

## EFFECT OF CRYSTALLINE PHASE FORMATION ON COAL SLAG VISCOSITY

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### INTRODUCTION

The Texaco Gasification Process (TGP) employs a high temperature and pressure slagging gasifier, in which the viscosity of the slag plays a key role in determining operating conditions. For all the feedstocks to TGP, the viscosity of the slag at the operating temperature has to be low enough to ensure a smooth flow out from the gasifier. The slag viscosity behavior in the gasifier has been studied through experimentation under reducing atmosphere as well as using empirical models. As in the oxidizing conditions, some coal slags exhibit the classical behavior of a glass: a continuous increase in viscosity as the temperature decreases, while others exhibit a rapid increase in viscosity when temperature is lowered below a certain temperature which is referred as the temperature of critical viscosity ( $T_{cv}$ ). Below  $T_{cv}$ , it is believed that slag changes from a homogeneous fluid to a mixture containing crystallized phase(s). For glassy slags, the viscosity-temperature behavior has been modeled fairly successfully using empirical models based on slag composition, such as Watt-Fereday,<sup>1</sup> Si Ratio,<sup>2</sup> Urbain,<sup>3</sup> or modifications of those models.<sup>4-6</sup> However, when the viscosity is modified by crystalline phase formation, the empirical models fail to predict correct slag viscosity behavior. Even though the importance of the crystalline phase formation on the bulk flow properties of the slag has been long recognized, only limited information is available for prediction of  $T_{cv}$  or crystalline phase formation.<sup>7,8</sup>

Formation of crystalline phases and its effect on slag viscosity under gasification conditions were investigated with 4 coal slags. Slag viscosity was measured under reducing atmosphere at temperatures between 1150 - 1500 °C. Crystalline phases in slag samples were identified, and related to the observed viscosity.

### EXPERIMENTAL

**Set Up:** The schematic of our high temperature slag viscometer is shown in Figure 1. The Haake Rotovisco RV-100 system with a coaxial cylinder sensor system was employed for viscosity measurements. The sensor system, stationary crucible and rotating bob with tapered bottom, is made of high density alumina, and placed in a high temperature furnace. The heating elements (Kanthal Super ST) of the furnace are completely isolated from the viscometer assembly by a mullite tube which runs from the top to the bottom of the furnace. This protects the brittle heating elements from breaking during loading and unloading of the sensor system. The furnace temperature control and the data acquisition of shear rate vs. shear stress were obtained through PARAGON software on an IBM PC. To simulate a reducing condition, a 60/40 mix of CO/CO<sub>2</sub> was passed over the sample at 300 cc/min. The gas mixture entered from the bottom of the furnace and exited through the top. The viscometer was calibrated with a NBS borosilicate glass (Standard Reference Material 717).

**Procedures:** A cylindrical crucible is placed in the furnace. The crucible is locked into the bottom plates of the furnace, to prevent the crucible from rotating. The bottom plates are made of low density alumina to minimize conductive heat loss from the sample. Then, the CO/CO<sub>2</sub> sweep gas is turned on, and the furnace is heated to 1480 °C. When the furnace reaches 1480

°C, a few grams of pelletized ashes are fed from the top. This feeding process is slow to allow the pellets to completely melt and degas before the next feeding to prevent the slag from boiling over. Once the desired level of the melt is obtained, the bob is lowered from the top, guided by an alignment pin and a stopping plate. In this way, the viscometer is assembled in the same way every time, assuring that the bob is placed in the middle of the slag sample, both horizontally and vertically. Once the viscometer assembly is complete, the temperature is decreased at the rate of 56 °C/hr. The viscosity measurements are made every 10 minutes. After the experiment, the slag is cut as shown in Figure 1 and polished for Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) phase analysis. The elemental composition of the slag before and after the viscosity experiments were determined by Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) and the phase analysis was also conducted by X-Ray Diffraction (XRD).

