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ON

**Slag Characterization and Removal Using Pulse Detonation
for
Coal Gasification**

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The research activities performed for the project in the fourth quarter of 1995, reporting period from October 1, 1995 to December 31, 1995 are Summarized below.

The kick off meeting for the project, after the account was set-up at Prairie View A & M University (PVAMU), was held on November 6, 1995 at the campus of the University of Texas at Arlington (UTA). The meeting was attended by Dr. Ziaul Huque from PVAMU, Dr. Wilson from UTA and Dr. Lou Hunter and Mr. Don Couch from Lockheed Martin Co. Discussion of the meeting concentrated on the plan of action and research activity sequences to finish the project in a timely fashion.

In the meeting it was concluded that the experiments will mainly focus on breaking the bonds within the slag itself using detonation wave. For the experiments, initial suggestion was to build up slag deposit around a representative tube by placing it inside the convection pass of an actual boiler at the Northern States Power Company. But it was later concluded that once the tube is cooled to room condition, the thermal stress will greatly reduce the bonding between the heat transfer surface and the slag. It was concluded that the slag will be attached to the tube using high density epoxy resin. High density epoxy will be used so that they do not diffuse into the slag and strengthen the bonding within the slag. Suggestions on candidate epoxy are provided by MTI lab. MTI also provided PVAMU with different kinds of slags for testing.

Initial Setup Design

Figure 1 shows the schematic of the initial design of the experimental set up. The tube with slag attached will be placed vertically at the exit of the detonation chamber with the help of the clamp and bolts. The purpose is to make the tube with slag and its attachment, a separate unit so that it can be bolted in place when experiments are carried out and removed when not required. After attachment, the tube can be move closer or away from the exit of the detonation chamber. The actual location for each experiment will be determined from the CFD analysis. The tube can also be rotated along its axis in order to study the effect of orientation.

Pulse Detonation Technology Studies

A preliminary study using CFD (performed at Lockheed Martin) shows the development of the blast waves as they exit the detonation tube. A nozzle has been added in the preliminary study to the detonation tube. This study is limited to the effects of a single shot wave. In order to set up the initial flow conditions for the CFD run, a one dimensional algebraic analysis, which includes the solution of the detonation wave and the expansion wave which follows the detonation combustion wave is used as an input into 2-D Navier Stokes CFD solutions. The expansion wave brings to rest the moving

detonation products. In our solutions, there will be several zones of flow between the detonation wave zone and the at-rest zone. The time accurate Navier Stokes will then predict how the blast wave develops as it leaves the end of the detonation tube and strikes the target sample of slag deposited on a section of heat exchanger coated with ash. The following six figures show the wave as it expands into the exhaust nozzle. Currently the tube configurations are being modeled to be included in the CFD analysis. Time dependent pressure, velocity, temperature and surface shears will be calculated.

Figure 2 and Figure 3 shows the normalized pressure distribution. In Figure 2 the blue color in the nozzle indicates the atmospheric pressure. Figure 3 is the normalized pressure condition a few milliseconds after the blast wave expands into the nozzle. Figure 4 and Figure 5 shows the normalized velocity distribution. In Figure 4 again the blue color in the nozzle indicates the ambient velocity. Figure 5 shows the velocity distribution a few milliseconds after the blast wave expands into the nozzle. Figure 6 and Figure 7 shows the normalized temperature. As before in Figure 6 the blue color indicates the ambient temperature. Figure 7 shows the temperature distribution a few milliseconds after the blast wave expands into the nozzle. The experiment work to study the effectiveness of detonation wave in breaking the bonds within slags will consists of 2 HZ detonation impingement and single shot impingement.

Slag Technology Studies

The slag characterization studies were performed by MTI and provided to PVAMU.

