

VISCOSITY OF SYNTHETIC COAL ASH SLAGS

Karl S. Vorres and Sherman Greenberg†

Chemistry Division, Building 211
†Materials Science and Technology Division, Building 212
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

INTRODUCTION

Coal used for energy conversion contains a considerable amount of mineral matter. During the conversion process the mineral matter is heated, and in the higher temperature reactors is converted to a molten material which flows from the reactor at a rate dependent on the viscosity of the slag. In studies of coal slags obtained from electric utility boilers (1,2,3) this behavior has been studied and correlations have been determined between the viscosity of the slag and the chemical composition. These studies have been carried out in a range of gaseous environments typical of the combustion furnace with a range of oxygen concentrations from almost zero to 15%.

The purposes of this study included a determination of the viscosity behavior of synthetic slags over a range of compositions and temperatures characteristic of slagging gasifier operation. The compositions were chosen to be broadly representative of a range of coals from both the eastern and western U.S. The temperatures were chosen to be in the range of satisfactory gasifier operation, and within the limits of the experimental equipment. The gaseous environments were selected to have the low oxygen partial pressure (about 10^{-8} to 10^{-9} atm) typical of the slagging gasifier.

The viscosity data were to be used as input for an associated refractory/slag corrosion program. Accordingly, the data obtained for the first few slags were compared with correlations developed by Watt and Fereday (1,2) based on chemical composition and by Hoy, Roberts and Williams (3), using a modified version of the silica ratio. In order to simplify the systems for study, the synthetic slags were limited to the five components: SiO_2 , Al_2O_3 , FeO , CaO and MgO . Since they contained no Na_2O or K_2O , the slag compositions were outside the range of the earlier correlations. If this difference was neglected, then the composition of all but four of the synthetic slags used in this program fell outside the range of the compositions for which the correlations were developed (10% Al_2O_3 or 0% MgO or low silica ratio or high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio) and the correlations did not, in general, represent the data obtained for the synthetic slags.

EXPERIMENTAL

Slag: The viscosities of 21 synthetic slags, covering the range of compositions expected in slags derived from American coals were determined in this

study. The synthetic slags were prepared from reagent grade chemicals. The synthetic slags were mixed with water and pressed into pellets using a pressure of 15000 psig. The pellets had a slightly smaller diameter than that of the containment crucible. The composition of the slags is given in Table 1.

Viscometer: The apparatus and technique have been described in detail (4). Essentially a Brookfield Rheolog(TM) was used to replace the sample head in the rotating cylinder slag corrosion apparatus used in slag/refractory corrosion studies at ANL (5). Appropriate seals and ceramic structural components permit maintenance of the desired low oxygen activity within the measuring chamber. The viscosity measuring "bob" was a cylinder 12.7 mm diameter and 11.1 mm high. For measurement at lower oxygen partial pressures the "bob" and connecting shaft were fabricated of molybdenum; in an air environment the molybdenum was replaced by platinum. The slag was contained in Al2O3 crucibles. The "bob" and measuring system were calibrated at room temperature using a series of NBS oils ranging from 10 to 600 poise.

Procedure: Viscosity measurements were usually made in a decreasing temperature mode at 50 C. intervals after the slag sample had been slowly heated to the desired temperature, typically about 1400-1550 C. The slag was kept at each temperature long enough to demonstrate constant viscosity (about 30-60 minutes). In one case, slag 12, measurements were also made in an increasing temperature mode to determine if there were hysteresis effects. None were observed in this slag and other work confirmed this (4). Measurements made in other laboratories with other slags have shown hysteresis (6). The desired oxygen partial pressure was maintained by flowing H₂-CO₂-N₂ (or A) mixtures of the required composition through the interior of the measuring chamber throughout the experiment. The variation of oxygen partial pressure with gas composition and temperature was calculated using a NASA-developed code (4).

RESULTS AND DISCUSSION

The data obtained were plotted as viscosity versus temperature for the different materials and displayed the expected exponential increase in viscosity as the temperature decreased. In most of the runs a characteristic sudden increase in viscosity was noted, as in some related studies (1,3). Some typical results are shown and compared with the Watt-Fereday and modified silica ratio projections, assuming a liquid phase, in Figures 1 and 2, (slags 1 & 12).

