SLAG FOAMING IN ENTRAINED FLOW GASIFIERS

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Introduction

In the entrained flow type of gasifiers, the slag viscosity is an important parameter which determines gasification conditions.[1] The slag viscosity has been measured experimentally under a reducing condition, and also estimated by various empirical models.[2-4] Most viscosity measurements were conducted under isothermal conditions or very low cooling rates such as 2 or 3°C/min. These data were used to determine the gasification temperature in the slurry-feed gasifiers to ensure continuous flow and, therefore, continuous removal of slag. In the dry-feed gasifiers which operate at temperatures well above 1500°C, the viscosity is used as a guide for minimizing the refractory wear. The isothermal measurements, however, do not render any information on slag behavior under rapid cooling conditions at the slag tap.

As the cooling rate increases, the viscosity at a given temperature decreases,[5] and the slag remains fluid to quite low temperatures. The low viscosity helps the slag flow out of the slag tap, so it was not a concern until one particular coal, Denisovsky coal, was tested. Denisovsky coal was a Russian sub-bituminous coal and was one of the nine coals tested under the project, "Development of fundamental Technologies for the IGCC systems," funded by Korean Ministry of commerce, Industry and Energy.[5] All nine coals were tested in two pilot scale entrained flow gasifiers: a 3-ton/day dry-feed gasifier at the Institute of Advanced Engineering (IAE), Suwon, Korea, and an 1-ton/day slurry-feed gasifier at Korean Institute of Energy Research (KIER), Taejeon, Korea. While the Denisovsky coal slag didn't cause any operational problem at the high temperature of the dry-feed gasifier, slag foaming filled up most volume of the slurry-feed gasifier vessel, resulting a major repair of the unit.

The cause of foaming was investigated in the laboratory. The slag viscosity was measured at two cooling rates, 2 and 10°C/min, and the cooled slag was examined using (a) Scanning Electron Microscope (SEM).

Experimental

Slag sample: The slag produced from the IAE dry-feed gasifier was used. The composition of the slag is shown in Table 1. The Denisovsky slag contains high concentrations of SiO_2 and Al_2O_3, and low concentration of CaO. The numbers in Table 1 were normalized to give 100, excluding refractory components such as Cr_2O_3 and ZrO. The concentration of refractory components varied widely from sample to sample. The average concentration of refractory components was 3-4%, but some contains over 10% of Cr_2O_3.

Table 1. Normalized Composition of Denisovsky Coal Slag

Al_2O_3	SiO_2	Fe_2O_3	CaO	MnO	TiO_2	MgO	K_2O	Na_2O	P_2O_5
30.5	49.3	9.13	5.63	0.19	0.99	1.70	1.68	0.53	0.44

Viscometer: Brookfield HB-DVIII viscometer with Searle type coaxial cylindrical cell was used in viscosity measurements.[6] The cell(stationary crucible and the rotor) was made of high density alumina and was placed in a high temperature furnace with the maximum attainable temperature of 1600°C. In order to simulate a reducing atmosphere, 80/20 (volume %) mix of CO_2/CO was injected from the bottom of the furnace at 1000cm^3/min. Approximately 70g of slag samples were broken into the sizes less than 2mm and slowly fed to the crucible at 1550°C. When all the slag was fed and the rotor was assembled, the temperature of the furnace was lowered at the rate of 2 or 10°C/min. The viscosity was measured every 30s at the shear rate of 10 rpm, until the torque on the rotor reached the 90% of the viscometer limit. Then, the rotor was removed from the molten slag and the whole assembly was allowed to cool down naturally. The cooled slag was cut as needed and examined using a SEM (Hitachi model).