Introduction

Micro beam Technologies Incorporated is working with Prairie View to develop and demonstrate a new method to remove deposits from coal-fired utility boilers. MTI is providing background information on fuel properties, ash formation, ash deposition, and ash removal. In addition, MTI is providing deposits collected from a full scale utility boiler. Ash deposits on fireside heat exchange surfaces of power plants significantly decrease plant efficiency and are aggravated by variability in coal quality. Deposit formation is related to coal quality (chemical and physical characteristics of the inorganic material), system operating conditions, and system design (1). Variations in coal quality can significantly influence ash deposition on heat transfer surfaces resulting in decreased plant performance and availability. Deposits in the radiant and convective pass heat transfer surfaces of the boiler require soot blowing and load shedding for removal, both of which decrease plant efficiency and availability. Ash accumulations on heat transfer surfaces require annual or semi-annual shutdowns for cleaning which result in cleaning costs and lost revenues from being off-line. In addition, maintaining slag flow in wet bottom boilers and cyclone-fired boilers can require co-firing of other fuels and outages to remove frozen slag resulting in decreased efficiency and availability.

The deposits sent to Prairie View are from the convective pass of coal fired utility boiler that fires a sub bituminous coal. The boiler type and operating conditions that led to the

formation of the deposit are known as well as the fuel that was fired when the deposit formed. The characteristics of these deposits also represent those found in some advanced power generation systems such as fluidized bed combustion systems including circulating fluidized bed and bubbling bed systems. The deposits used in this initial work are similar in characteristics to those found in systems operating under oxidizing conditions. Deposits produced under reducing environments such as those found in integrated gasification combined cycle systems do not contain the same types of phases and therefore will likely have different properties. There is very little information available on the characteristics of deposits produced in gasification systems.

Background

Coal Characteristics

The ash-forming constituents or inorganic components in coal is highly variable in abundance and have a diverse distribution of associations. The association and abundance of major, minor and trace elements in coal is dependent upon coal rank and depositional environment. The inorganic components in lower rank sub bituminous and lignitic coals are associated with the organic and mineral portions of the coal matrix. The lower rank coals contain high levels of oxygen some of which are in the form of carboxylic acid groups that can act as sites for actions such as ash Ca^{2+} , Mg^{2+} , Na^{+1} , K^{+1} , Sr^{+2} , and Ba^{+2} . Unlike lower ranked coals, the inorganic components associated with bituminous and anthracite are primarily in the form of minerals. The major mineral groups include quartz, clay minerals, pyrite, and carbonates. The mineral grains found in the coal vary in size and association. Some of the minerals are bound or locked within coal particles and others are liberated from the coal particles. The size and association of the mineral grains and abundance and type of organically-associated inorganic elements influence the characteristics of the ash forms produced upon conversion. The abundance and association of minerals in coal has been reviewed and published in *Fundamentals of Coal Combustion for Clean and Efficient Use* (1).

Ash Formation and Deposition Processes

During combustion or gasification the inorganic materials are transformed into ash species that are in the form of gases, liquids, and solids. These intermediates are complex and variable; their characteristics reflect the interactions of the inorganic components in the coal during combustion. Research on ash (fly ash) indicate a bimodal size distribution (1). The sub micron size particles form as a result of condensation of flame-volatilized species upon gas cooling. Flame volatilized species may also condense on the surfaces of larger particles or deposits. The larger particles are sometimes referred to as residual ash, which is largely derived from mineral grains. The composition and size distribution of the larger particles result from the transformations and interactions between discrete mineral grains in higher rank coals.

In lower rank coals the interaction of the organically-associated inorganic elements with mineral grains occurs as well as mineral-mineral interactions. In addition, the low-rank coals that contain high levels of organically-associated calcium and other alkali and alkaline earth elements produce high levels of very small, $< 5\mu\text{m}$, calcium-rich particles. The chemical composition, mineralogy, and size of the ash particles ultimately determine the likelihood of the ash depositing on heat transfer surfaces or causing other operational problems.

The size of the intermediate ash species in the flue-gas stream, boiler design, gas velocity, and temperature determine how the ash particles are transported to heat-transfer surfaces. The ash species are transported to the heat transfer surfaces by several mechanisms based on their size and state. Sub micron particles are transported to the surfaces by diffusion and thermophoresis. Larger particles are transported to the surface by inertial impaction. Ultimately, one has to understand both the size and chemistry of the particles entrained in the bulk gas flow through the boiler in order to understand how ash deposits form.

Although there are many types of ash deposits, the most common deposits can be categorized into two major groups: high-temperature silicate-based deposits, and low-temperature calcium-based deposits. These deposit types form under very different temperatures and from very different ash materials.