To understand the Newtonian characteristics of the slags, plots of logarithm of viscosity versus temperature were made. These indicated straight lines or two line segments. For runs with a sudden increase in viscosity at lower temperatures, two segments were observed. Shear rates were not varied and the various types of non-Newtonian behavior were not explored. The observed straight lines are consistent with Newtonian behavior.

Arrhenius plots were then made. These plots typically involve the logarithm of a rate constant and the reciprocal of the absolute temperature. Viscosity is not a rate parameter, but is defined as the shear stress divided by the shear rate. The reciprocal of the viscosity is the shear rate per unit shear stress and was used in the plots. A typical example is shown in Figure 3. Slag 1 shows a typical high temperature low activation energy regime with a transition to a high activation energy, low temperature regime. This behavior was noted in most of the

runs. The other behavior was, as in the case of slag 12, a single straight line covering the range of the data. The slopes and activation energies for runs without the transition tended to be intermediate in the range of the values for runs with the transition.

In order to compare the viscosity behavior of the different compositions for the higher temperature regime and the slags with no transitions, separate plots superimposing the sample series with a constant weight % SiO₂ were made and are shown in Figures 4,5 and 6. Note the vertical change in scale in Figure 6. The solid portion of the lines represents the actual range of data. The dashed part of the lines was added to facilitate visual comparison. Examination of the plots shows two general tendencies. The reciprocal viscosities or fluidities tend to increase for series with lesser amounts of SiO₂ in them. Although the envelopes of data are broad, this observation can be made. Additionally, for a given series with a fixed weight % SiO₂, the fluidities are greater for the lower amounts of Al₂O₃.

A similar study of the lower temperature regime will be made later.

Activation energies and the temperature range of data are given in Table 2. Initial statistical analyses have not shown a strong correlation of activation energies with any of the slag constituents.

A wide range of activation energies with very high values was obtained for the lower temperature regime. The transition from the higher to the lower temperature regime generally occurred in the 1300-1400 C range. In order to interpret the data the ternary equilibrium phase diagrams for the systems SiO₂-Al₂O₃-MO were examined where MO is either CaO, FeO, or MgO. The mole fractions of each of the constituents were calculated as also shown in Table 2, and the ternary diagram corresponding to the major base in the group CaO, FeO or MgO was selected. Usually a ternary eutectic was found in the temperature region which would be expected for a system most closely corresponding to the sample composition. This eutectic temperature was close to the observed transition temperatures in the viscosity data. Many of the highest temperatures used were significantly below those associated with the appearance of a solid phase from the melt. This solid phase could have been present through the entire series of measurements on the slag.

CONCLUSIONS

A series of 21 synthetic coal ash slags were studied. It was observed that: (1) Plots of the logarithm of viscosity versus temperature showed one or two straight line segments, indicating Newtonian behavior in the temperature range studied. (2) Plots of the logarithm of the reciprocal of viscosity versus reciprocal of absolute temperature also showed one or two straight line segments, indicating one or two mechanisms were operative over the temperature range. (3) For three series, varying in SiO₂ content, those with the greatest SiO₂ content had the highest viscosities. (4) Within a series of given SiO₂ content, those members with the highest Al₂O₃ content had the highest viscosity. (5) For slags exhibiting a transition in behavior, the transition temperature could usually be associated with a ternary eutectic temperature in the phase equilibrium diagram for the most closely related ternary system. (6) Many of the slags probably had a

solid phase precipitating from the liquid phase during the cooling period before the transition temperature.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the U. S. Department of Energy. KSV acknowledges support from the Chemical Sciences Division of the Office of Basic Energy Sciences, while SG acknowledges support from the Surface Gasification Materials Program.

