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9 AUTHORS, INCLUDING:

Thomas H. Fletcher
Brigham Young University - Provo Main Cam…

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The Surface Characteristics and Reactivity of Residual Carbon in Coal Gasification Slag[†]

Xianglong Zhao,[†] Cai Zeng,*[,†] Yanyan Mao,[†] Wenhua Li,[†] Yun Peng,[‡] Tao Wang,[‡] Boris Eiteneer,[§] Vladimir Zamansky,[‖] and Thomas Fletcher[⊥]

[†]*Coal Polygeneration Technology Lab and* [‡]*Materials Characterization Lab, GE Global Research, Shanghai, 201203, China,* [§]*Fuel Conversion Laboratory,* [‖]*Energy and Propulsion Technologies, GE Global Research, Irvine, California 92618, USA, and* [⊥]*Brigham Young University, Provo, Utah 84602, USA*

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In a slagging entrained-flow coal gasifier, a large portion of the inorganic matter will form liquid slag that may have strong physical and chemical interactions with char. Understanding the char−slag interaction is important for improving the modeling and design of gasifiers. This paper reports the characteristics of residual carbon in both coarse and fine slag from a typical entrained-flow coal water slurry gasifier. The surface characteristics of slag and residual carbon in slag were evaluated by scanning electron microscopy and energy dispersive X-ray spectroscopy. The reactivity of the residual carbon in slag was compared through thermal gravimetric analysis. It was observed that fine inorganic matters in the slag tend to exist in spherical shape whereas residual carbons tend to stay as loose floccule. A melting test on fine carbon−slag mixture validated that inorganic matters have a tendency to agglomerate into large carbon-free spheres when melting in a carbon powder matrix due to surface tension change. It was also found that the reactivity of the carbon in fine slag was lower than carbon in coarse slag, which implies the formations of the carbon in fine and coarse slag are different.

Introduction

Both China and USA are rich in coal reserves but limited in oil and natural gas, therefore the development of clean coal technologies is of extraordinary importance to these two countries and attracted lots of attention. As the first step of IGCC and coal-to-chemicals technologies, coal gasification plays a key role in producing energy and chemicals. In addition to coal, gasifier feedstocks may also include biomass, petrol coke, refinery residues, wastes, etc.[1] This is why gasification technologies have grown so fast in the past 20 years.

Among various gasification technologies, entrained-flow gasification has become one of the most important technologies due to its high efficiency and friendly environment effects.[2] In an entrained-flow gasifier, the inorganic matter in coal usually melts, forming liquid slag, and flows down along the gasifier refractory wall. During its residence time in the gasifier, the molten slag will have complex physical and chemical interactions with char, leading to impact on overall carbon conversion efficiency.[3]

In an ideal gasification process the inorganic matter goes into slag, while the combustible matter produces syngas. The separation of inorganic matter happens in several steps in a standard coal water slurry entrained-flow gasifier. The first step comprises molten slag flowing down along the gasifier refractory wall. Then molten slag is quenched in a quench tower, and eventually enters a lock hopper for discharge. The slag discharged from the lock hopper is usually referred to as coarse slag. Not all inorganic matter ends up in coarse slag; some of the inorganic matter at fine size is entrained and exits with the syngas. Syngas cleanup, via a process such as a water scrubber, is usually applied to capture the remaining inorganic matter. The solid in the wastewater from scrubber is deposited and filtered to collect as fine slag.[4] In practice, most black water from the quench tower and other units is also mixed with this wastewater stream, contributing to additional inorganic matter in the fine slag. The carbon content in coarse slag and fine slag is different[4] due to the different formation processes. Normally, the fine slag contains considerable amount of carbon, and therefore it may be recycled to be mixed with the feedstock in gasification plants.

The carbon carried in slag, both as found in coarse and fine, is a key factor that influences the carbon conversion of a gasifier. Till now, only very limited open research has been carried out to characterize the carbon in slags from entrained-flow gasifier.[4] Thus, understanding the char−slag interaction is of increasing interest in order to better model and design a gasifier. This study reports some preliminary studies on the characteristics and reactivity of slag samples with high carbon content from entrained-flow gasifiers.

Experimental Section

1. Slag Preparation. Three slag samples, that is, fine slag, coarse slag, and refractory brick slag, collected from an entrained-flow gasifier in China, were studied in this study. The coarse slag was sampled directly from the outlet of the slag lock hopper, and therefore it mostly comes from the molten slag that flowed along the gasifier wall. In a normal operation of

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*To whom correspondence should be addressed. Telephone: +86 21 38772100; E-mail: cai.zeng@ge.com.

