THE EFFECT OF SOLIDS AND PHASE COMPOSITION ON VISCOSITY BEHAVIOUR AND $T_{CV}$ OF SLAGS FROM AUSTRALIAN BITUMINOUS COALS

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ABSTRACT

The flow behaviour of coal mineral matter at high temperatures is an important parameter for coal use in entrained-flow gasification technologies. Recent research [1-4] has studied in some detail the viscosity behaviour of slags from Australian coal ashes, covering a wide range of compositions suitable as feedstock for entrained flow gasifiers. Slag flow behaviour is characterised by the temperature dependence of slag viscosity, and by the temperature of critical viscosity ($T_{CV}$).

Viscosity behaviour and $T_{CV}$ strongly depend on slag composition. Moreover, at temperatures below the liquidus temperature this compositional dependence is complicated by precipitation of solids, and the resultant change in chemical composition of the liquid phase. In this study, the viscosity behaviour of selected slag compositions is investigated in terms of dynamics of solids precipitation, compositional changes, and morphology of crystallised solids. Relationships between slag microstructure, phase composition and viscosity behaviour are described on the basis of viscosity measurements, thermodynamic calculations, and slag quenching experiments. It is shown that viscosity–temperature behaviour of specific slag compositions was dependent on the amount and size of the solids in the slag, silica/alumina ratio (S/A) and compositional changes of the liquid phase due to solid phase precipitation.

Key words: slag, viscosity, $T_{CV}$, gasification, phase composition

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1. Introduction

Recently there has been a significant increase in interest for more efficient and environmentally-cleaner technologies for energy production such as Integrated Gasification-Combined Cycle (IGCC) power generation. The most common gasification process for this application is entrained-flow gasification due to its high throughput and fuel feedstock flexibility. In all types of entrained-flow gasifiers, a high operating temperature is usually required to maximise the rate of carbon conversion. At such temperatures, the coal mineral matter melts and is removed through a slag tap system; entrained-flow gasifiers are therefore slagging gasifiers. Smooth operation of such gasifiers depends strongly on steady and reliable removal of slag, which is strongly dependent on the flow behaviour of the slag.

There are two aspects used to characterise slag flow behaviour: viscosity dependence on temperature, and the temperature of critical viscosity. For the majority of bituminous coal slags, viscosity exponentially decreases with an increase in temperature [1]. At viscosities below ~25 Pa s, slag flows down the gasifier walls and is discharged through the tapping device. However, if the slag viscosity drops below 2 Pa s, it may become too fluid and potentially cause some problems in the gasifier, such as excessive wear of refractory walls (e.g. GE and ConocoPhillips E-gas technologies) or excessive heat loss through water-cooled walls (e.g. Shell or Siemens technologies). Thus, the slag viscosity at slag tapping temperature should ideally be greater than 2 Pa s and less than 25 Pa s. The optimal range of slag viscosities for operation of entrained flow gasifiers is generally considered to be between 5 and 15 Pa s at the slag tapping temperature [4].

The slag flow behaviour (including temperature dependence of slag viscosity) as described above is influenced mainly by the composition of the coal slag. The other
possible factor affecting slag flow behaviour - oxygen partial pressure in the gasifier - is more a function of a gasifier design and operation, and during the normal operating conditions is negligibly low. The four major components: silica, alumina, ferric oxide and calcium oxide; usually comprise about 90–95 wt.% of Australian coal ashes with small amounts of MgO (~0.1–4%), Na₂O (~0.1–2.3%), K₂O (~0.1–4%) and TiO₂ (typically 0.6–3%). Silicon dioxide (SiO₂) is the dominant network former, and the addition of most of the other oxides to SiO₂ will usually lead to a decrease in viscosity. The alkali oxides (Na₂O, K₂O) can all be classified as network modifiers, thus their presence usually leads to a decrease in viscosity. The alkaline earth oxides (e.g. MgO, CaO) play more complex structural roles depending on the overall composition of the melt, although they mostly act as network modifiers, reducing the slag viscosity.

