J. Min. Metall. Sect. B-Metall. 49 (2) B (2013) 201 - 206

Journal of Mining and Metallurgy,
Section B: Metallurgy

REDUCTION KINETICS OF LEAD-RICH SLAG WITH CARBON IN THE TEMPERATURE RANGE OF 1073 TO 1473 K

X. Hou[a, b], K.C. Chou[a], B. Zhao[a,*]

[a] State Key Laboratory of Advanced Metallurgy and School of Metallurgical and Ecological Engineering,
University of Science and Technology Beijing, China
[b] School of Chemical Engineering, The University of Queensland, Qld 4072, Australia

(Received 23 August 2012; accepted 25 March 2013)

Abstract

Extensive experiments have been carried out on the reduction of lead-rich slag in graphite crucible at temperature range of 1073 to 1473K. The reduction kinetics was also compared between industrial sinters and synthetic slags. The extent of reduction was measured by the volume of $CO-CO_2$ gas produced at a given temperature and time. It was found that, at a given temperature, the reaction rate between the slag and carbon was initially fast and then slow as the extent of the reaction increases. Only limited reaction between slag and carbon occurred at temperatures below 1173K. At temperatures above 1173K, the reaction rate increased significantly with increasing temperature. The reduction reaction was found to be mainly liquid-solid reaction, which was chemically controlled at initial stage and diffusion controlled at later stage. The apparent activation energy was calculated to be 83.8 kJ/mol at chemically controlled stage and 224.9 kJ/mol at diffusion controlled stage for reduction of industrial sinter. For the synthetic slag, the reaction activation energy was 102.9 kJ/mol at chemically controlled stage and 259.4 kJ/mol at diffusion controlled stage. The difference of the activation energy between industrial sinter and synthetic slag can be explained by the difference in their CaO/SiO_2 ratios.

Keywords: *Reduction reaction; Lead-rich slag; Kinetics; Activation energy.*

1. Introduction

The lead blast furnace is still the predominant technology used in the production of primary lead metal [1]. For most operations, the feed to the furnace is in the form of oxidized lead sinter from lead sulphide concentrates. The sinter plant has the disadvantage that it produces a high volume of low SO_2 offgas and lead fugitive emissions. By contrast, the use of lead-rich slag results in a greatly simplified operation with more efficient capture of SO_2 and lead fugitive emissions. In addition, the high lead slag product is lower in sulfur (<0.5%) compared to sinter and thus reduces the environmental problems in the blast furnace operation [2]. Therefore, more and more lead smelters have used lead-rich slag to replace sinter as feedstock to blast furnace for the production of lead metal [3, 4].

To assist in the optimization of the lead blast furnace operations, it is important to obtain a fundamental understanding of the reaction kinetics occurring within the furnace. Solid carbon (coke) is a common reductant in the production of lead metal. Some works have been reported in the literature about the reduction of lead oxide or lead slag [5-10]. Upashya [5] investigated the reduction kinetics of the lead oxide in liquid slag by carbon dissolved in iron at 1673K. It was shown that the reaction rate at initial stage was governed by the chemical reaction and then controlled by the mass transport. Kinaev et al. [6] measured the reduction rate of $PbO-FeO-Fe_2O_3-CaO-SiO_2$ slags using carbon with the concentration of PbO ranging from 3 to 100 wt% at the temperature of 1423-1573K. It was shown that the reduction of lead slags with carbon is chemically-controlled reaction. In addition, Zhao et al. [7] carried out the experiments on the microstructure and reduction characteristics of industrial lead sinters and synthetic lead slags in CO/CO_2 gas mixtures. Yang et al. compared the mechanical properties and reduction behavior of lead-rich slag and sinter [4, 8, 9]. 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 temperature range of 1073-1473K which is of industrial importance.

