**Relationship between Submicron Ash Aerosol Characteristics and Ash Deposit Compositions and Formation
Rates during Air- and Oxy-Coal Combustion**

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Abstract

Deposition of ash on heat transfer surfaces is a major factor in determining boiler performance. Deposits so formed consist of tightly bound “inside” deposits close to the heat transfer surface and loosely bound “outer” deposits that are easily dislodged. This paper describes research focusing on both the *composition* of inner and outer deposits, and also on the *rate* of deposition of the inner deposit layer. Presented are selected results from a wide ranging study concerned with mechanisms governing the formation of fouling deposits during air and oxy-coal combustion in a 100 kW test rig. The primary focus is on establishing a relationship between the size segregated composition of the coal ash aerosol, and the spatially resolved composition of the deposit layer, and this is accomplished by experimentation that addresses the impacts of conversion from air-firing to oxy-firing. Experiments involved three different coals (Powder River Basin or PRB, Illinois and a 60/40 Blend of Illinois and PRB), each burned under air- and oxy-coal combustion conditions. Data for the PRB coal suggested that changes in the composition of the inner deposit layer were caused by variations in sub-micron aerosol compositions, but that these occurred only when there were significant changes in flame temperature. An increase of the latter also led to increasing submicron particle concentrations and deposition rates. Although both aerosol and deposit compositions depended greatly on coal compositions, rates of deposition of the inner deposit layer correlate linearly with the concentration of the submicron aerosol in the flue gas, for all three coals, and under all air- and oxy-firing conditions for which data are available. This result suggests the amount rather than the (variable) composition of the submicron aerosol is important. There was no correlation between deposition rates and total ash concentrations.

Keywords: coal ash, aerosols, fouling, deposition, oxy-combustion.

1. Introduction

1.1 Motivation

A major impediment to being able to predict accurate heat transfer rates in air-coal, oxy-coal and advanced oxy-coal combustion conditions is a lack of predictability of fouling rates on heat transfer surfaces. Fouling deposition is the deposition process for ash that sticks on the steam tubes located in the convection zone, in contrast to slagging which describes the process through which hardened melted deposits are deposited in the burner zone and radiation zone [1, 2]. These ash deposition processes (slagging and fouling) on heat transfer surfaces produce resistances to heat transfer that can control boiler performance. Fouling deposits can be controlled by soot blowing, where the

frequency of soot blowing is determined by the rate of ash deposition on the heat transfer tubes, and by the “stickiness” of the deposits.

The importance of ash deposition in thwarting validation between simulations of radiative heat flux and experimental measurements is demonstrated in Reference [3], which shows comparisons between advanced simulations and measurements of heat flux in a 1.5 MW horizontal test furnace [3]. Both simulations and measurements utilized the most advanced techniques currently available, and were components of an ongoing project to demonstrate the use of exascale computing to facilitate deployment of advanced oxy-combustion processes. Although trends along furnace length were simulated, the discrepancies between experiment and theory, which were considerable, were attributed to absence of accurate ash deposition models.

1.2 Scope of this paper

This paper is concerned wholly with fouling deposits, not with slagging deposits. The focus is on effects of changes of coal composition, and of oxidant composition on the characteristics and composition of the fouling deposits formed, and on the ash aerosol formed during the air- and oxy-firing of pulverized coal. In contrast to previous work [4, 5], special efforts were made here to relate both the size segregated ash aerosol compositions and the ash aerosol particle size distributions not only to the *compositions* of the deposit layer, but also to the *rates of deposition* of the sticky deposit layer. It is hoped the results can be used in simulations requiring predictions of deposition rates and deposit qualities under air and oxy combustion conditions. The purpose of this paper therefore is to summarize in one place the key results and conclusions of the research, in order to produce a cohesive picture of how deposits are formed and to provide tools that may ultimately allow prediction of both rates of formation of ash deposits and their properties.