To increase the range of coals that can be processed in entrained flow slagging gasifiers, a common practice is to blend the feedstock with either flux or with other coals of suitable composition to produce a feed with appropriate slag viscosity behaviour. The silica ratio (SiO₂ content normalised to total of SiO₂, Fe₂O₃, CaO and MgO) has generally been used for initial evaluations of slag viscosity behaviour. A ratio <80% is considered suitable for entrained flow processes. A flux, generally limestone, would appear necessary for coal ashes with high silica ratios. For a wide range of Australian coals, a SiO₂/Al₂O₃ ratio of 1.6–2.0 appears optimum to minimise limestone flux requirements [4].

Another key component of slag flow behaviour is the temperature of critical viscosity (T_cv). Definitions of T_cv can vary between researchers and the most common are summarised by Vargas [5]. For the present purposes, T_cv is recognised as a sharp break in the exponential viscosity versus temperature curve; this is assumed
to be due to crystallisation of solids in the melt in amounts sufficient to alter the slag flow behaviour [5, 6]. For entrained flow gasifiers, the temperature of critical viscosity should be comfortably below the slag tapping temperature to avoid slag tapping problems.

It is currently impossible to make an accurate prediction or estimation of the $T_{CV}$ of a specific slag based on chemical composition of the slag alone; however, it is known that $T_{CV}$, as with viscosity, is strongly dependent on slag composition. Previous work by the authors investigated a potential relationship between $T_{CV}$ and the amount and composition of the precipitated solids. A method to predict the $T_{CV}$ on the basis of initial chemical composition of the coal ash and thermodynamic modelling was developed [7]. The amount and type of solid phases precipitated in the silicate melt at the $T_{CV}$ were assessed for a variety of slags, chosen from an extensive database of measurements of slag flow behaviour. The assessment provided only general trends relating slag phase compositions to $T_{CV}$. No direct correlations between solid phase content, solid phase composition of the melt and $T_{CV}$ were found.

This work suggested that the viscosity behaviour of slags below their liquidus temperature (and, consequently, a $T_{CV}$ transition) is a complex event, driven by the interaction of a number of factors, including:

i) Change in chemical composition of the melt due to solid phase precipitation

ii) The effect on the melt of precipitated solids with different shapes and size distributions, which is in turn dependant on the nature of solids and cooling rates [8]
iii) Concentration of minor oxides, K$_2$O, Na$_2$O, TiO$_2$, PO$_3$, which may promote the nucleation process [9], or, in case of mixed alkali systems, lower critical cooling rates [10].

The work presented in this paper investigates how these factors affect the viscosity behaviour and $T_{CV}$ of coal slags. Slag compositions were selected to separately isolate and interrogate the impact of the factors listed above on slag flow behaviour. Selected slag compositions were investigated in terms of the viscosity behaviour, dynamics of solid precipitation, compositional changes and morphology of the solids.

2. Experimental

2.1, Sample selection

The silica to alumina ratio (S/A) is one of the important characteristics of slag composition affecting the slag’s viscosity behaviour. As the majority of Australian bituminous coals have S/A ratio between 1.0 and 4.5 (Figure 1a), the coal slag compositions used in this work were chosen to cover this range. Since iron and calcium oxides play an important role in slags as network modifiers, the samples used in this work were categorised according to their CaO and Fe$_2$O$_3$ compositions, and for each of these series the S/A ratio was selected to allow slag flowability over the range of 1400–1500 °C.

The iron oxide content of Australian thermal coal ashes typically varies between 1 and 30 wt.% (Figure 1b), therefore the samples used in this work were consistent with this range. In the present study, samples were selected on the basis of the four major components, such as SiO$_2$, Al$_2$O$_3$, CaO and Fe$_2$O$_3$, and with low
concentrations of the minor elements such as K, Na and Ti in order to minimise complications arising from their effect on solids growth in the melt.

It was expected that the effect of solid formation would be clearly seen in the slags with extreme contents of iron and calcium oxides, as the liquid phase changes have a more dramatic effect on viscosity. Samples were chosen and this assumption and within each of the categories, based on iron and calcium oxides content, the S/A ratio varied between 1.1 and 5.1 in order to cover a wide range of slag compositions. The chemical compositions, measured by ICP analysis, and the primary phase fields of the investigated slags are listed in Table1. Concentrations of Mn$_3$O$_4$, P$_2$O$_5$ and SO$_3$ are below 1wt.% and are not included here.

