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THE EFFECT OF COAL RATIO ON THE HIGH-LEAD SLAG REDUCTION PROCESS

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Abstract

The effect of coal ratio on the high-lead slag reduction was reported in this article. First, the phase diagrams of the PbO-FeO-SiO_2-2%CaO-10%ZnO slag system at various temperatures and coal ratios were thermodynamically constructed. Next, the density, the melting temperature, the viscosity, the chemical composition and the phase transformation of the reduced slag were investigated. The thermodynamic results indicated that the variation of coal ratio could affect the chemical composition of the reduced slag, which led the physical properties of the reduced slag to change further. The experimental results illustrated that the content of lead and copper in the reduced slag decreased, while the contents of iron, silicon, calcium and zinc in the reduced slag increased as the coal ratio increased, which led the density and viscosity of the reduced slag to decrease further. The melting temperature of the reduced slag increased sharply when the coal ratio varied in the range of 1.5% to 3%. The mineralogy of the reduced slag indicated that lead mainly existed in the reduced slag in the form of metallic lead, while the iron and zinc were mainly enriched in the reduced slag in the form of a silicate phase. The industrial verification test results demonstrated that the average recovery rate of the lead exceeded 96.0%, the average lead content in the reduced slag was below 2.0% and the average fume rate was approximately 12.0%.

Keywords: *Coal ratio; High-lead slag; Reduction; Slag property*

1. Introduction

Lead has a strategic and industrial importance, due to its wide application in storage batteries, cable shields, shipbuilding and radiation protection [1,2]. At present, the lead sulfide concentrate is the main raw material for the production of lead. The traditional routes for lead extraction from lead sulfide concentrate is achieved through the pyrometallurgical method, which involves the bath smelting to obtain high-lead slag, followed by blast furnace reduction to produce crude lead [3-6]. The oxygen-enriched bottom-blown smelting for the extraction of lead from the lead sulfide concentrate is widely applied in the industrial production in many smelting processes [7,8]. Moreover, the oxygen-enriched bottom-blown smelting has better mixing performance and reaction kinetics conditions compared to other processes, which are based on its own reaction heat, to ensure the stability and continuity of smelting [9].

The reduction of high-lead slag is an important part of the lead smelting process. Traditionally, a slag containing lead oxide could be reduced to crude lead in the blast furnace. During this process, the molten high-lead slag requires cooling and casting first, before it could be processed in the blast furnace, which wastes the latent heat of the molten high-lead slag and causes severe environmental pollution [10-13]. Therefore, there is an urgent demand for the molten high-lead slag direct reduction technology with high-efficiency, cleaning and lower energy consumption. At present, a novel technology of the direct reduction of the molten high-lead smelting slag has been proposed and considered to be a popular treatment process, which could utilize the latent heat of the molten high-lead slag, reducing the energy consumption and solving the environmental pollution problem [14,15]. The coal ratio is an important technological parameter in the direct reduction process of the molten high-lead smelting slag, which determines the extent of reduction reaction and the distribution behavior of valuable metal and impurity elements between the metal phase and the slag phase during reduction. Also, the distribution behavior of valuable metal and impurity elements between the metal phase and the slag phase is closely related to the reduced slag properties, indicating that the coal ratio plays an important role in the reduction process [16]. When contrasted, the effect of coal ratio on the direct reduction of the molten high-lead smelting slag is still unclear.

Therefore, in the present work, the phase diagrams of the PbO-FeO-SiO_2-2%CaO-10%ZnO slag system at various temperatures and coal ratios were

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established through the thermodynamics software FactSage [17,18]. The density, the melting temperature, the viscosity, the chemical composition and the phase transformation of the reduced slag were investigated in the laboratory and the mechanism of anterograde high yield during reduction was further addressed. Simultaneously, industrial verification testing was carried out.

