

Reduction kinetics of lead-rich isasmelt slag at the temperature range of 1073 to 1473K

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Abstract: The use of the ISASMELT furnace results in a greatly simplified operation with more efficient capture of SO₂, and lead fugitive emissions. In addition, the high lead slag product is low in sulfur (<0.5%) compared to sinter, reducing the environmental problems with the blast furnace operation. Therefore, the ISASMELT furnace has a promising application in the field of lead production and has replaced the conventional sinter plant in modern lead production. Lead-rich slag produced from the IsaSmelt furnace is used as feedstock to a lead blast furnace for the production of lead metal. To assist in the optimization of the lead blast furnace operations, it is essential to obtain a fundamental understanding of the reaction and kinetics occurring during the reduction of the lead slag in the blast furnace. In this study, extensive experiments have been carried out on the reduction of lead sinters in carbon crucibles at temperature range from 1073 to 1473K. A comprehensive study has been carried out on industrial sinters and synthetic slags to compare the reduction kinetics. The extent of reaction for each sample is measured by measuring the volume of gas produced at a given temperature and time. For all slag investigated at fixed temperature, the reaction rate between the slag and carbon is initially fast and then the rate becomes slower as the extent of reaction increases. Only limited reaction between slag and carbon occurs at temperatures below 1173K. At temperatures above 1173K, the reaction rate increases significantly with increasing temperature. For industrial sinters slag, it was found that a layer of metallic lead was formed at the interface between the sinter sample and carbon at the temperature of 1473K, indicating that the metallic lead layer reduces the contact area between the sinter and carbon thereby reducing the overall rate of reaction. For the slag compositions investigated liquid starts to form at approximately 1073K. Proportion of liquid phases increases with temperature increasing. The reduction reaction belongs to liquid-solid reaction. The reaction kinetics was chemical reaction controlled at initial stage and diffusion controlled at longer time interval. The apparent activation energy was calculated to be 83.8 kJ/mol (chemical controlled) and 224.9 kJ/mol (diffusion controlled) for reduction of sinter slag. For the synthetic slag, the reaction activation energy was 102.9 kJ/mol at initial stage and 259.4 kJ/mol at diffusion controlled stage.

Keywords: Reduction reaction, lead-rich slag, kinetics

1. Introduction

Compared with the lead blast furnace, which is still the predominant technology used in the production of primary lead metal [1], the use of the ISASMELT furnace results in a greatly simplified operation with more efficient capture of SO₂ and lead fugitive emissions. In addition, the high lead slag product is low in sulfur (<0.5%) compared to sinter and thus reduces the environmental problems with the blast furnace operation [2]. Therefore, the ISASMELT furnace has a

promising application in the field of lead production and will replace the conventional sinter plant in modern lead production. For instance, at the YMG plant in Qujing, Yunnan province, China, the sinter plant has been replaced with a lead ISASMELT furnace and gotten some success to some degree [3, 4].

During the process using the ISASMELT furnace, lead-rich slag produced from the IsaSmelt furnace is used as feedstock to a lead blast furnace for the production of lead metal. To assist in the optimization of the lead blast furnace operations, it is essential to obtain a fundamental understanding of the reaction and kinetics occurring during the reduction of the lead slag in the blast furnace. Solid carbon is a commonly used reagent for the reduction of lead from lead-rich slag. Some work has been reported in the literature about the reduction kinetics of lead oxide or lead slag. Upashya K.[5] investigated the reduction kinetics of the lead oxide in liquid slag by carbon dissolved in iron at 1673K. It showed that the reaction rate at initial stage was governed by the chemical reaction and then controlled by the mass transport. N. N. Kinaev et al. [6] measured the reduction rate of PbO-FeO-Fe₂O₃-CaO-SiO₂ slags using carbon with the concentration of PbO ranging from 3 to 100% at the temperature of 1423-1573K. The results showed that the reduction of lead slags with carbon is the chemical reaction controlled. In addition, B. J. Zhao et al. [7] carried out the experiments on the relative microstructure and reduction characteristics of industrial lead sinters and synthetic lead slags in CO/CO₂ gas mixtures. Besides these, little information is available in the literature concerning the corresponding reduction behavior of lead-rich slag using solid carbon as reduction agent at low temperature, i.e. 1073-1473K which is of industrial importance.

