

GASIFICATION SLAG RHEOLOGY IN TITANIUM-RICH, IRON AND CALCIUM-ALUMINOSILICATE GLASSES

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INTRODUCTION

The Texaco Gasification Process (TGP) employs a high temperature, high pressure slagging gasifier to produce synthesis gas for power, hydrogen, and chemicals. During gasification most of the ash collects on the refractory wall to form a molten glass or slag. The viscosity of the slag plays a key role in determining operating conditions. Insufficient operating temperatures can cause erratic slag flow from the unit, while excessive operating temperatures can result in rapid refractory wear.

Waste streams that are high in titanium (e.g. plastics and tires where TiO_2 is used as a pigment) are being tested for gasification by Texaco. Texaco has developed a process to liquify both used plastics and tires with heated oil to produce a pumpable feed referred to as plastic-oil or tire-oil. Other major elements found with the titanium in these feeds include calcium, aluminum, iron, silicon, and zinc. The zinc sublimes during gasification, leaving behind a titanium-rich calcium-aluminosilicate glass with various amounts of iron.

The rheology of iron and calcium-aluminosilicate glasses within a gasifier has been studied through experimentation under reducing conditions, and by comparing this data to empirical models. Our initial study¹ indicated that: i) most calcium-rich gasification slags should exhibit the classical behavior of a newtonian glass (a continuous slow increase in viscosity as the temperature decreases), and ii) iron-rich slags can exhibit either newtonian or non-newtonian behavior (very low viscosity at high temperatures with a rapid increase in viscosity at some critical temperature (T_{cv})). At temperatures below T_{cv} , the slag is thought to change from a homogeneous fluid to a mixture of a fluid and rapidly crystallizing phase(s). Slag rheology under oxidizing conditions has been modeled rather successfully with empirical models based on slag composition. These models include Watt-Fereday,² Urbain³, Si Ratio⁴, or modifications of those models⁵. However, these models are limited to 0-5% TiO_2 , and do not predict T_{cv} .

A study by Monteiro, et al⁶, using titanium-rich, calcium-aluminosilicate glass was conducted in which up to 15% TiO_2 was used as a nucleation catalyst. The end result was a reduction in the melting point of the glass by the titanium dioxide. To extend the data base to higher titanium levels, in both calcium and iron-rich, aluminosilicate slags under reducing conditions, viscosity testing was conducted using 0-30% TiO_2 added to both synthetic glasses and gasification slags obtained from commercial units. The experimental viscosity curves were then compared to the empirical curves to determine how well the empirical curves could predict high titanium slag rheology under reducing conditions.

EXPERIMENTAL

Set Up: A 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, all composed of high density alumina, are 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_2 was passed over the sample at a flow rate of 300 cc/min. The gas mixture entered from the bottom of the furnace and exited through the top. The viscometer was calibrated with a National Bureau of Standard (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 composed of low density alumina to minimize conductive heat loss from the sample. The CO/CO_2 sweep gas is turned on, and the furnace is heated to 1480°C. When the furnace reaches 1480°C, a few grams of pelletized ash are fed from the top. This feeding process is slow enough to allow the pellets to completely melt and degas before the next feeding to prevent the slag from boiling over the sides of the crucible. 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. This method allows for the viscometer to be 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 phase analysis was conducted by X-Ray Diffraction (XRD).

During the viscosity measurements, 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^{-1} . The resulting shear rate-shear stress curve is that of a newtonian fluid at high temperatures and characteristic of a non-newtonian fluid at low temperatures. For the viscosity-temperature plot, the viscosity at the highest shear rate was used. Temperature calibration of the equipment was conducted as reported in Oh, et al¹.

Materials: Six synthetic glasses and two coal slags were used in the test program. The synthetic glasses consisted of +99.0 percent pure oxide components as listed in Table 1a. Composition 1 was formulated to match the chemical composition of the ash for a potential plastic feedstock. For Compositions 2 and 3, approximately 10% and 27.5% TiO_2 were added, respectively, to the base case. Barium and magnesium oxides were eliminated from Compositions 4 and 5, and the amounts of calcium and silica were changed while the TiO_2 was held constant. Composition 6 was similar to Composition 3, but without barium oxide being added to the mix.

