	6.5	11.5	4.0	0.0
Y2-actual	49.8	10.9	16.3	6.4	11.4	5.1	0.0
Y3-planned	51.5	11.2	16.8	6.7	11.8	0.0	2.0
Y3-actual	50.8	11.1	16.6	6.6	11.6	1.3	2.0

 Table 2. The target and actual compositions of lead-rich slags for reduction experiments.

The typical microstructures of Y2 and Y3 are shown in Figure 2 as the typical microstructures of Y1 have been reported in a previous study [10]. It appears that 5.1 wt% Al_2O_3 in Y2 and 2.0 wt% MgO in Y3 did not make a significant difference in the microstructure. The major phases presented in Y2 and Y3 are spinel, melilite and lead silicate 6PbO·FeO_{1.5}·SiO₂ (PFS) [21]. In addition, Ca₂SiO₄ (C2S) and larsenite PbZnSiO₄ (PZS) [22,23] are also present in both samples. The spinel crystals are present on the surface of the melilite indicating that spinel is the primary phase field. Spinel and melilite were precipitated at relatively higher temperatures and the other phases were precipitated at lower temperatures. The compositions of the phases present in these slags were measured by EPMA and are shown in Table 3.



Figure 2. Typical microstructures of slow-cooled lead-rich slags: Y2 (**a**,**b**) and Y3 (**c**,**d**). S = spinel, M = melilite, PFS = 6PbO·FeO_{1.5}·SiO₂, C2S = Ca₂SiO₄, PZS = PbZnSiO₄.

flag	DI	Composition (wt%)									
Slag	Phase	Fe ₂ O ₃	ZnO	Al_2O_3	MgO	CaO	SiO ₂	РЬО			
2/2	Spinel	49.4	34.7	15.4	0.2	0.1	0.0	0.2			
	Melilite	2.7	17.2	6.1	0.1	33.7	33.6	6.6			
ΥZ	PFS	5.3	0.6	0.8	0.0	0.0	5.4	87.9			
	Ca_2SiO_4	0.2	0.4	0.0	0.0	17.2	18.4	63.7			
	Spinel	64.1	24.0	5.1	6.6	0.1	0.0	0.1			
2/2	Melilite	0.7	14.8	1.1	4.5	34.4	37.5	6.9			
¥3	PFS	3.8	0.9	0.4	0.0	0.0	5.2	89.7			
	PbZnSiO ₄	0.2	21.5	0.2	1.3	1.5	18.3	57.0			

Table 3. Compositions of the phases present in the melted slags measured by EPMA.

6.2. Reduction

Thermodynamically both CO and CO₂ can be formed during the reduction of lead-rich slag by carbon. However, excess carbon can rapidly consume CO₂ to form CO which has been confirmed by the experimental measurements [8]. CO is therefore considered to be the only exit gas from the graphite crucible in the present study. The main reactions between carbon and liquid slag containing Fe₂O₃, PbO and ZnO include:

$$PbO(l) + C(s) = Pb(l) + CO(g)$$
⁽²⁾

$$Fe_2O_3(l) + C(s) = 2FeO(s) + CO(g)$$
(3)

$$ZnO(l) + C(s) = Zn(g) + CO(g)$$
(4)

The reduction degree is calculated according to Equation (5):

$$\alpha = V_m \times 100\% / V_T \tag{5}$$

where V_m is the experimentally measured gas volume (mL), V_T is the total volume of the theoretical gas volume generated from Equations (2)–(4) (mL) by 5.00 g slag, and α is the reduction degree (%).

Isothermal reduction experiments have been carried out in the temperature range of 1073 to 1473 K. The reduction degrees of Y1, Y2 and Y3 as a function of reaction time are shown in Figures 3–5, respectively. It can be seen from these figures that the reduction degree increases rapidly at the beginning of the reduction and then increases slowly with time. The reduction process includes two stages: the chemically controlled stage and the diffusion-controlled stage that has been reported in previous studies [8,10,11]. Additionally, at temperatures below 1173 K the reaction of both Y2 and Y3 with carbon is limited. Once the temperature is above 1173 K, the reduction degree has a significant increase at the same reaction time.



Figure 3. Reduction degree of Y1 as a function of reaction time [10].



Figure 4. Reduction degree of Y2 (Al₂O₃ addition) as a function of reaction time.



Figure 5. Reduction degree of Y3 (MgO addition) as a function of reaction time.

