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Experimental and Modelling Evaluation of Slagging Behaviour of German Lignite

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ABSTRACT

The behaviour of mineral matter is important for the characterisation of coal for use in entrained-flow gasification technologies. We investigated four behavioural characteristics—ash fusion temperatures (AFT), slag viscosity versus temperature profiles, temperatures of critical viscosity (TCV), and slag phase compositions—of Rhenish lignite coal ash using laboratory and modelling tools.

Our modelling of AFT using coal ash composition provided a wide range of data, with only one (modified) model demonstrating agreement with experimental data. Experimental slag viscosity data were obtained over a temperature range from 1200°C to 1500°C. Where relevant, TCV was also measured. Comparison of these data to the calculated viscosities using several models from the literature revealed variation in the accuracy of the models due to the different databases used. Models that calculate TCV on the basis of ash composition fail to predict the data due to very high silica:alumina ratio. However, models based on AFT data match well with the experimental TCV values.

The formation of solids in the slags in the temperature range below liquidus was calculated using thermodynamic modelling tools and compared with the microstructure of laboratory quenched samples. This revealed a strong relationship between solids formation and increasing viscosity.

We also examined a modification of slagging behaviour by blending the Rhenish ash with ash of an Australian coal in different ratios. We show that greater viscosity and a wider operational temperature can be achieved by using an appropriate blending ratio.

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1. Introduction

Integrated gasification combined cycle (IGCC) technology is one of the most promising approaches to reducing the environmental impact of using coal as a power source. The technology allows precombustion separation of polluting gases in power plants, as well as the use of coal as a chemical feedstock. Much effort has been spent in the investigation of the different fields of development of this technique. One of the most challenging aspects is the coal gasification, which includes slag formation if an entrained-flow gasification reactor is used. Several parameters have been developed to describe the characteristics of the slag. The viscosity over temperature trend and the temperature of critical viscosity (T_{CV}) describe the behaviour of the molten slag, whereas the ash fusion temperature (AFT) shows the melting process of the ash. Even though the experimental AFT test is relatively cheap and reliable, some models have been developed to predict the AFT on the basis of the ash composition, or using slag at the liquidus temperature (T_{liq}), below which the first solids in the slag appear (Gray, 1987; Yin et al., 1998; Jak, 2002).
In an entrained-flow reactor, the slag has to be removed continuously, but a protective layer also needs to be built up on the reactor walls. To ensure these requirements, its viscosity has to be within the range of 2–25 Pa·s (Patterson and Hurst, 2000; Ilyushechkin et al., 2011a). For most bituminous coal slags, the viscosity rises logarithmically as the temperature falls (Schobert et al., 1985). A common theory of slag structure describes it as a SiO₂ network. SiO₂, Al₂O₃, and TiO₂ are recognised as network formers, which increase slag viscosity, whereas CaO, MgO, Fe₂O₃, Na₂O, and K₂O are network breakers, which decrease the viscosity (Vargas, 2001; Hilgman and van der Burgt, 2008; Mills, 2011; Kekkonen et al., 2012). By adding flux (e.g., CaCO₃) to the slag, the viscosity can be reduced to meet slag requirements and enlarge the operational range of the process. A silica/alumina (S:A) ratio of 1.6–2.0 is optimal to minimise limestone flux requirements (Patterson and Hurst, 2000). Coal blending is another approach to change slag composition (S:A ratio and/or CaO content) in order to produce slag viscosity suitable for continuous tapping and to minimise flux consumption (Wang and Massoudi, 2013).

Slag viscosity modelling is a useful tool for the preliminary assessment of slagging behaviour of coal mineral matter in entrained-flow gasifiers. Several models have been developed to predict the viscosity vs. temperature trend from the slag or ash composition. Most of these models, however, do not consider the presence of solids in the slag. Only a few models were found to take solids into account by modifying the viscosity values of the other models (Annen, 1983; Oh et al., 1995; Vargas, 2001). The amount of solid phases in the slag can be determined either using a thermodynamic modelling tool (e.g., FactSage) or experimentally, by quantitative X-ray diffraction, by scanning electron microscopy (SEM) or optical microscopy image analysis, and by electron probe microanalysis (EPMA) analysis of the quenched slag, with determination of slag phases and calculation of the mass balance for different components in the phases.