The viscosity measurements take 6 mins. The rotation rate of the bob is ramped from 0 to 65 rev/min for 3 mins and back to 0 for the next 3 mins. The shear rate is varied from 0 to 18.2 s<sup>-1</sup>. The resulting shear rate-shear stress curve is that of a newtonian fluid at high temperatures, and the characteristic of a non-newtonian fluid is typical at low temperatures. For the viscosity-temperature plot, we took the viscosity at the highest shear rate.

**Temperature Calibration:** During viscosity measurements, there is no way to measure the sample temperature without disturbing the flow. Separate experiments were conducted to calibrate the slag temperature against the furnace temperature. Four thermocouples were placed in the slag as shown in Figure 1 to measure temperature distribution throughout the sample. Figure 2 plots the temperature differences from the mid-thermocouple (TC2) as a function of the TC2 temperature. As can be seen, the deviation was less than ±2 °C most of the time as the temperature decreases from 1480 to 1090 °C at the rate of 56 °C/hr. One thermocouple (TC4) was placed in the center of the bob to measure the thermal inertia of the bob. The temperature difference between TC2 and TC4 was less than 5 °C most of the cooling time, proving that the alumina bob did not give much thermal inertia. In order to estimate the sample temperature during the viscosity measurements, TC2 was calibrated against the furnace control thermocouple.

**Materials:** The four coals include SUFCo (Hiawatha seam, high volatile C bituminous rank), Pittsburgh #8 bituminous, and two Powell Mountain coals [unwashed (PMA) and washed (PMB) coals]. SUFCo and PMA were gasification slag samples which were further ashed to remove any remaining organic carbon. Pittsburgh #8 and PMB samples were prepared from coal by ashing at 750 °C under air. We found that alumina from the crucible and the bob dissolved into the slag during viscosity measurements and raised the concentration of alumina. Table 1 presents the normalized composition after the experiments.

## RESULTS

**Slag Viscosity:** Figure 2 plots the viscosities of the four slags as a function of temperature. The viscosity of SUFCo and PMB slags exhibit the glassy slag behavior, while the viscosity curves of Pittsburgh #8 and PMA are typical of a crystalline slag. The SUFCo slag contains high concentrations of SiO<sub>2</sub> and CaO, and low concentrations of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. The high concentration of SiO<sub>2</sub> in SUFCo causes the slag to have a higher viscosity than the others at high temperatures, and to act as a glassy slag showing a gradual increase in viscosity as the temperature decreases. Compared to SUFCo slag, Pittsburgh #8 slag has a lower SiO<sub>2</sub> and CaO, but higher Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. Even though it exhibits the behavior of a crystalline slag, it has a low T<sub>v</sub>: the slag remains the most fluid among the four slags at temperatures above ~ 1285 °C.

As expected from a washed coal, PMB has a lower concentration of  $\text{Fe}_2\text{O}_3$  than PMA. The  $\text{SiO}_2$  concentration was very similar in both samples, and both contain a very low concentration of  $\text{CaO}$  and a high concentration of  $\text{Al}_2\text{O}_3$ . Since it is believed that the higher iron content usually lowers the slag viscosity, the higher viscosity of PMA with  $T_{cv}$  of  $1425^\circ\text{C}$  is opposite of what is expected. PMB shows a viscosity of less than 1000 poise even at  $1300^\circ\text{C}$ .