Results and Discussion

Figure 1 shows the viscosity of Denisovsky coal slag as a function of temperature at two cooling rates. The viscosity was typical of a glassy slag at both cooling rates, and, as expected, shows lower values at 10°C/min. Under 2°C/min cooling rate, the maximum viscosity measured was about 5000 poise at 1380°C, while at 10°C/min, was 4000 poise at 1350°C. Measurements at a higher cooling rate were not possible due to the large mass of the cell and slag employed, and also due to excessive swelling, as discussed below. Once the hot slag boils over the crucible, it damages the furnace seriously.

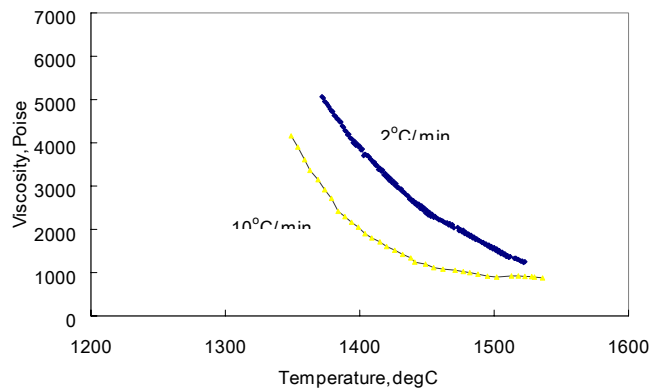
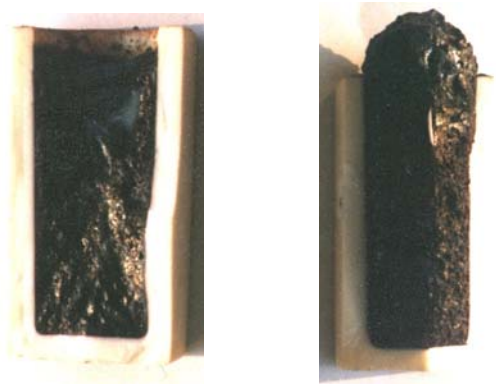


Figure 1. Viscosity of Denisovsky coal slag as a function of temperature at two cooling rates.

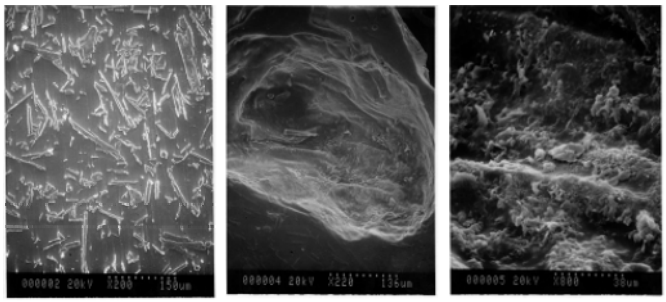


(a) After 2℃/min Cooling (b) After 10℃/min Cooling

Figure 2. Photographs of Denisovsky coal slag after viscosity measurements.

Figure 2 shows the shape of Denisovsky coal slag after viscosity measurements. At 2°C/min cooling, the slag remained inside the crucible, but filled the space which had been occupied by the rotor. The slag contained large number of small spherical pores though out the sample. At 10°C/min, the slag shows excess swelling. The slag not only filled out the rotor space, but also expanded above the crucible. The portion extruded above the crucible had rusty color coating and relatively high strength. The hardness decreased towards the bottom of crucible, becoming very brittle to the point that it could be crushed by hand. Many big spherical pores were observed at the bottom of crucible. Excess swelling or foaming of the slag after viscosity measurements was not observed in any other coal slags tested.

The SEM micrographs of the extruded top portion of the slag cooled at 10°C/min are shown in Figure 3. The overall area (Figure 3(a)) shows glassy background with needle-shape crystalline phases. The analysis by SEM/EDX identified these crystals as Al-Cr-oxide, a phase found in the refractory of the IAE gasifier. SEM/EDX composition analysis of a pore (Figures 3.b and 3.c) revealed that the pore had higher concentration of Fe than the glassy matrix, and the Fe concentration decreased towards the edge of the pore.