2.2. Measurement of Slag Viscosity

Some of the viscosity data used in this work, particularly for high-iron slags, has been taken from previously published work [12]. In all cases, slag viscosity measurements were made with a Haake high temperature viscometer using the rotational bob technique described previously [11]. Samples were pre-melted in molybdenum crucibles at 1600ºC in a neutral atmosphere. To ensure the absence of oxygen, the crucible was placed in a sacrificial graphite liner. Viscosity measurements were taken using a cylindrical molybdenum rotating sensor. The temperature cooling step for each set of measurements was of 50ºC at low viscosities and 25ºC at viscosities above 8 Pa s, with at least 30 min intervals to equilibrate temperature inside the crucible. At each temperature point, the slag viscosity was measured several times to ensure the repeatability of measurements. The average of these measurements was used as the value of viscosity.
2.3. Thermodynamic calculations

A thermodynamic equilibrium calculation of slag in relevant reducing atmospheres has been developed for prediction of phase compositions in the slags at temperature in the range 1000–1600°C. The thermodynamic phase equilibria package used in this work was FactSage, version 5.4 [13]. This package has been used previously for prediction of melting behaviour of coal mineral matter and viscosity of slags [14-16]. Databases used for calculations of compounds and solutions were FACT53 and FToxid. The gaseous elements included in these computations are major non-metals (C, H, N, O). Slag was presented as a mixture of the salts and oxides of Si, Ca, Al, Mg, Fe, K, Na, Mn and Ti.

2.4. Preparation and Characterization of Quenched Slags

Slag quenching experiments were performed in order to estimate the accuracy of modelling prediction in terms of slag composition and to analyse the morphology of any solids formed in the slag. A sample of pelletised ash mixture was placed in a platinum envelope and suspended on a platinum wire in the cold zone at the bottom of the vertical tube furnace. The lower end of the work tube was sealed with a plastic film and submerged in water. The furnace tube was flushed with nitrogen during all experiments and graphite was attached to the platinum envelope to ensure reducing conditions similar to those used in the viscosity measurements described above. The sample was raised to the hot zone of the furnace and equilibrated at the specific temperature (in the range 1250–1450°C) for 5–15 hrs and then quenched by dropping into the water.

Analysis of the quenched sample provides information about the phase compositions existing at equilibrium temperature. The microstructure of the quenched
slags was investigated using Scanning Electron Microscopy (SEM) in backscattering mode and Electron Probe Microanalysis (EPMA) was carried out to identify solid and liquid phase compositions of quenched samples.

3. Results and discussion

3.1 Assessment of thermodynamic model used for liquid solid phase prediction

Slag phase composition analysis and model predictions of solid phase content were made using a test slag samples (compositions are listed in Table 1) to check the validity of thermodynamic model predictions. Compositions of test slags were selected from mullite and feldspar primary phase fields, since these fields are corresponds to the compositions of majority of the slags presented in this study. EPMA measurements were used to estimate the solid phase content in the slags for comparison with FactSage calculations. Since the composition of the liquid phase changes with precipitation of solids, the results of EPMA analysis of quenched slags were used to estimate the amount of solids.

Figure 2a and 2b show solid phase content in the test samples at different temperatures as calculated by the model and as determined experimentally. SEM micrographs of the slag samples quenched at different temperatures are shown in Figure 2c, 2d and 2e and illustrate some of the data presented in Figure 2a and 2b. Phases observed in quenched tests samples and the amount are in corresponds well with FacSage calculations. In test sample 1, the amount of feldspar, shown as dark-grey coloured structures (figure 2c and 2d), decreases with increasing equilibration temperature. At 1200°C silica as second phase starts to precipitate. In test sample 2, mullite starts to precipitate at temperatures below 1350°C, and about 5-10% of this
phase was observed in the sample quenched at 1320°C (figure 2e). At temperatures below 1300°C feldspar was detected as a second crystallised phase.

It is clear that the experimental and calculated results are in good agreement. Therefore, the thermodynamic model was used for determination of phase compositions and phase concentrations in the investigated slags.