The aim of the present study is to examine the reduction behavior of Isasmelt slag at low temperature. The reduction characteristics of industrial lead sinters and synthetic lead slags will be measured and compared. Based on this, the reduction kinetics will be analyzed.

2. Experimental

2.1 Preparation of lead sinter and slag samples

The sinter sample used in this study is a kind of typical lead sinter supplied by industrial operations at the YMG plant in Qujing, Yunnan province, China. The bulk compositions of the initial sample used for reduction experiments are given in Table 1. Iron may be present in both ferric and ferrous in the samples but no separate analyses of the species were carried out. All iron has been calculated to Fe₂O₃ for presentation purpose based on assumption that the samples were produced by oxidation in air.

Synthetic lead slags have been prepared in the laboratory from high purity PbO, ZnO, Fe₂O₃, CaCO₃ and SiO₂ powders. The sample has approximately the same PbO and Fe₂O₃ concentrations while with lower CaO/SiO₂ ratio (as shown in Table 1).

The pelletized mixture of about 1000g was placed in an aluminosilicate crucible and heated in a furnace to 1373 to 1423K for 60 minutes. After that, the slag was slowly cooled within the crucible. Argon gas with 5000 ml/min flow rate was used throughout the experiment to stir the slag.

Table 1. Compositions of the initial samples used for reduction experiments

Sample	Compositions (wt%)					
	Fe ₂ O ₃	ZnO	CaO	SiO ₂	PbO	CaO/SiO ₂
Sinter slag	16.1	9.1	12.0	9.3	53.6	1.30
Synthetic slag	16.9	11.4	6.7	11.9	51.8	0.56

2.2. Reduction experiment

The assembly of the reduction experiment is shown in Fig. 1. The experiments were carried out in a 19mm ID alumina reaction tube. The test procedure involves introducing the crucible into the reaction tube from the bottom of the furnace. The crucible (18mm OD, 14mm ID and 40mm high), made from pure graphite, was held on a platform consisting of an upturned alumina crucible supported on an alumina thermocouple sheath. A Pt/Pt-13%Rh thermocouple was used to monitor slag temperature. Air was flushed from the reaction tube using high purity argon gas. The platform and graphite crucible were slowly raised on the alumina tube into the hot zone of the preheated furnace. The temperature of the furnace was predetermined according to requirement. When the crucible reached the hot zone the gas flushing was stopped and the reaction tube was properly sealed.

In the experiment, 5.00g slag sample (~1mm diameter size) was added from the top of the furnace into the crucible. Once the slag sample touched the graphite crucible the reaction started. CO/CO₂ gas produced from the reaction between graphite and slag was captured in a water-containing pressure device and resulted in the displacement of water into a container on a balance (as shown in Fig.2). The volume of the CO/CO₂ gas produced from the reduction was continuously measured by the weight of the water displaced. The reaction was stopped by lowering the sample and crucible from the hot zone to room temperature under Ar gas flow. Preliminary experiments have been carried out on the reduction of lead sinters and synthetic slags in carbon crucibles at temperature range from 1073 to 1473K.

