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THE EFFECTS OF HETEROGENEOUS SLAG CHARACTER ON VISCOSITY AND SLAG FLOW IN IGCC GASIFIERS

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ABSTRACT

The accepted criterion for flow of slag required for its removal from entrained flow coal fired gasifiers is the slag viscosity, with laboratory measurements of the viscosity of homogeneous (fully liquid) slags prepared from ash being used to establish the suitability of particular coals for the technology, and the necessity for adding flux during firing to lower viscosity. This Communication raises issues related to the direct application of the viscosity measurements, by examining the nature of slags sampled from pilot-scale gasifiers which has revealed their non-homogeneous nature.

Key Words:

Slag viscosity, IGCC, Slag flow

1. INTRODUCTION

In Integrated Gasification Combined Cycle (IGCC), pulverised coal is gasified in an entrained flow reactor. The ash products form a slag layer which flows down the refractory wall under gravity and out the bottom of the gasifier into a water quenching system. For slag to flow from IGCC gasifiers, it is generally accepted that the slag viscosity must be sufficiently low at the temperature of tapping, typically less than 15-25 Pa.s at temperatures from 1400-1500°C. This may be termed the *slag flow criterion*. In addition, as slag is cooled and solids (crystals) are formed, the viscosity becomes non-Newtonian at a temperature known as the temperature of critical viscosity (T_{cv}). The effect of the solids is to increase the apparent viscosity of the slag. This temperature depends the slag chemistry and on the cooling rate. The slag should be removed at a temperature above the T_{cv} so that the effect of solids is not too great. This may be termed *the* T_{cv} *criterion*. Both the criteria must be met.

For coals with ash compositions of low to moderate levels of CaO and Fe_2O_3, the addition of limestone as a flux is needed to achieve the slag flow criterion. The limestone calcines to CaO and then impacts and dissolves into the slag as it runs down the wall. Typically, an equivalent CaO level of 30% is needed so that the bulk composition approaches the low temperature eutectic on the SiO_2 – Al_2O_3 – CaO phase diagram. There are efficiency and economic penalties for the addition of flux, and therefore its addition should be minimised.

The aim of this paper is to highlight some of the problems associated with estimating the viscosity of a slag in a real situation from laboratory viscosity data and thermodynamic predictions. SEM analysis of four slags from gasifiers (three slags from Gasifier A, and one slag from Gasifier B) are used to illustrate the heterogeneity of real gasifier slags. Both gasifiers are pilot scale with firing rates of between 20 and 40 kg/hr.

2. VISCOSITY MEASUREMENTS ON HOMOGENEOUS SLAGS

Substantial viscosity and T_{cv} data has been generated for coal ash derived slags using a rotating bob viscometer[1]. Viscosity data have been correlated with the slag chemistry and temperature on the basis that the slag is homogeneous and fully liquid. However, predictions made by the thermodynamic equilibrium package FACT[2] for the slags indicate that a substantial proportion of the viscosity data is at sub-liquidus temperatures, where solids are present at thermodynamic equilibrium. Figure 1 shows a plot of liquidus temperature calculated using FACT versus the measured T_{cv} for 52 synthetic SiO_2 – Al_2O_3 – CaO – FeO slags. It can be clearly seen that the measured T_{cv} is a sub liquidus event by as much as 250°C. This suggests that the slags are super saturated and hence not at equilibrium in the viscometer for the times allowed in the experiment, this being typically 45 minutes. It should be noted that this time is considerably longer than the time for slag to run down the wall of a gasifier, which is typically 5-15 minutes. Slags in practical systems are therefore not expected to be at equilibrium, and the experimental viscosity data will apply.

Examination of the slags showed almost complete molten character, with little evidence of crystallisation. This observation indicates the gasifiers are operated at temperatures above the liquidus or the slags are not reaching equilibrium before they are quenched.

3. EFFECT OF SOLIDS ON SLAG VISCOSITY

The effect of solids on bulk viscosity has been well studied[3] for spherical, non-interacting particles of equal size. For volume fractions of less than 10% by volume, liquids show a linear increase in viscosity with the volume fraction of solids. For volume fractions greater than 10%, a number of empirical expressions have been developed which show exponential increases in viscosity with volume fraction of solids[3]. These expressions are affected by shape and size distribution and as such, slags containing needle-like crystals would not be expected to closely follow them. At temperatures below the T_{cv}, the slag is non-Newtonian. This means that the apparent viscosity is, by definition, a function of the shear rate. In order to accurately predict the apparent viscosity of a slag containing solids, the shear rate at the slag tap must be known.

