Viscosity Models for Fluxed Australian Bituminous Coal Ashes

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ABSTRACT

The development of coal based integrated gasification combined cycle (IGCC) power generation technologies has led to interest in the prediction of the viscosity versus temperature characteristics of Australian coal ashes. Empirical viscosity models for Northern Hemisphere coals cover only a part of the compositional ranges of Australian bituminous coals. In the present work, viscosity versus temperature curves have been determined for both fluxed coal ash slags and synthetic slags in the SiO_2-Al_2O_3-CaO and the SiO_2-Al_2O_3-CaO-5%FeO systems. The viscosity data at 1450°C and 1500°C has then been used to develop new modified Urbain type models which allow improved viscosity predictions over the anorthite region of these phase systems. Further data is being accumulated to improve and extend the range of the present models and to cover the SiO_2-Al_2O_3-CaO-10% FeO system.

The data developed for fluxed coal ash slags assists in evaluating the suitability of Australian bituminous coals for use in slagging gasifiers. Data for the synthetic melts will also be useful in theoretical viscosity modelling in this important quaternary system.

1. INTRODUCTION

The need for higher efficiency and better control of gaseous emissions of environmental concern has led to the development of coal fired integrated gasification combined cycle (IGCC) plants for power generation. An IGCC demonstration plant of 250MW capacity is now operating at Buggenum, Netherlands, and additional plants are planned. These plants often include an entrained-flow gasifier operating in a slagging mode, and so it is essential that the molten slag has a viscosity which is low enough for optimum slag tapping at temperatures in the range 1400-1500°C. Australian high volatile bituminous coals appear well suited for use in IGCC technologies excepting that many have ash fusion temperatures > 1500°C or even > 1600°C, and thus will require either the addition of a flux, usually limestone, or blending with coals with low ash fusion characteristics[1]. This has led to interest in the prediction of the viscosity of fluxed Australian coal ash slags.

A number of empirical models have been reported for the estimation of the viscosities of coal ash slags[2,3]. More recent models[4,5] have been proposed and their use has been reviewed[5,6]. The higher silica contents, silica/alumina ratios and lower calcium oxide contents of Australian bituminous coals compared with USA and European coals means that some care should be taken with the use of these viscosity models based on chemical composition. The most favoured is the Urbain[4] model, which relates to SiO_2-Al_2O_3-CaO (SAC) mixtures, and where the effect of FeO may be simply treated. It appears the most suitable for fluxed coal ash slags[5,6] and this paper presents new modified Urbain type models which cover the range of normalised composition of fluxed Australian bituminous coal ash slags in the anorthite region for the SAC and the SiO_2-Al_2O_3-CaO-5%FeO (SACF) phase diagrams[7].

These models cover the compositional and temperature range of practical interest in slagging gasifiers and form the basis for accurate viscosity predictions to be made for fluxed Australian bituminous coal ash slags. The work forms part of a CSIRO priority program to evaluate the suitability of Australian bituminous coals for use in future IGCC power generation technologies[1].

2. EXPERIMENTAL

A total of 25 fluxed slags containing < 2.5 wt% FeO and 15 fluxed slags containing 2.5 < wt% FeO < 7.5 were prepared from Australian bituminous coal ashes using Unilab laboratory grade calcium carbonate as flux. Examples of the normalised compositions and the viscosities determined at 1450°C and 1500°C of the fluxed slags for two of the coal ashes are given in Table I.

In addition, 19 synthetic mixtures were prepared from BDH aluminium oxide, silica, iron III oxide and calcium carbonate, with compositions selected to cover the anorthite region at the 5 weight % FeO level in the quaternary SACF system. The compositions examined and measured viscosities are shown in Table I.

Viscosity measurements were made under reducing conditions with a Haake-1700 high temperature rotational viscometer, using molybdenum rotors and crucibles. A sacrificial graphite external liner was used to ensure the removal of any oxygen in the nitrogen gas stream, with the carbon monoxide produced forming a reducing atmosphere. Ferric/ferrous ratios of about 0.1 were measured for several slags under these conditions. The melts were heated to about 100°C above the previously determined melt temperature, and viscosity measurements were taken at 30°C intervals during stepwise cooling until the melt recrystallised. A minimum of 30 minutes equilibration was allowed at each temperature.

The rotor speed, the torque on the rotor and the sample temperature, recorded with a type B, (Pt/6% Rh // Pt/30% Rh) thermocouple, were collected and processed by the Rotovisco software. The parameters for the rotor crucible combination had previously been found from measurement of a standard reference material[8] over the range 1000-1300°C.

