Viscosities of Fluxed Australian Coal Ash Slags Containing 10-15 wt% FeO

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ABSTRACT

This work completes a survey of the suitability of Australian bituminous coal for use in advanced power generation using integrated gasification combined cycle (IGCC) technology. Viscosity measurements of slags may be used to determine the amount of CaO flux required to obtain a viscosity < 25 Pa.s in the slag tapping range of 1400-1500^{o}C for entrained flow slagging gasifiers. The work covers viscosity measurements on slags containing 10-15 wt% FeO and presents two empirical Urbain-style viscosity models based on the quaternary system SiO_2-Al_2O_3-CaO-FeO covering the ranges 10-12.5 and 12.5-15 wt% FeO.

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. Several IGCC demonstration plants are now operating, 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 in the range 1400-1500^{o}C and a temperature of critical viscosity T_{CV} lower than this temperature range, so that blockage of the slag tapping hole does not occur.

A survey of the suitability of Australian bituminous coals for IGCC was undertaken[1] and viscosity measurements have been presented[2] for fluxed coal ash slags with FeO content up to 10 wt%. In order to obtain sensible empirical models that dealt with the fluxing effect of FeO, the slag compositions were normalised to the quaternary SiO_2-Al_2O_3-CaO-FeO system and divided into four ranges 0-2.5, 2.5-5, 5-7.5 and 7.5-10 wt% FeO. An Urbain-style model was used for viscosity predictions. For representation on triangular graphs and for comparison with viscosity measurements for synthetic melts at the 0, 5, 10 and 15 wt% FeO levels[3-5], the slag compositions are renormalised to these FeO wt% levels.

This work continues the survey of Australian bituminous coals up to 15 wt% FeO, and presents two empirical Urbain-style viscosity models based on the quaternary system SiO_2-Al_2O_3-CaO-FeO covering the ranges 10-12.5 and 12.5-15 wt% FeO.

2. EXPERIMENTAL

Target compositions to cover the range of interest were prepared using coal ashes with FeO content in the range 10-12.5 and 12.5-15 wt% or by blending available coal ashes and adjusting the flux levels using laboratory grade Fe_2O_3 and $CaCO_3$. The samples were melted in a premelt furnace in an inert atmosphere. The viscosity measurements were made using a Haake 1700 rotational viscometer with molybdenum rotors and crucibles. The experimental procedure has been previously described[2].

3. VISCOSITY MODELLING

The most commonly used viscosity model was derived by Urbain[3] (Model 1) from a limited number of viscosity measurements covering the whole range of compositions for the SAC system. In this case, iron oxide is treated as a modifier with a similar effect to calcium oxide. The present CSIRO treatment uses a modified Urbain method, based on a least squares fit to the transformed Weynman equation (3)

$$\eta = A\ T \exp(B/RT) \qquad (1)$$

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

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

where η is the viscosity in Pa.s and x and y are the respective normalised mole fractions $m_s/(m_s+m_a+m_c+m_f)$, and $(m_c+m_f)/(m_a+m_c+m_f)$. This size was selected using the singular value decomposition method, as larger polynomials did not offer any significant improvement in the sum of the squares of the residuals. A polynomial fit of viscosity at 1450°C and 1500°C with composition is obtained from the experimental data. Then, for any composition within the range, values of A and B in equation (2) can then be calculated from the simultaneous equations at the two temperatures. Predicted viscosity values covering the temperature range close to 1400-1500°C may be calculated using equation (2).

This work adds two new empirical viscosity models (9 and 11) to the present series of models shown below:

Model 1	Urbain model
Model 2	Synthetic slag SAC model[4]
Model 3	Coal ash slag model for < 2.5% FeO[2]
Model 4	Synthetic slag SACF model for 5% FeO[5]
Model 5	Coal ash slag SACF model for 2.5-5% FeO[2]
Model 6	Coal ash slag SACF model for 5-7.5% FeO[2]
Model 7	Synthetic slag SACF model for 10% FeO[5]
Model 8	Coal ash slag SACF model for 7.5-10% FeO[2]
Model 9	Coal ash slag SACF model for 10-12.5% FeO
Model 10	Synthetic slag SACF model for 15% FeO[6]
Model 11	Coal ash slag SACF model for 12.5-15% FeO

4. RESULTS

4.1 Coal ash slags containing 10-12.5 wt% FeO

The normalised SACF compositions of the coal ash slags used for the viscosity Models are given in Table 1. These are then renormalised to 10 wt% FeO for convenient plotting to give the viscosity contours shown in Figure 1. Predicted viscosities at 1450 and 1500°C using Models 1, 7 and 9 are compared with the experimentally determined values in Table 1, and in Figure 2 for slag 12 of Table 1. The polynomial coefficients for use in the modified Urbain style equations are given in Table 2.