**Crystalline Phase Formation:** The crystalline phases in the four slags, which were examined by XRD, OM, and SEM, are listed in Table 2. The SEM micrographs of the four slags are shown in Figure 4. The SUFCo slag shows glass (40-45 vol. %) and anorthite (55-60 %) as major phases. Pittsburgh #8 slag contains glass, both large crystals and dendrite of hercynites, and needle-like corundum and mullites. Both large crystals and dendritic hercynites were iron rich, with the composition of  $\text{Fe}(\text{Al},\text{Fe})_2\text{O}_4$ . The PMA slag shows extensive formation of dendritic hercynites ( $\text{FeAl}_2\text{O}_4$ ) along with long needles of mullites. In contrast, the PMB slag has long, needle-like crystals of corundum and large crystals of hercynites. The anorthites in SUFCo and the mullite and corundum crystals in the other three were all aligned to the direction of the flow. The alignment of the crystals suggests that the crystals were formed during the viscosity measurement, not during the cooling. The crystal size of corundum in PMB was much larger than those found in Pittsburgh #8 sample. The examination of the interface between the slag and the aluminum crucible also showed that the nucleation of corundum occurred at the alumina crucible and the bob. As the nucleated particles grew into elongated crystals, they were broken off from the wall and mixed into the melt.

## DISCUSSION

$T_{cv}$ 's observed in our experiments were compared to the model proposed by Watt<sup>7</sup> which correlates  $T_{cv}$  as a function of slag composition. While  $T_{cv}$  for Pittsburgh #8 showed fair agreements between observed ( $1285^\circ\text{C}$ ) and predicted ( $1223^\circ\text{C}$ ), the predicted  $T_{cv}$  for PMA was much lower than observed ( $1255$  vs.  $1425^\circ\text{C}$ ). The biggest failure of the model is for SUFCo, a glassy slag: the predicted  $T_{cv}$  was  $2440^\circ\text{C}$ .

The glassy slag behavior of SUFCo and PMB suggests that the large elongated crystals do not cause a rapid increase in viscosity. In addition, precipitation of corundum and hercynite in PMB lowers the concentration of  $\text{Al}_2\text{O}_3$  in the melt, while increasing  $\text{SiO}_2$  concentration which may cause the melt to behave as a glassy slag. The two crystalline slags, Pittsburgh #8 and PMA, showed dendritic hercynites. From our experiment, it is not clear whether dendrites were formed during quenching after the viscosity measurements or at around  $T_{cv}$ . If the dendrites were formed during quenching, the increase in the viscosity cannot be explained. For the PMA slag, as mullites precipitate out, the remaining melt should have a lower aluminum and higher iron which would result in a lower viscosity, not higher. However, the high concentration of iron in the melt also makes it susceptible for precipitation of a Fe-phase such as hercynite. Therefore, it is more likely that the dendrites were formed at around  $T_{cv}$  and caused a rapid solidification of the slag. Watt and Fereday<sup>7</sup> also observed the frequent occurrence of the spinels in their slags samples from the viscometer, and stated that the formation of phases under the experimental conditions is determined more by the rate of crystallization than the phase equilibria.

The only model, we found, which incorporate the effect of crystalline phases on the slag viscosity was the model proposed by Annen et al.<sup>9</sup> They treated the slag as a mixture of the melt and crystalline phases, and modeled the viscosity of the mixture ( $\mu_{\text{mixture}}$ ) as a function of liquid's viscosity ( $\mu_{\text{liq}}$ ) and the solid content:

$$\mu_{\text{mixture}} = \mu_{\text{liq}} (1 + 2.5 c + 9.15 c^2)$$

where  $c$  is the volume fraction of solids. For the viscosity of liquid phase, they employed the Watt-Fereday model. The solid's concentration and the liquid composition in the mixture were calculated using a chemical equilibrium code. The above equation is valid for solids present in the shape of spheres at low concentrations. For those slags that contained elongated crystals of mullites and corundum, the above equation may not be appropriate. The model also does not describe the effect of the particle size we observed in large crystals of spinel vs. dendritic spinels. However, the above model or variations of the above may still provide an improved first approximation to model the effect of crystalline phase formation on slag viscosity.

The success of the model by Annen et al. also depends on the accuracy of the solid's concentration predicted as a function of temperature. The thermodynamic equilibrium calculations were made for the four coal slags using normalized compositions of the five major components ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{FeO}$ , and  $\text{MgO}$ ). It was assumed that the liquid phase was an ideal mixture of various silicate species. The predicted crystalline phases at 900 °C agreed well with the observation as shown in Table 2. However, the concentration of solids predicted as a function of temperature did not improve the viscosity predictions for Pittsburgh #8 and PMA.