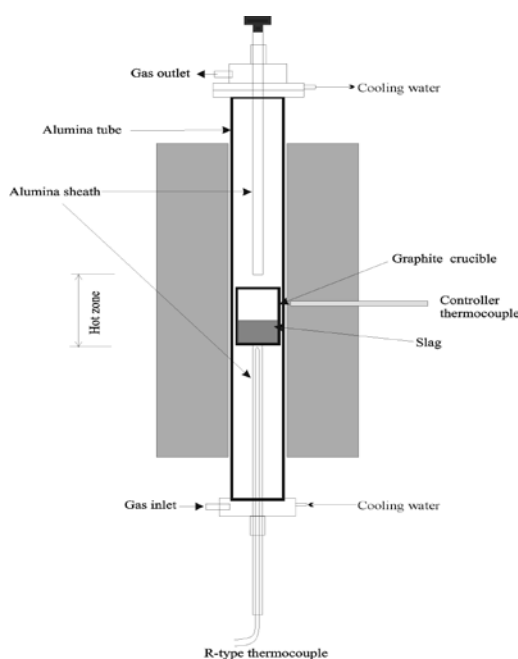


Fig. 1 Assembly of reduction experiment in vertical furnace

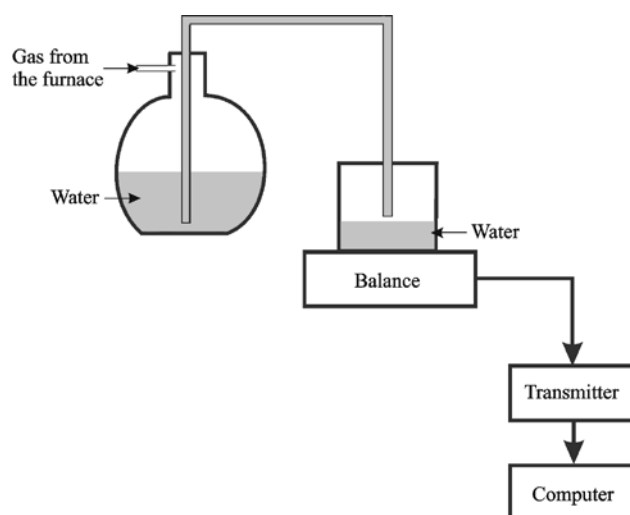


Fig.2 Assembly of gas collection and data record system

2.3 Microstructural analysis

The initial and reduced samples were mounted in epoxy resin, polished and examined using optical and scanning electron microscopy to identify the phases present. The compositions of the glass and solid phases present in the slags were determined using electron probe X-ray microanalysis (JEOL 8200L EPMA; Japan Electron Optics Ltd., Toyo, Japan). The EPMA was operated under 15-kV accelerating voltage and 15 nA probe current with Duncumb-Philibert measurements. ZAF correction procedure was applied. The average accuracy of the EPMA measurements is within ± 1 wt %.

3. Results and discussion

3.1 Liquidus in the lead-rich slag-carbon system

As reported in the literature, lead-rich slags only transferred to liquid phase above 1473K [5-7]. In the investigated temperature range, lead-rich slags existed in both solid and liquid phases. The reaction between carbon and lead-rich slags is a complex process which involves solid-liquid and solid-solid reactions. By comparison, the solid-liquid reaction, i.e. liquid slag and carbon is preferred from chemical reaction viewpoint. The amount of liquid phase can be predicted using thermodynamic computer modeling package FactSage in conjunction with the optimized thermodynamic database for this system developed by the authors [8]. The proportions of the major phases present in the system of lead-rich slag-carbon at different temperatures are presented in Table 2. It can be seen that liquid phase appears from 1073K and its proportion increases with temperature increasing, which leads to the reduction reaction to occur more easily at higher temperature.

Figs.2 a and b show the typical microstructures of sinter slag (a) and synthetic slag (b) reduced at 1073K for 60 minutes in graphite crucible respectively. Some amount of liquid phase exists in both slags besides the crystal phases, which is in agreement with the predict result of FactSage. Extensive measurements have been carried out in the liquid

phase fields. The results of the EPMA measurements of the liquid phase are reported in Table 3. It can be seen that the contents of the liquid compositions examined in the experiment are close to that predicted by FactSage, further verifying the reasonability of the software.

One thing should be pointed out that ferrite oxide exists in the form of Fe_2O_3 in the slag. Since the experiments were carried out in the graphite crucible, Fe_2O_3 will be reduced to FeO. Therefore, the content of ferrite oxide was predicted in the form of FeO when using the software of FactSage.

Table 2. Liquidus compositions of lead-rich slag at different temperature predicted by FactSage

Sample	Compositions (wt%)						
	Liquid phase content (wt%)	FeO	PbO	CaO	SiO ₂	ZnO	
Sinter slag	1073K	39.2	4.16	86.922	0.438	6.13	2.35
	1173K	43.9	7.36	80.9	1.18	8.05	2.51
	1273K	51.7	8.92	76.4	2.12	9.42	3.14
	1373K	69.3	9.72	68.5	4.76	10.6	6.42
	1473K	100	12.4	55.1	8.44	13.0	11.06
Synthetic slag	1073K	10.5	5.82	89.9	0.998	1.792	1.49
	1173K	57.4	7.63	85.3	1.67	2.79	2.61
	1273K	65.7	9.54	79.5	2.88	3.62	4.46
	1373K	74.6	12.4	67.3	6.36	6.31	7.63
	1473K	91.8	14.3	55.6	11.9	9.01	9.19