Figure 8 illustrates the type of liquid components present in deposits as a function of temperature. At lower temperatures, sulfates dominate, while at higher temperatures, silicates are more prone to cause deposits. In high-temperature fouling, the bonding of particles is due to silicate liquid phases and in low-temperature fouling, the bonding is a result of the formation of sulfates. Condensed sulfur species, principally in the form of CaSO_4 , are stable and form the matrix or bonding material in the low-temperature deposits.

High temperature fouling occurs in regions of the utility boiler where temperatures exceed the stability of the sulfate-bearing phases ($> 1700^\circ\text{F}$). In combustors burning coals that contain high levels of alkali and alkaline earth elements, high-temperature fouling can be a significant problem. Much work has been done on high temperature fouling due to sodium. In most cases, the innermost layers consist primarily of small particles, rich in flame-volatilized species such as sodium and sulfur, which are transported to the surface by vapor phase diffusion and thermophoresis. Larger particles also impact the surface. The initial deposit layers may provide a sticky surface for trapping inertially impacting particles which are not sticky. In addition, the initial layers may provide fluxing materials that will cause larger particles to melt. These particles provide sites for continued deposition to form islands of particles. These initial islands are the precursors of the more massive upstream deposits that form in the secondary superheater and reheater sections of a utility boiler. Coatings also form on the surfaces of entrained ash particles as a result of the condensation and reaction of

Analytical Techniques for Coal, Ash, and Deposit Characterization

The application of new analytical techniques has resulted in data and understandings that are very useful in determining ash behavior in utility boilers. Many of the operational problems encountered during combustion of coal in utility boilers are related to the ash-forming constituents of the coal. These problems include: deposition of heat transfer surfaces; formation of fine particulate that is difficult to collect; and erosion and corrosion of boiler parts. Using traditional methods of analysis, accurate prediction of ash behavior during combustion as a function of coal composition and combustion conditions is not possible. For example, traditional methods use the composition of the coal ash produced under ASTM (American Society for Testing and Materials) ashing conditions as a crude guide to predict the behavior of inorganic constituents of a specific coal during combustion. The ASTM technique is limited in that it can be used to predict only the *average properties* of the ash since all ash-forming components are combined and allowed to interact during the ashing process. However, examination of fly ash shows that many different types of particles are present, each having its own composition and its own melting behavior. The wide variation of fly ash types is related to the wide variability in the abundance and distribution of inorganic constituents in coal.

MTI's analytical techniques much more completely describe the inorganic components and mechanisms that control ash formation and deposition. As a result of these improvements in characterization techniques and our understanding of the critical mechanisms, we can now better predict and minimize ash behavior problems.

The coal's inorganic components (from which the fly ash and ash deposits form) must be quantitatively determined in order to predict and minimize ash deposition. In the case of low-rank coals from the western U.S., the inorganic components include both small mineral particles and elements that are attached to the oxygen in the coal (mainly alkali- and alkaline-earth elements, Na and Ca, that are atomically dispersed in the organic part of the coal). The amounts of the various organically-associated inorganic elements present control the size, chemistry, and melting points of the ash produced as a result of burning the coal in the boiler. In order to determine the precise amounts and types of inorganic constituents in low-rank coals MTI uses two methods: 1) CCSEM (computer-controlled scanning electron microscopy) which tells us the size and chemistry of mineral particles in coal, and 2) chemical fractionation which tells us the amounts, chemistry, and associations of organically associated elements.

A combined CCSEM and chemical fractionation approach can be used to quantify all inorganic constituents in coals. Coal ash chemistries calculated from CCSEM and chemical fractionation analysis correlate with more standard bulk ash chemistry analysis performed by the ASTM procedures.

flame-volatilized species to form a molten or plastic surface. Condensation on surfaces of deposited ash particles can also occur. As a result of the insulating effect of the deposit layer on the tube, the outer layers of the deposit are formed at higher temperatures. The higher temperature causes melting and interaction of the particles to form a liquid phase. Once a liquid phase has formed on the outside of the deposit, it becomes an efficient collector of ash particles, regardless of the individual melting characteristics of the particles.