4.2 Coal ash slags containing 12.5-15 wt% FeO

The normalised SACF compositions of the coal ash slags are given in Table 3. These are then renormalised to 15 wt% FeO to give the viscosity contour plot shown in Figure 3. Predicted viscosities at 1450 and 1500^{o}C using Models 1, 10 and 11 are compared with the experimentally determined values in Table 3, and in Figure 4 for slag 7 of Table 3. The coefficients for use in the Urbain style equations are given in Table 2.

5. DISCUSSION

The small number of data points and the small compositional range covered for the coal ash slags limited the usefulness of the empirical viscosity Models 9 and 11. The small values for the factor s^2 for the goodness of fit given in Table 2 was mainly due to the limited degrees of freedom. Figures 2 and 4 show that the Urbain Model 1 over estimated the viscosities, while the synthetic Models 7 and 10 gave acceptable viscosity predictions, and best agreement with the experimental values was obtained for Models 9 and 11.

One unexplained experimental observation was the presence of non-Newtonian slag behaviour at temperatures around 1500^{o}C in excess of the melting temperature, which had not been seen in our previous viscosity measurements of coal ash slags containing less FeO. The large number of slags with non-Newtonian behaviour is shown in Figure 5, and this caused an unexpected delay in measuring a sufficient number of slags for the model. The use of the thermochemical program FACT[7] provided a possible reason for this behaviour for the group of slags containing about 50 wt% SiO_2. After the initial premelting and cooling, the high temperature phases, mullite and alumina, could form and would only slowly dissolve into the melt at the temperature of 1500^{o}C used at the start of the viscosity measurement. Raising the initial temperature to a limit of 1600^{o}C had no effect on this behaviour. However, no evidence for this was provided by a SEM study of the cooled slags. No suitable explanation could be advanced for the other slags with non-Newtonian behaviour, except that a very high temperature melting component might be present in the coal ashes.

Measurements of synthetic SACF slags in the anorthite region at the 10 and 15 wt% FeO levels resulted in viscosity values, which were smaller than the optimum viscosity value of 15 Pa.s for slag tapping over the temperature range of 1400-1500^{o}C. The need to measure slag compositions at the 10 wt% FeO level similar to those used in entrained-flow gasifiers[8] shown in Figure 6, led to slags more in the tridymite and mullite than the anorthite region, which resulted in smaller overlap with the previously measured synthetic slags. This limited the useful compositional range of the synthetic Models 7 and 10 for predicting viscosities of gasifier slags. Where possible, the coal ash slag models presented here should be used.

6. CONCLUSIONS

Viscosity contours of coal ash slags with compositions at the 10-12.5 and 12.5-15 wt% FeO levels have been presented at 1450 and 1500^{o}C. These enable the degree of flux addition or blending of coals to be estimated for use in entrained flow gasifiers to give viscosity values at the optimum and maximum slag tapping values of 15 and 25 Pa.s, respectively. More slag viscosity measurements are needed with a wider range of compositions so that more accurate contours and improved model parameters may be obtained. More work on the cause of non-

Newtonian behaviour is needed. There is also a need for a global model to overcome the limitations of the many empirical models.

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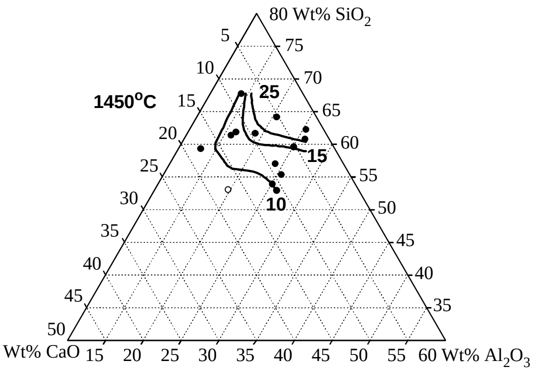

Figure 1 Viscosity contours (Pa.s) for coal ash slags containing 10-12.5 wt% FeO

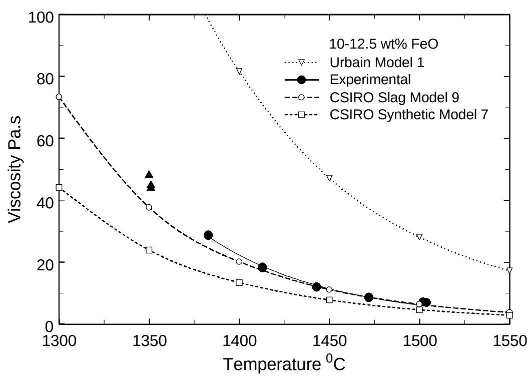

Figure 2 Comparison of experimental and predicted viscosities (slag 12, Table 1)