First, the differences found between inner and outer deposits is described. This distinction is important because, while compositions of both inner and outer deposits yield useful information on their formation mechanisms, deposition rates can only be precisely determined for the tightly bound inner deposits. The outer deposits are too loose to allow reproducible rate data to be obtained for practical coal combustion situations. Second, the methodology used to obtain the data to be presented is briefly recapped, although details can be found elsewhere [4, 5]. Third, the effects of air and oxy combustion of various coals on the *composition* of deposits and on the *size segregated composition of the ash aerosol* are explored. Finally *the rates of formation of inside deposits* are explored under air-firing and oxy-firing conditions. Correlations to allow prediction of deposition rates, using

knowledge of the ash aerosol particle size distribution are presented, and are found to correlate all the data obtained here, for all coals, all oxidants and all conditions investigated.

1.3 Mechanisms: inner and outer deposit layers

It has been found [5] that fouling deposits can be divided into two types: 1) tight, sticky “inner” deposits that strongly adhere to available surfaces, especially to the heat transfer surfaces, and 2) loose “outer” deposits that are easily dislodged and potentially re-entrained by the flue gas. From a practical point of view, we define the loose “outer” deposits as those that are easily dislodged by vigorous shaking, and the sticky “inner” deposits as those that remain attached, and can only be removed by scraping the surface of the deposit probe. For this reason, precise measurements of deposit rates may be made only of the tight, sticky “inner” deposits, since these are not sensitive to re-entrainment by flue gases and to being lost during extraction of the deposit probe. Therefore, in this paper much of the discussion emphasizing differences in deposition rates is valid only for the sticky inner deposits, although both “inner” and “outer” deposits are considered as far as composition differences are concerned.

Figure 1 depicts a deposit probe of finite length inserted into a flue gas flowing downwards past it. In the absence of turbulence, the vertical face can receive deposits only through particle diffusion mechanisms. The scanning electron microscope (SEM) of the vertical deposits (Figure 1) shows only small sub-micron particles, and these are highlighted in the ash aerosol particle size distribution shown on the right hand side of the figure. The inside deposit shows a mix of larger particles (comprising most of the mass of the deposit) together with small sub-micron particles, while the outer layer shows primarily large super micron particles. By varying the deposit surface temperature it has been found [5] that at a constant flue gas temperature the deposition rate on the *vertical* surface depends on the collection probe surface temperature, suggesting that particle diffusion by thermophoresis [6], is the dominant mechanism of deposition there. It should be noted that the vertical deposits are sticky and not easily removed from the surface, other than by physical scraping.

A reasonable hypothesis to be tested here is that for the inside deposits shown on the SEM on Figure 1, the small particles form the “glue” that holds the larger particles together, and thereby form the sticky inner deposits. The small particles (comprising the “glue”) in both inner and vertical deposits are both likely to have been transported by thermophoresis, and have been shown [5] to have similar compositions. The larger particles in the horizontal inner deposits are transported by inertial impaction, not diffusion, and provide the bulk of the mass of those deposits.

Hence deposition *rates* of the horizontal inner deposits would be expected to be substantially greater than those of the vertical deposits, where large particles are absent.

1.4 Mechanisms: ash aerosol formation and deposition

Figure 2 shows the relationship between ash aerosol formation mechanisms and deposit formation mechanisms. An important feature is that submicron particles are formed by vaporization and subsequent condensation of semi-volatile metals, while super micron sized particles are generally formed by fragmentation [7]. Hence one describes ash aerosol size distributions in terms of vaporization modes, caused by sequential vaporization and nucleation/condensation of metals, and fragmentation modes caused by burnout of hollow or solid char particles. Little is available in the literature, in which both the ash aerosol is characterized in detail, and in which that information is linked to the spatially resolved composition of the deposit and to deposition rates. It was the objective of this research to provide these links and to use them to determine any special features in mechanisms governing the formation of deposit layers during oxy-coal combustion compared to those formed during combustion in air.

Several vaporization modes have been observed (see Figure 1), where each mode depends on the dew point of the condensing mineral matter. Typically, a vaporization mode with particle diameter $d_p < 0.1 \mu\text{m}$ (see Figure 1) is due to condensation of a vaporized metal fume in the cooled sampling probe, while a mode between $0.1 \mu\text{m}$ and $0.7 \mu\text{m}$ (see Figure 1) is normally due to metal vaporization, nucleation, condensation and growth within the furnace prior to sampling.