The coal slags used in the test program were; i) SUFCo (Hiawatha seam, high volatile C bituminous rank) from a commercial plant, and ii) Pittsburgh #8, a bituminous coal, gasified in a pilot unit. The samples were washed and screened to remove most of the carbon. Titanium dioxide was then added at 20% of the slag weight. The chemical composition of the SUFCo slag used in this study contained more calcia, and less silica than previous SUFCo slags that have been used for the calibration runs. For reference purposes, both SUFCo slag viscosities are plotted together.

RESULTS

Final Slag Composition: Both the alumina crucible and bob partially dissolved into the slag and raised the concentration of alumina. Table 1b gives the final composition of the slag, and these values were the ones used in the empirical models. Approximately three percent alumina was added to the SUFCo slag and one percent to the Pitts. #8, which is consistent with previous runs. The calcium and titanium-rich slags dissolved much more alumina, apparently because of the lower slag viscosities at high temperatures. The final chemistry of Composition 2 was not analyzed for this study, because the crucible was destroyed twice before a reasonable viscosity curve could be generated (a phase analysis study is being conducted on the slags from these failed runs in which the chemical analysis will be reported).

Slag Viscosity: Figure 2a contains the viscosity curves of four synthetic slags, SUFCo slags, and SUFCo slag with titanium as a function of temperature. The only slag that exhibited a classic newtonian behavior was the SUFCo slag. Each of the synthetic slags exhibited non-newtonian behavior to varying degrees in which the slags had very low viscosities until a critical viscosity temperature was reached in which the viscosities increased moderately, and then quickly, which led to the spindle snapping. Based on the curves generated during this study; i) at low calcium and high titanium concentrations, the slag starts out fluid, but reaches a critical viscosity at a high temperature (1370°C), ii) at high calcium and moderate titanium levels, the slag is very fluid at low temperatures (1150°C), and iii) at high calcium and high titanium levels, the slag is fluid even at high temperatures, and then reaches a critical viscosity at intermediate temperatures (1270°C).

Figures 2b and 2c contain the viscosity curves of SUFCo and Pitts. #8 slags. Both slags exhibit glassy (newtonian) slag behavior. The result of adding titanium to the SUFCo slag is consistent with the corresponding synthetic slag in that the titanium lowered the viscosity. A critical viscosity may have begun at 1150°C , but the run automatically terminated. For the high iron, Pitts. #8 slag, the addition of titanium appears to have no effect on the viscosity. As a point of reference, the Pitts.#8 slag used in this study is newtonian in behavior compared to the Pitts. #8 generated in our original study which had a dramatic viscosity rise at the critical temperature.

Crystalline Phase Formation: The furnace was turned off at 1190°C and the slags were rapidly cooled by the CO/CO_2 gas mix. After cooling, the crystalline phases and glasses in the slags were examined by SEM. The phases identified were TiO_2 (rutile) and $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite). Both phases were physically aligned with one another. All samples were sent to a university for further analysis and will be reported on at a later date.

DISCUSSION

None of the slags exhibited sharp increase in viscosity at their normal critical viscosity temperature as seen in some previous tests. Therefore, the chemical compositions of the final slags were used in the various models to determine how well the models correlated with the experimental data. Based on the limitations of the models as shown in Table 2, the Watt-Fereday model most closely matches the test conditions.

The actual viscosity of each slag was plotted against the four models. Based on these plots, the Urbain model most closely matches the slag viscosity for the calcium-rich slags, and all of the titanium-rich slags. The only slag samples that the Urbain model did not predict well were the high iron, Pitts. #8 and the intermediate calcium, titanium-rich slag (none of the models were in agreement with this composition).