Figures 6 and 7 illustrate the relationship between the reduction degree and temperature at the chemically controlled stage (50 s) and diffusion-controlled stage (3500 s). They show that the reduction degree of three slags increases with increasing temperature in both the chemically controlled stage and diffusion-controlled stage. The increment is more significant at higher temperatures. The addition of MgO (Y3) seems to increase the reduction degree slightly. The presence of Al_2O_3 in the lead-rich slag significantly decreased the reduction degree and the reaction rates at temperatures below 1173 K are very low. It has been reported [24] that the presence of $4 \text{ wt}\% Al_2O_3$ in the lead-rich slag can increase the liquidus temperature in the spinel primary phase field. As a result, the proportion of the liquid phase is lowered with the addition of Al_2O_3 which causes a low reaction rate between the slag and carbon.



Figure 6. Comparison of reduction degree of three slags after 50 s reaction; the symbols are experimental results and the lines are data fitting.



Figure 7. Comparison of reduction degree of three slags after 3500 s reaction; the symbols are experimental results and the lines are data fitting.

The typical microstructures of Y2 and Y3 after the reaction at 1173 K and 1373 K for 3500 s are shown in Figure 8. The compositions of the phases present in the samples were measured by EPMA and are given in Table 4. It can be seen from Figure 8a that a large proportion of glass phase is present in the high- Al_2O_3 slag after the reduction at 1173 K. The presence of lead metal indicates that significant amount of lead oxide had been reduced. However, the extent of the PbO reduction was limited, resulting in a large proportion of PbO-containing liquid retained at 1173 K. The microstructure is shown in Figure 8a and also indicates that this part of the sample was cooled quickly and low-melting point phases did not precipitate. It can be seen from Figure 8b that after the reduction at 1373 K for 3500 s, only a small proportion of the PbO-containing glass is present and more lead metal was formed. Figure 8c shows the reduced MgO-containing slag at 1173 K. It can be seen that the proportion of the glass in this sample is lower than that shown in Figure 8a indicating that more PbO was reduced when MgO is present. After the reduction at 1373 K, it can be seen from Figure 8d that the glass phase is not present in the sample. Two new phases, olivine $(Fe,Ca)_2SiO_4$ and willemite $(Zn,Fe)_2SiO_4$ appeared. It is clear from the microstructures that the extent of the PbO reduction in the MgO-containing sample (Y3) is higher than other samples because less PbO-containing phases are present after the reduction. This is confirmed from the phase compositions shown in Table 4. All phases present in the reduced Y3 from 1373 K do not contain significant PbO. In contrast, ZnO is present in all phases indicating that ZnO was not easy to be reduced.



Figure 8. Microstructure of slow-cooled slag of Y2 and Y3 after reaction at 1173 K and 1373 K for 3500 s: (a) Y2 1173 K; (b) Y2 1373 K; (c) Y3 1173 K; (d) Y3 1373 K. G = glass, S = spinel, M = melilite, Pb = lead metal, PZS = PbZnSiO₄, PFS = 6PbO·FeO_{1.5}·SiO₂, Wil = willemite, O = olivine.

Table 4. Compositions of	of the phases present in th	e slags after reduction	measured by EPMA.
=		-	-

<u><u> </u></u>	Temperature		Composition (wt%)								
Slag	(K)	Phase	FeO	ZnO	Al_2O_3	MgO	CaO	SiO ₂	РЬО		
		Glass	4.2	1.2	2.7	0.0	0.2	12.2	79.6		
	1173	Spinel	42.9	36.8	19.5	0.3	0.2	0.0	0.3		
¥2		Melilite	2.2	18.0	5.2	0.1	33.1	34.5	6.8		
12		Glass	22.2	14.1	4.5	0.1	13.6	33.9	11.6		
	1373	Spinel	45.9	33.7	19.9	0.2	0.1	0.1	0.0		
		Melilite	3.2	19.1	3.1	0.1	33.2	36.3	5.1		
		Spinel	61.5	25.4	6.2	6.5	0.2	0.1	0.2		
	1170	Melilite	0.6	16.9	1.0	3.3	32.8	37.7	7.7		
	11/3	PFS	3.6	1.3	0.3	0.0	0.0	5.8	89.0		
¥3		PbZnSiO ₄	1.0	19.3	0.1	2.0	1.3	18.4	57.9		
15		Spinel	65.5	21.7	9.1	3.0	0.2	0.5	0.1		
	1070	Melilite	3.3	16.7	0.7	2.6	34.8	38.5	3.3		
	1373	Willemite	10.8	48.6	0.2	9.5	0.2	30.7	0.0		
		Olivine	48.0	10.0	0.1	5.7	4.7	31.6	0.0		

6.3. Kinetics

As shown in Figures 3–5, the reduction of the lead-rich slag by carbon includes chemically controlled stage and the diffusion-controlled stage. The reaction between the lead-rich slags and graphite is mainly liquid-solid reaction. The experimental results of the lead-rich slag reduction are analyzed in two steps.