Table I Melt compositions (wt%) and measured viscosities (Pa.s) at 1450°C and 1500°C

SiO_2	Al_2O_3	CaO	FeO	Pa.s. 1450°C	Pa.s. 1500°C
		Fluxed	Slags		
43.8	29.7	24.7	1.8	4.20	2.50
57.6	23.3	14.6	4.6	21.7	12.6
		SACF	Melts		
37.5	20.8	36.5	5.2	0.85	0.55
37.5	26.0	31.3	5.2	1.24	0.73
37.5	31.3	26.0	5.2	2.36	1.48
37.5	36.5	20.8	5.2	3.83*	2.61
42.4	20.9	31.4	5.2	1.56	0.99
42.4	26.2	26.2	5.2	2.57	1.60
42.4	31.4	20.9	5.2	4.38*	2.78
42.4	36.7	15.7	5.2	8.58	5.19
47.4	21.1	26.3	5.3	3.20	1.95
47.4	26.3	21.1	5.3	9.97*	6.15
52.4	15.9	26.5	5.3	1.33	0.75
52.4	21.2	21.2	5.3	8.15	4.76
52.4	31.8	10.6	5.3	16.3	9.65
57.5	16.0	21.3	5.3	7.34	3.89
57.5	21.3	16.0	5.3	23.7	13.5
57.5	26.6	10.6	5.3	44.2	23.2
62.6	16.0	16.0	5.3	35.9	20.0
62.6	21.4	10.7	5.3	92.6*	45.7*
62.6	26.7	5.4	5.3	133*	68.6*

* Extrapolated from Newtonian curve

3. RESULTS

3.1 Slags containing < 2.5% FeO

The compositions examined and measured viscosity values have been previously reported[9] and are summarised in the viscosity contour plots shown in Figure 1. This shows a regular decrease in viscosity as the CaO content increases. A viscosity of < 25 Pa.s would be considered suitable for slag tapping[1].

For comparison purposes, a contour plot determined from the viscosity measurements of 42 SAC melts by Machin et al.[10] is shown in Figure 2. It can be seen that the plots are in reasonable agreement indicating that the minor components present in the fluxed coal ashes do not have a marked effect.

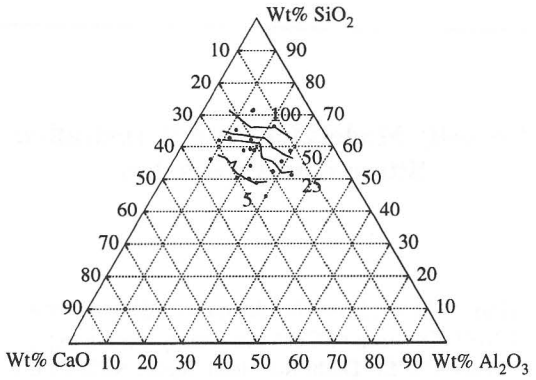

Figure 1 Viscosity contours at 1500°C for fluxed slags containing < 2.5% FeO.

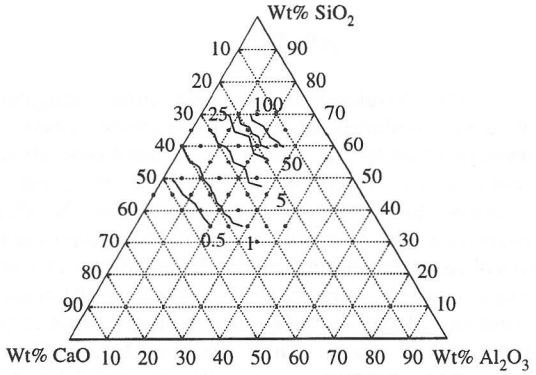

Figure 2 Viscosity contours at 1500°C for SAC melts.

3.2 Slags containing 2.5-7.5 % FeO

The compositions of artificial SACF melts examined and viscosity values determined at 1450 and 1500°C are given in Table 1. The viscosity contour plot is shown in Figure 3. Similar trends are evident at the 5% FeO level as in the SAC melts (Figure 2), but the viscosities are lower at similar CaO levels. Thus, increased FeO reduces the amount of CaO (and hence flux addition) required for slag tapping.

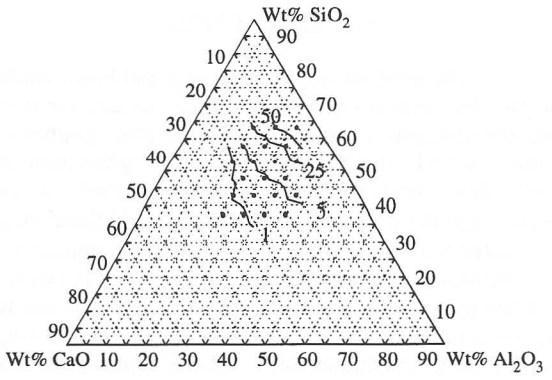

Figure 3. Viscosity contours at 1500°C for SACF melts at the 5% FeO level

At this time, insufficient data for fluxed coal ash slags is available for contour plotting , but similar results are expected.