3.2. Viscosity behaviour and phase composition

3.2.1. Low iron and calcium slags

The results for the low iron, low calcium slags are given in Figure 3. The viscosity behaviour of these slags is mainly determined by the viscosity of the liquid phase, which in turn depends on the S/A ratio. Over the measured temperature range, the viscosity slowly increases as the temperature decreases (Figure 3a). No sharp break in the viscosity-temperature curve associated with Tcv is observed.

Composition SA1 corresponds to a silica primary phase field and has a high S/A ratio (4.98). The viscosity of the slag is above 200 Pa·s even at high temperatures, and gradually increases as temperature is reduced. The liquidus temperature for this composition is below the minimum temperature at which the experiments were conducted, hence there is no precipitation of solids which may affect the viscosity (thus no chart of solids content vs temperature is included in Figure 3).

The other two low-iron, low-calcium slags (SA2, SA3) have relatively low S/A ratios and consequently their viscosities are lower than those of SA1. Both compositions lie at higher liquidus temperature regions than the SA1 composition, and correspond to mullite primary phase fields. Precipitation of solid phases starts at temperatures below 1600°C for SA2 (Figure 3b) and 1500°C for SA3 (Figure 3c). The solids formation and accompanied increase of the S/A ratio have very little effect
on viscosity; the amount of solids is still quite low and relative change in S/A ratio not significant (10% and 25% of initial S/A ratio for composition SA2 and SA3, respectively). In terms of calcium and iron concentrations, the liquid phase compositional change is not considered, as their content is low.

3.2.2. High iron and low calcium slags
The high iron and low calcium category of slags used in this work is further separated into two groups for clarification of discussion, depending on the S/A ratio. The first group (Figure 4) has an intermediate S/A ratio (2.88 and 2.39 for SAF1 and SAF2 slags, respectively). Due to their compositions, and particularly high FeO\textsubscript{x} content, their viscosities are below 25 Pa\textperiodcentered s at temperatures of 1325°C and above (Figure 4a). At temperatures below 1250°C, the viscosity in both compositions increases more steeply than observed for the low-calcium, low-iron slags.

The compositions of these samples are located in different primary phase fields, and the viscosity increase at temperatures below 1225°C is associated with solid phase growth. For SAF1, which corresponds to the leucite primary phase field, solids start to precipitate on cooling at temperatures below 1350°C. The amount of solids remains very low until the temperature decreases to 1225°C, where feldspar and spinel replace the leucite (Figure 4b). For SAF2, mullite appears as a primary phase at temperatures below 1375°C, where both the amount of solid phase and S/A ratio gradually increase with a temperature decrease, as shown in Figure 4c. At 1225°C, the second solid phase, silica (as trydimite), starts to precipitate. The calculated total amount of solids at this temperature for both compositions is approximately 12 wt.% and viscosity is high. When crystallisation of solids begins, the iron oxide content change in the liquid phase is small, and unlikely to affect viscosity. From the shape of the viscosity curves, Tcv can be identified only approximately, since the
changes in the viscosity are not acute enough. However, the $T_{CVS}$ are lower than the temperatures where the high viscosity limit of 25 Pa·s has been achieved and so are unlikely to be of practical significance.

The second sub-group of high iron, low calcium slags (compositions having a low S/A ratio of 1.1 and 1.25) are shown in Figure 5. Viscosity increases for these slags are very steep (Figure 5a and 5d) as soon as solids start to precipitate, which occurs at a higher temperature than the samples discussed previously. All compositions are in the mullite primary phase field. The first break in viscosity occurs for all compositions when the amount of solids (mullite) reaches a level of approximately 10 wt.%. A second sharp break is observed in Figure 5a, when slags SAF3 and SAF4 have about 20 wt% of mullite (as indicated in Figure 5b and 5c). At this point, viscosities of both slags start to show non-Newtonian behaviour.

For compositions SAF5 and SAF6 (Figure 5d), as the temperature is reduced below 1500°C, the viscosities rapidly increase above the level 25 Pa·s, and the samples show non-Newtonian behaviour. This corresponds to a solids (mullite) concentration of approximately 10–15 wt.% for both compositions. For all compositions in this group solid phase content growth is accompanied by increasing S/A ratio (up to 85, 62, 80 and 53 % of the initial S/A ratio for SAF3, SAF4, SAF5 and SAF6, respectively) and some increasing of iron oxide in the slags liquid phase.