The aim of the present study is to examine the reduction behavior of lead-rich slag in the temperature range of 1073-1473K. The reduction characteristics of industrial lead sinters and synthetic lead slags will be

---

* *Corresponding author: baojun@uq.edu.au*

DOI:10.2298/JMMB120823012H

MOLTEN12 - Conference Special Issue
Ninth International Conference on Molten Slags, Fluxes and Salts

measured and compared. The reduction kinetics will be discussed based on the experimental data.

2. Experimental

2.1 Preparation of lead sinter and slag samples

The sinter sample used in this study is a typical industrial sinter and its bulk composition is given in Table 1. Iron may be present in both ferric and ferrous states in the samples but no separate analyses of the species were carried out. All iron has been calculated to Fe_2O_3 for presentation purpose based on the assumption that the samples were produced by oxidation in air.

Synthetic lead slag was prepared in the laboratory from high purity PbO, ZnO, Fe_2O_3, $CaCO_3$ and SiO_2 powders. The sample has approximately the same PbO and Fe_2O_3 concentrations while with lower CaO/SiO_2 ratio compared to the sinter (as shown in Table 1).

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

Table1. *Compositions of the initial samples used for reduction experiments*

Sample	Compositions (wt%)					
	Fe_2O_3	ZnO	CaO	SiO_2	PbO	CaO/SiO_2
Sinter	16.1	9.1	12	9.3	53.6	1.3
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 Figure 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 inside the alumina sheath 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 into the hot zone of the preheated furnace. The temperature of the furnace was predetermined according to the requirement. When the crucible reached the hot zone the gas flushing was stopped and the reaction tube was properly sealed.

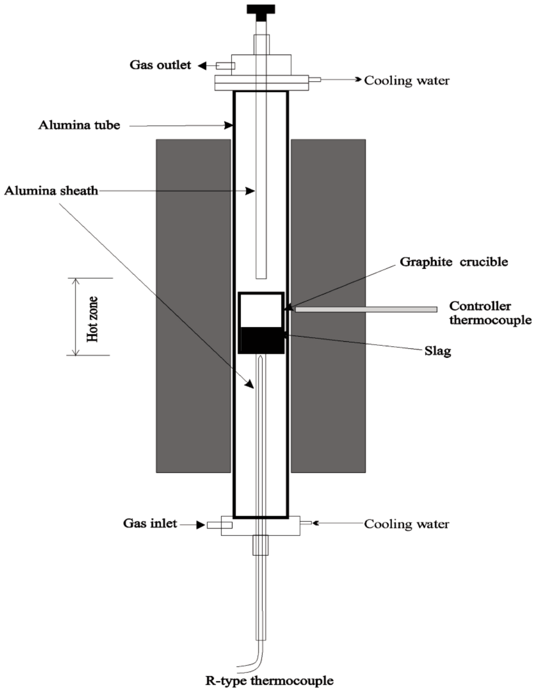

Figure 1. *Assembly of reduction experiment in vertical furnace*

In the experiment, 5.00g sample (~1mm diameter size) was added from the top of the furnace into the crucible. Once the sample touched the graphite crucible the reaction started. CO/CO_2 gas produced from the reaction between the graphite and the sample was captured in a water-containing pressure device and resulted in the displacement of water into a container on a balance (as shown in Figure 2). The volume of the CO/CO_2 gas produced from the reduction was continuously measured by the weight of the water displaced (converted to volume at a given

