The effect of ZnO/PbO and FeOx/SiO2 on the viscosity of the PbO-ZnO-Fe3O4-SiO2-CaO slag was measured using the rotating spindle method. The slag viscosity decreased with decreasing ZnO/PbO mass ratio because of the depolymerization of the silicate structures. The viscosity decreased with increasing FeOx/SiO2 mass ratio as the experimental temperature was above 1623 K, while the viscosity increased significantly with the increase of FeOx/SiO2 as the experimental temperature below 1623 K because of the phase transition and the change of slag melting point. According to XRD analysis of as-quenched slag, the spinel and the zincite phase increased with increasing FeOx/SiO2. Increasing ZnO/PbO and FeOx/SiO2 could enhance the crystallization capacity of the slag. FTIR analysis revealed that the degree of polymerization of the as-quenched slags decreased with decreasing ZnO/PbO and increasing FeOx/SiO2. The temperature dependencies of the viscosity on ZnO/PbO and FeOx/SiO2 were investigated, and the apparent activation energies of each system were found to be between 169.5 to 227.4 KJ/mol, and 151.1 to 676.4 KJ/mol, respectively.

Keywords: Viscosity; High lead and zinc slag; Slag structure; Apparent activation energy

1. Introduction

Lead sulfide concentrate is the main raw material for lead smelting. The traditional routes of extracting lead from lead sulfide concentrate include a desulfurization process in a bath smelting process, followed by a reduction process to obtain metal lead. The oxygen-enriched bottom blown smelting in a desulfurization process is widely used in lead and copper smelting processes in China due to low energy consumption and due to it being environmentally friendly [1-2]. The limited resources of high grade lead concentrate have aroused interest in the use of alternative lead bearing material which is seldom used in the bottom blown furnace due to the restrictions on the composition of raw materials in the existing lead smelting processes. The high Zn content raw materials such as lead and zinc mixed concentrate are especially abundant in China. Due to the high zinc content these raw materials will lead to the reduction of PbO in the oxidation slag, the variation in the mass transfer in desulfurization process, the increase of slag melting point, and the change of slag viscosity. Viscosity is one of the important physicochemical properties of slag, and low viscosity could promote the efficiency of the desulfurization reaction of slag. Considering the effect of slag composition on its physical properties, the slag composition must be optimized to accommodate changes to its viscosity.

FeOx/SiO2 is an effective means to adjust slag physical property in the desulfurization process of lead smelting [3]; it is important to study the effect of FeOx/SiO2 on the viscosity of slag with high ZnO content. Therefore, in order to make the oxidation furnace operate effectively, it is necessary to understand the dependence of slag viscosity on temperature and composition. Gupta [4] studied the viscosity of PbO-SiO2 melts and found that the viscosity of slag decreased with the increasing content of PbO because of the depolymerization of the silicate network structure. Battle and Hager [5] found that the addition of SiO2 increased the viscosity of lead smelting slag, while the additions of ZnO decreased the viscosity at high temperatures, but raised the slag liquidus temperature. Lv et al. [6] investigated the effect of FeO content on the viscosity and structure in the SiO2-MgO-FeO-CaO-Al2O3 slag system. The results showed that the viscosity decreased and the mass fraction of the suspended particles increased with the increase of FeO content.

The final desulfurization slag can usually be approximately considered a mixture of oxides including PbO, ZnO, FeOx, SiO2, and CaO from the oxidation of lead raw material and the flux of oxygen-
enriched bottom blown furnace. However, there is a lack of the available data with respect to the viscosity of PbO-ZnO-Fe_3O_4-SiO_2-CaO system slag. Therefore, the effect of ZnO/PbO and FeO/X/SiO_2 on the viscosity in PbO-ZnO-Fe_3O_4-SiO_2-CaO system was initially investigated in this article, and the effect of ZnO/PbO and FeO/X/SiO_2 on the activation energy (E_η) for the viscous flow was estimated as well. The phase relations of the slag were studied by XRD. Furthermore, Fourier transform infra-red (FTIR) techniques were used to obtain the structural information of the molten slag.

2. Experimental

2.1 Sample preparation

The slag used in this experiment was synthesized with analytical pure grade PbO, ZnO, Fe_3O_4, SiO_2, and CaO provided by Sinopharm Chemical Reagent co., Ltd. The slag composition (FeO/X/SiO_2=1.08, CaO/SiO_2=0.5) was based on the chemical composition of oxidation slag of typical oxygen-enriched bottom blown furnaces in the lead smelting industry in China. The reagent was weighted according to the required composition given in Table 1 and mixed to become homogeneous. The loss caused by PbO volatilization [7] at high temperature was compensated by the excess addition of PbO (~1.09 times the theoretical quantity).