4. VISCOSITY MODELLING

The most commonly used viscosity model was derived by Urbain[4] from a limited number of viscosity measurements covering the whole range of compositions for the SAC system. This treatment uses a modified Urbain method[9], based on a least squares fit to the transformed Weynman equation (3)

$$\eta = ATexp(B/RT) \quad (1)$$

$$\ln(\eta) = \ln(A)+\ln(T) +B/RT \quad (2)$$

$$\ln(\eta) = a_0 + a_1y + a_2y^2 + a_3x + a_4xy + a_5xy^2 + a_6x^2 + a_7x^2y + a_8x^2y^2 + a_9x^3 + a_{10}x^3y + a_{11}x^3y^2 \quad (3)$$

where x and y are the respective mole fractions $m_s/(m_s+m_a+m_c+m_f)$, and $(m_c+m_f)/(m_a+m_c+m_f)$. Values of A and B in equation (2) can then be calculated from the determined viscosity values at each temperature so that predicted viscosity values may be calculated covering the temperature range close to 1400-1500°C.

The method has been previously applied[9] to viscosity measurements at 1450 and 1500°C for the range of compositions of SAC melts[10] shown in Figure 2. This paper covers its application to fluxed coal ash slags containing < 2.5% FeO shown in Figure 1 and to the synthetic SACF melts at the 5 wt% FeO level shown in Figure 3. The least square coefficients for the viscosity fits at 1450 and 1500°C using equation (3) are shown in Tables II, III and IV.

The sums of the squares of the residuals s^2 for the synthetic SAC and SACF melts were smaller than for the fluxed slags containing < 2.5 wt% FeO. This reflects the irregular spacing of the data points and the presence of other minor components having an effect on the viscosity values in the latter case.

Table II Coefficients for viscosity fits to SAC melts

Coeff.	1450°C	1500°C
a_0	8.897807E+01	-8.165074E+01
a_1	-1.847283+02	1.634541E+02
a_2	8.150640+01	-8.223458E+01
a_3	-5.836806E+02	3.682653E+02
a_4	1.252480E+03	-6.682820E+02
a_5	-5.958102E+02	2.870640+02
a_6	1.238935E+03	-4.657219E+02
a_7	-2.673720E+03	6.908098+02
a_8	1.287301E+03	1.904705E+02
a_9	-8.087798E+02	-1.991040E+02
a_{10}	1.768936E+03	1.706461E+02
a_{11}	-8.486441E+02	-7.005842E+01
s^2	0.23	0.33

Table III Coefficients for viscosity fits to fluxed slags containing < 2.5% FeO

Coeff.	1450°C	1500°C
a_0	1.979740E+03	-3.767907E+02
a_1	-6.266818E+03	1.258838E+02
a_2	4.922969E+03	5.996328E+02
a_3	-1.171434E+04	3.278496E+02
a_4	3.705226E+04	4.486744E+03
a_5	-2.907575E+04	-7.139734E+03
a_6	2.245315E+04	2.169530E+03
a_7	-7.101869E+04	-1.636148E+04
a_8	5.570585E+04	1.904705E+04
a_9	-1.401185E+04	-2.761384E+03
a_{10}	4.439712E+04	1.419628E+04
a_{11}	-3.483867E+04	-1.467699E+04
s^2	2.63	3.23

Table IV Coefficients for Viscosity Fits to SACF Melts

Coeff.	1450°C	1500°C
a_0	3.945617E+02	4.830969E+02
a_1	-6.311380E+02	-8.307334E+01
a_2	-7.966081E+00	8.861615E+01
a_3	-1.726069E+03	-2.059431E+03
a_4	1.842723E+03	2.450195E+03
a_5	1.506686E+03	1.354258E+03
a_6	2.328394E+03	2.666599E+03
a_7	-3.112448E+02	-5.698979E+02
a_8	-5.521809E+03	-5.898616E+03
a_9	-9.1824206E+02	-9.762760E+02
a_{10}	-1.586113E+03	-1.892178E+03
a_{11}	4.955243E+03	5.538116E+03
s^2	0.26	0.22

An examples of the predictive use of these models is shown in Figures 4, for a fluxed slag containing < 2.5 wt% FeO.