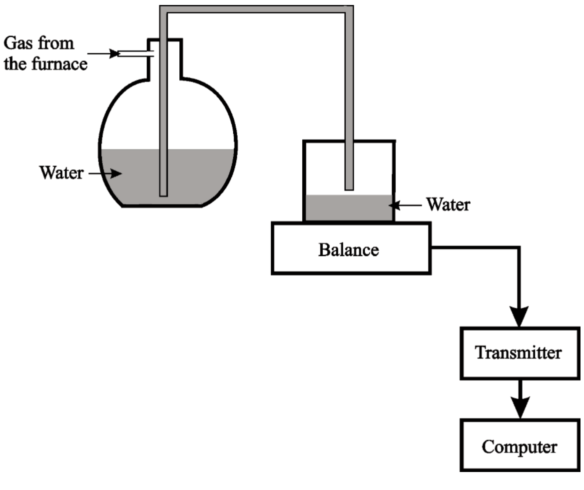

Figure 2. *Assembly of gas collection and data record system*

room temperature). The reaction was stopped by lowering the sample and crucible from the hot zone to room temperature under Ar gas flow. A series of experiments have been carried out on the reduction of lead sinter and synthetic slag in carbon crucibles in the temperature range from 1073 to 1473K.

2.3 Sample examination

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 all phases present in the samples were determined using electron probe X-ray microanalysis (JEOL 8800L EPMA; Japan Electron Optics Ltd., Toyo, Japan). The EPMA was operated under 15-kV accelerating voltage and 15 nA probe current. The Duncumb-Philibert ZAF correction procedure was applied. The average accuracy of the EPMA measurements is within wt %.

3. Results and discussion

3.1 Thermal calculation

As reported in the literature, the liquidus temperatures of lead-rich slags are usually above 1473K [5-7]. In the investigated temperature range, both solid and liquid phases are present in the lead-rich slags. The reaction between carbon and lead-rich slags is a complex process which involves solid-liquid, solid-gas, liquid-gas and solid-solid reactions. The solid-liquid reaction, i.e. liquid slag and solid carbon is preferred from chemical reaction viewpoint. The proportion of liquid phase present at temperature is therefore important in understanding of the reaction and it can be predicted using thermodynamic computer modeling package FactSage in conjunction with the optimized thermodynamic database [10]. The proportions of liquid phase present in the sinter and the lead-rich slag, and their compositions, at different temperatures are presented in Table 2. It can be seen that proportions of liquid phase increase with increasing temperature, which leads to the reduction reaction to occur more easily at higher temperature.

Figures 3a and 3b show the typical microstructures of lead sinter in air quenched from a) 1173 and b) 1273K respectively. It can be seen clearly that the proportions of the liquid phase increased with increasing temperature, which is in agreement with the result predicted by FactSage. In addition to the liquid phase, melilite (dark phase) and spinel (grey phase) are also present in both samples.

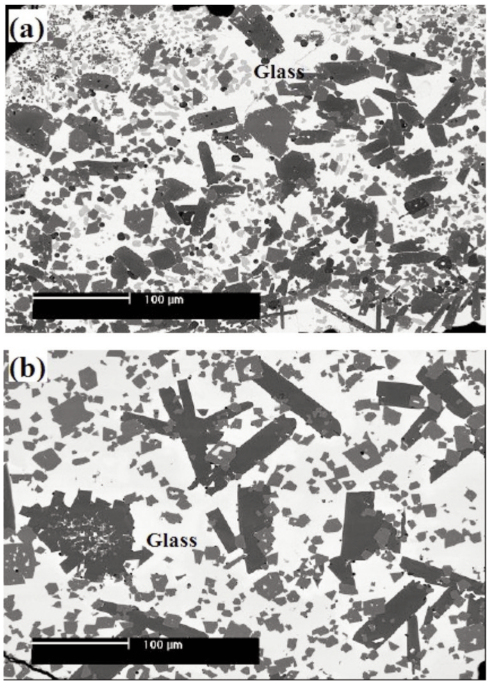

Figure 3. *Typical microstructures of lead sinter in air quenched from a) 1173K; b) 1273K*

Table 2. *Proportions of liquid and their compositions of sinter and slag at different temperature predicted by FactSage*