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gasifier, the coarse slag contains a very small amount of carbon; but under some special operating conditions, it may contain a lot. To study the properties of carbon in coarse slag, a coarse slag sample with high carbon content was analyzed in this study. The fine slag was sampled from the black water handling unit. It should be noted that some of the fine slags come from the water scrubber, and the rest came from the black water out of the quench tower and slag handling unit. The inorganic matter from the scrubber was from the fly ash that exited the gasifier with the syngas, while the rest of the fine slag mainly came from the melting slag along the wall. The refractory brick slag sample was a refractory brick whose surface was covered by slag in the gasifier. Though the slag had already solidified and therefore was different than the on-spot flowing molten slag in the gasifier, examination of this sample could be beneficial for gaining the insights into char–slag interaction.

2. SEM-EDS. The surface morphology and composition of the as-received slag samples were investigated using a JEOL JSM 6460LV scanning electron microscopy (SEM) equipped with an OXFORD Inca energy dispersive spectroscopy X-ray analyzer (EDS). The EDS uses a semiquantitative analysis model by referencing standard spectra collected by the manufacturer. Algorithms of varying accuracy were used, taking into account of differences between the experimental conditions during the standard and sample spectra. The accuracy of such morphological, geometrical, and elemental composition analysis is highly sample dependent. Elements with atomic number less than that of sodium cannot be quantified accurately. Therefore, the concentrations of light elements in Tables 1–3 are only semiquantitative, although the data value has a precision of 0.1 wt % due to the retestability of the EDS.

3. TGA. The reactivity of the carbon in the slag samples was evaluated using a Mettler-Toledo TGA/SDTA 851e thermal gravimetric analyzer (TGA). To compare the reactivity of the slag sample with that of coal, a coal sample from the same plant was tested. The coal sample and slag samples with weight of about 25 mg were respectively loaded to an alumina crucible and heated in a stream of air at a flow rate of 70 mL/min. A non-isothermal heating program was used to evaluate the reactivity of samples. An indicator to the reactivity is the peak temperature where the rate of weight loss reaches a maximum. However, the peak temperature changed at different heating rates. At higher heating rates, the weight loss rate curves of coal and coarse slag showed broad maxima, and it was therefore hard to determine the peak rate position. Thus, the TGA test was performed at a slow heating rate of 5 °C/min.

Results and Discussion

1. Surface Characteristics of Slag Samples. Typical morphology of the fine slag sample by SEM is shown in Figure 1. The surface of the fine slag sample was covered with small spheres and fine floccules. EDS analysis for the spheres and floccules are shown in Table 1. The floccule contains more carbon than the spheres.

Table 1. EDS Analysis of the Fine Slag Sample

spectrum	C	O	Na	Mg	Al	Si	S	K	Ca	Fe	total
floccule, wt %	54.2	24.8	0.6	0.5	3.5	7.7	0.2	0.5	4.3	3.8	100.0
sphere, wt %	21.7	30.3	4.1	0.8	9.9	17.3		1.4	9.0	5.5	100.0

Table 2. EDS Analysis of the Coarse Slag Sample

spectrum	C	O	Na	Mg	Al	Si	S	K	Ca	Fe	total
floccule, wt %	62.6	18.0	0.6	0.2	2.2	4.3	0.4		4.6	7.1	100.0
sphere 1, wt %	16.2	33.5	1.4	0.9	3.9	10.1			20.6	13.4	100.0
sphere 2, wt %	39.2	16.2	3.8	0.6	10.8	13.2		0.9	4.8	10.6	100.0

Table 3. EDS Analysis of the Refractory Brick Slag Sample

spectrum	C	O	Na	Mg	Al	Si	K	Ca	Fe	Total
rough surface 1, wt %	33.2	32.0	1.2	0.7	8.0	18.7	2.5	2.8	1.0	100.0
rough surface 2, wt %	46.7	29.1	0.8	0.5	5.0	12.9		3.6	1.4	100.0
smooth surface, wt %		47.7	0.9	0.6	11.5	27.1		10.3	1.9	100.0

The morphology of the coarse slag sample is shown in Figure 2. The surface of the coarse slag sample was also covered with spheres and fine floccules, but the particle size distribution is continuous, so it was difficult to distinguish the floccules from spheres. This is different from fine slag, in which the spheres could be clearly distinguished from the floccules. Such morphology difference may attribute to the different formation processes of fine slag and coarse slag. The fine slag mainly came from the water scrubber, thus it most likely carries much soot and ash, and the ash usually appears as spheres. The coarse slag was formed from the melting slag that was cooled and broken in the quench tower. During the sudden quenching process, the inorganic matter may form the broad and continuous particle size distribution. The EDS analysis of the coarse slag sample is shown in Table 2. The floccule in the coarse slag sample also contains high carbon similar to the floccule in the fine slag sample.