The composition of the slag after the experiment was presented in Table 2; it can be seen that there were some changes in the composition of the slag after the viscosity measurement. Besides, the test results showed that Al_2O_3 concentration (less than 2.5 wt. %) was dissolved in the slag from the corrosion of the crucible in viscosity measurement. In addition, the Al_2O_3 content in the slag before and after the viscosity measurement was measured. The results illustrated that the Al_2O_3 content varied in the range from 2.32 wt. % to 2.45 wt. %, and the change of Al_2O_3 content before and after the viscosity measurement was less than 0.15 wt. %, which indicated that the enrichment of Al_2O_3 in the slag from the corrosion of the crucible in viscosity measurement could be neglected. The same method was used to measure the viscosity of copper smelting slag [8-9], and the results demonstrated that the solubility of Al_2O_3 was negligible in the copper smelting or “Cu_2O”-SiO_2-Al_2O_3 melt slag under experimental conditions.

2.2 Experimental apparatus and procedures

In this research, the viscosity of molten slag was determined by the rotating cylinder method. Fig. 1 shows the schematic diagram of the viscosity experimental device. An alumina crucible (inner...
A diameter: 40 mm, height: 115 mm) was put in a vertical tube furnace with MoSi2 heating elements. The Pt-13 pct Rh/Pt thermocouple at the bottom of the crucible was used to monitor the slag temperature. Meanwhile, the furnace temperature was controlled by the computer program. The rotating bob was made of alumina, and the viscometer was calibrated with castor oil with known viscosity before the experiment. It should be pointed out that the bob which was used to measure the viscosity had almost no change in the diameter before and after the experiment, which indicated that the influence of the diameter variation on the viscosity measurement could be neglected.

About 250 g of mixture was heated to 1623 K and equilibrated for 1 h to obtain the homogeneous slag. The bob was inserted into the molten slag and maintained at 10 mm above the bottom of the crucible, and then the viscometer (model: RTW-10) started measuring with the spindle at a fixed rate of 200 rpm. The value of slag viscosity was calculated and recorded by the computer. The Ar was introduced into the furnace at a flow rate of 1.2 L/min to prevent the oxidation of slag. The errors of viscosity measurement were less than 0.002 Pa·s. When the temperature reached at each target temperature, the slag equilibrated at each experimental temperature for 30 minutes.

Kim and Sohn [10] used the breaking temperature to describe the property of slag. The breaking temperature is the critical temperature at which the viscosity varied greatly during the cooling cycle. The molten slag could be assumed to be full liquid above the breaking temperature [11].

After the viscosity measurement, the slag was reheated to the target temperature. Subsequently, parts of the slag were removed from the slag by the iron rod and quenched in water for the structure analysis. The slag phase and the structure were analyzed by X-ray diffractometer (Bruker, D8 ADVANCE, Germany) and Fourier Transform Infrared Spectrometer (Nicolet, iS50, USA), respectively.

3. Results and Discussion
3.1 Effect of ZnO/PbO on slag viscosity
Fig. 2 shows the viscosity changes of the PbO-ZnO-Fe3O4-SiO2-CaO system as a function of temperature with varying ZnO/PbO and a constant FeO/SiO2 of 1.08 and CaO/SiO2 of 0.5. The variation of ZnO/PbO in PbO-ZnO-Fe3O4-SiO2-CaO slag system has a significant influence on the slag viscosity. The viscosity increased as the ZnO/PbO increased. A further increase of ZnO/PbO above 1 had a remarkable effect in enhancing the viscosity. According to work done by Gupta [4] and Jin [12] et al., both PbO and ZnO suggested to be a weak basic oxide in a silicate melts, which could have decreased the slag viscosity by depolymerizing the slag network structure. It seems that PbO is better than ZnO in
depolymerizing the network structure; thus, increasing PbO/ZnO decreases the slag viscosity. According to the study of Jin et al. [12], the increasing ZnO content in slag would lead to the increase of crystallization capacity of the slag. In this study, the breaking temperature increased rapidly with the increase of PbO/ZnO, which further confirmed this point.

Fig. 3 shows the XRD analysis of the as-quenched slags with various ZnO/PbO in the PbO-ZnO-Fe₃O₄-SiO₂-CaO slag system. It can be seen that the main crystalline phase for the ZnO/PbO = 0.33 (ZnO=15 wt.%, PbO=45 wt.%) was identified as the spinel phase (ZnₙFe₃₋ₙO₄₊₂). The peaks intensity of the spinel phase was gradually increased as the increase of ZnO/PbO. When the ZnO/PbO increased to 0.714 (ZnO=25 wt.%, PbO=35 wt.%), the diffraction peaks for the zincite phase (ZnO) emerged. As the ZnO/PbO continued to increase, the diffraction peaks for ZnO and Fe₃O₄ became more pronounced. It is reported that the increase of the spinel and the zincite phase in the slag is the main reason for the increase of viscosity in the lead bath smelting process [13]. Thus, a subsequent decrease of ZnO/PbO ratio showed an increase effect in lowering the slag viscosity.