(1) The reduction degrees can be calculated as a function of time at a fixed temperature. At the chemically controlled stage, the reaction rate constant is commonly calculated using Equation (6) [17–20]:

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

where α is the reduction degree, *t* is reaction time, and *k* is the reaction rate constant.

Several models have been developed to describe the diffusion-controlled reactions. The equation suggested by Dickinson [17] was found to be the best fitting one for the experimental data and is used to simulate the experimental results in the diffusion-controlled stage.

$$[(1 - \alpha)^{-1/3} - 1]^2 = kt \tag{7}$$

The definition of α , t and k in the diffusion-controlled stage is the same as the Equation (6). Kinetic curves are calculated from the experimental data using Equations (6) and (7). The reaction rate constant is determined by the slope of the tangent line of the kinetic curve. The experimentally determined reaction rate constants in the chemically controlled stage and the diffusion-controlled stage are given in Table 5.

Table 5. Experimentally determined reaction rate constants.

Slag	Chemically Controlled Stage					Diffusion Controlled Stage					
	1073 K	1173 K	1273 K	1373 K	1473 K	1073 K	1173 K	1273 K	1373 K	1473 K	
Y1	$3.8 imes$ 10^{-5}	$\begin{array}{c} 3.9\times\\10^{-5}\end{array}$	$1.2 imes 10^{-4}$	$3.1 imes 10^{-4}$	$5.3 imes 10^{-4}$	$3.6 imes 10^{-9}$	$4.3 imes$ 10^{-7}	$\begin{array}{c} 5.1 \times \\ 10^{-6} \end{array}$	$9.8 imes$ 10^{-6}	$\begin{array}{c} 4.0\times\\10^{-5}\end{array}$	
Y2	-	$7.2 imes 10^{-6}$	$4.8 imes 10^{-5}$	$1.8 imes 10^{-4}$	$3.2 imes 10^{-4}$	$2.3 imes 10^{-10}$	$5.8 imes 10^{-8}$	$\begin{array}{c} 5.8 \times \\ 10^{-7} \end{array}$	$4.2 imes 10^{-6}$	$\begin{array}{c} 2.9 \times \\ 10^{-5} \end{array}$	
Y3	$4.6 imes 10^{-5}$	$9.8 imes$ 10^{-5}	$8.9 imes 10^{-5}$	$2.1 imes 10^{-4}$	$3.4 imes 10^{-4}$	-	$3.9 imes 10^{-7}$	$6.9 imes 10^{-6}$	$1.1 imes$ 10^{-5}	$7.2 imes 10^{-5}$	

(2) The activation energy in the chemically controlled stage or the diffusion-controlled stage can be calculated using the Arrhenius equation, where the reaction rate constant as a function of temperature can be expressed as:

$$k = Ae^{-E/RT} \tag{8}$$

where *A* is the pre-exponential factor (s⁻¹), *E* is the activation energy (J·moL⁻¹), *R* is the gas constant (8.314 J·moL⁻¹·K⁻¹) and *T* is the absolute temperature (K).

The activation energy can be obtained from a linear relationship between ln(k) and 1/T. Equation (8) can be rewritten as:

$$ln(\mathbf{k}) = -\frac{E}{RT} + A \tag{9}$$

Figures 9 and 10 illustrate the relationships between ln(k) and 1/T in the chemically controlled stage and diffusion-controlled stage, respectively. In the chemically controlled stage shown in Figure 9, the activation energies of Y1, Y2 and Y3 are determined to be 95, 185 and 62 kJ/moL, respectively. The activation energies of Y1 and Y3 are significantly lower than those of Y2. It seems that both CaO and MgO can decrease the activation energy in the chemically controlled stage to accelerate the reaction. On the other hand, the presence of Al₂O₃ in the slag suppresses the reaction rate of the reduction.

It can be seen from Figure 10 that in the diffusion-controlled stage, the activation energies of Y1, Y2 and Y3 are determined to be 294, 371 and 233 kJ/moL, respectively. It is clear that the activation energies in the diffusion-controlled stage are much higher than those in the chemically controlled stage. Similarly, CaO and MgO can accelerate the reaction and Al₂O₃ suppresses the reduction in the diffusion-controlled stage. Hou et al., [10] reported that the activation energy was 83.8 and 102.9 kJ/moL at chemically controlled stage for lead sinter and synthetic lead-rich slag, respectively. At the diffusion-controlled stage, the reaction activation energy was 224.9 and 259.4 kJ/moL for lead sinter and synthetic lead-rich slag, respectively. The activation energies obtained in the present study are in the same range with those of industrial lead sinter [10].



Figure 9. The relationship between ln(k) and 1/T for the reduction reaction in the chemically controlled stage; the symbols are experimental results and the lines are data fitting.



