

VISCOSITIES OF LEAD SLAGS

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Abstract

In this paper, experimentally determined viscosities of industrial lead slags at various temperatures are reported. Previous correlation models in literature are briefly reviewed. Based on the data from this study and other two investigations, an empirical viscosity model has been developed to correlate the viscosities of industrial lead slags with composition and temperature. The calculated results using this viscosity model are in good agreement with the measured data. It is found that the viscosities of lead slags increase with increasing SiO_2 and Al_2O_3 contents.

Introduction

The viscosity of lead-smelting slag is very important for quantifying the flow properties of the slag. In addition, it influences the amount of entrained metal in the slag, mass transfer at the slag/metal interface, heat transfer through the slag, and the service life of refractory materials. Low viscosity slags, which should contain less entrained lead and should be easily skimmed from the furnace, are preferable for production. The preferable slags should also melt at lower liquidus temperature over a narrow temperature range to avoid lead volatility. It is expected that those slags with the best combination of viscosity and liquidus temperature range would improve lead smelting operation.

Numerous studies have been carried out to measure the viscosities of synthetic lead containing systems, such as binary system PbO-SiO₂, ternary systems PbO-SiO₂-MgO, PbO-SiO₂-CaO, and PbO-SiO₂-Al₂O₃ [1-7]. A couple of studies on viscosities of industrial lead slags with low lead oxide content are also documented [8, 9]. It has been found that although temperature is the determinant of the slag viscosity, slag composition, oxidation-state, and the presence of entrained solid particles such as spinels, magnetite or other ferrites also affect viscosity. Low order synthetic slags containing 3 or 4 constituents normally cannot reproduce viscosities of industrial slags that have much more complicated constituents. In this paper experimentally determined viscosities of industrial lead-smelting slag samples are reported in the temperature range between 1050°C and 1300°C. The resulting experimental data, along with selected literature values, are correlated with temperature and composition.

Experiments and Results

Viscosity measurements of a total of 27 different industrial lead smelting slag samples were carried out in the temperature range between 1050°C and 1300°C. A Brookfield RVTDV-II digital viscometer with graphite components was used in the viscosity measurements. These slags studied have relatively high contents of lead and copper. The chemical analyses of the industrial lead slag samples studied are tabulated in Table I. The detail information about the apparatus for viscosity measurements and experimental procedure has been reported in our previous paper [10].

Viscosity measurement results are tabulated in Table II. It is found that the viscosities of the lead slags decrease with increasing temperature and the natural logarithm of viscosity against reciprocal temperature closely follow a linear relation over the reported ranges of temperature.

Discussion

Composition dependency of viscosity

Generally, the viscosity of lead slags increases with increasing the content of network forming oxides, such as SiO₂, and decreases with increasing the proportion of network modifiers, such as PbO, MgO, CaO, FeO, and ZnO. The amphoteric oxides such as Al₂O₃ may act either as network formers or as modifiers depending on the contents of the slags [11, 12]. Although all metallic oxides play similar role in the slag, i.e., breakdown the continuous Si-O-Si network by supplying nonbridging oxygen ions and cause the viscosity to decrease, the effect of various metallic oxides is quite different. At constant silica content, the substitution of the metallic oxides with a high melting point such as MgO, CaO, and ZnO for ones with a low melting point such as PbO will raise the liquidus temperature of the slags and result in a higher viscosity [6, 9].

Industrial lead slags usually have 8 to 12 major components that typically account for 90-95% of the slag composition. All the composition variables are functionally related each other. The variation of any individual component may result in the changes of one or more other slag components. It is not feasible to determine the effect of each individual chemical component on the viscosity by changing only one slag component at a time and fixing rest of others. To figure out the effect of each individual slag component on the variation of the slag viscosity, it is necessary to develop a quantitative correlation of viscosity with composition. A satisfactory correlation model should not only discriminate chemical components by the categories of the network former and the network modifier but also recognize the characteristic of each individual component.