As we and the others observed, the formation of crystalline phases in those slags may be governed by the kinetics factors. Better understanding of the rate of crystallization of various phases as well as more realistic treatments of silicate melts in thermodynamic equilibrium analysis are needed.

## CONCLUSIONS

The slag viscosities of SUFCo and PMB coals exhibited the behavior of a glassy slag, of which the viscosity gradually increases as the temperature decreases. The other two, Pittsburgh #8 and PMA, showed the behavior of a crystalline slag with  $T_{ev}$  of 1285 and 1425 °C, respectively. Crystalline phase analysis of the slag samples revealed that extensive network formation of dendrite spinels in Pittsburgh #8 and PMA caused a rapid increase in the viscosity, while anorthites in SUFCo and large crystals of hercynites and elongated particles of corundum in PMA did not affect the slag viscosity as much. The prediction of crystalline phase formation under a given experimental condition and its effect on the viscosity remains to be a challenging task. Thermodynamic equilibrium analysis with a realistic treatment of silicate melt system may improve the predictions of phase formation as a function of temperature. In addition, better understanding of the rate of crystalline phase formation is needed.

## REFERENCES

1. Watt, J. D., and Fereday, F., *J. Inst. Fuel*, 42, 99-103, 1969
2. Urbain, G., Cambier, F., Deletter, M., and Anseau, M. R., *Trans. J. Brit. Ceram. Soc.* 80, 139, 1981
3. Corey, R. C., US Bureau Mines Bull. No. 618, 1964
4. Schobert, H. H., Streeter, R. C., and Diehl, E. K., *Fuel*, 64, 1611, 1985
5. Kalmanovitch, D. P., Weinmann, J.R., Ness, S.R., and Benson, S. A., DE90-011398, 1990
6. Jung, B., and Schobert, H. H., *Energy Fuel*, 6, 387, 1992
7. Watt, J. D., *J. Inst. Fuel*, 42, 131-134, 1969
8. Kalmanovitch, D. P., Sanyal, A., Williamson, J., *J. Inst. Energy*, 59, 20, 1986
9. Annen, K., Gruninger, J., and Stewart, G., *Proc. Flames Res. Foundation*, 3-1, 1983

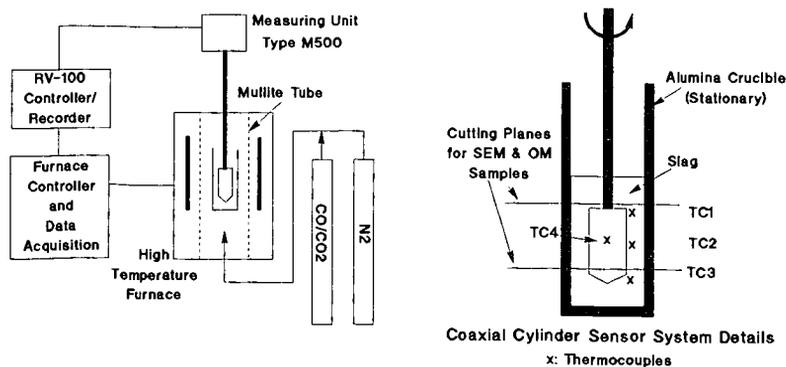
**Table 1. Normalized Composition of Four Coal Slags**