Figure 10. The relationship between ln(k) and 1/T for the reduction reaction in the diffusion-controlled stage; the symbols are experimental results and the lines are data fitting.

6.4. Thermodynamic Analysis

The optical basicity is a useful parameter to characterize the properties of the silicate slag. Based on the data given in Table 1 and the bulk compositions of the lead-rich slags in Table 2, the apparent optical basicity of Y1, Y2 and Y3 is calculated to be 0.727, 0.723 and 0.735, respectively. The relationships between the activation energies and slag apparent optical basicity are shown in Table 6 and Figure 11. It can be seen from Figure 11 that the activation energies at the chemically and diffusion-controlled stages decrease with

increasing the slag apparent optical basicity. It suggests that increasing the apparent optical basicity can stimulate the progress of the reduction.

Table 6. The apparent optical basicity and activation energies of the lead-rich slags.

Slag	Apparent Optical Basicity	Chemically Controlled Stage (KJ/moL)	Diffusion-Controlled Stage (KJ/moL)
Y1	0.727	95	294
Y2	0.723	185	371
Y3	0.735	62	233



Figure 11. The relationships between the activation energies and slag apparent optical basicity at the chemically and diffusion-controlled stages.

It is clear from Figure 11 that the activation energies at the chemically controlled stage are much lower than those at diffusion-controlled stage. This difference can be explained by the concentrations and activities of PbO and ZnO in the liquid slag. Previous studies [7,8,10,11] confirmed that the reduction reactions mainly occurred between the liquid slag and reductants. The compositions of the liquid slag and the activities of PbO and ZnO in the liquid can be calculated by the thermodynamic model FactSage 8.1 [16] for a given bulk slag composition and temperature. The optical basicity of a liquid slag can be calculated from its composition. Table 7 shows the compositions of the liquid slag for Y1, Y2 and Y3 at 1473 K and their liquid optical basicity. The activities of PbO and ZnO in the liquid slag are also calculated from the FactSage. It can be seen from Figure 12 that the activities of PbO are much higher than those of ZnO and they all increase with increasing the optical basicity of the liquid slag. High activity of a component in the liquid slag indicates that the component can be relatively easier to be reduced. In the initial stage of the reduction the main reaction is the reduction of PbO to Pb in the liquid slag by carbon. High concentration and activity of PbO in the liquid (Table 7) results in a fast reaction. After PbO in the liquid is rapidly reduced, ZnO starts to be reduced. As a result of PbO reduction, the proportion of the liquid decreases and the viscosity of the liquid increases. Therefore, the reduction of ZnO is a diffusion-controlled reaction and this reaction is much slower than the reduction of PbO. On the other hand, it can be seen from Figure 12 that the activities of PbO and ZnO increase with increasing the optical basicity of the liquid slag. This explains the trends shown in Figure 11 where the activation energies at the

chemically controlled and diffusion-controlled stages decrease with increasing apparent optical basicity.

Table 7. The compositions and activities of the liquid slags at 1473 K are calculated by FactSage; the liquid optical basicity is calculated from liquid compositions and the data in Table 1.

Slag	Compositions (wt%)							Liquid Optical	Activity	
	PbO	ZnO	Fe ₂ O ₃	CaO	SiO ₂	Al_2O_3	MgO	Basicity	PbO	ZnO
Y1	57.0	9.2	11.7	7.4	13.1	1.3	0.0	0.723	0.21	0.094
Y2	57.7	7.4	8.9	7.4	13.2	5.1	0.0	0.717	0.19	0.075
Y3	59.0	9.1	8.0	7.7	13.5	1.3	1.4	0.731	0.27	0.1



Figure 12. The relationship between optical basicity of liquid slags and the activity of PbO and ZnO at 1473 K.

7. Conclusions

The isothermal reduction of lead-rich slag by carbon has been investigated in the temperature range of 1073–1473 K by accurate measurements of the gas volume generated from the reactions. Experimental results and thermodynamic calculations are combined to explain the effects of CaO, MgO and Al₂O₃ on the reduction kinetics and mechanisms. It was found that the activation energy was 62–185 kJ/moL at the chemically controlled stage and 280–392 kJ/moL at the diffusion-controlled stage for the lead-rich slags investigated. All activation energies increase with increasing optical basicity of the slag. Both CaO and MgO can decrease the activation energy and accelerate the reduction of the lead-rich slag by carbon. In contrast, Al₂O₃ increases the activation energies at both chemically controlled and diffusion-controlled stages resulting in a lower reaction rate. As a result, MgO-containing lead concentrate and refractories are encouraged, and in contrast, use of Al₂O₃-containing lead concentrate and refractories should be carefully considered.

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