### 3.2.3. High calcium and low iron slags

Results for the high calcium and low iron slags are given in Figure 6. The primary phase field for the high calcium and low iron slags depends on the S/A ratio: composition SAC1 is in the silica primary phase field and compositions SAC2 and SAC3 are in the feldspar primary phase field. For the silica rich coal slag (SAC1,
S/A=5.14) viscosity gradually decreases with temperature (Figure 6a) and solids (trydimite) are found at temperatures lower than the minimum temperature used for viscosity measurements for this sample (therefore no chart of solids formation is presented).

Compositions with lower S/A ratios lay in the high liquidus temperature region and solids (feldspar) start to precipitate at temperatures below 1450°C where viscosities of the slags are low. Sharp increases in the viscosities (Tcv events) occur when the solids level exceeds 20 wt.% (Figure 6b and 6c). In the case of composition SAC2, the solids are feldspar phase only; for composition SAC3, the solids are feldspar (primary solid phase) and mellilite as a second solid phase. The viscosity break is sharper for composition SAC3 with lower S/A ratio (1.19) compared with composition SAC2 (S/A = 2.13). The S/A ratio in these slags also increases with decreasing temperature up to S/A = 2.85 and 1.65 for SAC2 and SAC3 slags, respectively. CaO concentration increases by only 10% throughout the temperature range where solids start to precipitate; this is unlikely to significantly affect the viscosity change.

3.2.4. High calcium and high iron slags

The final category of slags investigated is those having both high calcium and iron contents (Figure 7). The two considered compositions are from feldspar (SACF1) and spinel (SACF2) primary phase fields. As the temperature decreases, the viscosity and solids content for these slags increases. A sharp break in the viscosity curve (Tcv) occurs when the feldspar level in composition SACF1 (Figure 7b) exceeds 30–35% and spinel appears as a second solid phase. For composition SACF2, viscosity increases significantly with decreasing temperature at a spinel level of about 20%
with formation of feldspar as a second phase (Figure 7c). At these points, the S/A ratio in both melts increases and may affect the viscosity behaviour. Concentrations of Fe and Ca in the liquid phase are also changing: for SACF1 some increasing of Ca concentration is accompanied by a decrease in Fe content in the liquid phase; for SACF2 composition, precipitation of spinel leads to depletion of Fe in the liquid phase.

3.2.5. Microstructure of quenched slags

An observation of the microstructure of the quenched slags and analysis of the slag phase compositions reveal that in general, calculated and observed slag compositions correspond well, particularly in terms of liquidus temperatures, appearance and concentration of the primary phases. However, some contradictions between predicted and observed phases are found in the appearance of secondary precipitated solid phases in some of the slag compositions. For example, according to FACTSage calculations, it is expected that SACF2, at temperatures below 1300°C, would form spinel with feldspar as a second solid phase. In fact, the microstructure of quenched slag contains feldspar with mellilite (Figure 8a). Furthermore, the microstructure of SAC3 slag quenched from 1370°C contains large feldspar crystallites with needle like alumina, instead of the predicted feldspar with mellilite as a second solid phase (Figure 8b). These examples indicate that the applied calculations may not be suitable particularly in low temperature regions.

When considering the morphology of the solid phases, some interesting features are observed in quenched slag samples near potential $T_{CV}$ events. Mullite solids are found at 1400°C in sample SAF4 as 10–50 μm plate-like crystallites (Figure 9a) or as dispersed 50–100 μm agglomerates of small crystallites in SAF3
The difference in the morphology of the crystallites is likely to be associated with the different crystallisation rates in those samples. Sample SAF4 has a liquidus temperatures about 50–60°C lower than sample SAF3 and has a smaller difference between liquidus and equilibration temperatures. During solids formation in this sample, nucleated mullite precipitates have sufficient time to grow as large crystallites. For sample SAF3, precipitation rates are higher than crystal growing rates, so solids appear as a large number of precipitates which formed agglomerates.