Owing to the buildup of solids in slag at lower temperatures, a sharp increase in the viscosity trend can occur. In this work, the temperature at which this increase starts is referred to as TCV. The tapping temperature of an entrained-flow reactor should always be higher than TCV to avoid the formation of solids in the slag flow. The value of TCV can be calculated based on the slag composition, or using AFT data, if they are available. The difficulties of prediction based on slag composition have been mentioned in previous work (Ilyushechkin et al., 2011a) and also attributed to the variations in the definition of TCV in the literature (Vargas, 2001).

The present work analyses the slugging characteristics of some German lignite using different models. The modelling results are compared with experimental values, and the suitability of the models is discussed. Due to the determined properties of the coal ash slag, blending with another coal was considered. By applying a suitable model relevant to the composition of the slag used in this study, the viscosity of the blends at different blending ratios was investigated and experimentally confirmed.

2. Experimental Methods

2.1. Sample preparation and analysis

The German lignite was analysed in two different states: TUF101 is the lignite as received without any further treatment, whereas TUF104 is the same lignite crushed to a particle size of 45–180 μm and predried. Ash from both samples was produced in an air furnace at 770°C and then mixed before the slag experiments were carried out. Artificial ash mixture (sTUF1400), reproducing TUF101–104 ash without S, was prepared by mixing laboratory or analytical grade Al₂O₃, CaO, Fe₂O₃, K₂CO₃, MgO, Na₂CO₃, SiO₂, and TiO₂ powders. This composition was confirmed later by an X-ray fluorescence (XRF) analysis of quenched slag samples. Slag from an Australian coal (CRC702-s102) was used for the blending experiments. The blends were produced in a ratio of TUF101/104slag:CRC702-s102 of 66:33 (blend 1) and 75:25 (blend 2).

Slag samples were obtained before and after viscosity measurements (described below) using the cold-rod quenching technique. Additional slag samples were obtained from a drop-tube furnace by equilibration of selected slag compositions at 1200–1400°C in a molybdenum (Mo) envelope. Quenched slags were analysed using SEM in backscattering mode. EPMA was used to identify the composition of solid and liquid phases in the slag samples.

Slag and ash bulk chemical compositions are listed in Table 1. Compositions were determined by XRF according to ASTM D3174-12 standard (ASTM International, 2012), and confirmed by EPMA for fully liquid slags. The ash fusion test was carried out according to the ASTM standard D1857-87 (ASTM International, 2000).

2.2. Viscosity measurements

The viscosity vs. temperature trend was experimentally determined in a Haake 1700 rotating bob viscometer. The sample was placed in a Mo crucible. To ensure reducing conditions, the viscometer was purged with a nitrogen flow of 200 mL/min, and the sample was surrounded by a sacrificial graphite holder. The sample was heated to 1400–1500°C for 5–6 hours and held for 6 hours to prepare slag. After premelting, the viscosity rotating bob (Mo) was inserted into the slag mixture, which was homogenised by stirring. The viscosity was measured through the heating and the cooling cycle in 50°C steps and at different shear rates at 1200–1550°C. The temperature was kept constant for 30 minutes to enable equilibrium in the slag before measurement commenced.