Previous correlation models

Many theories dealing with the temperature dependence of viscosity have been proposed for the liquid state. The theoretically derived viscosity equations have not been verified adequately for liquid silicates because of the incomplete knowledge of the physical properties of such liquids. Several empirical viscosity equations are available in literature for the estimation of the viscosity of lead slags and liquid silicate melts [8, 9, and 11-13]. In many cases the viscosity measurements reported were found to obey an Arrhenius type equation

$$\eta = A \exp(E/RT) \quad (1)$$

The fit to an Arrhenius type equation gives parameters in terms of the pre-exponential constant A and the activation energy E. Based on different theories, the modified forms of the simple Arrhenius equation can be written as a generalized form

$$\eta = AT^n \exp(E/RT) \quad (2)$$

where n is a constant. $n = 0.5$ was derived by both Glasstone et al. [14] based on reaction rate theory and Bockris and Reddy [15] based on the hole theory. $n = 1$ was derived by Weymann based on the hole theory [16]. Hu and Reddy [17] and Reddy and Hebbar [18] considered the changes of network structure of silicate melts on the addition of alkali oxides and extended Bockris and Reddy equation [15] to binary silicate melts.

Battle and Hager [9] separated oxides into two groups, basic oxides and acidic oxides, and then lumped them together to a composition dependent variable, the weight ratio of basic oxides to acidic oxides. Using an Nth-order polynomial equation, they correlated the viscosities of lead slags with the weight ratio and obtained the correlation coefficients. A good estimate of the viscosities of lead slags was reported. Battle and Hager method is somewhat cumbersome because the different sets of coefficient values are needed at various temperatures.

Using an Arrhenius type equation Altman et al. [8] correlated the viscosities of lead slags with temperature and composition. Similarly, a weight ratio of constituents was used as the composition dependent variable. However, the MgO content was summed with the acidic oxides SiO_2 and Al_2O_3 rather than with the basic oxides to describe the tendency of the viscosity increase with increasing MgO at low concentrations.

An empirical model in the modified form of the simple Arrhenius equation was developed by Ribound et al. [13] to estimate the viscosity of mould powders. In this model the slag constituents were classified into five different categories. The model coefficients were expressed as a function of the mole fractions of these categories.

The models by Battle and Hager [9], Altman et al. [8], and Ribound et al. [13], in common, have an obvious flaw, that is, they all consider that the oxides in the same category

provide same effect on the viscosity. Therefore, they predict same viscosity value for all systems with different compositions but with equal total amounts in the categories, although it is a known fact that, for example, the viscosities of SiO₂-CaO and SiO₂-FeO can not be same at a particular SiO₂ content. The cations of different metallic oxides show different polarization strength on the shared oxygen of adjacent Si-O bonds resulting in different weakening effect on the network linkage.

Bottinga and Weill [11] developed an empirical model to estimate the viscosity of complex alumino-silicates with emphasis on the magmatic silicate liquids. They observed that logarithmic viscosity of silicate solutions varied as a linear function of composition over restricted composition intervals in simple systems and extended their observations to multicomponent systems based on the Arrhenius mixing rule. The viscosity could be calculated with equation (3)

$$\ln \eta(T) = \sum_i X_i D_i(T) \quad (3)$$

where $\eta(T)$ is the viscosity in poise at temperature T , $D_i(T)$ is a constant characteristic viscosity contribution of the component i of mole fraction X_i . This model emphasized the specific effect of each individual component in various systems. Apparently, the disadvantage of the Bottinga and Weill method is that many $D_i(T)$ are needed for the viscosity correlation at various temperatures.

Estimation of the viscosity of lead smelting slags

Because it is found from our experimental data and most of viscosity measurements reported in literature that the logarithm of viscosity obeys a linear dependence against reciprocal temperature, therefore, the Arrhenius type equation is adopted in this study. The composition dependence of viscosity for liquid silicate can be qualitatively explained in terms of the structure of liquid silicate, which considers the liquid silicate as a non-periodic array of SiO₄ tetrahedra linked together by strong Si-O covalent bonds. Viscous flow must undergo the rupture and replacement of some of the Si-O bonds. The fluidity is strongly dependent on the strength of linkage between flow units and the sizes of the flow units, which is determined by the concentration of network forming oxides. Therefore, the contents of network forming oxides are chosen as composition variables in the pre-exponential term of our model. The addition of metallic oxides to the network forming oxides results in a breakdown of the complex polyions into smaller flow units making the flow easier. Since the liquidus temperature of the silicates with various metallic oxides is quite different, the contents of the network modifiers are considered as composition variables in the temperature term of our model.