Feldspar is also observed as particles with a range of different sizes: the test slag sample has 10–20 µm plate-like crystallites dispersed in liquid phase (Figure 2b); SACF1 has ~100 µm crystallites (Figure 10a); and SAC2 has millimetre-size crystallites (Figure 10b). The microstructures of SACF1 and SAC2 correspond to a temperature below the $T_{CV}$. At high temperatures these slags have solid phases about one order of magnitude smaller in size, similar to solids observed in the test slag. It seems that the difference in the size of the feldspar also depends on the ratio between precipitation rates (cooling rates) and crystal growth rates.

The data and discussion above suggest that viscosity-temperature behaviour of specific slag compositions, as expected, depends on a number of complex and interrelated parameters. Generally, coal slag behaviour is consistent with the theoretical behaviour of molten silicate melts, as depicted in Figure 11. Figure 11, (area a), depicts the case when the entire viscosity range of interest can be obtained experimentally with little difficulty. Abrupt increases in viscosity in this case (i.e. $T_{CV}$ events) are associated with significant amounts of solids formation and very often accompanied with transformation of the viscosity behaviour from Newtonian to non-Newtonian. The viscosity measurements of the Australian bituminous coal slags were
focused on the determination of the viscosity range applicable for entrained flow gasification, and in cases when the limit of 25 Pa·s has been achieved no further measurements were conducted to detect a non-Newtonian behaviour and/or Tcv.

The case illustrated in area a of Figure 11 is typical for coal slags with relatively high liquidus temperatures and low S/A ratio (e.g. samples SAF3–SAF6) due to the significant amount of crystallised solids over the viscosity measurement temperature range. The crystallisation of solids complicates the viscosity behaviour of the liquid phase, in particular if the precipitation of solids favours silica enrichment. TCV events can be clearly seen in the low calcium-high iron compositions when the amount of solids exceeds 15 or 25 wt. %, depending on S/A ratio. In lower S/A ratio compositions, fewer solids are required to observe sharp viscosity increases.

In the investigated low iron-high calcium compositions, the sharpest viscosity increase is observed in the composition with lowest S/A ratio. For those compositions, viscosity at temperatures below TCV has non-Newtonian behaviour. When the S/A ratio is relatively high, viscosity increases are not so dramatic. With low solids content, and high S/A ratio, viscosity decreases gradually with temperature over the range of practical interest as depicted in Figure 11 (area b) and TCV-like events are not measured.

Both the amount of solids and the size of the crystals increase at temperatures near Tcv events. If precipitation rates are faster than the rate of crystal growth then the solids form agglomerates (e.g. Figure 9b); conversely, if the rate of solid phase growth is greater than precipitation rates, then the size of the solids can be an order of magnitude greater at the temperatures near a Tcv event.

The viscosity of a slag near the TCV (i.e. a slag with significant and changing solids content) has been described by Goldsmith et al [17] as:
\[ \eta_{\text{mixture}} = \eta_r(1 + cu + du^2) \quad (1) \]

where \( u \) is the fractional volume of dispersed solid assemblies, \( \eta_r \) is the viscosity of “residual slag”, and \( c \) and \( d \) are constants related to the shape of the dispersant and solids-melt hydrodynamic interaction, respectively. Annen et al. [18] modelled the viscosity of a mixture of melt and crystalline phases using Goldsmith’s equation (Equation 1) and reported coefficients of \( c = 2.5 \) and \( d = 9.15 \) for solids as spheres at low concentration. In the cases presented in the current work, most of the solids have a bar like or plate like shape and \( c \) and \( d \) will be a composite of individual coefficients for each precipitated phase \((c_i, d_i)\).

In the present study, the viscosity behaviour of the selected slags delivered from Australian bituminous coals has a trend corresponding to the Equation (1) with some extension. From our observations the viscosity of ‘residual slag’ can be expressed as:

\[ \eta_r = \eta_o(T) + \Delta \eta \quad (2) \]

where \( \eta_o(T) \) is the temperature dependent viscosity of pure liquid slag before solids crystallisation and \( \Delta \eta \) is viscosity change due to compositional changes of the liquid phase and likely to be inversely proportional to the silica/alumina ratio in the bulk slag composition.