2. Experimental

2.1. Materials

The high-lead slag utilized in this study was taken from the bottom-blown oxidizing smelting Smelter, as supplied from Yuguang Gold & Lead Co., Ltd. Henan, China. The main chemical composition of high-lead slag was as follows: Pb 51.67%, Fe 12.4%, Cu 0.37%, Zn 7.93%, SiO_2 9.61%, CaO 1.63%, As 0.86% and S 0.29%. The coal was utilized as the reductant and fuel in the reduction process, and the main chemical composition was as follows: C 80.32%, H 0.51%, O 1.38%, N 1.49% and S 0.67%. The XRD pattern of high-lead slag, presented in Fig. 1, demonstrated that lead mainly existed in the high-lead slag in the silicate form, while zinc mainly occurred in the form of zinc silicate, ferrite and zinc oxide, whereas the iron mainly occurred in the silicate form.

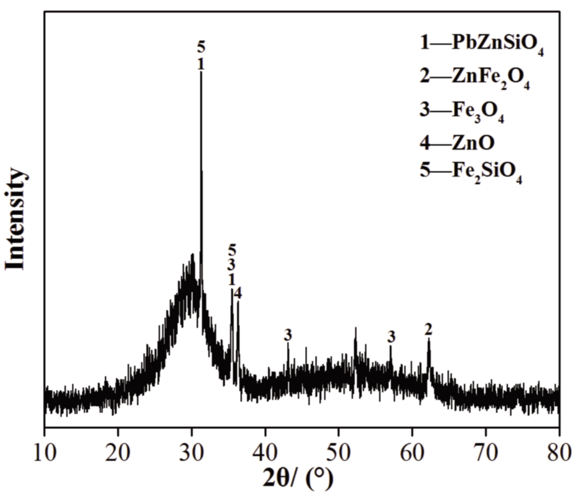

***Figure 1**. XRD pattern of high-lead slag*

2.2. Experimental procedure

100 g of high-lead slag and a certain amount of coal were mixed together and added to the clay crucible. Following, the clay crucible was placed into the electric furnace for reduction smelting. The reduction was carried out at 1250 °C for a reduction time of 1 h. Subsequently, the crude lead and reduced slag were weighed and analyzed, respectively.

2.3. Analysis and testing

The crystal phases of the high-lead and reduced slag were determined through x-ray diffraction analysis (Cu Kα, λ=0.154056 nm; Rigaku-TTR III). The melting temperature of the reduced slag was measured with the RDS-05 automatic tester for slag melting point and the melting speed. The viscosity of the reduced slag was determined with a D-Y type internal cylindrical rotating high-speed high-temperature viscosity meter. The chemical analysis of metal elements in the reduction process was conducted through ICP-AES (Agilent 725) and spectrophotometry (722S).

3. Results and discussion

3.1. Thermodynamic analysis

Fig. 2 presents the phase diagrams of the PbO-FeO-SiO_2-2%CaO-10%ZnO slag system at various temperatures and coal ratios. Based on the phase diagrams, it could be observed that the coal ratio change caused the slag chemical composition variation at the same temperature, which consequently changed the slag liquid phase zone area. This meant that the coal ratio variation would affect the chemical composition of the reduced slag first, whereas consequently the melting temperature of the reduced slag would be affected in turn. Moreover, the shape and size of the slag liquid phase zone differed at various temperatures and coal ratios. According to Fig. 2(a), the slag liquid phase zone was rendered as a triangle at 1050 °C, which was closer to the SiO_2-FeO side as the coal ratio increased. According to Fig. 2(b) and (c), the slag liquid phase zone area increased sharply as the coal ratio increased at the temperature beyond 1050 °C. Also, the slag liquid phase zone area mainly increased in the SiO_2-FeO side and FeO vertice direction. Therefore, it was of high significance to control the reasonable reduction temperature and coal ratio for the anterograde high yield and economy.

