Analysis of the Combustion Behavior of Iron in Coal Combustion by In-situ X-ray Spectroscopy

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The chemical states of iron compounds have a significant effect on their stickiness under coal combustion conditions. For example, crystalline magnetite and hematite, the end products of pyrite oxidation, are non-sticky. Several intermediate products are molten, however. These include the sulfide pyrrhotite and its oxy-sulfide derivatives, which may be either molten or solid, depending upon temperature and extent of reaction.

During combustion, iron may also become incorporated into glassy aluminosilicate-derived ash particles. Because glassy particles are often sticky, these particles may also deposit on and adhere to available surfaces. In prior research conducted at PSI, particle stickiness has been shown to be a function of particle viscosity. Thus, knowledge of the precise composition of iron-containing glass particles is an important parameter in determining their viscosity and stickiness. In addition to composition, the oxidation state of iron-containing glasses must also be known. For iron dissolved in glass, the (+2) oxidation state results in a significantly lower viscosity than does the (+3) oxidation state.

To understand and eventually predict the deposition of iron-containing ash particles, it is, therefore, critical that the precise chemical state of iron at the point of encounter with an impaction surface be known. X-ray spectroscopy is one technique useful for determining the chemical speciation of iron. Typically X-ray spectroscopic analysis is conducted on a sample that has been quenched and removed from the combustion process. While this provides valuable insight into the possible states of iron, the possibility of quench induced phase formation cannot be avoided.

In this program, an in-situ X-ray combustion furnace and measurement cell has been constructed by PSI, Univ. of Kentucky, and BNL personnel to permit measurement of the forms of iron and other elements without the need for quenching and sample removal. This permits the state of iron to be measured in deposit samples at elevated temperatures.

Details of the furnace and measurement techniques are given in previous publications.

A series of in-situ combustion runs were made with feeds of; 1) pyrite, 2) Kentucky #9 tailings from a coal cleaning plant with more than 90% ash, and 3) Pittsburgh #8 washed coal. In these runs, the ash composition was measured by X-ray spectroscopy at elevated temperatures as the ash was collected on a probe. In addition, a series of combustion runs were made with the

same furnace off-line with ash samples collected in a sample cup and subsequently analyzed by X-ray spectroscopy and by Mössbauer spectroscopy.

The results of the in-situ runs as analyzed by X-ray spectroscopy are given in Table 1. Not enough samples were collected in these runs to permit Mössbauer analysis. The results of the off-line experiments as analyzed by Mössbauer spectroscopy are given in Table 2. The X-ray spectroscopy data of Pittsburgh #8 ash do not show any dramatic changes with changing combustion conditions. However, third derivatives of the X-ray spectroscopy data exhibit similar composition to those measured by Mössbauer spectroscopy.

Discussion

The retention time in the drop tube furnace for all runs was about 2.5 sec. Typical retention times in utility boilers are around 1-2 sec. Thus, the retention time in these experiments was a bit on the high side. Typical temperatures in the heat exchange system of utility boilers are about 600°C-700°C at the superheater tube surface and are around 400°C to 500°C at the steam generator tube surface. Thus, although the collection surface differs in the experimental system (alumina vs. steel) the collection temperatures are in the right range. In a real utility system, however, the gas temperature (particle temperatures) will be much higher.

Pyrite In-situ Results

Previous work (Huffman, PESC, 1990, 16, 243-251) has indicated that the transformation products formed from pyrite at gas temperatures of 1038-1454°C and residence times of 0.07 to 1.2 sec in a 95% N_2:5% O_2 atmosphere primarily were magnetite as the dominant oxide and pyrrhotite as the dominant sulfide. In these experiments with approximately the same conditions except for residence time hematite was the dominant oxide and pyrrhotite the dominant sulfide. It appears that at residence times in the range of 2.5 sec the magnetite is oxidized to hematite. One notes that the deposits were sticky even in the case where the analysis indicates only hematite. Small amounts of oxysulfides not detected by this analytical technique could have provided the stickiness characteristic.

