Prediction of Temperature of Critical Viscosity for Coal Ash Slag

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Introduction

The need for greater efficiency for future power generation has led to an increase in integrated gasification combined cycle (IGCC) technologies, which can reduce emissions of greenhouse gas, sulfur dioxide, nitrogen oxides and trace elements.[1,2] IGCC plants commonly utilize entrained flow gasifiers, which are generally operated in slagging mode at high-temperatures (1400–1800°C), and pressures (20–70 bar).[3,4] To ensure reliable slag tapping, the operation temperature of the gasifier should be above the temperature of critical viscosity of the slag,[5] T_{cv}. This temperature is recognized as a sharp break in the viscosity vs. temperature curve and marks the division between crystal-affected viscosity and viscosity not affected by the presence of crystals.[6] The difficulty and high cost of measuring the T_{cv} value of slag derived from coals with varied ash analyses has led to many predictive models based on ash fusion temperature (AFT) and chemical composition.[7]

Sage Model

Sage and McIlroy[8] found the hemispherical temperature of coal ash slag T_h, to be an adequate guide for T_{cv}

$$T_{cv} = T_h + 111 \tag{1}$$

The hemispherical temperature of coal ash is defined according to the ASTM ash fusion test as the temperature at which a cone collapses to a hemispherical lump (height = 1/2 × width).

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Corey Model

Corey[9] proposed a relationship between T_{cv} and the softening temperature T_s, defined as the temperature at which a cone fuses to a lump with height = width

$$T_{cv} = T_s \tag{2}$$

Marshak Model

Marshak and Ryzhakov[10] also showed the T_{cv} of a coal ash slag to be a function of T_s

$$T_{cv} = 0.75 \cdot T_s + 548[K] \tag{3}$$

Analysis of coal ash compositions shows that they consist mainly of SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO,[11,12] so that the properties of coal ashes at high-temperature might be modeled by a five component SiO_2-Al_2O_3-Fe_2O_3-CaO-MgO synthetic ash. Moreover, since the composition of synthetic ash samples can be easily controlled, the experimental conditions can be simplified and can exclude any interference by trace elements. Thus, we have measured the T_{cv} values of 40 synthetic ash samples formed by mixtures of these five oxides (SiO_2, Al_2O_3, CaO, Fe_2O_3, and MgO), as well as eight Chinese coal ash samples. The computer software package FactSage has been used to calculate the temperatures corresponding to different proportions of liquid phase of synthetic ash samples. An empirical liquidus model has been derived to correlate the T_{cv} values of the 40 synthetic ash samples with their liquidus temperatures calculated by FactSage. This model was then used to predict the T_{cv} values of the coal ash samples.

Experimental

Coal ash and synthetic ash samples

Eight representative Chinese coal samples were used in the study. The coal ash samples were prepared in a muffle

Table 1. Ash Composition, AFTs, Liquidus Temperatures, Measured T_{cv} Values, and Critical Viscosities for Coal Ash and Synthetic Ash Samples