It should be noted that the floccules always contain more carbon than spheres. Further experiments were carried out to understand the interaction between carbon and inorganic

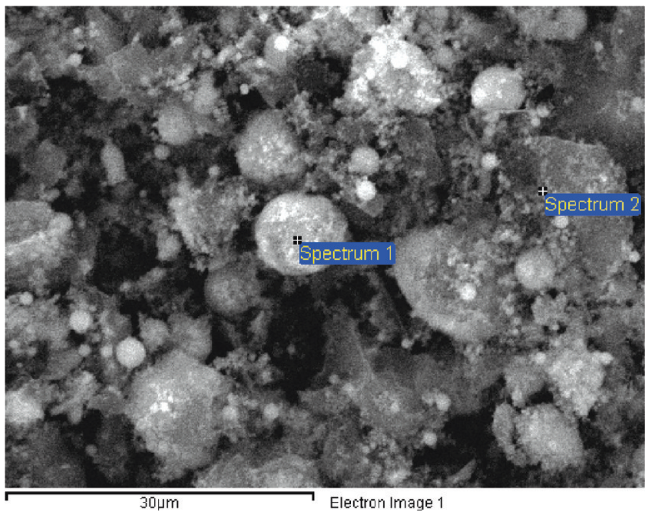

Figure 1. Surface characteristics of the fine slag sample.

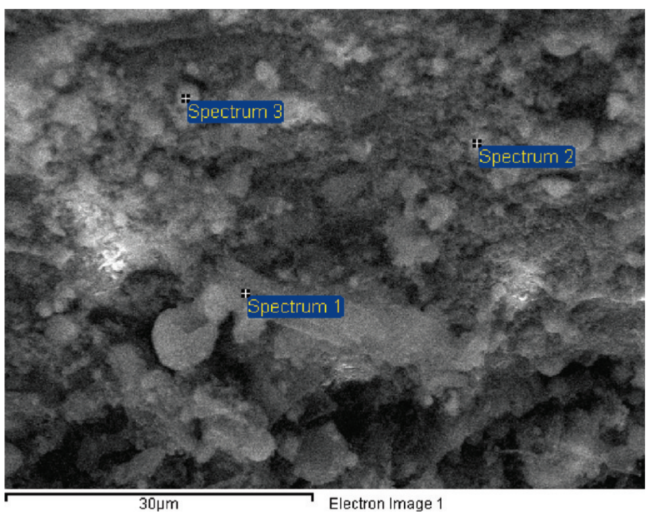

Figure 2. Surface characteristics of the coarse slag sample.

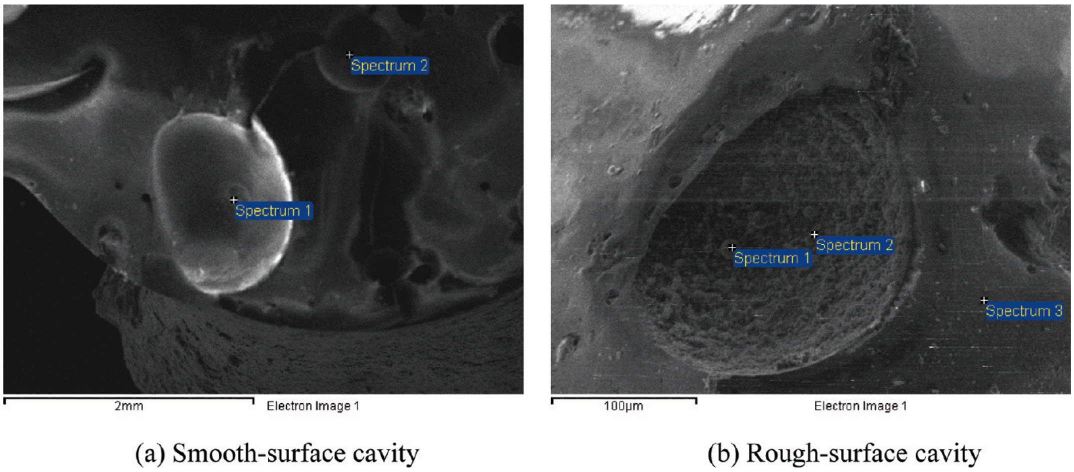

Figure 3. Surface characteristics of the wall slag sample. (a) Smooth-surface cavity and (b) rough-surface cavity.