Kentucky #9 In-situ Tailing Results

Kentucky #9 tailings did show some pyrrhotite, but it was less than 10%. There was not much Fe^{xx} and Fe^{xxx} glass formation though there was a substantial amount of clay in the sample, i.e., pyrite oxidized to Fe-oxides without reacting with the clay to form a glassy phase. Glass is normally found when both the pyrite and the clay is in the coal particle.

As anticipated under the conditions of this experiment, magnetite formed at the lower temperatures and hematite at the higher. At stoichiometric ratios (SR) from 0.6 to 2 the transition from pyrrhotite to magnetite to hematite appears to be more sensitive to furnace temperature increase than to SR, but when the SR is reduced to 0.2, pyrrhotite is preserved. It is somewhat unusual for pyrrhotite to remain essentially unoxidized at a SR as high as 2 but this is probably

due to a low rate of oxidation at the corresponding low temperature. (The maximum gas temperature is approximately 125°C lower than the furnace set point).

Pittsburgh #8 In-situ Results

X-ray spectroscopy analysis was sufficient only to indicate that iron oxide and iron in glass were found under the various operating conditions. Quantitative data were obtained by M`ssbauer analyses of the off-line runs.

Pittsburgh #8 Off-line Results

In general the fraction of the iron in the glassy phase is lower in the low temperature experiments. This trend is consistent with data in the literature (Fuel, Cat. 100, 262-270, 1995) and may be due to the higher coalescence rates between clays and pyrite at high temperatures. The data exhibits a trend of both increasing amounts of ferrous iron in glass and increasing magnetite/hematite ratios with decreasing stoichiometric ratios.

Conclusions

In general the results with the dynamic in-situ combustion furnace and X-ray analysis concur with the literature results using quenched samples.

It is planned to explore a more unique use of in-situ X-ray spectroscopy by observing the molten Fe-O-S phase that is believed to be formed by the exothermic oxidation of pyrrhotite (unobservable in quenched samples) by the use of a static high temperature cell in which an appropriate sample is heated and observed by X-ray spectroscopy in a combustion gas atmosphere with varying oxygen partial pressures.

Table 1
Results of In-situ Experiments

Feed	Furnace Temp. ^{O}C	Probe Temp. ^{O}C	% O_2	S.R.	Ash Composition by X-ray spectroscopy	Stickiness
Pyrite	1300	520	5	2	$Fe_{1-x}S$-Fe_2O_3	High
	1300	560	14	5	Fe_2O_3	High
Ky #9 Tailings	1200	400	20	2	$Fe_{1-x}S$	High
	1300	480	20	1	$Fe_{1-x}S$-Fe_3O_4	High
	1400	500	20	1	Fe_3O_4	High
	1500	650	20	.6	Fe_2O_3	High
	1500	700	5	.2	$Fe_{1-x}S$-Fe_2O_3	High
Pitts #8 Washed	1300	600		.7	Iron oxide/iron in glass	Low
	1300	600		.9	Iron oxide/iron in glass	Low
	1300	600		2.5	Iron oxide/iron in glass	Low
	1400	650		.7	Iron oxide/iron in glass	Low
	1400	650		.9	Iron oxide/iron in glass	Low
	1400	650		1.6	Iron oxide/iron in glass	Low

Table 2
Results of Off-line Experiments

Feed	Furnace Temp.^{O}C	SR	Ash Composition	% Fe	M/H
Pitts #8	1200	1.2	Fe^{xx}/Glass Fe^{xxx}/Glass Fe_2O_3 Fe_3O_4	3 4 56 37	.66
	1200	2	Fe^{xxx}/Glass Fe_2O_3 Fe_3O_4	9 78 13	.16
	1200	10	Fe^{xxx}/Glass Fe_2O_3 Fe_3O_4	7 74 19	.25
	1400	1.2	Fe^{xx}Glass Fe^{xxx}/Glass Fe_2O_3 Fe_3O_4	16 14 31 39	1.25
	1400	10	Fe^{xxx}/Glass Fe_2O_3 Fe_3O_4	10 61 29	.47