	Composition (wt %)						Ash fusion temperature (°C)					
Sample	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	A/B[a]	IDT	ST	HT	FT	T_{cv}Exp (°C)	η(Pa.s)
Yulin	36.74	12.00	28.81	10.23	7.83	1.04	1130	1160	1185	1230	1290	38.23
Huafeng	37.16	19.92	26.65	5.75	6.04	1.48	1075	1150	1170	1185	1298	15.11
Shierkuang	42.00	20.67	12.63	15.44	2.83	2.03	1185	1210	1255	1285	1323	24.89
Wulanqiceng	45.19	19.42	13.18	17.34	0.69	2.07	1205	1235	1250	1290	1331	19.58
Huainan No.2	44.36	24.82	24.62	3.15	0.91	2.41	1285	1310	1325	1340	1424	24.35
Huainan No.1	46.66	26.10	20.63	3.31	0.96	2.92	1320	1395	1410	1420	1471	33.14
Dazhuang	49.36	24.93	12.21	9.13	1.51	3.25	1200	1210	1265	1300	1398	17.73
Gaoyang	43.11	36.67	9.48	5.25	1.94	4.79	1395	1420	1455	1475	1550	32.38
1	35.71	14.28	15.00	15.00	20.00	1.00	1155	1200	1210	1250	1413	24.98
2	31.20	20.80	30.00	15.00	3.00	1.08	1125	1170	1185	1230	1333	22.51
3	37.14	14.86	30.00	15.00	3.00	1.08	1060	1130	1150	1180	1287	25.33
4	37.86	15.14	15.00	15.00	17.00	1.13	1140	1180	1190	1225	1380	24.83
5	35.20	23.80	25.00	15.00	1.00	1.33	1080	1145	1160	1180	1310	42.58
6	40.71	16.29	15.00	25.00	3.00	1.33	1135	1185	1200	1250	1300	34.11
7	34.20	22.80	25.00	15.00	3.00	1.33	1080	1130	1165	1200	1317	13.52
8	43.57	17.43	15.00	15.00	9.00	1.56	1200	1135	1175	1210	1285	26.71
9	40.62	21.38	30.00	5.00	3.00	1.63	1100	1170	1175	1190	1307	52.50
10	44.29	17.71	15.00	20.00	3.00	1.63	1100	1155	1160	1190	1293	34.45
11	44.29	17.71	30.00	5.00	3.00	1.63	1090	1150	1160	1185	1307	31.22
12	42.59	22.41	15.00	15.00	5.00	1.86	1140	1175	1180	1210	1320	35.85
13	46.43	18.57	15.00	15.00	5.00	1.86	1100	1160	1165	1200	1314	37.34
14	36.55	30.45	15.00	15.00	3.00	2.03	1200	1250	1265	1310	1390	28.34
15	47.85	19.16	25.00	5.00	3.00	2.03	1165	1205	1220	1250	1340	18.88
16	43.90	23.10	15.00	15.00	3.00	2.03	1170	1210	1225	1280	1334	23.04
17	43.90	23.10	25.00	5.00	3.00	2.03	1180	1240	1255	1290	1389	17.25
18	46.06	20.94	15.00	15.00	3.00	2.03	1155	1200	1215	1255	1314	26.72
19	40.20	26.80	15.00	15.00	3.00	2.03	1180	1240	1255	1290	1355	16.06
20	15.46	51.54	15.00	15.00	3.00	2.18	1360	1410	1415	1455	1533	10.34
21	25.13	41.87	15.00	15.00	3.00	2.18	1350	1355	1360	1385	1500	17.11
22	43.90	23.10	15.00	15.00	3.00	2.09	1210	1250	1275	1310	1395	35.48
23	49.64	19.86	15.00	15.00	0.50	2.27	1200	1240	1250	1290	1364	30.41
24	49.50	22.50	10.00	15.00	3.00	2.57	1150	1215	1225	1275	1345	40.10
25	47.17	24.83	10.00	15.00	3.00	2.57	1180	1225	1240	1300	1346	30.08
26	43.20	28.80	15.00	10.00	3.00	2.57	1230	1285	1290	1315	1421	65.52
27	51.43	20.57	20.00	5.00	3.00	2.57	1275	1280	1300	1350	1385	45.77
28	51.43	20.57	10.00	15.00	3.00	2.57	1185	1210	1225	1245	1303	17.33
29	39.27	32.73	15.00	10.00	3.00	2.57	1270	1320	1330	1345	1433	37.16
30	51.43	20.57	15.00	10.00	3.00	2.57	1170	1215	1230	1280	1349	16.66
31	47.17	24.83	20.00	5.00	3.00	2.57	1250	1270	1285	1320	1427	40.75
32	47.17	24.83	15.00	10.00	3.00	2.57	1190	1240	1250	1285	1395	24.63
33	49.50	22.50	15.00	10.00	3.00	2.57	1175	1225	1235	1265	1367	25.20
34	52.94	24.06	5.00	15.00	3.00	3.35	1225	1265	1270	1335	1421	25.77
35	50.45	26.55	5.00	15.00	3.00	3.35	1225	1270	1290	1315	1435	21.64
36	55.00	22.00	15.00	5.00	3.00	3.35	1195	1225	1240	1325	1370	38.15
37	42.31	37.19	15.00	5.00	0.50	3.87	1330	1390	1410	1370	1455	12.35
38	57.14	22.86	2.00	15.00	3.00	4.00	1235	1280	1295	1340	1416	45.90
39	57.86	23.14	15.00	1.00	3.00	4.26	1225	1270	1280	1325	1407	23.46
40	45.27	37.73	5.00	5.00	7.00	4.88	1400	1420	1425	1440	1523	17.04

A/B=(SiO_2+Al_2O_3)/(Fe_2O_3+CaO+MgO);1-40: synthetic ash sample; η: Critical viscosity

furnace at 815°C for 24 h according to the Chinese standard GB/T1574-1995. Chemical analysis of the coal samples was carried out using X-ray fluorescence (XRF). Forty synthetic ash samples, covering the range of composition of most of the Chinese coal ash samples, were prepared from Sinopharm Chemical Reagent Corp. Laboratory reagent silicon dioxide, aluminum oxide, ferric oxide, calcium oxide and magnesium oxide. The chemical composition of coal ash and synthetic ash samples is given in Table 1.