Even though the Urbain model most closely matches the data, at high titanium concentrations the model predicts higher viscosities than the test run data. The most likely cause for the discrepancy would be the formation of a calcium-titanium-silicate glass phase that has; i) a lower melting point than the calcium-aluminosilicate glass, and ii) a flatter liquidus within its phase boundaries than anorthite. The large crystalline phases that formed during cooldown appear to have little effect on the viscosity as indicated by their orientation to the flow direction within the slag as it spun around the bob.

The Watt-Fereday and Si Ratio model gave the best fit for the high iron slag. Again, based on the compositional limit in Table 2, the Watt-Fereday model contains the most elements within the boundary conditions. In previous runs with Pitts. #8, hercynitic spinels came out of solution rapidly creating a critical viscosity. The difference between the Pitts. #8 used during this test and that used in the prior work was; i) the presence of more iron, and ii) the iron was more likely to be in the +2 valence state (the slag was reduced in the gasifier, while the Pitts. #8 ash used in the first study may not have fully reduced during testing).

The lack of change in viscosity of the Pitts. #8 slag when titanium was added was unexpected. The glass phase should be of fayalite composition which has a low melting point. In previous tests, hercynitic spinels crystallized out of solution, and one would suspect that with the added TiO_2 , $FeTiO_3$ (ilmenite) which was present would crystallize out of solution near 1300° C and affect the viscosity more noticeably. The combined presence of $FeAl_2O_4$ and $FeTiO_3$ should abruptly raise the slag viscosity which was not seen. Several additional runs, along with phase prediction will be done in the future.

CONCLUSIONS

The slag viscosity data for calcium and titanium-rich feeds are consistent with previous studies in that; i) titanium will lower the melting point of a calcium aluminosilicate glass for TiO_2 up to 27.5%, and ii) the higher the calcium concentration, the more fluid the glass will be with or without titanium, for CaO contents up to 30%. The most consistent model for the calcium-titanium aluminosilicate system under reducing conditions is the Urbain Model. For higher iron slags, the Watt-Fereday Model appears to be a better system for predicting viscosity. However, a high iron slag will have a greater likelihood of nucleating a high melting spinel or ilmenite phase, causing a critical viscosity to develop as iron is rapidly withdrawn from the glass phase.