REFERENCES

1. J. D. Watt and F. Fereday, "The Flow Properties of the Slags Formed from the Ashes of British Coals. Part I. Viscosity of Homogeneous Liquid Slags in Relation to Slag Composition", J. Inst. Fuel 42, 101 (1969).
2. J. D. Watt, "The Flow Properties of Slags Formed from the Ashes of British Coals. Part 2. The Crystallizing Behavior of the Slags", J. Inst. Fuel 42, 131 (1969).
3. H. R. Hoy, A. G. Roberts, and D. M. Williams, "Behavior of Mineral Matter in Slagging Gasification Processes", IGE Journal 5, 444 (1965).
4. J. Chen, S. Greenberg, and R. Poeppel, "The Viscosity of Coal Slags as a Function of Composition, Temperature and Oxygen Partial Pressure", ANL/FE-83-30 (in press).
5. S. Greenberg, R. Poeppel et al, "The Corrosion of Ceramic Refractories in Synthetic Coal Slags Using the Rotating Cylinder Technique: An Interim Report", ANL/FE-83-31 (in press).
6. R. C. Streeter, E. K. Diehl and H. H. Schobert, "Measurement and Prediction of Low-Rank Coal Viscosity", Preprints Am. Chem. Soc. Div. Fuel Chem. 28(4) 174 (1983).

TABLE 1 SLAG COMPOSITIONS

COMPOSITION	NO.						
	1	2	3	4	5	6	7
SiO ₂	50	50	50	50	50	50	50
CaO	5	5	5	5	5	5	5
Al ₂ O ₃	10	10	20	20	20	30	30
FeO	15	25	25	15	5	15	5
MgO	20	10	0	10	20	0	10

COMPOSITION	NO.						
	8	9	10	11	12	13	14
SiO ₂	40	40	40	40	40	40	40
CaO	15	15	15	15	15	15	15
Al ₂ O ₃	10	10	20	20	20	30	30
FeO	15	25	25	15	5	15	5
MgO	20	10	0	10	20	0	10

COMPOSITION	NO.						
	15	16	17	18	19	20	21
SiO ₂	30	30	30	30	30	30	30
CaO	25	25	25	25	25	25	25
Al ₂ O ₃	10	10	20	20	20	30	30
FeO	15	25	25	15	5	15	5
MgO	20	10	0	10	20	0	10

Table 2. Activation Energies, Range of Temperatures and Mole Fractions

Slag #	Ea	Temperature Range	Mole Fractions				
			SiO ₂	Al ₂ O ₃	CaO	FeO	MgO
1	43.9	1440-1332	.483	.057	.052	.121	.288
2	44.2	1460-1314	.515	.061	.055	.215	.154
3	42.0	1456-1350	.568	.134	.061	.237	.000
4	40.1	1513-1337	.529	.125	.057	.133	.158
5	60.2	1462-1312	.495	.117	.053	.041	.295
6	366	1550-1500	.584	.209	.063	.147	.000
7	65.2	1515-1415	.543	.192	.058	.045	.162
8	77.6	1353-1192	.384	.056	.154	.120	.286
9	13.1	1455-1297	.409	.060	.164	.214	.152
10	55.5	1454-1335	.451	.133	.181	.235	.000
11	37.6	1439-1310	.420	.124	.169	.132	.156
12	103	1436-1262	.393	.116	.158	.041	.293
13	36.9	1535-1447	.464	.205	.186	.145	.000
14	50.8	1484-1401	.431	.190	.173	.045	.161
15	104	1434-1339	.286	.056	.255	.119	.284
16	77.6	1390-1265	.272	.060	.272	.212	.151
17	29.5	1451-1299	.335	.132	.299	.234	.000
18	106	1448-1377	.313	.123	.279	.131	.155
19	20.0	1459-1352	.293	.115	.261	.041	.291
20	55.1	1402-1294	.345	.203	.308	.144	.000
21	116	1532-1415	.321	.189	.286	.045	.159