3.2. Effect of coal ratio

Table 1 depicts the density and chemical composition values of the reduced slag at various coal ratios at 1250 °C for 1 h of reduction. From Table 1, it was discovered that the content of lead and copper in the reduced slag decreased as the coal ratio increased, which led to the density of the reduced slag to be reduced. The lead content in the reduced slag was lower than 2% and the copper content in the reduced slag was as low as 0.036% at the coal ratio of 3.5%, indicating that lead and copper in the high-lead slag mainly entered the metal phase during reduction. Moreover, the contents of iron, silicon, calcium and

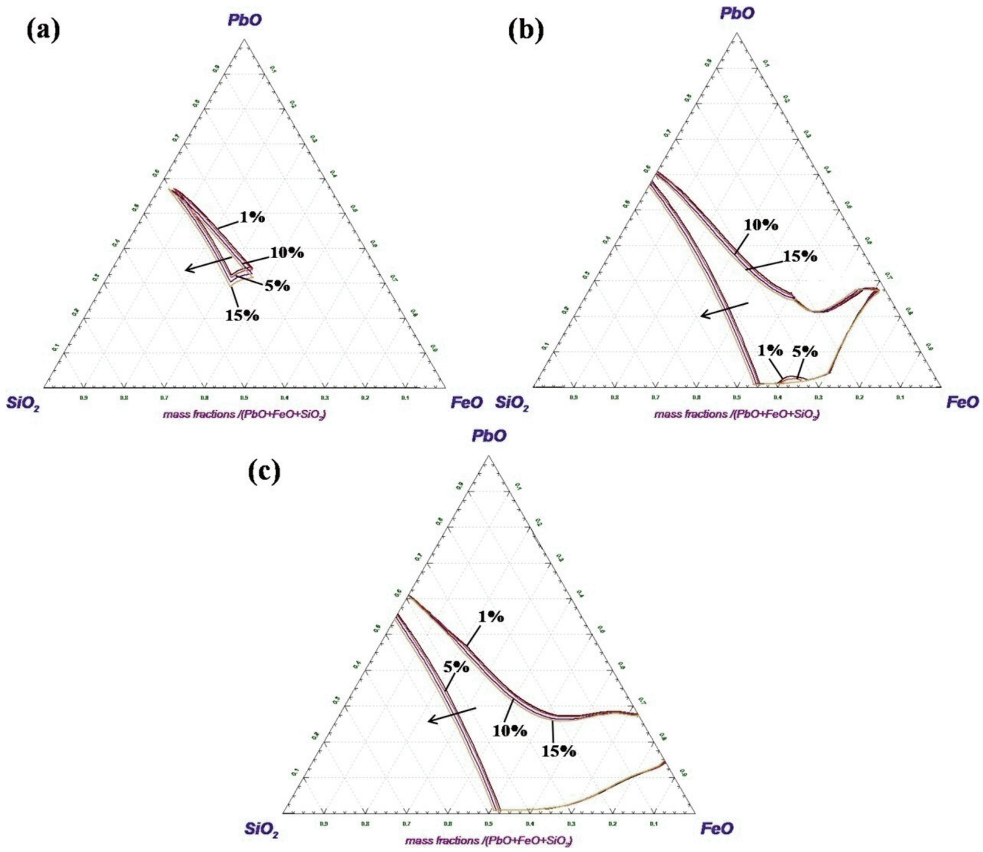

***Figure 2**. Phase diagrams of the PbO-FeO-SiO_2-2%CaO-10%ZnO slag system at various temperatures and coal ratios (coal ratios in the direction of the arrow are 1%, 5%, 10% and 15%, respectively) (a) 1050 °C; (b) 1100 °C; (c) 1150 °C*

zinc in the reduced slag increased as the coal ratio increased which could lead to the iron and zinc enrichment achievement in the slag.

Fig. 3 illustrates the melting temperature of the reduced slag at various coal ratios. It was observed that the melting temperature of the reduced slag varied in the range of 1170 K~1190 K at the coal ratio below 1.5%. The melting temperature of the reduced slag increased sharply as the coal ratio changed in the range of 1.5%~3%. Furthermore, the melting temperature of the reduced slag increased slowly at the coal ratio beyond 3%, which was in agreement with the thermodynamic analysis. Therefore, it was conducive to facilitate the reduction reaction carried out as the temperature increased.