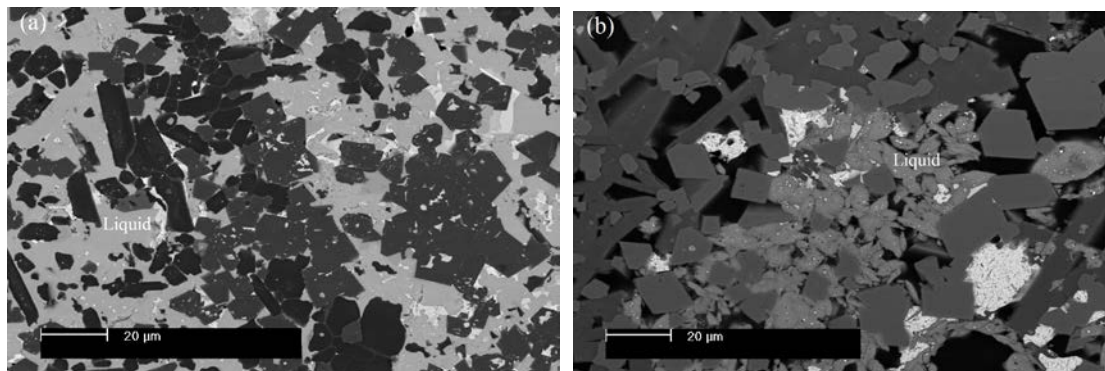


Fig.3 Backscattered scanning electron micrograph of lead-rich slag after reaction at 1073K for 60 minutes in graphite crucible (a) sinter slag; (b) synthetic slag

Table 3. Experimentally determined phase compositions for the liquid phase in slags at 1073K

Sample	Compositions (wt%)					
		FeO	PbO	CaO	SiO ₂	ZnO
Sinter slag	1073K	5.2	89.0	0.1	4.3	1.1
	1073K	5.0	90.3	0.1	3.1	1.3
	average	5.1	89.7	0.1	3.7	1.2
Synthetic slag	1073K	2.1	77.2	0.3	18.0	2.6
	1073K	2.7	72.9	1.2	21	2.3
	average	2.5	75.1	0.75	19.5	2.45

3.2 Isothermal reduction experiments

Isothermal reduction experiments were carried out at the temperature range of 1073 to 173K with 100K interval. Note that the gas produced from the reaction between sinter/slag and carbon is actually a mixture of CO and CO₂. The ratio of CO to CO₂ was not determined in the present study. However, the total volume of the CO and CO₂ produced from the reaction represents the relative extent of the reduction reactions.

Figs 4 and 5 show the experimental results for the reduction of sinter and synthetic slag respectively. For each sample the results are presented in the form of gas evolution volumes as functions of reaction time. It can be seen from Figs 4 and 5 that at fixed temperature the gas volume evolved initially increases rapidly and then became slower as the reaction proceeds. It indicates the reduction kinetics is chemical controlled at initial stage and diffusion controlled at longer time interval. Metal lead can be observed in the liquid phase (as shown in Fig.3), indicating the chemical reaction takes place at the interface of liquid slag and carbon.

It can also be seen that only limited reaction between sinter/slag and carbon occurs at temperatures below 1173K. At temperatures above 1173K, the gas volume evolved increased significantly with increasing temperature. Over the whole temperature range investigated sinter slag has a higher gas volume evolved (Fig.4) than that of synthetic slag (Fig.5) but the difference varies with temperature. The main reason is probably that the liquid proportion in the sinter slag sample is higher than those of the synthetic slag (as shown in Table 2), which lead to larger reaction surface liquid/solid reaction.

In view of the reduction reaction of sinter slag (Fig.4), it can be seen that for the first 20 minutes, the gas volume evolved increases with increasing temperature. However, after 20 minutes reaction the gas volume evolved at 1473K is lower than that at 1373K. On inspection of the 1473K sample it was found that a layer of metallic lead was formed at the interface between the sinter sample and carbon. It appears that in this case the metallic lead layer reduces the contact area between the sinter and carbon thereby reducing the overall rate of reaction.