4. EROSION OF GASIFIER REFRACTORY

The most unexpected feature of the slags obtained from gasifier A is the quantity of refractory material found. All samples had significant quantities of undissolved chromium oxide refractory, which have been eroded from the gasifier wall. Extensive growth of crystals of Cr_2O_3 / Al_2O_3 and Cr_2O_3 / FeO were observed. In addition to these particles, the chromium oxide content of the continuous slag phase was as high as 13%. The presence of the refractory will have a dramatic effect on the viscosity of the slag due to the increase in solids content, chromium oxide in the liquid and the removal of other components into solid solutions which will change the liquid phase viscosity.

5. EFFECT OF GAS BUBBLES ON SLAG VISCOSITY

Examination of SEM micrographs showed that slags can contain significant amounts of gas bubbles of various sizes and would be expected to affect the apparent bulk viscosity. However, these gas bubbles do not appear to be evenly distributed through the slag.

The majority of literature on the flow of gas – liquid mixtures centres on very high gas holdups (i.e. foams or sprays) rather than dispersed gas bubbles of less than 10% volume. A number of expressions were found which related the gas and liquid viscosities and the volume fraction of gas to the apparent bulk viscosity[4]. The effect of dispersed gas bubbles on the bulk viscosity is not well understood and requires further investigation. The degree to which gas bubbles influence bulk viscosity is, most likely, a function not only of volume fraction, but of bubble size and applied shear rate. If the bubble size is small and the shear rate is sufficiently low that the bubbles do not deform, then they will behave as solid spheres and increase viscosity. If the shear rate is high enough for the bubbles to deform or even tear, then the bulk viscosity will decrease.

6. PARTITIONING OF MINERALS INTO SLAG AND FLY ASH

In slagging gasifiers, coal particles are directed towards the walls so that the remaining mineral matter can form a slag layer. Larger ash particles have enough momentum to impact the wall and become part of the slag layer. Smaller particles that do not have the momentum to impact the wall stay in the gas stream (fly ash) and are removed in cyclones. This size partitioning can have a compositional effect on the slag viscosity. For example, if a coal ash is composed of silica particles which are relatively fine compared to the other minerals present, then a greater proportion of the silica will be carried out as fly ash. This will result in the slag being depleted in silica and hence will have a viscosity lower than that expected from laboratory measurement. Table 1 shows the composition of the ash from Coal 4 and of the slag produced when that coal was fired in Gasifier B. A significant enrichment in silica in the slag can be seen. This is because the starting ash contained large quartz particles which became part of the slag and proportionally more of the other minerals were removed as fly ash. This bulk slag composition, however, can also be misleading if the ash contains minerals too large to dissolve into the slag. Figure 2 shows large undissolved silica particles in the gasifier slag. These particles will produce a bulk composition high in silica whilst the continuous liquid phase is relatively low in silica.

By analysis of the laboratory ash by CCSEM to provide particle size distributions of the various minerals and knowledge of the size fraction removed in the fly ash, any enrichment of the slag by a particular component may be predicted.

7. CHAR CARBON IN SLAG

In order to determine whether penetration of char into the slag was important to slag flow, the three slags from gasifier A were examined by SEM for the presence of unreacted char. No such char was found in any sample. In addition, the slags were analysed for total dissolved carbon content, including forms such as iron carbide. It was found that the carbon content of the three slags ranged between 0.08% and 0.28% carbon. Thus it was concluded that it was unlikely that char penetrates the slag, as no unreacted particles were evident. Also, the levels of carbon in the slag were considered too low to have a dramatic effect on the slag viscosity.

8. ATMOSPHERIC EFFECTS ON VISCOSITY

Atmospheric conditions inside a gasifier are highly reducing. This leads to the problem of the reduction of iron oxides to form metallic iron. When the iron is reduced to its metallic form, it is separated from the slag into dispersed globules. Figure 3 shows an SEM micrograph of Slag 4 from gasifier A. Because of this separation, the liquid slag becomes depleted in iron causing the viscosity to increase. Examination of slags from the three coals fired in gasifier A showed not all the iron oxide was reduced to metallic form. EDS analyses of the continuous slag phases showed between 2 and 6% FeO still present in the slag. Prediction of how much FeO will finally be in the slag, based on laboratory ash analyses, will be complicated firstly by fly ash partitioning and then by reduction of the iron species. Further investigation is required for accurate modelling of the fate of iron oxides.