The temperature dependence of viscosity can be represented by the Arrhenius equation [8].

\[ \ln \eta = A + \frac{E_\eta}{R \cdot T} \]

where \( \eta \) is the viscosity, Pa·S; \( A \) is a constant, Pa·S; \( R \) is the gas constant, 8.314 J/mol·K⁻¹; \( T \) is the absolute temperature, K; \( E_\eta \) is the apparent activation energy stand for the sensibility of viscosity to temperature, and the change of \( E_\eta \) can illustrate the variation in the frictional resistance of viscous flow and the change of the slag structure [14], J/mol.

Fig. 4 shows a linear fit between the natural logarithm of the viscosity (ln \( \eta \)) and the reciprocal temperature (1/T).

Frictional resistance for viscous flow [12], which was similar to the change of measured viscosity.

3.2 Effect of FeOₓ/SiO₂ on slag viscosity

Fig. 5 shows the viscosity variation of the PbO-ZnO-Fe₃O₄-SiO₂-CaO system as a function of temperature with varying FeOₓ/SiO₂ and a constant ZnO/PbO of 1.18 and CaO/SiO₂ of 0.5, it can be seen that the increase of FeOₓ/SiO₂ could lower the viscosity of the slag as experimental temperature was
at 1623 K. The basic oxide behavior of FeO, which, like CaO, is a modifier of the network structure of silicate [15]; it was confirmed by the FTIR results as well. The same result was reported by other investigators [6]. However, when experimental temperature was below 1598 K, the viscosity increased significantly with the increase of FeO/SiO$_2$. Note that the increase of FeO in lead smelting slag can increase the melting point of the slag, thus causing various viscosity [13]. With the increase of FeO/SiO$_2$, the gradient of the viscosity curve got sharper below the breaking temperature, which further confirmed that the breaking temperature of the slag increased with the increase of Fe/SiO$_2$.

In order to know the relationship between the viscosity and the slag composition with the increase of FeO/SiO$_2$, the XRD analysis of the as-quenched slags with various FeO/SiO$_2$ in the PbO-ZnO-Fe$_3$O$_4$-SiO$_2$-CaO slag system was carried out. As shown in Fig. 6, the main crystalline phase of the slag was identified as zincite when FeO/SiO$_2$ was at 0.65. With FeO/SiO$_2$ increasing to 0.86, the diffraction peaks for the spinel phase became observable. Moreover, the spinel phase increased as FeO/SiO$_2$ continued to increase. This illustrated that the addition of silica could inhibit the formation of the spinel phase.

Based on the above study results, the increase of FeO/SiO$_2$ would not only increase the slag melting point, but also led to the phase transformation of the slag. This could be the reason that led to the change of the slag with various FeO/SiO$_2$ ratio as experimental temperature was below 1598 K.

The viscosities of various FeO/SiO$_2$ slag as a function of reciprocal of the temperature were shown in Fig. 7. $E_\eta$ in this system was estimated to be between 151.1 and 676.4 KJ/mol, and the corresponding $E_\eta$ with various FeO$_x$/SiO$_2$ was listed in Table 4.

### Table 1

<table>
<thead>
<tr>
<th>Slag Number</th>
<th>Range of Temperature (K)</th>
<th>$E_\eta$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>1523 to 1623</td>
<td>151.1</td>
</tr>
<tr>
<td>10</td>
<td>1573 to 1623</td>
<td>182.8</td>
</tr>
<tr>
<td>11</td>
<td>1573 to 1623</td>
<td>676.4</td>
</tr>
</tbody>
</table>

### 3.3 FTIR Analysis

It is generally considered that the viscosity is related to the degree of polymerization of silicate slag [16-17]. The FTIR transmittance of the as-quenched...
slag as a function of wavenumbers at different ZnO/PbO and FeO\textsubscript{x}/SiO\textsubscript{2} are exhibited in Figure 10 and 11. The infrared spectra of the silicate slag is mostly concentrated in the wavenumber range of 1200 to 400 cm\textsuperscript{-1} [18-20]. This wavenumber region includes the stretching vibration bands of the [SiO\textsubscript{4}]\textsuperscript{tetrahedra} (wavenumber: 1100-850) and [AlO\textsubscript{4}]\textsuperscript{tetrahedra} (wavenumber: 750-590), and the Si-O bending vibration bands (wavenumber: ~500), respectively [6].