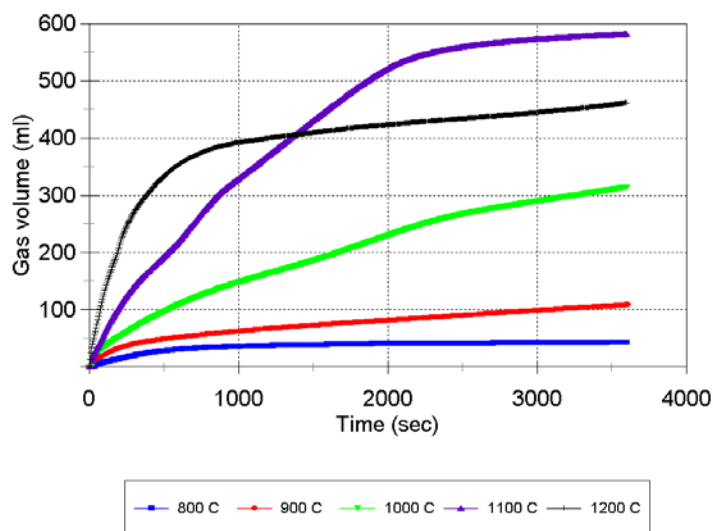


Fig.4. Gas evolution of sinter lead slag in graphite crucible as a function of reaction time

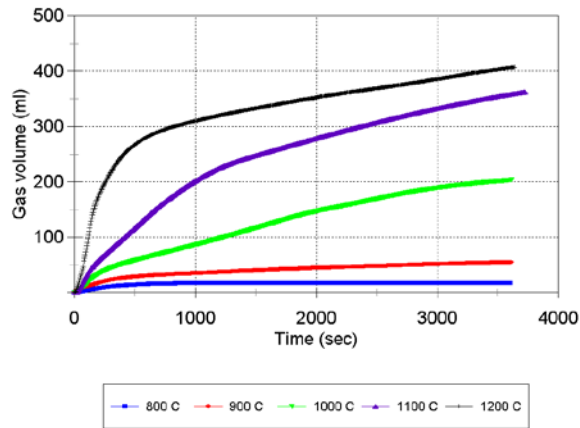


Fig.5 Gas evolution of synthetic slag in graphite crucible as a function of reaction time

3.3 Microstructural analysis

Fig.6 shows the typical microstructures of sinter slag (a) and synthetic slag (b) reacted at 1173K for 60 minutes in graphite crucible. It can be seen from these backscattered electron micrographs that metal lead exists in the both systems, indicating the reduction reaction has been taken place at this temperature. It can also be observed that some porosity (shown as black areas in Fig.6) is created due to the solidification of metal lead from liquid phase to solid phase. The present of metallic lead among the liquid slag (as shown in Fig.6) verifies the reduction reaction mainly took place at the liquid-solid interface, i.e., liquid slag-carbon interface.