Table 2 presents the reduced slag viscosity values at various temperatures and coal ratios. As presented in Table 2, the viscosity of the reduced slag decreased gradually as the temperature increased at the same coal ratio. Similarly, the viscosity of the reduced slag

***Table 1.** Chemical composition and density of the reduced slag at various coal ratios (wt.%)*

Coal ratio/ %	Density/ kg/m^3	Pb	Fe	Cu	Zn	SiO_2	CaO
0	6.058	51.67	12.4	0.37	7.93	9.61	1.63
1	5.477	41.41	15.16	0.31	9	11.56	2.25
1.5	4.951	31.55	18.1	0.17	10.82	13.27	2.63
2	4.699	20.89	22.48	0.16	13.54	15.34	3.12
2.5	4.334	11.64	25.44	0.072	15.7	18.77	3.8
3	4.189	5.28	29.07	0.065	17.49	20.84	4.13
3.25	4.092	2.11	29.37	0.04	17.21	23.33	4.07
3.5	4.084	1.35	29.48	0.036	17.6	24.71	4.08

was reduced as the reduction reaction continued at the same temperature. The temperature for the same viscosity of the reduced slag also decreased gradually along with the lead content reduction in the slag. The viscosity of the reduced slag was below 0.5 Pa•s at the coal ratio of 3.5% and at the temperature beyond 1313 K, which was conductive to facilitate the reduction reaction execution.

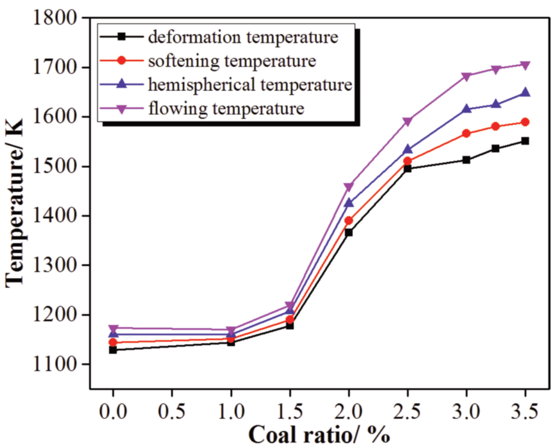

***Figure 3**. Melting temperature of the reduced slag at various coal ratios*

The XRD patterns of the reduced slag at various coal ratios are presented in Fig. 4, which demonstrated that the lead existing in the form of a silicate phase could be converted into metallic lead; the zinc phase in the reduced slag could change from zinc ferrite ($ZnFe_2O_4$) to zinc silicate (Zn_2SiO_4) and the iron phase could be firstly converted from zinc ferrite ($ZnFe_2O_4$) to an intermediate phase (Fe_3O_4), and then the Fe_3O_4 could be converted into a silicate ($(Fe,Mn)_2SiO_4$). All these conversions occurred as the coal ratio increased. The reduction product of FeO was generated and the metallic lead phase disappeared at the coal ratio of 3.5%, indicating that the reduction of lead was complete. According to Fig. 4(f), the metallic lead phase could not be distinguished in the XRD patterns. This might be due to the low lead content in the reduced slag and the volatilization of lead during reduction. The aforementioned analysis demonstrated that the lead in the reduced slag mainly existed in the form of metallic lead, while the iron and zinc were mainly enriched in the reduced slag in the form of a silicate phase.

From the latter analysis, it could be observed that the coal ratio affected the high-lead slag reduction reaction, especially the chemical composition. As a result, the density, the melting temperature and the viscosity of the reduced slag varied accordingly. Simultaneously, the slag physical properties variation would have an important effect on the metal recovery rate and metal content in the slag during reduction, which consequently affected the anterograde high yield of the reduction.

3.3. Industrial verification test

The industrial verification test of the direct reduction of the molten high-lead smelting slag was carried out under the conditions of 1100~1200 °C for the reduction temperature, 250~300 Nm^3/h for the natural gas consumption, 580-620 Nm^3/h for the oxygen flow rate, 6.5%~8.5% for the coal ratio and 14~16:10~12:4~4.5 for the proportion of $FeO:SiO_2:CaO$ in the slag. Table 3 presents the analysis results of the industrial verification test. It was observed that the average recovery rate of the lead reached up to 96.84%, the average lead content in the reduced slag was below 2.0% and the average fume rate was 12.23%.