The effect of minor elements in the slag such as K, Na, Ti was neglected in our study in order to minimise the number of dependent variables. This was possible as their concentrations in the investigated samples are very low. However, if their concentration is relatively high (>2–3 wt.%) their effect on the viscosity has to be considered [9, 19], since they may change phase equilibria in the whole slag system. In addition some of the elements (e.g. K\textsubscript{2}O or Na\textsubscript{2}O) may work as network modifies in the liquid phase.
4. Conclusions

Experimental measurements of slag viscosity, thermodynamic calculations and quenching experiments have been used to investigate the relationships between slag viscosity behaviour and the presence of solid phases in the melt. From the perspective of coal use in entrained flow gasification technologies, the following conclusions can be drawn from this work:

- Above the liquidus temperatures (i.e. where no solids are likely to be present in the slag), slag viscosity depends on the slag bulk composition, particularly the S/A ratio and concentration of CaO and FeO;
- Below the liquidus temperature (i.e. with solids appearance in the melt), slag viscosity increases proportionally to the amount of solids;
- A sharp increase in viscosity (i.e. a $T_{CV}$ event) is observed in compositions with relatively low S/A ratio (< 2) and where the solid content reaches a certain level (generally above 15 wt.%) and/or significantly increases the size of the crystals;
- A high S/A ratio in the slag is usually sufficient to mask sharp increases in slag viscosity from solids precipitation (i.e. $T_{CV}$ event);
- Changes of S/A ratio and/or CaO, FeO content in the liquid phase due to crystallisation of solids also affects slag viscosity behaviour, but this effect is secondary to the total amount of solids content and initial S/A ratio.

The composition of the majority of Australian coal slags is in the range where some amount of solids is likely to be present in the slag under typical gasification conditions. Therefore, the results presented and discussed in this work will improve the initial screening and assessment of coal suitability for entrained flow gasification from the slag flow behaviour point of view.
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References


Table 1 Chemical and Phase Compositions of Slags.

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<td>36.08</td>
<td>30.21</td>
<td>29.56</td>
</tr>
<tr>
<td><strong>High CaO, high Fe₂O₃ slags</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SACF1</td>
<td>35.64</td>
<td>22.3</td>
<td>19.85</td>
</tr>
<tr>
<td>SACF2</td>
<td>26.51</td>
<td>24.71</td>
<td>19.35</td>
</tr>
</tbody>
</table>

* Composition was obtained from the coal ash fluxed with Fe₂O₃ and CaO to desired concentrations.
**Figure captions**

Figure 1. S/A ratio (a) and distribution of iron oxide concentrations (b) in Australian coals suitable for entrained flow gasification.

Figure 2. Calculated and measured solid phase concentration in test-slag 1 (a) and test-slag 2 (b), and microstructure of test-slag 1 quenched from 1200 °C (c), 1400 °C (d) and test-slag 2 quenched from 1320 °C (e). Legend: L- former liquid phase, F-feldspar, S-silica, M-mullite.

Figure 3. Viscosity behaviour (a), solid phase content and liquid phase change in low iron and calcium slags: SA2 (b) and SA3(c).

Figure 4. Viscosity behaviour (a), solid phase content and S/A ratio of the liquid phase in high iron low calcium and high SA slags: SAF1 (b), SAF2 (c). FeO* is initial concentration in liquid phase.

Figure 5. Viscosity behaviour (a, d), solid phase content and liquid phase changes (b, c, e and f) in high iron low calcium and low SA slags. FeO* is initial concentration in liquid phase.

Figure 6. Viscosity behaviour (a), solid phase content liquid phase change in low iron and high calcium slags: SAC2 (b), SAC3 (c).

Figure 7. Viscosity behaviour (a), solid phase content liquid phase change in high iron and high calcium slags: SACF1 (b), SACF2 (c). FeO* and CaO* are initial concentrations in liquid phase.

Figure 8. Microstructure of SACF2 slag quenched from 1300 °C (a) and SAC3 slag quenched from 1370°C. Legend: L-former liquid phase, S-spinel, Me-mellilite, F-feldspar, A-alumina.

Figure 9. Microstructure of SAF4(a) and SAF3(b) slags quenched from 1410 °C. Legend: L-former liquid phase, M-mullite.
Figure 10. Microstructure of SACF1 slag quenched from 1280 °C (a) and SAC2 quenched 1320°C (b). Legend: L-former liquid phase, F-feldspar

Figure 11. Typical viscosity behaviour in ash coal slags.
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