9. THE APPLICABILITY OF THE VISCOSITY DATA FOR HOMOGENEOUS SLAG TO PRACTICAL SITUATIONS

This paper has highlighted some of the differences between real gasifier slags and those used in the laboratory to study slag properties. These include:

- Super saturation of the slag which prevents accurate determination of the T_{cv},
- Formation of metallic iron and the associated removal of iron oxide from the slag;
- The erosion of refractory material;
- Gas bubbles, and
- Size separation of ash particles producing component enrichment.

Care should be exercised in the direct use of laboratory results in the prediction of coal performance in gasifiers. Models should be developed which can account for the heterogeneity of real gasifier slags.

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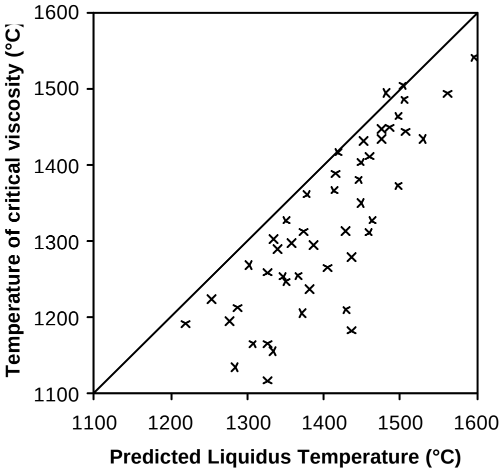


Figure 1. Comparison of measured T_{cv} and Liquidus temperature predicted by FACT

Table 1. Compositions of starting ash from Coal 4 and slag produced from Gasifier B.

Component	Laboratory Ash	Gasifier Slag
SiO_2	41.4	63.1
Al_2O_3	12.6	12.7
Fe_2O_3	25.3	10.0
CaO	10.5	9.6
MgO	1.7	1.7
Na_2O	1.0	1.5
SO_3	6.1	0.18

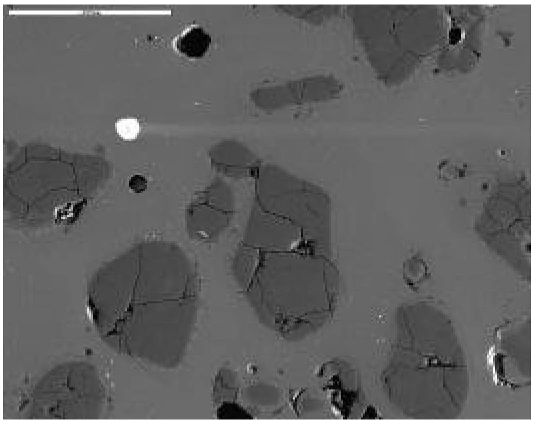
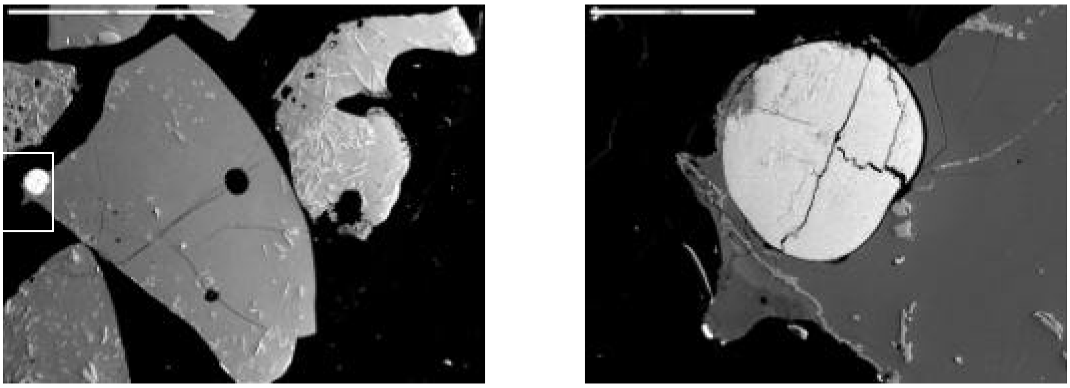


Figure 2. SEM image of Slag 4 containing large undissolved silica particles from Gasifier B. (Scale bar = 200mm)



(a)

(b)

Figure 3. SEM micrographs of Slag 2 from Gasifier A showing metallic iron globule. (a) Scale bar = 2mm. (b) Close up of area indicated (Scale bar = 200mm).