In the study of silicate melt structure, the average number of non-bridge oxygen (NBO/Si) is often used to illustrate the polymerization of silicate slag structures [21], where the lower NBO/Si indicates the higher degree of polymerization of the molten slag [11]. The wavenumber region between 1200 and 800 cm\textsuperscript{-1} is widely known to be the [SiO\textsubscript{4}]\textsuperscript{tetrahedra} peaks with various NBO/Si (NBO/Si=1, 2, 3, 4). According to the study of B. O. Mysen et al [22], the wavenumber region of 1100-1050 cm\textsuperscript{-1}, 980-950 cm\textsuperscript{-1}, 920-900 cm\textsuperscript{-1}, 880-850 cm\textsuperscript{-1} represent the band groups of [SiO\textsubscript{4}]\textsuperscript{tetrahedral} with NBO/Si = 1 (sheets), 2 (chains), 3 (dimers) and 4 (monomers), respectively. Clearly, as shown in Fig. 8, the [SiO\textsubscript{4}]\textsuperscript{tetrahedra} peaks at about 750 to 1150 cm\textsuperscript{-1} got weaker when the ZnO/PbO was decreased, which demonstrated that the structure of the slag could be depolymerized by the decrease of ZnO/PbO. The results observed in Fig. 9 show that the characteristic stretching vibration band for the large silicate network structures became less pronounced and the depth of the convoluted band became shallower, which illustrated that the increase of FeO\textsubscript{x}/SiO\textsubscript{2} was likely to depolymerize the silicate network structure into simpler polymer type units. Therefore, the depolymerization of the silicate network structure could reduce the polymerization degree of complex viscous units, thus decreasing the slag viscosity.

4. Conclusion

The viscosities of PbO-ZnO-Fe\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}-CaO lead smelting slags were measured using the rotational spindle method, and the phase structure was studied by XRD and FTIR analysis. The following conclusions could be obtained:

1. The viscosity of the molten slag decreased as the ZnO/PbO mass ratio decreased from 1.18 to 0.33, and the decrease trend was more obvious when ZnO/PbO was less than 0.714 and the temperature was below 1523 K.

2. The effect of FeO\textsubscript{x}/SiO\textsubscript{2} in PbO-ZnO-Fe\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}-CaO system on the viscosity was complicated due to the phase transition of the basic slag and the change of the slag melting point ranging from 1523 to 1573 K. XRD analysis of as-quenched molten slag samples revealed that the phase could be changed in the slags with the lower FeO\textsubscript{x}/SiO\textsubscript{2} mass ratio.

3. The apparent activation energy of viscosity at different ZnO/PbO and FeO\textsubscript{x}/SiO\textsubscript{2} was estimated to 169.5 to 227.4 KJ/mol, and 151.1 to 676.4 KJ/mol, respectively. The variation of the apparent activation energy was similar to the change in the viscosity.

4. The PbO or FeO\textsubscript{x} is likely to be a network modifier and provided free O\textsuperscript{2-} to depolymerize [Si\textsubscript{x}O\textsubscript{y}]\textsuperscript{n-tetrahedra} into simpler polymer type units, which resulted in the decrease of the viscosity.

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Reference


UTICAJ ODNOSE ZnO/PbO I FeOx/SiO$_2$ NA VIZKOZNOST OLOVNE ŠLJAKE


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Apstrakt

Uticaj ZnO/PbO i FeO$_x$/SiO$_2$ na viskoznost PbO-ZnO-Fe$_3$O$_4$ i SiO$_2$-CaO šljake izmeren je korišćenjem metoda rotacione osovine. Viskoznost šljake opada sa opadanjem ZnO/PbO masenog odnosa zbog depolimerizacije silikatnih struktura. Viskoznost je opadala sa povećanjem masenog odnosa FeO$_x$/SiO$_2$ pri temperaturi iznad 1623 K, dok je viskoznost značajno porasla povećanjem FeO$_x$/SiO$_2$ pri temperaturi ispod 1623 K zbog faznog prelaza i promene tačke topljenja šljake. Prema XRD analizi kaljene šljake, faza spinela i cink oksida se povećala povećanjem FeO$_x$/SiO$_2$. Povećanje ZnO/PbO i FeO$_x$/SiO$_2$ je poboljšalo kapacitet kristalizacije šljake. FTIR analiza je otkrila da je stepen polimerizacije kaljene šljake smanjen sa smanjenjem ZnO/PbO i povećanjem FeO$_x$/SiO$_2$. Ispitivane su temperaturne zavisnosti viskoznosti na ZnO/PbO i FeO$_x$/SiO$_2$ i nađeno je da su energije aktivacije u ovim sistemima bile od 169.5 do 227.4 KJ/mol i od 151.1 do 676.4 KJ/mol, respektivno.

Ključne reči: Viskozitet; Šljaka sa visokim udelom cinka i olova; Struktura šljake; Energija aktivacije.