Low-temperature ash deposition occurs at temperatures in the range of 1000 - 1650 °F. In systems which exhibit low temperature fouling, the sulfate phases dominate the matrix or bonding mechanism between particles. Detailed examination of low-temperature deposits shows high levels of calcium in the deposits. Formation of low-temperature deposits is dependent upon the availability of small calcium oxide particles and the process of sulfation. Low-temperature deposits form when small calcium oxide particles in a deposit undergo sulfation through reaction with sulfur dioxide in the gas stream. This reaction produces calcium sulfate which causes particle-to-particle bonding and fills in the available pore space in the deposits. This pore filling produces very strong, brick-like deposits which are difficult to remove.

Figure 8. Distribution of liquid phases as a function of deposit temperature

Deposit Removability

The primary factors that influence the ability to be removed are the strength of the deposit and the adhesive bond between the ash deposit and the heat transfer surface. The removal of the deposit involves breaking the deposit matrix and/or breaking the bond between the deposit and heat transfer surface. Methods typically used to remove deposits include load reduction and on-line cleaning. Load reduction results in cooling of the deposits to cause the breaking of bonds between the deposit and heat transfer surface because of a differential in the thermal expansion coefficients between the deposit and heat transfer surface. On-line ash deposit cleaning devices are called sootblowers. The blowing medium is either high pressure steam or compressed air. The blowing medium is directed at the deposit through a nozzle. The impacting fluid causes the deposit to crack and be eroded away. The design of the blowers vary depending upon the location in the boiler. The wall blowers are short blowers that extend a short distance into the radiant section of the boiler and are rotated to remove the deposit in a circular pattern around the point of entry into the boiler. Long retractable blowers are required to clean the surface of the tube banks in the convective passes of utility boilers. For extremely difficult to remove deposits water-jet sootblowers have been used. These work well to remove large accumulations of deposits in the furnace. The impact of water is much greater than that of air or steam so it is effective in removing deposits. In addition, the water can quench or cool the deposit resulting in fracture of the deposit and breaking the adhesive bond with the heat transfer surface. The use of sootblowers varies widely due to fuel quality and ranges of operating conditions. Many operators will operate each sootblower every eight hours or once a shift. Some have the blower operation linked to boiler cleanliness monitors so cleaning can be made on demand. Some use visual observations to assist in determining sootblowing cycles. Sootblowing is a significant expense in terms of operation and maintenance. In addition, the use of sootblowers can cause tube wastage due to the impaction of deposits blown from heat transfer surfaces.

The removability of a deposit depends upon its physical structure. Wain and others (1992) initiated work to develop relationships between the nature of slag and the relevant thermal and mechanical properties that effectiveness of sootblowers. They examined ten different slag samples to determine the thermal conductivity, coefficient of thermal expansion, compressive strength and elastic modulus, porosity, and crystallinity. The ability of a deposit to be removed is dependent upon a thermal shock parameter. The thermal shock parameter is the change in temperature needed to develop crack propagation. When a sootblowing medium encounters a deposit, a change in temperature needs to occur to cause thermal stress leading to crack initiation and propagation. The operators of a boiler must be able to remove a deposit when it is still largely glassy and has a relatively high porosity. Deposits that have had sufficient time at temperatures that allow for significant strength development through viscous flow sintering will likely become very dense, highly crystalline and very hard to remove. Typically deposits having porosities of less than 25% are extremely difficult to remove.

Chemical fractionation uses a series of leaching procedures to determine the abundance and associations of inorganic elements in the coal. Water is used first to extract the elements most loosely bound to the coal and water-soluble minerals; water is followed by ammonium acetate, to extract elements more tightly bound to the organic matrix; finally hydrochloric acid is used to extract more tightly-bound phases and carbonate minerals. The inorganics remaining are the insoluble mineral phases which can be analyzed by CCSEM.

CCSEM is used to determine the size and chemistry of minerals in the coal. Basically, the CCSEM analysis finds dispersed inorganic particles (i.e. discrete minerals in coal) and quantifies their shape, size, and composition. Using CCSEM one can quantify both the mineralogy and size distribution of materials such as coal minerals and fly ash. Both the size and chemistry of minerals are important when trying to understand why ash deposits form.