Based on the above observations and considerations, an empirical viscosity model is developed from the Arrhenius type equation to correlate the viscosity of industrial lead slags with composition and temperature. The viscosity model can be expressed in natural logarithm form as follows:

$$\ln \eta = (A_0 + \sum A_i X_{A(i)}) + (B_0 + \sum B_i X_{B(i)}) \times 10^3 / T \quad (4)$$

where η is the viscosity in Pa.s, T is absolute temperature. $X_{A(i)}$ is weight percentage of network forming oxides $A(i)$ in the slag and $X_{B(i)}$ is weight percentage of metallic oxides or other non-network forming components $B(i)$ in the slag. A_0 , A_i , B_0 , and B_i are correlation

coefficients for species i in the composition ranges that the data covered. The weight percentage and correlation coefficient of all the elements and components other than the considered $X_{A(i)}$ and $X_{B(i)}$ are included in $X_{B(\text{others})}$ and B_{others} .

The data from three different investigations are used to generate the correlation coefficients: the results of this study, lead slag data from Altman et al. [8] and the lead slag data from Battle and Hager [9]. The correlation coefficients are obtained by least squares fitting equation (4) to a total of 319 viscosity observations on lead slag samples. The resulting constants are listed in Table III with the temperature range and the composition range that the observations span. The coefficient of multiple determination (R^2) for equation (4) is 0.89.

Figure 1 shows that the calculated results using this viscosity model are in good agreement with the measured data. From the regression analysis of the selected data, it is concluded that including the term $\ln T^n$ in equation (4), as suggested by equation (2), shows little improvement in goodness of fit.

From the signs and values of the correlation coefficients, further analysis about the effect of composition on the viscosities can be made. First, the coefficients show that the differences in the effect of various components on the estimated viscosity are existent but not significant. Secondly, the viscosity of the lead slags increases with increasing SiO_2 and Al_2O_3 contents. Thirdly, probably due to the limitation of the selected data, the signs and values of the constants indicate that the slope of $\ln \eta$ vs $1/T$ will increase with increasing the contents of metallic oxides. This does not agree with the general understanding on the effect of metallic oxides in terms of variations of the activation energy. Therefore, the form of equation (4) may not be valid over all composition ranges. Further study is required to optimize the correlation coefficients in equation (4) and recognize the physical meaning of the constant characteristics. The melting point of the metal oxides in the slags has been suggested as an indication to distinguish the specific effect of various metal oxides [6, 9].

Conclusions

Experimentally determined viscosities of industrial lead slags with various compositions are reported in the temperature range between 1050°C and 1300°C. A Brookfield RVTDV-II digital viscometer with graphite components was used in the viscosity measurements. These slags studied have relatively high contents of lead and copper.

The results show that viscosities of lead-smelting slags decrease with increasing temperature and $\ln(\eta)$ vs $10^4/T$ closely follows a linear relation over the reported ranges of temperature. The composition dependency of viscosity is discussed. Previous correlation models in literature are briefly reviewed.

Based on the data from this study and other two investigations, an empirical viscosity model has been developed to correlate the viscosity of industrial lead slags with composition and temperature. Our present model not only discriminates chemical components by the categories of the network former and the network modifier but also recognizes the characteristic of each individual component. In the meantime, the model correlates the viscosity with temperature in a simple form. According to the regressed model parameters, the differences in the effect of various components on the estimated viscosity are existent but not significant. The viscosity of lead slags increases with increasing SiO_2 and Al_2O_3 contents. Further study is required to optimize the model parameters.

The calculated results using this viscosity model are in good agreement with the measured data within the ranges that the data covered. Therefore, the derived viscosity model can be used to predict the viscosity of lead- and copper-smelting slags.