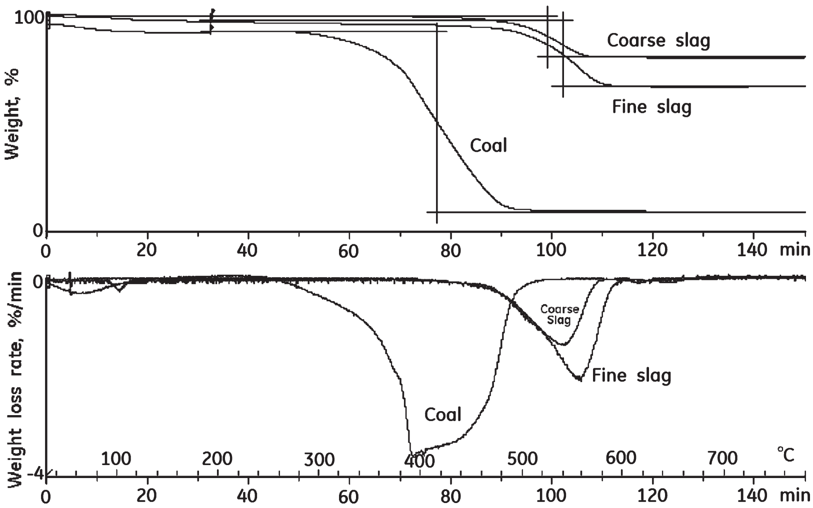

Figure 4. TGA curves for the samples studied.

matter. The carbon-containing slag was ground into powder, and then the powder was loaded into a high-temperature furnace with a temperature up to 1500 °C. This temperature is much higher than the ash fusion temperature of the sample. It was interesting to observe that the carbon-bearing slag does not melt like the carbon-free slag, but many small carbon-free spheres formed inside the pulverized slag after heating. Therefore, it seems that the inorganic matter in the slag melted and tended to fuse at high temperature but the carbon prevents aggregation, which results in the microcosmic melting and fusion of inorganic matter to form small carbon-free spheres. Carbon always remains as floccule morphology during the melting of the inorganic matter and does not incorporate into the formed ash spheres.

The surface morphology of the refractory brick slag is shown in Figure 3. The slag contains two types of cavities on the smooth inorganic surface. Typical smooth-surface cavities are shown in Figure 3a. EDS analysis revealed that these cavities are empty. Typical rough-surface cavities are shown in Figure 3b. EDS revealed that the rough surface contained a lot of carbon, as shown in Table 3. It is supposed that the molten slag will probably capture coal particles at its surface. Some coal particles will react completely if the conditions such as resident time and temperature, etc., are satisfied, and some will react partially, leaving residual carbon on the surface.

2. Reactivity of the Slag Samples. The reactivities of the carbon in slag samples and in coal were compared by the TGA. The time-dependent curves of the weight and weight loss rate are presented in Figure 4. Although it has been dried at 100 °C for 2 h, the coal sample still has a small amount of water, therefore there are weight losses before heating and at low temperature stage. However, the weight loss at low temperature does not affect the measurement of reactivity of samples. The combustible matter contents of the three samples are different, which is why their weight loss curves are different. The combustible matter accounts for ~90 wt % in the coal sample, ~33 wt % in the fine slag sample, and ~18 wt % in the coarse slag sample. The temperature points at which the samples' weights begin to decrease are different for all three curves. It is observed that the coal began losing its weight at a relatively low temperature due to pyrolysis, whereas the slag samples did not begin losing weight until the temperature was high enough to burn the carbon. The reactivities of carbon in fine slag and coarse slag were also different.

Two parameters were selected to represent the reactivity of the carbon in samples,[4] for example, the peak temperature and the burnout temperature. The two temperatures are summarized in Table 4. Both temperatures follow the following order: coal < coarse slag < fine slag. The reactivity of fine slag exhibits the lowest values of these parameters.

Table 4. The Reactivity of Residual Coal in Slag

sample	peak temperature, °C	burnout temperature, °C
coal	393	501
fine slag	558	582
coarse slag	544	571

The low reactivity of the fine slag is another evidence that the carbon in the fine slag formed in a different way with that in coarse slag. The fine slag contains the inorganic matter and carbon entrained by syngas, which has a short residence time; whereas the coarse slag contains the chars captured by flowing molten slag, which has a much longer residence time. However, the carbon in the coarse slag gives a higher reactivity despite of its longer residence time in gasifier. Therefore it implies that the carbon in the fine slag must be in a more stable form such as soot, which could be formed in the high temperature syngas and is very difficult to be burned out. The carbon in coarse slag should be unburnt char captured by the flowing slag, and having reactivity lower than that of coal but higher than that in fine slag.

Conclusions

The surface characteristics and reactivity of residual carbon in slag samples were investigated in this paper. It was found that the inorganic matter in the slag tends to form spheres while the residual carbon tended to stay as floccule morphology. A melting test validated that the inorganic matter has a tendency to agglomerate to form carbon-free balls. It was observed that the reactivity of the carbon in fine slag was lower than that in coarse slag, which indicates that the fine slag may contain soot.