4. Conclusion

In this work, the phase diagrams of the $PbO-FeO-SiO_2$-2%CaO-10%ZnO slag system were constructed. The density, the melting temperature, the viscosity, the chemical composition and the phase transformation of the reduced slag were investigated. Based on them, the industrial verification test of the direct reduction of the molten high-lead smelting slag was carried out.

The thermodynamic results indicated that the coal

***Table 2.** The viscosity of different reduced slag (Pa•s)*

Coal ratio/ %	T/ K								
	1273	1313	1333	1353	1373	1393	1413	1433	1453
1	-	-	-	4.258	1.11	0.72	0.529	0.359	0.278
1.5	-	-	-	2.704	0.256	0.134	0.065	0.049	0.034
2	-	-	-	3.614	1.164	0.606	0.248	0.232	0.191
2.5	-	-	3.989	1.319	0.529	0.426	0.358	0.379	0.366
3	-	4.106	2.038	0.447	0.232	0.264	0.248	0.232	0.228
3.25	-	3.134	0.569	0.47	0.407	0.403	0.39	0.375	0.374
3.5	2.325	0.475	0.321	0.24	0.063	-	-	-	-

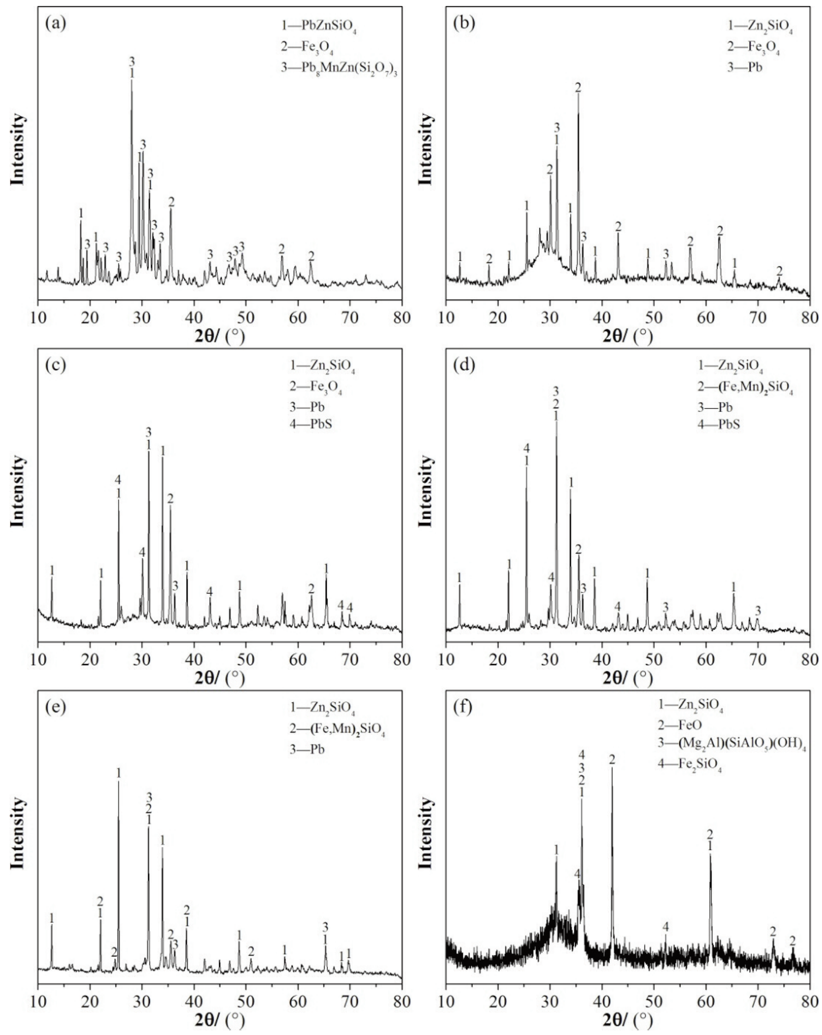

Figure 4. *XRD patterns of the reduced slag at various coal ratios: (a) coal ratio 1.0, (b) coal ratio 1.5, (c) coal ratio 2.0, (d) coal ratio 2.5, (e) coal ratio 3.0 and (f) coal ratio 3.5*