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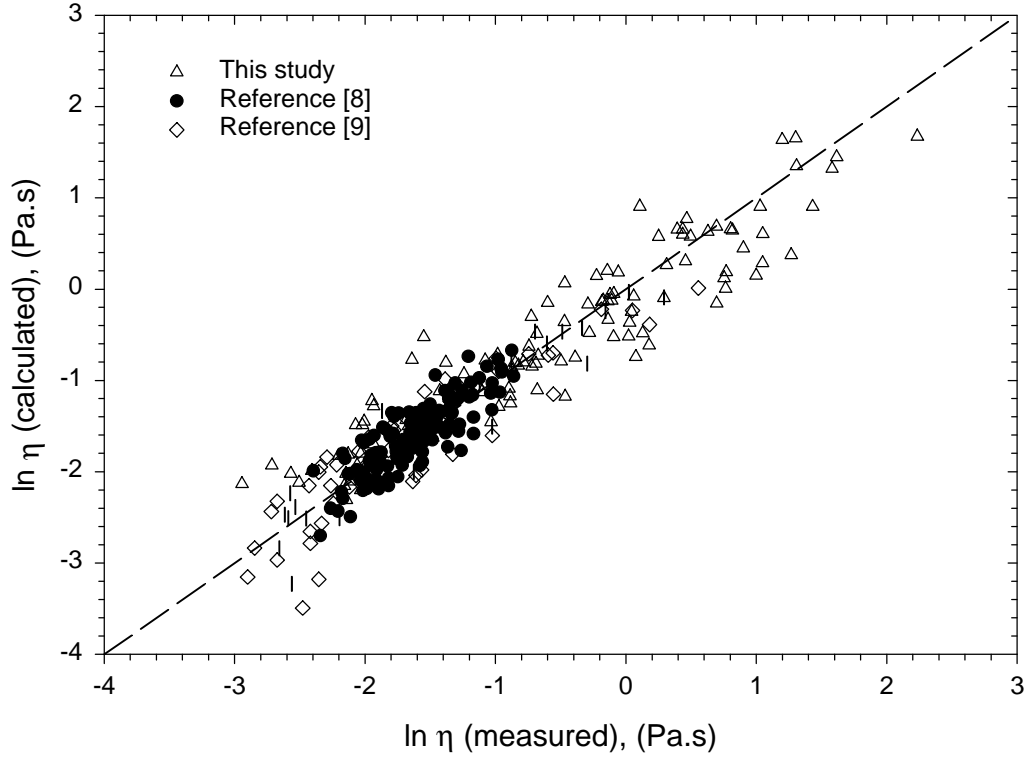


Figure 1: Comparison of calculated viscosity values with experimental results

Table I: Chemical analysis of slag samples

Sample No.	Chemical composition of samples in mass percentage											Sum
	SiO ₂	Al ₂ O ₃	MgO	CaO	ZnO	FeO	PbO	CuO	NiO	S	undisclosed elements	
1	16.47	2.53	0.35	6.24	4.57	12.31	30.27	16.16	2.05	2.51	4.29	97.75
2	13.11	2.12	0.53	4.97	3.44	9.39	34.30	23.25	1.90	3.42	3.85	100.27
3	18.18	2.30	0.52	7.43	4.37	13.35	38.51	5.19	1.53	0.13	4.6	96.12
4	23.75	8.15	0.29	8.75	4.73	18.29	23.42	3.34	0.98	0.12	4.02	95.84
5	13.93	2.94	0.64	5.73	3.07	10.90	40.23	10.47	2.57	0.07	5.75	96.30
6	25.04	8.01	0.58	10.10	5.78	21.56	14.87	3.17	0.83	-	4.37	94.30
7	14.75	2.56	0.77	8.61	3.51	13.39	28.77	15.57	2.19	2.29	5.06	97.48
8	25.64	4.34	0.44	10.80	4.26	19.90	22.10	2.52	0.60	0.13	4.38	95.11
9	23.18	3.70	0.35	8.99	4.46	22.15	22.10	2.22	0.73	0.38	6.21	94.47
10	22.93	5.52	0.74	6.81	3.41	13.98	31.67	4.97	1.39	0.38	3.32	95.12
11	21.08	5.28	<0.20	8.00	4.82	20.34	23.30	2.94	0.55	0.13	3.03	89.67
12	28.41	8.94	0.75	9.55	5.53	20.83	15.49	1.85	0.48	-	4.46	96.29
13	17.89	6.81	0.61	8.01	4.34	17.84	13.93	5.75	0.87	-	3.81	79.86
14	12.03	3.52	0.63	4.19	2.59	10.70	31.23	22.46	3.17	3.72	5.29	99.53
15	16.68	5.31	0.54	7.11	6.39	18.67	27.14	5.14	2.52	-	5.48	94.97
16	16.68	5.92	0.44	7.37	4.97	18.76	27.52	6.07	2.35	0.29	4.93	95.30
17	16.52	3.57	0.67	7.51	4.93	16.29	27.73	7.54	4.68	0.33	5.71	95.47
18	19.08	4.16	0.46	8.69	5.33	15.88	28.45	4.92	3.68	0.31	6.08	97.03
19	18.59	3.73	0.54	7.70	5.76	15.81	28.85	3.78	3.68	0.23	5.64	94.31
20	16.09	5.02	0.58	7.46	5.07	19.04	30.29	6.68	2.76	0.36	5.27	98.62
21	14.86	4.51	0.58	7.32	4.98	15.97	32.28	5.55	3.14	0.14	5.62	94.95
22	16.58	3.63	0.66	6.07	5.84	15.57	33.16	4.77	3.07	0.34	6.03	95.71
23	14.27	2.27	0.60	5.55	0.54	15.55	35.01	8.09	2.63	0.85	5.34	90.70
24	19.05	3.92	1.28	5.62	4.24	13.37	35.32	5.81	2.48	0.02	5.41	96.52
25	13.36	2.80	0.61	5.35	4.44	11.30	36.17	6.76	7.47	0.23	6.1	94.59
26	18.61	4.14	0.56	6.21	3.46	12.57	37.31	5.71	2.21	0.19	4.84	95.82
27	15.12	2.13	0.45	4.95	4.06	14.36	38.00	8.41	2.98	0.98	5.25	96.69