Ash fusion temperature test

We performed the ash fusion temperature tests by following the Chinese standard procedures (GB/T 219-1996) in a registered independent laboratory.[12] This test involved heating a sample cone of specified geometry at a rate of 5 K/min in an Ar atmosphere. The following specific temperatures are recorded for each sample, corresponding to specific shapes of the ash cones: Initial deformation temperature (IDT), softening temperature (ST), hemispherical temperature (HT), and flow temperature (FT). Table 1 presents the AFT data for coal ash and synthetic ash samples in an Ar atmosphere.

Measurement of T_{cv}

The apparatus for measurements of slag viscosity and T_{cv} value were described previously.[13] Viscosity measurements were then taken at the temperature at which the viscosity of slag was lower than 5.00 Pa·s with a bob speed of 25 rpm in

an Ar atmosphere. The higher partial pressure of oxygen was controlled by Ar/O_2 gas mixtures. Meanwhile, the lower partial pressure of oxygen was controlled by pure Ar gas; in addition, sacrificial graphite was used to remove few remaining oxygen in the Ar gas stream. The partial pressure of the oxygen was measured as approximately 10^{-6} atm at 1200–1500°C. The viscosity measurements were taken at 20°C intervals with stirring during the stepwise cooling process, allowing for equilibration of at least 60 min after each measurement. The T_{cv} value of the coal ash sample was determined based on the definition given by Dam-Johansen et al.[6] Their definition indicates a point of very abrupt change in the viscosity-temperature relationship. The measured T_{cv} values and critical viscosities of studied slag are listed in Table 1.

Thermodynamic modeling

Thermodynamic computer package FactSage[14] was used for predictions of multiphase equilibrium, liquidus temperatures and proportions of the liquid and solid phases in the Ar atmosphere for the multicomponent system SiO_2-Al_2O_3-CaO-Fe_2O_3-MgO. All available thermodynamic and phase formation data for this system were evaluated simultaneously in order to obtain a set of model equations for the Gibbs' energy of all phases; these then corresponded to functions of temperature and composition. FactSage could automatically predict the proportion of ferric and ferrous iron oxides as a function of composition, temperature, and gas atmosphere.[15]

FactSage performs complex thermodynamic model calculations (quasi-chemical and sublattice) for multicomponent and multiphase systems. It uses global conditions in elementary values, temperature, and total pressure as inputs. Global conditions could also be used as target variables after defining a target and represent the interaction of components for phase formation. The most frequently used targets are the given values of an extensive property, formation or disappearance of target phase, precipitation from target phase, or equilibrium mole fraction or activity.[16]

In this study, we used the method of Jak et al.[17] where thermodynamic properties calculated for samples by FactSage have been predicted from a five-component system SiO_2-Al_2O_3-Fe_2O_3-CaO-MgO, including, liquidus temperatures (temperatures at which first solid just starts to precipitate on cooling of a slag-liquid oxide melt), and the corresponding temperatures with different proportions of liquid phase. Once the phases have been determined, a total mass balance verifies the consistency of the system. For example, a four-component system of SiO_2-Al_2O_3-FeO-CaO (63.1, 27.7, 6.10 and 3.10 wt %, respectively), with the addition of 10 ± 1.5 g FeO per 100 g of initial sample, was selected for subsequent calculations.[18] As temperature decreased below the liquidus, the proportion of the mullite phase ($3Al_2O_3 \cdot 2SiO_2$) increased and the liquid proportion of the liquid phase decreased. At a temperature of approximately 1380°C, the tridymite phase (SiO_2) started to precipitate (in addition to the mullite phase). At approximately 1150°C, anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) started to form. Meanwhile, the mass of liquid and solid phases remained conservative from the single phase, to multiphase, and to liquid phase. For instance, at above 1550°C, the system comprised 100 g liquid phase; at 1300°C, the system comprised 71 g of liquid phase, 14 g of solid tridymite, and 15 g of solid mullite phase.

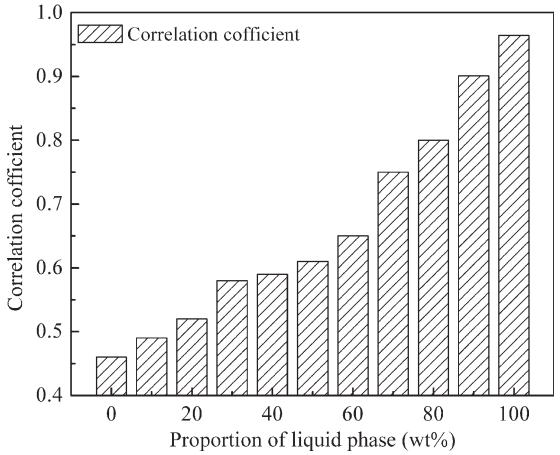

Figure 1. The effect of proportion of liquid phase on the correlation coefficients between the measured T_{cv} values and temperatures corresponding to different proportions of liquid phase for synthetic ash samples.