Table 3. *The analysis results of industrial verification test (wt.%)*

No.	Slag/ t	Slag grade/ %	Crude Pb/ t	Fume/ t	Fume grade/ %	Pb recovery rate/ %	Pb in slag/ %	Fume rate/ %
1	6133.86	49.56	2465.44	894	52.36	96.5	2.48	14.57
2	6631.34	48.55	2584.65	993	53.3	96.72	2.25	14.97
3	3493.21	46.84	1308.24	570	48.5	96.85	2.01	16.32
4	8562.65	49.56	3547.45	1158	49.2	97.02	1.87	13.52
5	9065.81	49.43	3784.3	1086	51.3	96.88	1.88	11.98
6	9807.96	47.11	3857.2	1126.4	54.6	96.79	1.89	11.48
7	4426.51	47.3	1683.93	700.8	48.2	96.56	1.96	15.83
8	8264.16	46.57	3232.82	1027.2	47.66	96.72	1.69	12.43
9	9944.73	47.97	4128.91	985.6	51.3	97.15	1.75	9.91
10	10719.51	48.79	4594.29	937.6	52.3	97.22	1.52	8.75
11	7323.91	44.68	2752.96	841.6	49.58	96.88	1.64	11.49
Average	-	-	-	-	-	96.84	1.9	12.23

ratio variation could affect the chemical composition of the reduced slag first, consequently affecting the physical properties of the reduced slag. The experimental results illustrated that the lead content in the reduced slag was below 2% and the copper content in the reduced slag was as low as 0.036%, when the coal ratio was 3.5%. The XRD patterns of the reduced slag demonstrated that lead mainly existed in the reduced slag in the form of metallic lead, while iron and zinc were mainly enriched in the reduced slag in the form of a silicate phase. The industrial verification test indicated that the average recovery rate of the lead reached up to 96.84%, the average lead content in the reduced slag was below 2.0% and the average fume rate was 12.23% at the coal ratio range of 6.5%~8.5%.

Acknowledgement

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EFEKAT RAZMERE UGLJA NA PROCES REDUKCIJE ŠLJAKE SA VISOKIM SADRŽAJEM OLOVA

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Apstrakt

U ovom članku se opisuje efekat koji ima razmera uglja na redukciju šljake sa visokim sadržajem olova. Prvo su termodinamički konstruisani fazni dijagrami sastava šljake PbO-FeO-SiO_2-2%CaO-10%ZnO na različitim temperaturama i sa različitim razmerama uglja. Zatim su ispitivani gustoća, temperature topljenja, hemijski sastav, i fazne transformacije redukovane šljake. Termodinamički rezultati su pokazali da varijacije u razmeri uglja mogu da utiču na hemijski sastav redukovane šljake, što je dovelo do toga da se fizičke osobine redukovane šljake i dalje menjaju. Eksperimentalni rezultati pokazali su da se sadržaj olova i bakra u redukovanoj šljaci smanjio, dok se sadržaj gvožđa, silicijuma, kalcijuma i cinka povećao u redukovanoj šljaci kako je razmera uglja rasla, što je dovelo do toga da su gustoća i viskoznost redukovane šljake i dalje opadali. Temperatura topljenja redukovane šljake je naglo porasla kada je razmera uglja varirala u opsegu od 1.5% do 3%. Mineralogija redukovane šljake pokazala je da je olovo uglavnom bilo prisutno u redukovanoj šljaci u obliku metalnog olova, dok su gvožđe i cink u redukovanoj šljaci uglavnom bili obogaćeni u obliku silikatne faze. Industrijska verifikacija rezultata testova pokazala je da je prosečna stopa dobijanja olova bila veća od 96.0%, da je prosečan sadržaj olova u redukovanoj šljaci bio manji od 2.0%, i da je prosečna stopa izduvnih gasova bila oko 12.0%.

Ključne reči: *Razmera uglja; Šljaka sa visokim sadržajem olova; Redukcija; Osobine šljake*