3. Results and Discussion

3.1. Ash fusion test

Gray (1987) developed models based on ash composition to predict the AFT for a wide range of New Zealand coals. An AFT model was also developed by Yin et al. (1998) for the composition of Chinese coal ashes. Both models are based on compositions close to the TUF101/104 composition used in present study; however, they do not predict all ash fusion temperatures, and the values are spread over a wide range (as shown in Figure 1). Jak (2002) offers the only model to predict all four ash fusion temperatures: deformation (Tᵈl), softening (Tˢ), hemisphere (Tʰ), and flow (Tᶠ). The model is based on Tliq, which was determined using the FactSage thermodynamic modelling program. The model shows the correct AFT trend for TUF101/104 ash; however, the values are lower than the experimental values. By adding 150 K to each AFT value of the Jak model, a good match to the experimental values was achieved, which is indicated by the “Jak+150” markers in Figure 1. The 150 K adjustment likely reflects the kinetic factor associated with ash fusion test: Ash melting characteristics of gradually heated samples (in AFT conditions) are different from ash at phase equilibria (thermodynamic modelling conditions). This modification was
chosen for this particular coal ash and must be confirmed in further investigations with other coal ash compositions.

3.2. Viscosity modelling and experimental data

The viscosity of TUF101/104 slag is very low (<2 Pa·s) at temperatures above 1240°C, and it significantly increases at temperatures below 1230°C. This indicates the presence of a very narrow temperature range in which TUF101/104 coal is suitable for entrained-flow gasification. The expected hysteresis in the heating and cooling cycle (Schobert et al., 1985) was confirmed in the TUF101/104 slag viscosity vs. temperature trend, which gives uncertainty in the determination of TCV as 1240 ± 10°C.

Postrun analysis of TUF101/104 slag revealed a high Mo content. The Mo dissolution from the crucible in the slag was assumed to be linked to the high sulphur content in the TUF101/104 ash, and this was confirmed in the run with artificial slag without sulphur. In slag produced from the artificial TUF101/104 mixture, much less Mo was dissolved (3 wt% in comparison with 10 wt% in the original TUF101/104 slag). This amount of Mo dissolution was recognised in experiments with other coals in earlier works and has a negligible effect on slag viscosity (French et al., 2001). The viscosity values of artificial TUF101/104 slag are very similar to original TUF101/104 slag with a slightly lower TCV. The difference in viscosities of these samples at low temperatures (near TCV) is associated with solids formation and is discussed in section 3.4.

To evaluate different model predictions for the German lignite used in this study, the modelling of the viscosity vs. temperature trend had to be separated into two parts: (i) models for slags without any solid content and (ii) models taking the solid content into account. Several different models were calculated for slags without solids, as shown in Figure 2. Except for the models of Lakatos, Wall, and Watt-Fereday, all models offered a prediction of the viscosity vs. temperature trend close to the experimental values. The modified Urbain model showed the best match of all models investigated. Therefore, this model was chosen for further modification to take into account the effect of solids on viscosity values.

Viscosity values were calculated for the different solid fraction inputs to the Annen and Einstein-Roscoe models. The solid-phase fraction was determined in FactSage calculations on the slag/ash bulk analysis (Annen/ER-ash) and on the EPMA analysis of the quenched slags above Tliq (Annen/ER-slag) to include the difference in ash and slag compositions listed in Table 1, which may affect viscosity values (Ilyushechkin et al., 2011b). To evaluate the accuracy of the FactSage predictions of solids content, the amount of solids was also estimated by a mass balance calculation on basic elements in the liquid (matrix) and solid phases (crystals) in the slags quenched below Tliq, and determined by EPMA (Annen/ER-mass balance). A higher viscosity value prediction from the Einstein–Roscoe model, compared with the Annen model, is illustrated in Figure 3. The values based on the FactSage

### Table 1

Sample composition determined by XRF

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Bulk composition [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
</tr>
<tr>
<td>TUF101ash</td>
<td>46.9</td>
</tr>
<tr>
<td>TUF104ash</td>
<td>46.8</td>
</tr>
<tr>
<td>TUF101/104slag</td>
<td>53.34</td>
</tr>
<tr>
<td>stTUF1400slag</td>
<td>51.20</td>
</tr>
<tr>
<td>CRC702slag</td>
<td>48.15</td>
</tr>
<tr>
<td>Blend 1</td>
<td>51.09</td>
</tr>
<tr>
<td>Blend 2</td>
<td>52.04</td>
</tr>
</tbody>
</table>

Note: Detection limit is 0.05 wt% for MgO and Na₂O and 0.02 wt% for all other components.
prediction of solids are also higher than the values based on the mass balance calculation. This difference is due to the FactSage prediction being based on equilibrium, which was not reached in the laboratory slag due to a relatively short residence time. Overall, the combination of the Einstein–Roscoe model based on the mass balance calculation is the best of the investigated models. However, even this model fails to predict the viscosity under 1225 °C, where the viscosity is significantly higher than any of the modelled values. Because only limited quenched samples were available, the EMPA data may not be representative. Further experiments are required to confirm these results.