Results and Discussion

Development of the Tcv correlation

Linear regression analysis was used to compare the correlations between the T_{cv} values of synthetic ash samples and the corresponding temperatures with different proportions of liquid phase calculated by FactSage. Generally, the reliability of the values calculated using such correlations is indicated by the correlation coefficient (R). The standard deviation, σ value, simply indicates how close the calculated value is to the experimental values. In our work, the R values have been used to analyze the correlations between the T_{cv} values of synthetic ash samples and their temperatures with different proportions of liquid. An R value of 0.7 is generally acceptable for predicting the T_{cv} values of ash samples, a value of 0.8 is good and 0.9 or higher is excellent.[7]

Figure 1 presents the effect of proportion of liquid phase on the correlation coefficients between the T_{cv} and the corresponding temperatures with different proportions of liquid phase calculated by FactSage for synthetic ash samples. Observations from Figure 1 indicate an increase in the T_{cv} corresponding to R values corresponding to the T_{cv} of synthetic ash samples as the proportion of liquid calculated by FactSage increases. When the proportion of liquid exceeds 70%, the value of the correlation coefficient is higher than 0.7. In particular, when the proportion of liquid increases to 100%, the corresponding R value for the T_{cv} is higher than 0.9, which is indicative of a significant correlation between the T_{cv} values of the synthetic ash samples and the liquidus temperature calculated by FactSage.

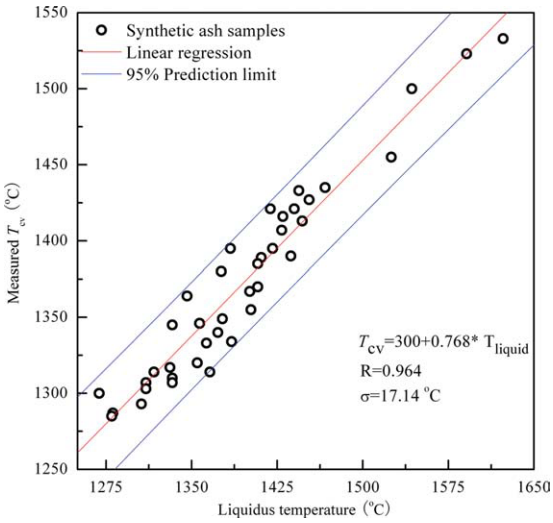

Figure 2. Correlation between the measured T_{cv} values and liquidus temperatures of synthetic ash samples.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2 shows the T_{cv} of the synthetic ash samples as a function of the calculated liquidus temperatures. Good correlations between the T_{cv} and liquidus temperatures can clearly be seen: the higher the liquidus temperature—the higher the T_{cv}. Moreover, the σ value is less than 20°C, which indicates that the accuracy of the results is within the experimental error.

The T_{cv} of the synthetic ash samples could be expressed as a linear function of the liquidus temperature according to the equation

$$T_{CV} = 300 + 0.768 \cdot T_{Liquidus} \tag{4}$$

where $T_{liquidus}$ is the liquidus temperature of the sample in degrees celsius (°C).

Comparison of the models

To test the accuracy of the various methods, the experimental T_{cv}, values of the synthetic ash samples were compared to predictions by each of models mentioned in the Introduction.

Figure 3 show parity plots of the measured T_{cv}, values vs. those predicted for synthetic ash samples by the Sage model,