Sample	*Compositions (wt%)*						
		Liquid phase content *(wt%)*	Fe_2O_3	PbO	CaO	SiO_2	ZnO
Sinter	1073K	39.2	6.5	89.9	1	1.1	1.5
	1173K	43.9	8.5	85.3	1.7	1.9	2.6
	1273K	51.7	10.6	79	2.9	3.1	4.4
	1373K	69.3	13.5	67.3	6.4	5.7	7.1
	1473K	100	16.1	53.6	12	9.2	9.1
Synthetic slag	1073K	10.5	5.1	86.4	0.4	5.7	2.4
	1173K	57.4	8.1	80.9	1.2	8.1	1.7
	1273K	65.7	9.9	76.1	2.1	8.7	3.1
	1373K	74.6	10.9	68.5	4.2	10.5	5.9
	1473K	91.8	13.3	56.4	7.3	13.1	9.9

3.2 Isothermal reduction experiments

Isothermal reduction experiments were carried out in the temperature range of 1073 to 1473K at 100K interval. Note that the gas produced from the reaction between sinter/slag and carbon is actually a mixture of CO and CO_2. The ratio of CO to CO_2 was not determined in the present study. However, the total volume of the CO and CO_2 produced from the reaction represents the apparent extent of the reduction reactions.

Figures 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 a function of reaction time. It can be seen from Figures 4 and 5 that at fixed temperature the gas volume evolved initially increases rapidly and then became slower as the reaction proceeds. It seems that the reduction is chemical controlled at initial stage and then diffusion controlled.

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 has a higher gas volume evolved (Figure 4) than that of synthetic slag (Figure 5) but the difference varies with temperature. The main reason may be due to the difference of the CaO/SiO_2 ratio which is 1.30 in the sinter and 0.56 in the slag.

In view of the reduction reaction of sinter (Figure 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.

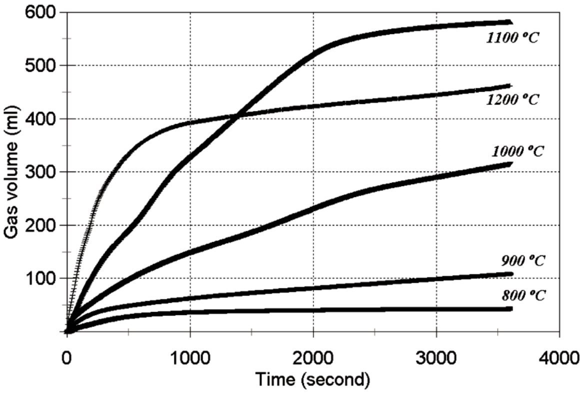

Figure 4. *Gas evolution of lead sinter in graphite crucible as a function of reaction time*

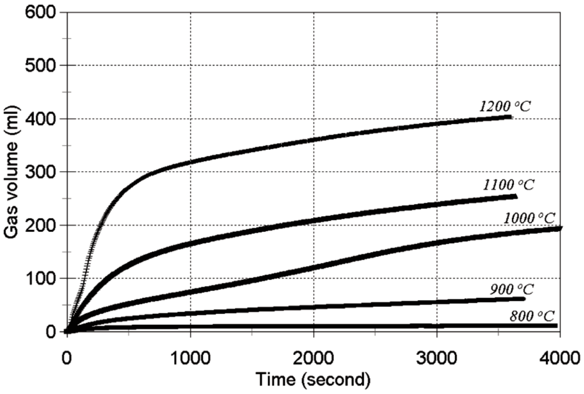

Figure 5. *Gas evolution of synthetic slag in graphite crucible as a function of reaction time*

3.3 Microstructural analysis

Figure 6 shows the typical microstructures of a) sinter and b) synthetic slag reacted at 1173K for 60 minutes in graphite crucible. It can be seen from these backscattered electron micrographs that lead metal is present in both samples, indicating the reduction reaction has been taken place at this temperature. The present of metallic lead among the liquid slag (as shown in Figure 6) verifies the reduction reaction mainly took place through the liquid-solid reaction.