At least two fragmentation modes have been observed [7]. A smaller fragmentation mode centered at $1\text{--}3 \mu\text{m}$ tends to contain non-agglomerated mineral inclusions originally within the shells of cenospheric char particles [7]. The larger fragmentation mode with resultant ash particles $> 5 \mu\text{m}$ is formed during the burnout of solid porous char with concomitant melting of mineral inclusions and their agglomeration prior to char fragmentation through oxidation. The larger fragmentation mode contains, typically, over 90% of the total ash aerosol, and is not shown on Figure 1 because of limitations in the particle size measurement device used there. The smaller central mode can contain over 90% of the mass within $\text{PM}_{2.5}$, (d_p smaller than $2.5 \mu\text{m}$) where those particles have sufficient surface area to allow condensation and/or surface reaction [7]. In this range the condensed or surface reacted metals have composition dependences of $1/d_p^2$ or $1/d_p$, depending on whether the process is film diffusion controlled or surface reaction controlled [8]. This leads to surface enrichment of vaporized metals on ash particles as particle size decreases.

These distinctions in aerosol formation mechanisms have profound effects on subsequent deposition mechanisms. Vaporization mode particles can be sticky and, as pointed out above (see Figure 1), are transported onto heat transfer surfaces through a diffusion (thermophoresis) mechanism. These particles may be condensed outside the boundary layer next to the heat transfer surface, or for the $d_p < 0.1 \mu\text{m}$ particles, within the thermal boundary layer. Note, however, that in Figure 1, over 90% of the total vaporization mode mass is contained in the mode between $0.1 \mu\text{m}$ and $0.7 \mu\text{m}$, that is, with vaporization mode particles formed in the hot furnace flue gases, outside the thermal boundary layer next to the heat transfer surface. Literature suggests that the composition of the sticky particles is important and consists largely of alkali sulfates [1, 2], although, results presented below will cast doubt on that conclusion.

Fragmentation mode ash particles will deposit on heat transfer surfaces primarily by inertial impaction. Our hypothesis is that the tight inside deposits referred to above consist of inertially impacted fragmentation mode particles sticking to one another and to the surface with the help of “glue” made up of thermophoretically deposited vaporization mode particles. The outer deposits that are only loosely bound together and to the deposit structure, contain relatively little of the vaporization mode particle containing “glue”. The inside deposit layer results from two mechanisms: 1) inertial impaction of fragmentation mode particles, a process that is dependent on the local aerodynamics in the neighborhood of the heat transfer surface; 2) thermophoresis of sticky vaporization mode particles to provide the glue to fix the deposit. One might expect the deposition rate to depend on both the concentration of the “glue” particles and that of the larger particles that comprise over 95% of the ash mass. Results presented below, however, will suggest that the deposition rate is controlled by only the “glue” particle concentration.

2. Methods and Materials

2.1 Experimental requirements

It is desirable to conduct systematic, reproducible tests that allow evaluation of the fouling potential various solid fuels. The following attributes of the experimental test system are required:

- i. The test should allow the solid fuel to be burned under as near practical conditions as possible.
- ii. The combustion rig should yield particle and gas species concentrations and time temperature histories of practical units since these determine the speciation and particles size of the ash aerosol from which the deposit is derived.

- iii. The combustion rig should be inexpensive to run and should allow a range of solid (and possibly liquid) fuels and a range of oxidants.
- iv. A suitable deposit probe must allow systematic collection of deposits, and preferably allow effects of particle impaction and diffusion to the deposit surface to be separated.
- v. The deposit probe should have a controllable surface temperature in order to simulate deposition to heat transfer surfaces at various temperatures.

To this end the oxy-fuel combustor and a surface temperature controlled deposit probe were designed and constructed, as summarized below.

2.2 Oxy-Fuel Combustor (OFC)

Details of the 100 kW (nominal) Oxy-Fuel Combustor (OFC) can be found elsewhere [9, 10] and so the test rig, as shown in Figure 3, is only briefly summarized here.