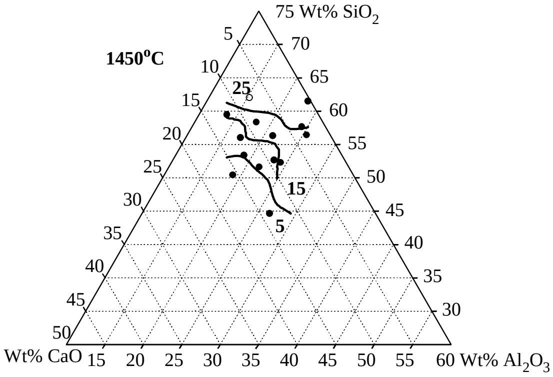

Figure 3 Viscosity contours (Pa.s) for coal ash slags containing 12.5-15 wt% FeO

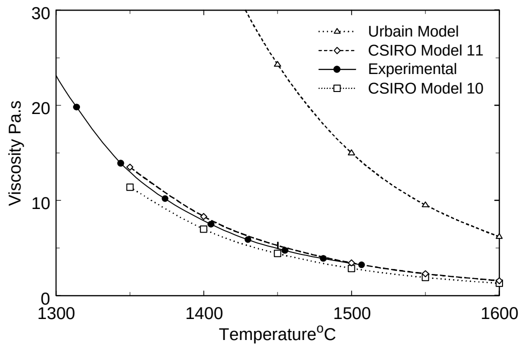

Figure 4 Comparison of experimental and predicted viscosities (slag 7, Table 3)

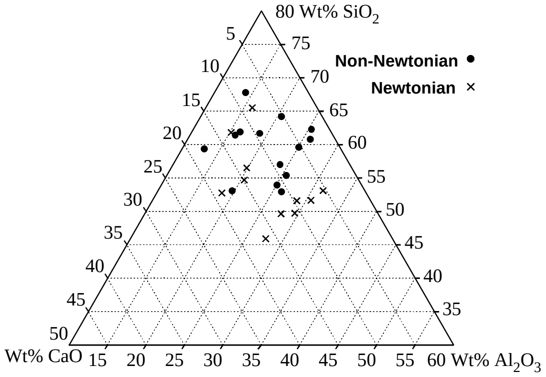

Figure 5 Slags with Non-Newtonian and Newtonian behaviour

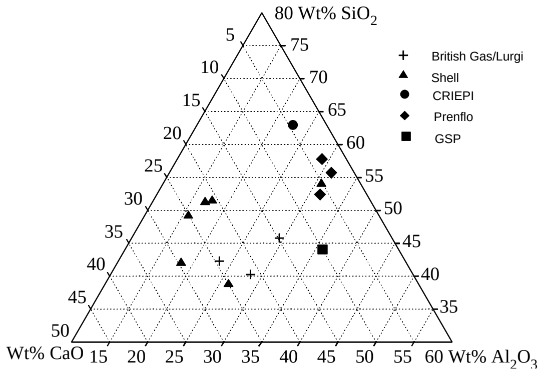

Figure 6 Gasifier slag compositions containing 7.5-12.5 wt% FeO

Table 1 Normalised Slag Compositions (wt%) at the 10.0-12.5 Wt% FeO Level and Experimental and Model Predicted Viscosities (Pa.s) at 1450 and 1500^{0}C

	Normalised Composition				1450^{0}C				1500^{0}C			
Ash	**SiO_2**	**Al_2O_3**	**CaO**	**FeO**	**1$^+$**	**7**	**9**	**Exp$^+$**	**1$^+$**	**7**	**9**	**Exp$^+$**
1	53.32	24.82	10.82	11.03	39.9	13.2	5.75	5.77	24.0	7.68	3.57	3.59
2	58.42	12.77	17.41	11.40	16.5	*	4.83	4.82	10.4	*	3.90	3.89
3	63.06	20.21	5.14	11.59	219	*	55.1	55.0	12.1	*	31.7	31.6
4	66.82	13.92	7.99	11.26	180	*	12.1	12.1	100	*	7.77	7.74
5	60.29	18.57	9.11	12.03	79.4	17.7	21.4	21.7	46.1	11.4	12.9	13.2
6	58.44	24.62	5.16	11.77	130	*	14.8	14.8	73.5	*	8.93	8.90
7	61.16	24.96	2.27	11.61	267	*	40.5	40.4	14.5	*	19.5	19.4
8	52.02	25.74	10.67	11.56	34.8	11.0	5.05	5.03	21.1	6.48	3.12	3.10
9	59.83	25.61	3.13	11.43	205	*	18.9	18.9	113	*	11.2	11.2
10	51.89	19.29	16.82	12.00	13.9	5.81	4.99	4.98	8.85	3.63	3.26	3.25
11	60.40	15.69	12.45	11.46	46.1	*	9.93	10.1	27.5	*	6.37	6.50
12	53.84	24.88	8.77	12.51	47.3	15.8	11.2	11.2	28.2	9.01	6.45	6.42
13	54.87	23.87	9.80	11.46	49.8	17.6	9.36	9.36	29.6	10.1	5.69	5.70
14	60.16	16.92	12.14	10.77	53.7	11.6	13.0	12.7	31.8	7.84	8.25	7.84
15	57.80	24.69	6.69	10.83	108	*	14.9	14.8	61.6	*	8.69	8.61