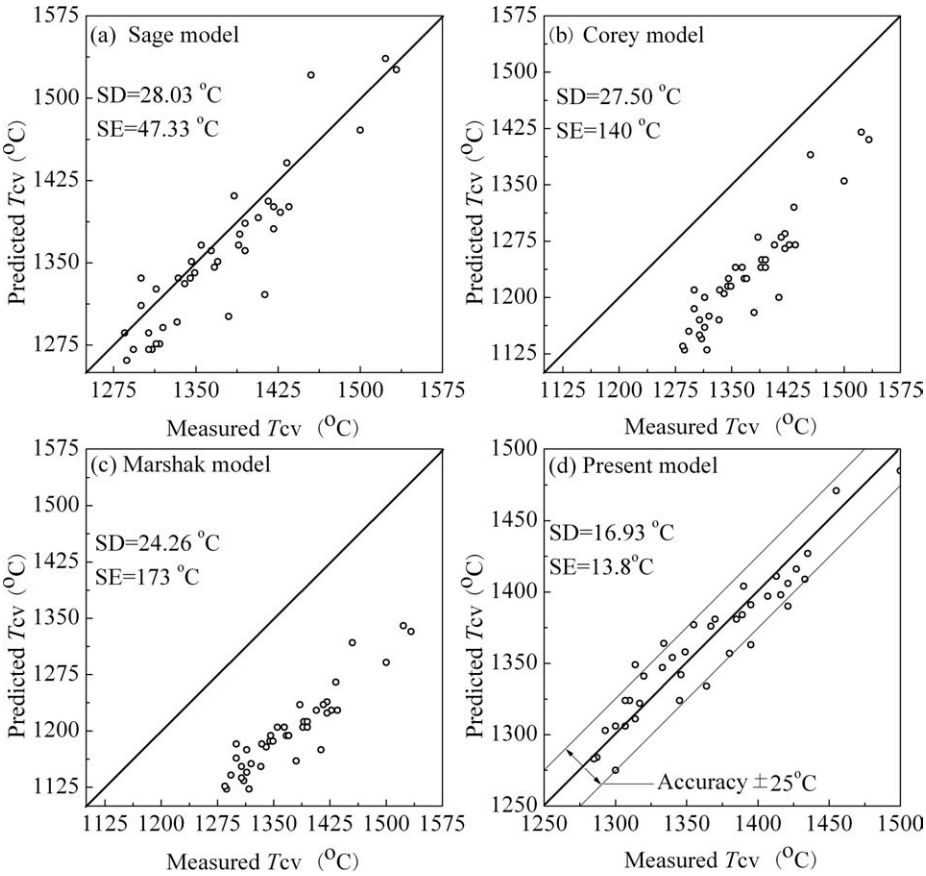

Figure 3. Comparison of the measured T_{cv} values with those predicted by (a) the Sage model, (b) the Corey model, (c) the Marshak model, and (d) the liquidus model for synthetic ash samples.

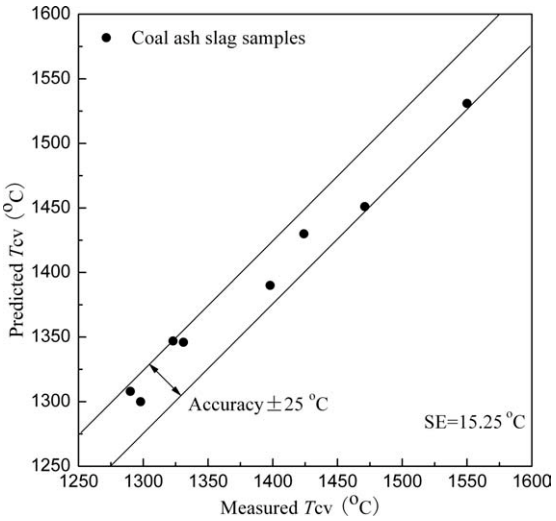

Figure 4. Comparison between measured and predicted T_{cv} values for coal ash samples.

the Corey model, the Marshak model, and the liquidus model, respectively. As can be seen from Figure 3a–c, these correlations significantly differ from the experimental measurements. Figure 3d shows a parity plot of measured T_{cv} values vs. those predicted for the synthetic ash samples by the liquidus model (Eq. 4). This model has the lowest bias and standard error, which is also demonstrated by the data lying close to the equivalence line. Most of the synthetic ash samples show deformation temperatures within experimental errors of $\pm$ 25°C; therefore, this model (Eq. 4) can predict T_{cv} of synthetic ash samples in an Ar atmosphere.

Prediction Tcv of Coal Ash Samples

In our work, the liquidus model (Eq. 4) was used to predict the T_{cv} of coal ash samples. Figure 4 shows a parity plot of the measured T_{cv} vs. the predicted T_{cv} for the eight Chinese coal ash samples. It can be seen that all of the coal ash samples show deformation temperatures within experimental errors of $\pm$ 25°C, which indicates that the liquidus model can predict T_{cv} of coal ash samples with a good level of accuracy.

Conclusion

In our work, an empirical equation has been derived to relate the T_{cv} of 40 synthetic ash samples with their liquidus temperature calculated by FactSage. An apparent linear correlation and good agreement between the T_{cv} of synthetic ash samples and the liquidus temperatures calculated by FactSage ($R > 0.90$, $\sigma < 20$°C) has been found. This equation has been used to predict the T_{cv} of eight Chinese coal ash samples with a good level of accuracy (SE < 20°C).

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