Results

Characteristics of Deposits for Testing

The deposits sent to Prairie View for testing range in characteristics from being a highly porous glassy type of deposit to a highly crystalline dense deposit. Initial testing will focus on the lower temperature deposits. These deposits are difficult to reach using conventional sootblowing techniques. The deposits from the reheater inlet-2 from the rear of the panel (MTI93-7) and reheater inlet front of panel (MTI93-8) have a medium-to-low porosity, low crystallinity, and are sulfate based. The sulfation processes fills pores and increases density. The sulfates form as a result of sulfation of deposited calcium-rich particles (3). The deposit from the economizer (MTI93-6) is highly porous and non-crystalline. This deposit formed at a sufficiently low temperature where the sulfation rate was slow resulting in only a minor amount of pore filling. This set of deposits represent a wide range of deposits found in the convective pass of a utility boiler firing a high calcium subbituminous coal. These subbituminous coals are being used extensively in the U.S. for power generation.

The boiler that produced these deposits is a Babcock and Wilcox opposed wall-fired pulverized coal-fired boiler. The unit is capable of generating 580 Mw gross. The fuel fired was a subbituminous coal from Wyoming.

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Future Work

1. The deposits will be analyzed to determine their chemical and physical characteristics.
2. Characterize deposit fragments removed during removal using Texas A&M device.
3. Report characteristics of the coal that led to the formation of the deposit.

References

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Figure 1. Test Chamber Schematic

NORMALIZED PRESSURE

CONTOUR LEVELS

0.00000
20.00000
40.00000
60.00000
80.00000
100.00000
120.00000
140.00000
160.00000
180.00000
200.00000
220.00000
240.00000
260.00000
280.00000
300.00000
320.00000
340.00000
360.00000
380.00000
400.00000
420.00000

3.000	MACH
0.00 DEG	ALPHA
$8.08 \times 10^{**5}$	Re
36.	TIME
175x51	GRID

Figure 2

NORMALIZED PRESSURE

CONTOUR LEVELS

8.00000
10.00000
12.00000
14.00000
16.00000
18.00000
20.00000
22.00000
24.00000
26.00000
28.00000
30.00000
32.00000
34.00000
36.00000
38.00000
40.00000

y

3.000 MACH
0.00 DEG ALPHA
 $8.08 \times 10^{+5}$ Re
 $2.00 \times 10^{+3}$ TIME
175x51 GRID

x

MACH NUMBER

CONTOUR LEVELS

0.00000
0.10000
0.20000
0.30000
0.40000
0.50000
0.60000
0.70000
0.80000
0.90000
1.00000
1.10000
1.20000
1.30000
1.40000
1.50000
1.60000
1.70000
1.80000

3.000
0.00 DEG
8.00x10**5
36.
175x51
MACH
ALPHA
Re
TIME
GRID

Figure 4

MACH NUMBER

CONTOUR LEVELS

0.00000
0.10000
0.20000
0.30000
0.40000
0.50000
0.60000
0.70000
0.80000
0.90000
1.00000
1.10000
1.20000
1.30000
1.40000
1.50000
1.60000
1.70000

3.000	MACH
0.00 DEG	ALPHA
$8.08 \times 10^{**5}$	Re
$2.00 \times 10^{**3}$	TIME
175x51	GRID

30 Nov 1995

Figure 5

NORMALIZED TEMPERATURE

CONTOUR LEVELS

1.00000
1.50000
2.00000
2.50000
3.00000
3.50000
4.00000
4.50000
5.00000
5.50000
6.00000
6.50000
7.00000
7.50000
8.00000
8.50000
9.00000
9.50000
10.00000
10.50000
11.00000
11.50000
12.00000
12.50000
13.00000
13.50000
14.00000
14.50000

3.000 MACH
0.00 DEG ALPHA
8.08x10**5 Re
36. TIME
175x51 GRID

30 Nov 1995

Figure 6

NORMALIZED TEMPERATURE

CONTOUR LEVELS

3.00000
3.25000
3.50000
3.75000
4.00000
4.25000
4.50000
4.75000
5.00000
5.25000
5.50000
5.75000
6.00000
6.25000
6.50000
6.75000
7.00000
7.25000
7.50000
7.75000
8.00000
8.25000
8.50000
8.75000
9.00000
9.25000

3.000	MACH
0.00 DEG	ALPHA
$8.08 \times 10^{+5}$	Re
$2.00 \times 10^{+3}$	TIME
175x51	GRID