* Composition outside of range $^+$ Model number and Experimental

Table 2 Coefficients for viscosity fits to fluxed slags containing 12.5-15 Wt% FeO

	Model 9, 10-12.5 wt% FeO		Model 11, 12.5-15 wt% FeO	
Coeff.	**1450°C**	**1500°C**	**1450°C**	**1500°C**
a_0	-1.2450503E+05	1.2227703E+05	1.8851531E+05	1.7884952E+05
a_1	-4.0355117E+05	-3.9335992E+05	-5.6648464E+05	-5.3411996E+05
a_2	3.2412878E+05	3.1351222E+05	4.2272386E+05	3.9618293E+05
a_3	-5.5399961E+05	-5.4602228E+05	-8.6616783E+05	-8.2060546E+05
a_4	1.7990718E+06	1.7590366E+06	2.6042295E+06	2.4500634E+06
a_5	-1.4478787E+06	-1.4041215E+06	-1.9440686E+06	-1.8166098E+06
a_6	8.2098173E+05	8.1212574E+05	1.3248044E+06	1.2525317E+06
a_7	-2.6713052E+06	-2.6201777E+06	-3.9854336E+06	-3.7385159E+06
a_8	2.1542184E+06	2.0948097E+06	2.9762948E+06	2.7706288E+06
a_9	-4.0522690E+05	-4.0237493E+05	-6.7453944E+05	-6.3600018E+05
a_{10}	1.3212287E+06	1.3002248E+06	2.0304764E+06	1.8976546E+06
a_{11}	-1.0676981E+06	-1.0412116E+06	-1.5169580E+06	-1.4055907E+06
s^2	0.001	0.004	0.018	0.008

Table 3 Normalised Slag Compositions (wt%) at the 12.5-15 Wt% FeO Level and Experimental and Model Predicted Viscosities (Pa.s) at 1450 and 1500°C

	Normalised Composition				1450°C				1500°C			
Ash	**SiO_2**	**Al_2O_3**	**CaO**	**FeO**	**1+**	**9**	**11**	**Exp+**	**1+**	**9**	**11**	**Exp+**
1	57.30	25.91	3.09	13.70	126	*	15.3	15.0	71.1	*	8.95	8.99
2	57.69	17.60	12.19	12.52	36.1	8.16	9.14	9.74	21.8	5.15	5.61	5.93
3	53.07	23.32	9.22	14.39	34.3	5.60	9.78	9.45	20.8	3.43	6.03	6.08
4	52.71	22.19	11.86	13.24	26.1	4.23	4.93	5.08	16.0	2.68	3.32	3.33
5	51.48	19.29	15.95	13.27	13.4	2.37	2.34	2.35	8.53	1.59	1.53	1.54
6	57.18	21.49	7.62	13.71	64.7	14.3*	11.0	11.6	37.9	8.11	7.11	7.29
7	54.52	19.27	12.97	13.24	24.4	4.42	5.27	5.05	15.0	2.87	3.45	3.33
8	60.81	13.91	12.12	13.16	23.0	*	9.99	10.0	14.3	*	6.51	6.47
9	59.11	18.25	8.72	13.92	60.2	*	13.7	12.6	35.4	*	8.38	8.00
10	53.84	24.88	8.77	12.51	47.3	7.84	11.1	11.2	28.2	4.71	5.98	5.91
11	45.31	26.98	13.93	13.77	12.3	2.22	2.75	2.75	7.89	1.43	1.86	1.86
12	58.34	24.54	3.10	14.02	137	*	32.6	33.2	77.3	*	18.5	18.4
13	63.26	15.59	7.66	13.30	107	*	43.3	43.6	61.3	*	22.8	23.0
14	61.80	23.27	0.36	14.57	287	*	45.1	45.1	156	*	25.8	25.8

* Composition outside of range + Model number and Experimental