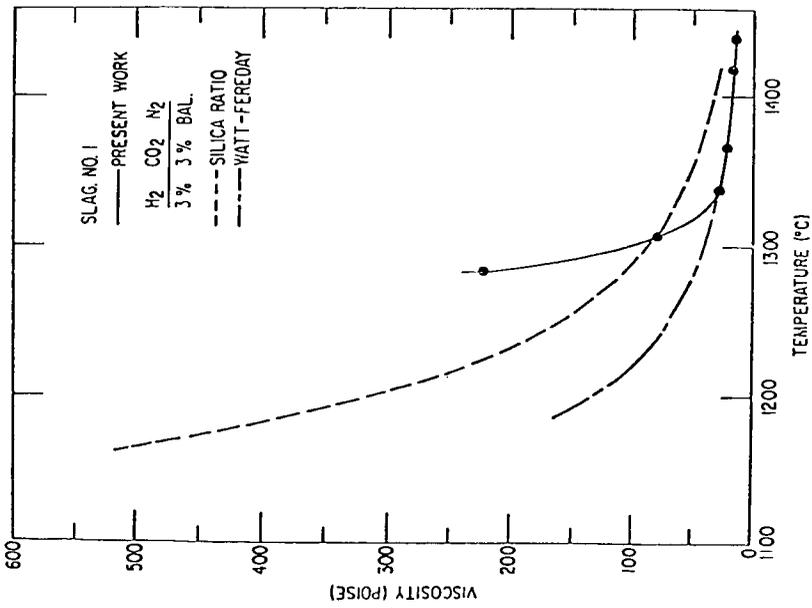


Figure 1. Viscosity of Slag 1

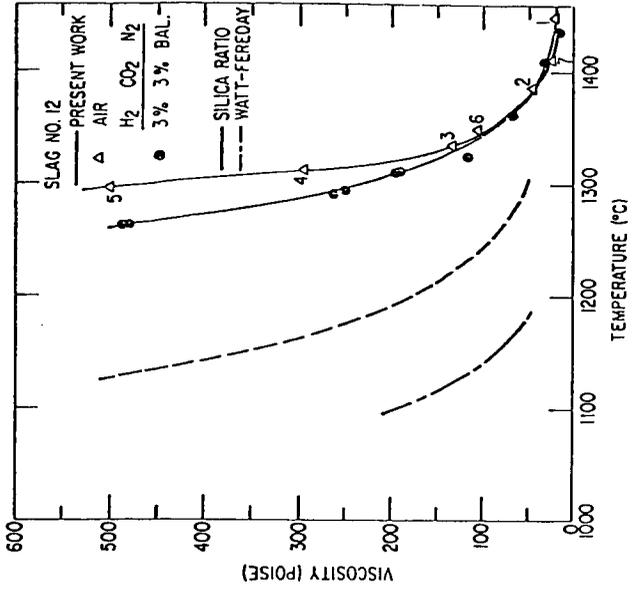


Figure 2. Viscosity of Slag 12

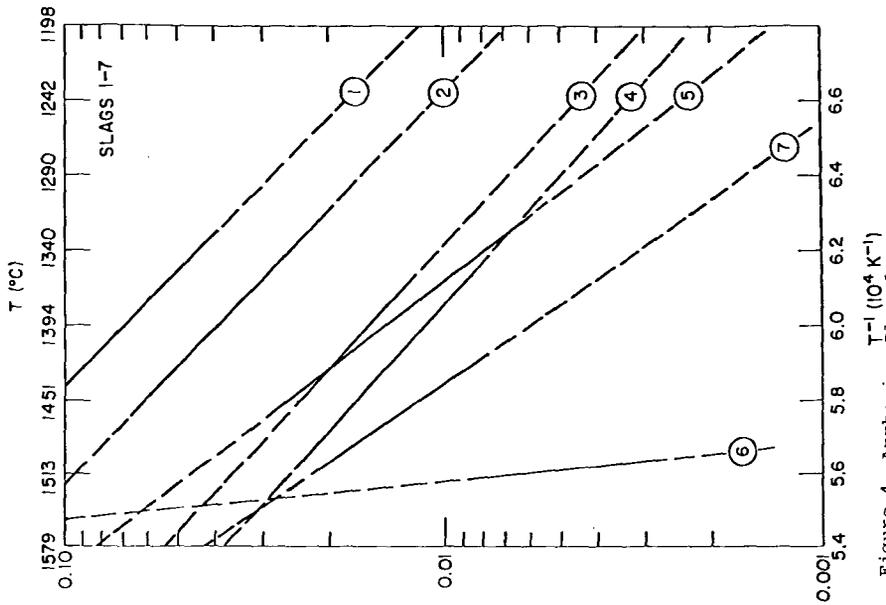


Figure 4. Arrhenius Plot for Slags 1-7