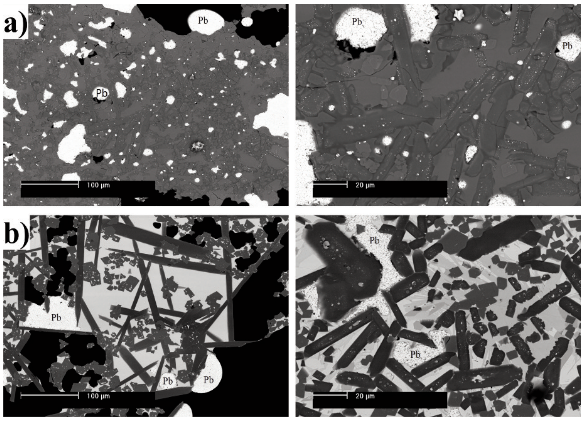

Figure 6. *Backscattered scanning electron micrographs of quenched samples after reaction at 1173K for 60 minutes in graphite crucible (a) sinter; (b) synthetic slag*

3.4 Reduction kinetics

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

$PbO(slag) + C(s) = Pb(l) + CO(g)$ ...(1)

$Fe_2O_3(salg) + C(s) = 2FeO(slag) + CO(g)$ ...(2)

$ZnO(slag) + C(s) = Zn(g) + CO(g)$ ...(3)

$FeO(slag) + C(s) = Fe(s) + CO(g)$ ...(4)

Since the concentrations of ZnO and FeO in the original slag were relatively low, their reactions with carbon can be neglected. Considering the reduction reaction mainly takes place with PbO and Fe_2O_3 in liquid, the amount of gas produced by Eq. (1) and (2) can be easily calculated from the proportions of the liquid and their compositions in the sinter and slag shown in Table 2.

It can be seen from Figures 4 and 5 that the reduction reaction between lead sinter/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 later stage. In the following section, the reaction kinetics will be analysed using shrinking core model [11-13].

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

$(\Delta m) = k_r t$ ...(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 the reaction. The relationship between the gas volume and the reaction time should also meet Eq. (5). From the above equation, the reaction constant at a given temperature can be obtained. Since the relationship between the reaction constant and the activation energy meet the Arrhenius equation [14]:

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

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

At later stage of the reaction, the reaction can be considered as diffusion controlled and described as follows [15]:

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

where k_d is the reaction constant. Since the reaction at 1473K was unusual and has been mentioned in the previous section, the reaction constant at this temperature is not taken into account when calculating the apparent activation energy. In an analogous way, the apparent activation energy can be calculated by the slope of ln(k) against 1/T (Figure 8) and the value is 224.9 kJ/mol.

In the same way, the apparent activation energy for the reaction of the synthetic slag and carbon can be calculated to be 102.9 kJ/mol at chemically controlled stage and 259.4 kJ/mol at diffusion controlled stage. The different activation energy for reduction of sinter and synthetic slag using carbon can be explained by the different CaO/SiO_2 ratio. The apparent activation energies calculated in the present study are different from that of the reduction of PbO [8], 200 kJ/mol. Since iron oxides in the liquid include ferric (Fe^{3+}) and ferrous (Fe^{2+}), the mobility of these species in the liquid and the ability to transfer electrons has a dramatic effect on the reduction of lead-rich slag. This phenomenon has been observed in the system of gaseous reduction of lead slags [7].

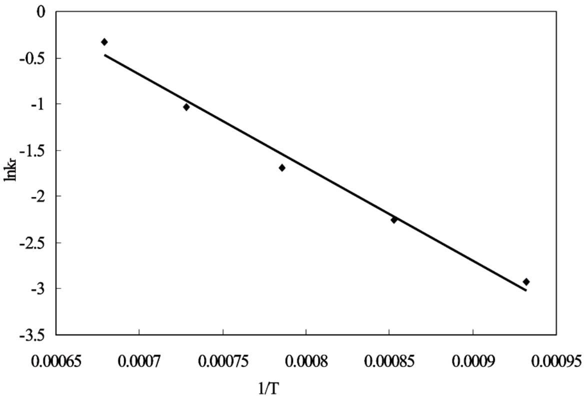

Figure 7. *The realtionship between ln(k) and 1/T for the reduction reaction of sinter at chemically controlled stage*