(a) Glassy Matrix (b) Pore (c) Inside of Pore

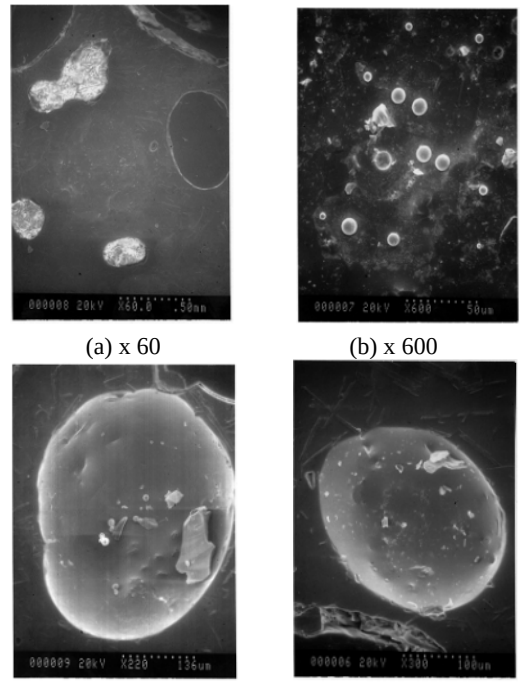
Figure 3. SEM micrographs from the top of Denisovsky coal slag cooled at 10°C/min.

The SEM micrographs of the bottom part of the slag are shown in Figure 4. The large spherical pores at the bottom have smooth, clear boundary which indicates their origin as gas bubbles in molten state. Figure 4(b) is the center area of Figure 4(a), magnified by 10 times, and shows the glassy matrix with Al-Cr-oxides and spherical droplets with white boundary. The SEM/EDX revealed that the droplets were made of metallic Fe. Metallic Fe droplets were also found in the large pores shown in Figure 4(c) and (d). Therefore, one can conclude that the pores were from O_2 gas bubbles which were released from Fe-oxides as they were reduced to Fe in a reducing gas atmosphere.

The SEM micrographs of the slag cooled at 2°C/min were similar to those in Figure 3. The top was also coated with the hard rusty red layer. The slag contained a high concentration of refractory components. Although the pores were smaller in size and number than those in 10°C/min slag, they also contained metallic iron inside.

The compositions of the top, middle, and bottom portion of 10°C/min slag cooled at 10°C/min, and one sample from 2°C/min slag were determined by XRF analysis. The compositions of 4 samples were very close to those shown in Table 1, confirming that there was no difference in composition between the hard top portion and porous bottom of the 10°C/min cooled slag, and also between the slags from two cooling rates.

The difference in pore size was resulted from the different actual cooling rates. When the cell assembly was allowed to cool down naturally after viscosity measurements, the cooling rate of the extruded portion of the slag is expected to be much faster than that of the bottom. The fast quenching and subsequent solidification of the slag inhibited the reduction of iron oxides and growth of bubbles, while, at the bottom, slow cooling allowed bubbles to expand to larger sizes.



(a) x 60 (b) x 600

(c) Pore at × 220 (d) Pore at ×300

Figure 4. SEM micrographs from the top of Denisovsky coal slag cooled at 10°C/min.

The difference in the extent of swelling of the slag samples from two cooling rates can be explained by the viscosity. When the reduction of iron oxides started, the oxygen bubbles grew more readily in the slag matrix with the lower viscosity.

Conclusions

Reduction of iron oxides to metallic Fe can cause excessive slag foaming by O_2 gas when it occurs in a relatively low viscous glassy slag. Even in the slag with high isothermal viscosity, the low viscous condition can occur under a rapid cooling condition, such as at the slag tap of the gasifier. The slag foaming by iron oxides reduction can cause a serious damage to gasifiers which operate at temperatures around 1300°C. The swelling tests under rapid cooling in a reducing atmosphere must be performed for glassy slags prior to gasification.

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