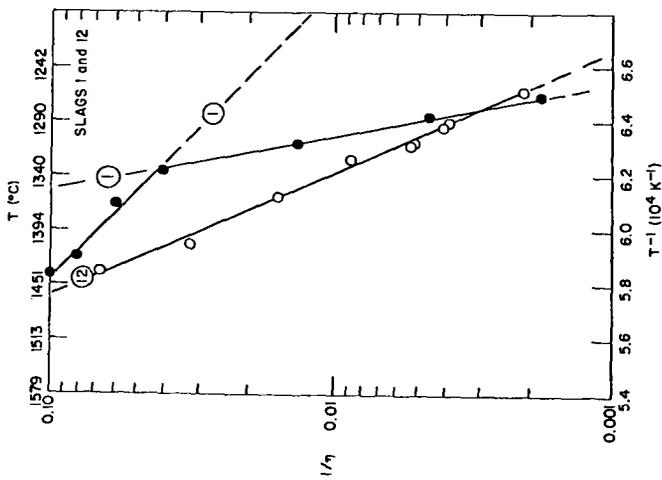
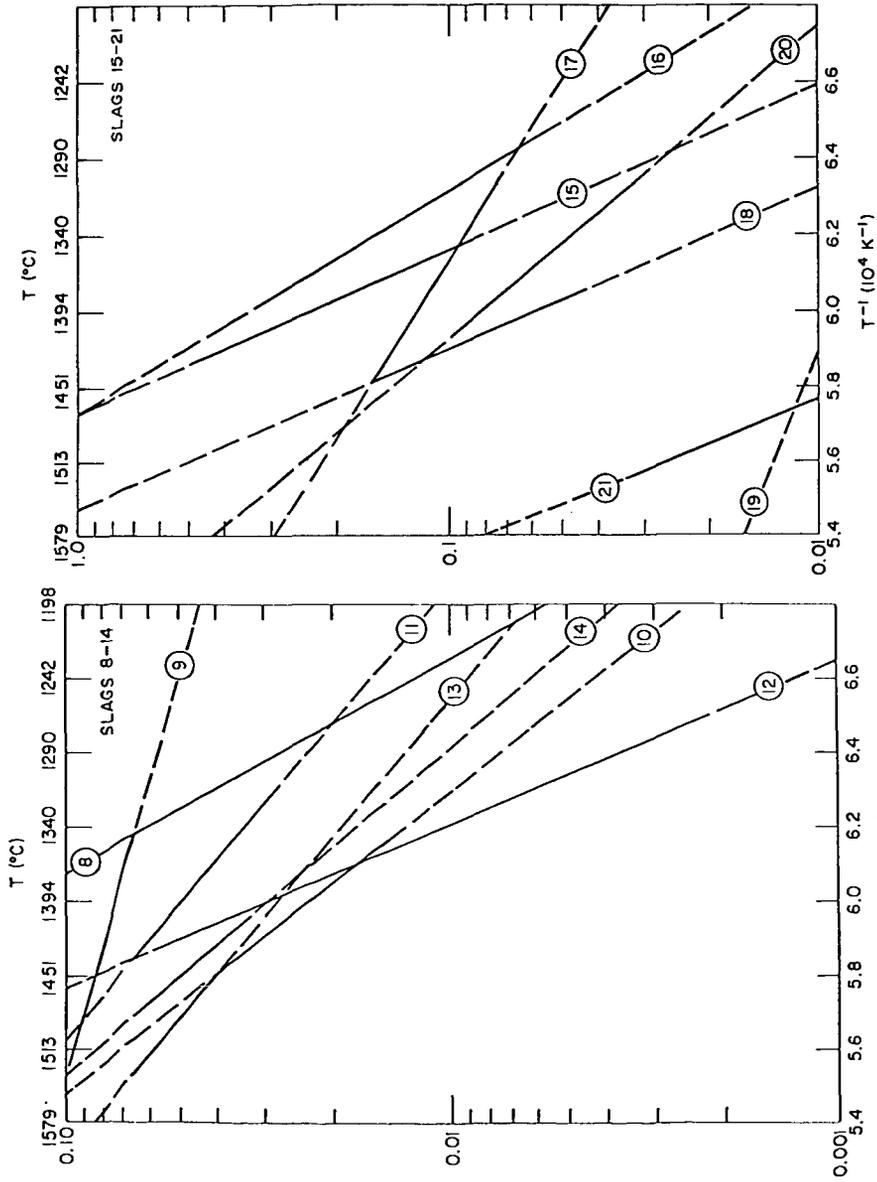


Figure 3. Typical Arrhenius Plots



Arrhenius Plots of Logarithm of Reciprocal Viscosity and Reciprocal Absolute Temperatures for Slags 8-14 and 15-21