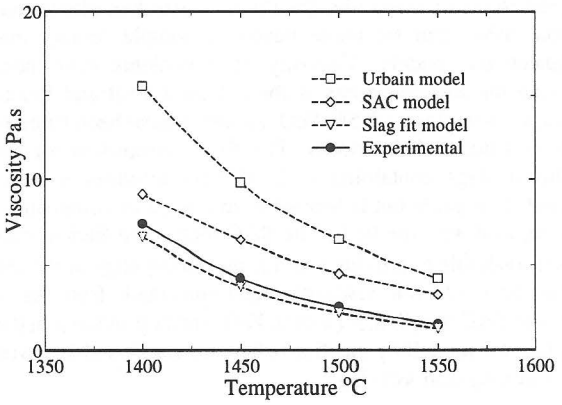

Figure 4. Comparison of experimental and predicted viscosity values for a fluxed slag with FeO < 2.5 wt%

Figure 5 shows a plot for a fluxed slag with 2.5 < wt% FeO < 7.5. Normalised compositions for these slags are given in Table I. The experimental viscosity-temperature relationship for the fluxed slags is compared with values predicted from the Urbain model[4] and the present models. Better predictions are obtained from the present models but at the cost of having a different version applicable to each FeO level and covering a smaller compositional range than the original Urbain model.

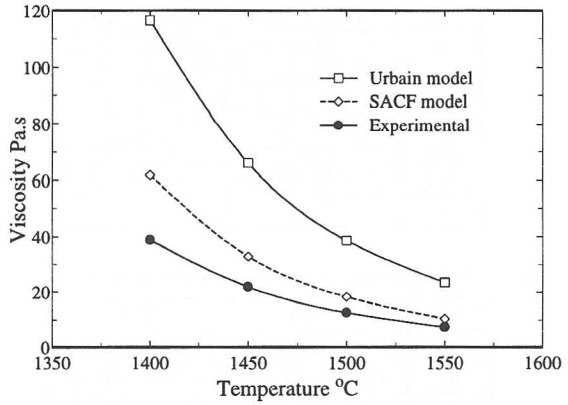

Figure 5. Comparison of experimental and predicted viscosity values for a fluxed slag with 2.5-7.5 wt% FeO.

The inclusion of further data for fluxed slags at the < 2.5% and especially the 5% FeO levels will improve the accuracy of the models. The next stage in the work involves viscosity predictions of fluxed slags at the 10% FeO level. This will allow the modification of the present viscosity models for fluxed slags with higher iron content, and will then help to cover most Australian bituminous coal ashes. The viscosity results for the artificial melts will also supply data for theoretical modelling.

5. CONCLUSIONS

The results demonstrate that reasonable predictions of viscosities for fluxed Australian bituminous coal ashes can be made based on simple ternary and quaternary models. Viscosity measurements have been made for artificial melts at the 5% FeO level and fluxed slags containing < 2.5% FeO and these have been fitted to a modified Urbain model. The fit of viscosities for the fluxed slags containing < 2.5% FeO provides a better predictive guide but is limited in the range of composition compared with the fit for the SAC melts. Insufficient data was available to provide a fit for the fluxed slags at the 5% FeO level. Overall, viscosity predictions made from the fit to the SAC and SACF (5 wt% FeO) melts provide a better guide for modelling gasifier behaviour for fluxed low iron containing coal ash slags.

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REFERENCES

1. D.J. Harris and J.H. Patterson, Aust. Inst. Energy J., Vol. 13, 1995, pp. 22-32.

2. R.C. Corey, Bureau Mines, Bull. 618, 1964, 64 pp.

3. J.D. Watt and F. Fereday, J. Inst. Fuel, Vol. 42, 1969, pp. 99-103.

4. G. Urbain, F. Cambier, M. Deletter and M.R. Anseau, Transactions of the British Ceramic Society. Vol. 80, 1981, pp. 35-43.

5. R.C. Streeter, E.K. Diehl and H.H. Schobert, Amer. Chem. Soc. Fuel Div., Vol. 28(4), 1983, pp. 174-191.

6. K.C. Mills and J.M. Rhine, Fuel, Vol. 68, 1989, pp. 193-200.

7. D.P. Kalmanovitch, A. Sanyal and J. Williamson, 3rd. Engineering Foundation Conference on Slagging and Fouling due to Impurities in Combustion Gases, Copper Mountain, Colorado, USA, 1984, pp. 537-553.

8. C.P. Broadbent, M. Franken, D. Gould and K.C. Mills, 4th. International Conference on Molten Slags and Fluxes, Sendai, Japan, ISIJ, 1992, pp. 439-443.

9. H.J. Hurst, F. Novak and J.H. Patterson, J.H.,. 3rd. Australian Melt Chemistry Symposium, Melbourne. 1996, pp.109-113.

10. J.S. Machin, T.B. Yee and D.C. Hanna, Journal of the American Ceramic Society. Vol. 35, 1952, pp. 322-5.