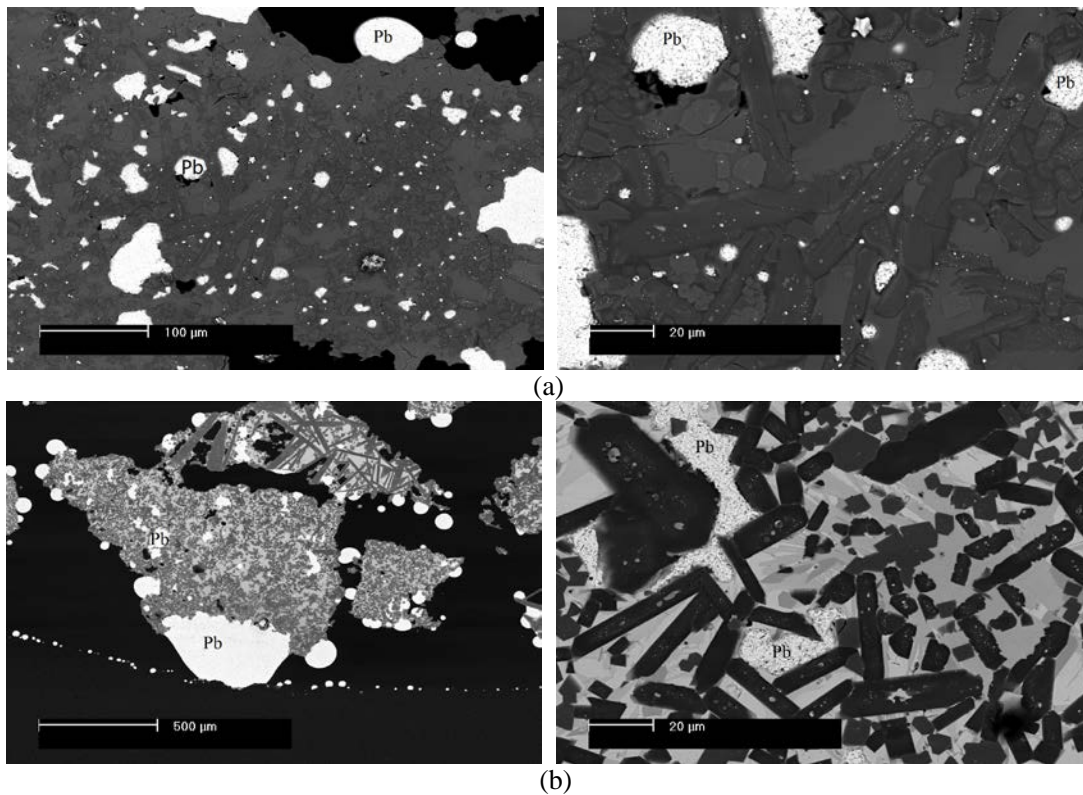
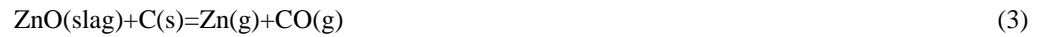


Fig.6 Backscattered scanning electron micrograph of lead-rich slag after reaction at 1173K for 60 minutes in graphite crucible (a) sinter slag; (b) synthetic slag

3.4 Reduction kinetics

Possible reactions between individual components of the liquid phases of the slag and carbon are following:



Since the content of ZnO and FeO in the original slag is very small, their reactions with carbon can be neglected. Only Eq. (1) and (2) occur for complete reduction. Considering the reduction reaction mainly takes place when PbO and Fe₂O₃ are in liquid. The proportion has been predicted by FactSage. Therefore, the gas amount produced by Eq.(1) and (2) can be easily calculated.

From above analysis, the reduction reaction between lead slag and carbon can be divided into two stages: at initial stage, the reaction was controlled by chemical reaction occurred at the liquid/solid interfaces and then diffusion controlled at longer time interval. In the following section, the reaction kinetics can be analysed using shrinking core model [9-11].

For sinter slag, at initial stage its reaction kinetics was controlled by chemical reaction and can be described by the following equation:

$$(\Delta m)=k_r t \quad (5)$$

where Δm is the mass change. k_r is the reaction constant and t is the reaction time. Since there exists linear relationship between the mass change and the gas volume produced by reaction. The relationship between the gas volume and the reaction time should also meet Eq.(5). From the above equation, the reaction constant at different temperature can be obtained. Since the relationship between the reaction constant and the activation energy meet the Arrhenius equation:

$$k=Ae^{-E/RT} \quad (6)$$

where k is the frequency factor ($\text{m}\cdot\text{s}^{-1}$), E is the activation energy ($\text{J}\cdot\text{mol}^{-1}$), R is the gas constant ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and T is the temperature (K). The apparent activation energy can be calculated by the slope of $\ln k$ and $1/T$ (Fig.7) to be 83.8 kJ/mol.

At longer time interval, the reaction was diffusion controlled and can be described as follows [12]:

$$(\Delta m)^2=k_d t \quad (7)$$

where k_d is the reaction constant. Since the reaction at 1473K was unusual which has been analyzed in the former section. The reaction constant at this temperature will not be taken into consideration when calculating the apparent activation energy. In an analogous way, the apparent activation energy can be calculated by the slope of $\ln k$ and $1/T$ (Fig.8) and the value is to be 224.9 kJ/mol.