3.3. Temperature of critical viscosity

The $T_{\text{CV}}$ can be determined from the viscosity trend as the temperature where a sharp viscosity increase occurs. Referring to the experiments, the $T_{\text{CV}}$ of the investigated slag is about 1240 °C. Several models to predict $T_{\text{CV}}$ were found in the literature, which are either based on the slag composition or refer to the AFT. The results of the modelling are shown in Table 2. The models based on the slag composition predict $T_{\text{CV}}$ values poorly; their overestimation of $T_{\text{CV}}$ can be explained by the strong influence of the S:A ratio (Vargas, 2001; Seggiani and Pannocchia, 2003). Because the S:A ratio for the investigated composition is much higher than mentioned for other coals (e.g., 1.6–2.0 for Australian coals), a high $T_{\text{CV}}$ value results from the calculation. The AFT-based models predict values closer to the experimental value, with the Corey model being very accurate. However, those models still show a relatively wide prediction range. Even to confirm the reliability of the Corey model, more experiments are required to confirm these results.

### Table 2

<table>
<thead>
<tr>
<th>Model</th>
<th>$T_{\text{CV}}$ (°C)</th>
<th>Refers to</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corey</td>
<td>1230</td>
<td>AFT</td>
</tr>
<tr>
<td>Sage–Mcllroy</td>
<td>1351</td>
<td>AFT</td>
</tr>
<tr>
<td>Marshak–Ryzhakov</td>
<td>1402</td>
<td>AFT</td>
</tr>
<tr>
<td>Watt</td>
<td>225,298</td>
<td>Slag comp. (wt%)</td>
</tr>
<tr>
<td>Seggiani–Pannocchia</td>
<td>8073</td>
<td>Slag comp. (mol%)</td>
</tr>
<tr>
<td>Sridhar</td>
<td>1016</td>
<td>Slag comp. (mol%)</td>
</tr>
</tbody>
</table>

with coals of the same or similar composition must be evaluated. The prediction of the $T_{\text{CV}}$ is very dependent on the composition of the slag and is therefore hard to predict using simple equations.

3.4. Formation of solids

The solid volume fraction has a strong influence on the viscosity trend. The appearance of solids in slags was investigated using FactSage thermodynamic modelling, with two different inputs for the slag composition: calculated from the EPMA analysis of the quenched real slag, and the artificial slag above $T_{\text{liq}}$. The modelling results were compared with the solid–phase fraction of samples quenched at different temperatures, which was estimated by a mass balance of the elements in the liquid and solid phases of quenched samples determined by EPMA.

Above 1300 °C, no solid phase was determined. TUF101/104 slag quenched at 1225 °C (Figure 4a) clearly shows crystals of different sizes in a matrix, which formed from the liquid phase. The composition of most crystals is similar to that of augite (enstatite, FeMgAl2Si2O6) and a second solid phase is powellite (CaMoO4). There are also some inclusions consisting of Mo (about 90 mol%) and sulphur (about 10 mol%). Consequently, not all the sulphur evaporated out of the slag, as was assumed for the calculation of the AFT, viscosity, and $T_{\text{CV}}$ models. The sample of TUF101/104 slag quenched at 1200 °C shows the same solid phases as the sample quenched at 1225 °C (Figure 4b), but the abundance of crystals is higher due to the lower temperature.