Table II: Results of viscosity measurements of lead slags

Sample No.	Viscosity η , (Pa.s)						
	1050 °C	1100 °C	1125 °C	1150 °C	1200 °C	1250 °C	1300 °C
1	-	-	2.230	1.366	0.757	0.411	0.111
2	-	-	-	-	-	0.408	0.119
3	-	-	-	-	-	0.204	0.090
4	-	-	-	0.867	0.485	0.194	0.078
5	-	-	-	-	1.022	0.413	0.136
6	-	-	3.553	2.125	0.624	0.252	0.143
7	-	-	-	0.799	0.476	0.240	0.077
8	-	-	2.849	2.149	0.910	-	0.133
9	-	-	2.717	2.006	1.080	0.377	0.131
10	-	-	-	-	1.046	0.340	0.145
11	-	-	-	-	1.195	0.627	0.145
12	-	-	-	-	0.549	0.213	0.063
13	-	-	2.264	1.579	0.872	0.289	0.126
14	-	4.862	-	2.462	1.029	0.332	0.143
15	-	1.547	-	0.898	0.456	0.185	0.117
16	-	1.547	-	0.886	0.510	0.250	-
17	-	2.003	-	1.063	0.609	0.355	0.150
18	-	2.856	-	1.340	0.678	0.218	0.128
19	3.698	1.642	-	0.831	0.428	0.252	0.129
20	-	1.285	-	0.748	0.417	0.224	0.121
21	-	1.482	-	0.840	0.486	0.260	0.116
22	5.032	1.877	-	0.872	0.439	0.189	0.082
23	-	1.114	-	0.626	0.374	0.134	0.053
24	9.350	4.191	-	2.159	1.137	0.507	0.197
25	3.315	-	-	-	0.418	0.228	0.117
26	-	2.802	-	0.944	0.505	0.240	-
27	3.681	1.595	-	0.911	0.502	0.248	0.131

Table III: Regression results for model correlation

Constant	Value	Input data range	
A_0	-31.981886	temperature	1050°C to 1433°C
A_{SiO_2}	0.543124	SiO_2	12.03 to 36.8 wt. %
$A_{Al_2O_3}$	0.548868	Al_2O_3	2.11 to 11.5 wt. %
B_0	-26.840100	MgO	0.2 to 9.5 wt. %
B_{MgO}	0.742236	CaO	3.3 to 21.7 wt. %
B_{CaO}	0.683681	ZnO	0.54 to 24 wt. %
B_{ZnO}	0.676625	FeO	9.37 to 34.7 wt. %
B_{FeO}	0.673338	PbO	0.13 to 40.23 wt. %
B_{PbO}	0.717893	CuO	0 to 23.18 wt. %
B_{CuO}	0.785696	NiO	0 to 7.47 wt. %
B_{NiO}	0.677901	S	0 to 6.8 wt. %
B_S	0.588837	viscosity	0.053 to 9.35 Pa.s
B_{Others}	0.737147		