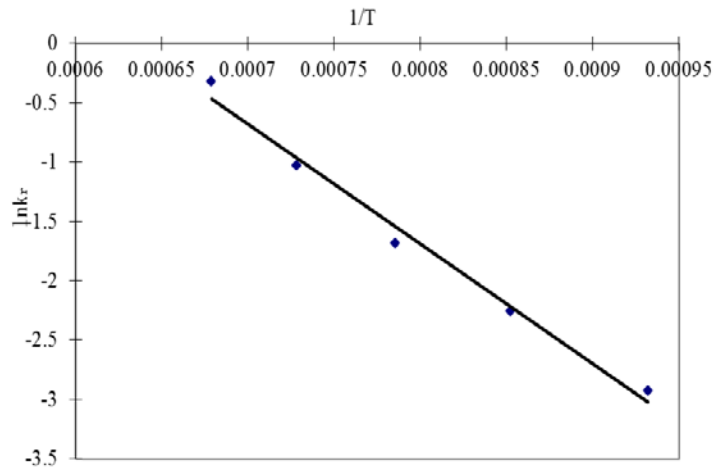


Fig.7 The relationship between $\ln k_r$ and $1/T$ for the reduction reaction of siter slag at initial stage

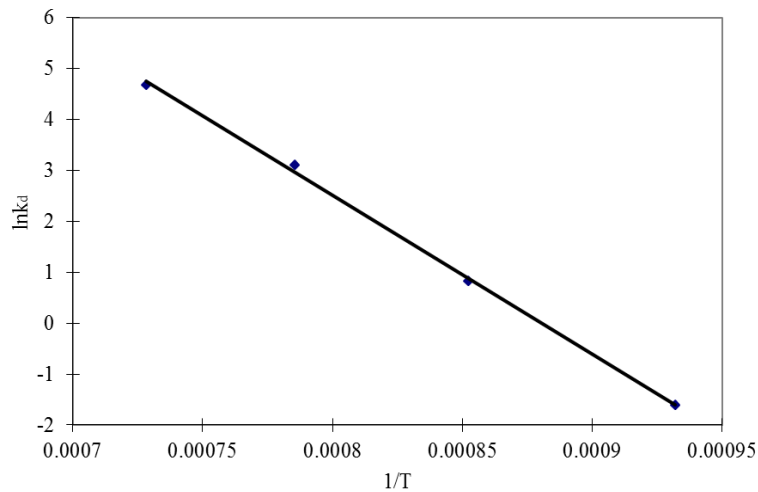


Fig.8 The relationship between $\ln k_d$ and $1/T$ for the reduction reaction of siter slag at initial stage

In the same way, the apparent activation energy for the reaction of the synthetic slag and carbon was calculated to be 102.9 kJ/mol at initial stage and 259.4 kJ/mol at diffusion controlled stage. The higher activation energy for reduction of synthetic slag using carbon can be explained from its microstructure (Fig.8b). The apparent activation energy is comparable with the value reported in the literature [8].

4. Conclusions

Samples of lead sinters and synthetic slag samples have been reduced using graphite at temperature range of 1073-1473K. The reaction rates between the lead-rich slags and graphite have been experimentally determined by measuring the gas volume evolved from the reaction. Thermodynamic calculations have been performed using FactSage computer program to predict the phase assemblages for selected slag compositions with carbon and in equilibrium with metallic lead. The results showed that:

- (1) For the slag compositions investigated liquid starts to form at approximately 1073K. Proportion of liquid phases

increases with temperature increasing.

(2) For all slags investigated at fixed temperature the reaction rate between the slag and carbon is initially fast and then the rate becomes slower as the extent of reaction increases.

(3) Only limited reaction between slag and carbon occurs at temperatures below 1173K. At temperatures above 1173K the reaction rate increases significantly with increasing temperature.

(4) The reduction reaction belongs to liquid-solid reaction. The reaction kinetics was chemical reaction controlled at initial stage and diffusion controlled at longer time interval. The apparent activation energy was calculated to be 83.8 kJ/mol (chemical controlled) and 224.9 kJ/mol (diffusion controlled) for reduction of sinter slag. For the synthetic slag, the reaction activation energy was 102.9 kJ/mol at initial stage and 259.4 kJ/mol at diffusion controlled stage.

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