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TABLE 1A - CHEMICAL ANALYSES (ICAP) - STARTING MATERIAL

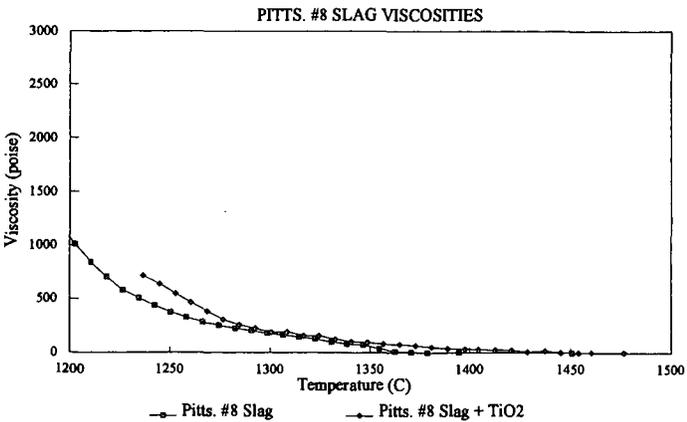
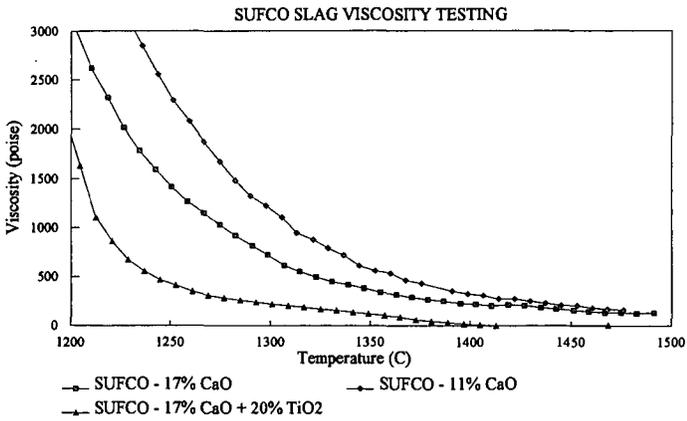
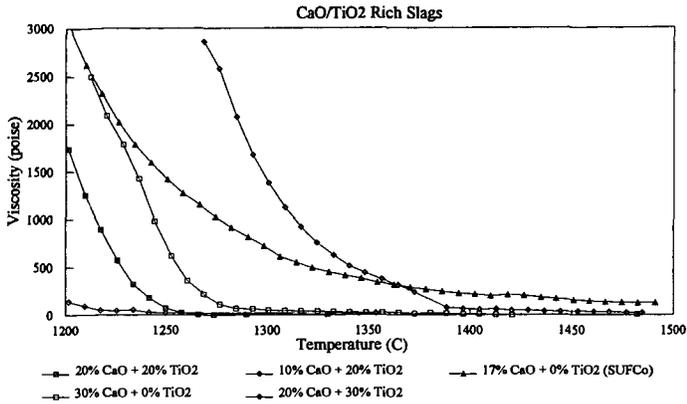
	SUFCo	Pitt. 8	Run1	Run2	Run3	Run4	Run5	Run6
SiO2	62.7	44.2	42.1	37	30.5	50	40	30
Al2O3	11.9	23.7	14.9	13.5	11	15	15	11
CeO	11.5	3.5	26.5	23.8	19.3	10	20	19.3
TiO2	1.1	1.1	0	10.8	27.4	20	20	27.3
Fe2O3	6.2	22.3	9.4	8.4	6.6	5	5	6.8
MgO	2.3	1	3.8	3.2	2.8	0	0	2.8
Na2O	2.6	1.7	0	0	0	0	0	0
BaO	0	0	3.25	2.9	2.4	0	0	0

TABLE 1B - CHEMICAL ANALYSES (ICAP) - END MATERIAL

	SUFCo + TiO2	Pitt. 8 + TiO2	Run1	Run3	Run4	Run5	Run6	Run6b
SiO2	53.4	33.3	40.5	27.1	46.7	40.4	29.7	30.1
Al2O3	15	24.6	21.2	21.4	18.5	15.8	17.1	15.5
CeO	9.6	2.7	20.4	14.8	8.1	16.8	15.8	16.1
TiO2	13	20	0	24.9	20.8	20.8	26.7	27.5
Fe2O3	5.4	18.8	9.3	8.1	5.9	5.4	6.8	6.8
MgO	1.9	0.8	3.4	2.4	0.2	0.2	2.8	1.9
Na2O	2.3	1.4	0	0	0	0	0	0
BaO	0	0	2.3	1.8	0	0	0	0

TABLE 2 LIMITATIONS OF MODELS

Oxides	Normalized		Riboud	Urban	W-F	SiRatio
	Wt. %	Wt %				
SiO2	40.4	40.8	34-56	43-73	30-60	30-59
Al2O3	15.8	15.8	0-12	8-14	15-35	15-30
FeO	5.3	5.4	8-46	2-28	3-30	5-31
MgO	0.2	0.2	8-46	0-7	1-10	1-15
CeO	16.8	16.8	8-46	1-9	2-30	0-30
Na2O	0	0.0	0-22	0-4	0	0
K2O	0	0.0	0-22	0-5	0	0
TiO2	20.8	21.0	0	0	0	0
P2O5	0	0.0	0	0	0	0
H2O	0	0.0	0	0-0.3	0	0
ZrO2	0	0.0	0	0	0	0
B2O3	0	0.0	0	0	0	0
CaF2	0	0.0	0-16	0	0	0



Figures 2a-c. Slag viscosity measurements of various slags.