Oxides	SUFCo	Pitt. #8	PMA	PMB
SiO <sub>2</sub>	60.21	46.77	43.79	43.37
Al <sub>2</sub> O <sub>3</sub>	15.60	24.67	26.04	29.28
Fe <sub>2</sub> O <sub>3</sub>	5.85	17.26	21.01	16.57
CaO	11.57	5.50	2.58	3.51
MgO	2.14	1.07	1.06	1.19
Na <sub>2</sub> O	2.67	1.00	0.45	0.51
TiO <sub>2</sub>	0.88	1.02	1.40	1.52
K <sub>2</sub> O	0.43	1.84	2.22	2.08
P <sub>2</sub> O <sub>5</sub>	0.26	0.32	0.70	0.98
BaO	0.08	0.11	0.15	0.20
SrO	0.12	0.18	0.26	0.46
PbO	0.00	0.05	0.08	0.08
Cr <sub>2</sub> O <sub>3</sub>	0.19	0.22	0.26	0.30

**Table 2. Crystalline Phases in Coal Slags**

Coal Slag	Observed	Crystalline Phases at 900 °C by Equilibrium Calculation
SUFCo	Anorthite	Anorthite Diopside
Pittsburgh #8	Mullite Fe-rich Hercynite Corundum	Mullite Hercynite & Spinel Anorthite
PMA	Mullite Hercynite	Mullite Hercynite & Spinel
PMB	Corundum Hercynite	Mullite Spinel

**Figure 1. Schematic of Slag Viscometer**



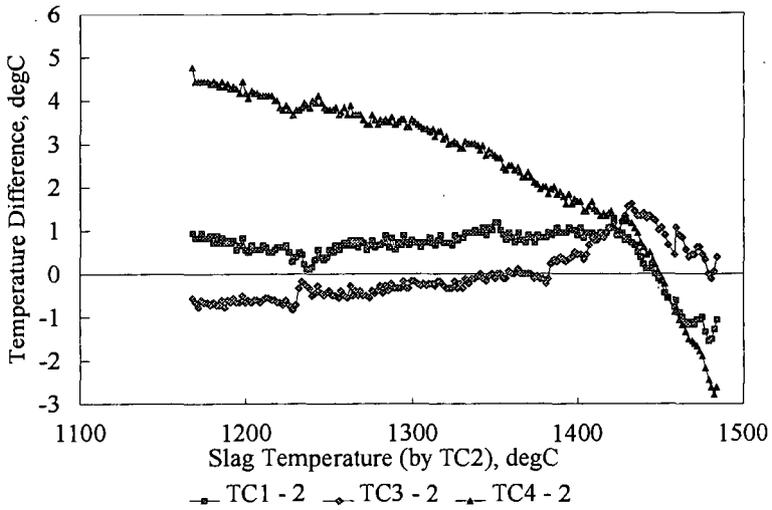


Figure 2. Temperature differences in slag sample from the mid-point.

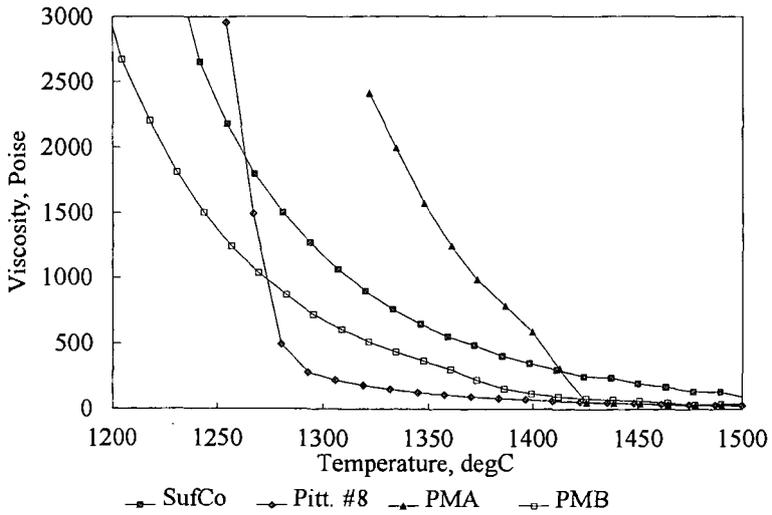


Figure 3. Slag Viscosity as a Function of Temperature

Figure 4. SEM Micrographs of Crystalline Phases in Coal Slags