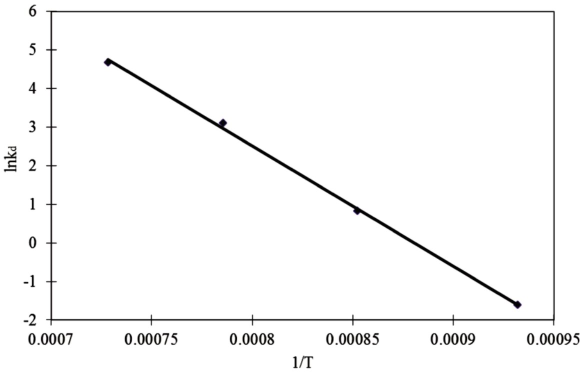

Figure 8. *The realtionship between ln(k) and 1/T for the reduction reaction of sinter at diffusion controlled stage*

4. Conclusions

Lead sinter and synthetic slag samples have been reduced using graphite in the temperature range of 1073-1473K. The reaction rates 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 compositions in air and in equilibrium with metallic lead. The results showed that:

(1) For the compositions investigated liquid phase starts to form at approximately 1073K. Proportion of liquid phases increases with increasing temperature.

(2) At fixed temperature the reaction rate between the sinter/slag and carbon is initially fast and then the rate becomes slower as the extent of reaction increases.

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

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

Acknowledgement

The authors express their appreciation to National Nature Science Foundation of China of No.51104012 for financial support.

References

[1] T. Imai, M. Sakata, K. Morita, Y. Kondo, A. Horiuchi, M. Kusano, Lead Smelters Survey. Lead & Zinc'05, Kyoto, Japan, 2005, p.419-478.

[2] H. T. He, Nonferrous Smelting, 1 (2003) 50-53.

[3] B. Errington, J. Wang, P. Arthur,Y. Dong. The ISA-YMG Lead Smelting Process. Lead & Zinc'05, Kyoto, Japan, 2005, p.587-599.

[4] J. K. Wang, B. Zhao, G. Yang, P. Hayes, Nonferrous metals，6 (2004) 5-8.

[5] K. Upashya, Metal. Mater. Trans. B 17B (1986) 271-279.

[6] N. N. Kinaev, E. Jak, P. C. Hayes, Scand. J. Met., 34(2005) 150-157.

[7] B. Zhao, B. Errington, E. Jak, P. Hayes,Can. Metall. Quart., 49(3)(2010) 241-248.

[8] G. Yang, B. Zhao, J. Wang, P.C. Hayes, Nonferrous Metals (Extractive Metallurgy), 4(2008) 5-7, 15.

[9] G. Yang, B. Zhao, J. Wang, P.C. Hayes, Nonferrous Metals (Extractive Metallurgy), 4(2006) 10-13.

[10] E. Jak, S. Degterov, P. C. Hayes, A. D. Pelton. 5th Intl. Conf. on Slags and Fluxes, Sydney, ISS, Warrendale, 1997, p.621-628.

[11] M.D. Pritzker, Chem. Eng. Sci., 58(2003) 473-478.

[12] F. Veglio, M.Trifoni, F. Pagnanelli, L.Toro, Hydrometallurgy, 60(2001) 167–179.

[13] A.Velardo, M. Giona, A. Adrover, F. Pagnanelli, L. Toro, Chem. Eng. J., 90(2002) 231–240.

[14] I. R. Johnson, J. H. M, Annals of Botany, 55(1985) 1-24.

[15] W. B. Jepson, J. Electrochem. Soc., 107(1) (1960) 53-55.