The SEM images of the artificial TUF101/104 slag quenched at 1220 °C and 1200 °C (Figures 4c and 4d) are different from those of the TUF101/104 slag prepared from real TUF101–104 ash. At 1220 °C, there are no crystals in the artificial slag, and enstatite and wollastonite (CaSiO3) are formed at 1200 °C. No powellite or Mo phase is formed in the artificial slag, which indicates a lower Mo content.

The blended compositions were quenched at 1500 °C, 1300 °C, and 1200 °C; no solid phases were determined, except for a small amount of the Mo and sulphur phase, as in the TUF101/104 slag. This is consistent with the viscosity measurement, where no $T_{\text{CV}}$ (and therefore no influence of solid phases) could be determined.

Figure 5 shows the FactSage prediction of solids based on the EPMA analysis of the artificial (sTUF1400) and TUF101/104 slag, as well as the experimental data for the quenched samples of the slag evaluated by the mass balance. The composition of the predicted phases fits to the experimental investigation. However, the predicted amount of solids is higher than in the quenched samples, indicating an overestimation of solids by FactSage. This was expected, because FactSage calculates the equilibrium, which was not reached in the experiments due to limited equilibrium times.

In the TUF101/104 slag, a Mo content of approximately 10 wt% was determined by the EPMA analysis, whereas the artificial slag shows a Mo content of about 3 wt%. The only difference between the two slags is the sulphur content, which is higher in the real slag. Therefore, an influence of sulphur on the Mo diffusion into the slag can be confirmed.

3.5. Blending approach

To modify the very low viscosity of the investigated slag and to narrow the operating temperature window suitable for entrained-flow gasification, a blending approach was investigated. The S:A
ratio of the TUF101/104 slag is very high (≈25) due to its low alumina content, and must be lowered, while CaO is relatively high and leads to low viscosity. In contrast, the Australian coal ash slag CRC702-102 has a high alumina content and low CaO content. It was therefore blended with the TUF101/104 slag to reduce both the S:A ratio and the CaO content. Based on modelling calculations (the Viscalc model was used, because it predicts this compositional range well), blending ratios of 66:33 (blend 1) and 75:25 (blend 2) of TUF101/104 and CRC702 were chosen to be investigated experimentally. The expected increase of the viscosity trend of the blends in comparison with the TUF101/104 slag was confirmed (Figure 6). A shift of the TCV to lower temperatures was recognised, which significantly extends the operational temperature range of blends suitable for entrained-flow gasification.

4. Conclusions

We investigated the slagging behaviour of the German lignite TUF101/104 and found a modified model for best AFT prediction. However, as the AFT test is relatively cheap and reliable, it may be appropriate to determine the AFT experimentally. Several viscosity prediction models were calculated for slags with and without solids, and a combination of the Einstein–Roscoe model with the modified Urbain model was found to fit the experimental data best.

![Fig. 4. Scanning electron microscope images of TUF101/104 slag quenched at (a) 1225°C and (b) 1200°C, and artificial TUF101/104 slag at (c) 1220°C and (d) 1200°C.](image)

L = former liquid phase; Py = clinopyroxene; Po = powellite; Mo = molybdenum (+sulphur); W = wollastonite.

![Fig. 5. Solids content in TUF101/104 ash slag (a) and artificial TUF101/104 slag (b) predicted by FactSage and measured by EPMA.](image)

Py = clinopyroxene; Po = powellite; W = wollastonite; visc = viscometer run.
A calculation of the $T_{CV}$ based on the ash/slag composition does not provide realistic $T_{CV}$ values, whereas one AFT-based calculation matched well with the experimental data. Nevertheless, an experimental determination seems to be needed to provide reliable $T_{CV}$ values.

A strong dependency of solids buildup on composition was shown. The phase fraction, as well as the solids composition, varied depending on the slag composition. The solids composition was correctly predicted using FactSage modelling and the EPMA slag bulk composition as input; however, the amount of solids was overestimated. In a blending approach, the composition and viscosity of the slag were modified to enlarge the operational temperature range and avoid the extensive buildup of solids below 1250°C.

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