The flame is a turbulent diffusion flame, but the flow becomes laminar as it progresses down the furnace, so that at Ports 5, 6 and 7, where fouling deposit samples were obtained, deposition of ash particles on horizontal surfaces of the probe occurs through a well defined particle impaction from laminar flow plus particle diffusion (thermophoresis). In addition, particle diffusion rates alone, and the composition of those diffusing particles can be determined by using a vertical deposition surface, parallel to the flow. In laminar flow the only deposition mechanism on such a surface is by particle diffusion, and this is found to be thermophoresis [5]. Clearly, deposition in field units would occur with turbulent impaction mechanisms also being important. However, it is hoped that deposition rates in the well defined laminar regime of this apparatus can be extrapolated to the turbulent aerodynamic regime of practical units through simulation and mathematical modelling. A more complete description is provided by Zhan et al [4, 5].

2.3 Deposit probe and deposits analyses

The deposit probe has been described in detail by Zhan et al [4, 5]. The coupon on which ash deposits is of stainless steel, and has a wall temperature that is controlled through an adjustable air flow and a thermocouple placed on the coupon wall. The coupon protruded halfway into the vertical section of the OFC and allows diffusion deposited ash to be collected on a vertical surface parallel to the laminar flow and impaction plus diffusion deposited ash to be collected on the horizontal portion of the coupon.

As described above, the horizontal deposits consisted of two layers, inner and outer layers, shown in the scanning electron micrographs on Figure 1. The inner layer was tightly bound to the deposit surface and could only be scraped off. The outer layer was friable and loosely bound and fell off with vigorous shaking. Clearly re-entrainment of loose particles by the flue gas makes the outer layer thickness dependent on the flue gas aerodynamics.

Composition of deposits was measured by two methods: Energy dispersive X-Ray spectroscopy (EDX) and Computer Controlled Scanning Electron Microscopy (CCSEM). EDX emphasizes the surface (to within a couple of microns) composition of particles, and provides reasonable bulk elemental compositions for micron and smaller sized particles. Particles are loose during analysis and EDX provides elemental analysis of the entire sample, taken as a whole. For CCSEM the particles are embedded in epoxy, ground to a flat plane, thus exposing the interior of (some of) the larger particles. Each (sometimes partially exposed) particle is then analyzed particle by particle, with the size of each particle noted. Since many (but not all) of the larger particles allow their interior compositions thus to be analyzed, CCSEM provides a closer approximation to the bulk analysis of each particle, than does EDX which emphasized the surface of all particles only. Acid digestion and atomic absorption or emission techniques would provide more accurate bulk particle compositions.

2.4 Ash aerosol sampling and characterization

An important feature of this work is to relate the ash aerosol to the ash deposits. The ash aerosol was sampled through Port 9 using an isokinetic dilution [8] and additional dilution as described in previous papers [4, 5]. A pre-separator cyclone removed the larger particles upstream of a Berner low pressure impactor (BLPI) which, with EDX, was used to obtain the size segregated composition of the ash aerosol. These data were supplemented with electron mobility (scanning mobility particle sizer, SMPS) and light scattering (aerodynamic particle sizer, APS) data to obtain finely resolved particle size distributions (PSD's) showing all existing PSD modes in the particle diameter range of 0.014 μm through 20 μm . One should be aware, however, that the BLPI and the SMPS/APS account for less than 10% of the total ash mass, the bulk of which is either removed in the furnace, in the pre-separator cyclone, or is beyond the size range measured by the APS.

2.5 Coal and ash compositions

Table 1 shows the coal and ash compositions pertinent to the results presented here. The coals are a Bituminous Illinois coal with high sulfur and high iron and silicon, a Powder River Basin sub-bituminous coal with high

moisture (loss on drying, LOD) and high calcium, and a 60/40 blend of both coals, similar to that originally planned for FutureGen 2.0.

3. Results and Discussion I: Composition of Deposits and Size Segregated Composition of Ash Aerosols

3.1 Deposit compositions for air (AIR) and oxy-combustion with 27% inlet O₂ (OXY27)

Data, not shown here, shows very little difference between the Air and OXY27 case as far as the size segregated composition and the particle size distribution of the ash aerosol. This result is independent of the extent of contaminant removal from the RFG, and is consistent with the results of Morris et al [11, 12].

Compositions of inner and outer deposits for AIR and OXY27 tests were obtained for three coals, namely the PRB sub-bituminous coal, the Illinois bituminous coal, and the 60% Illinois/40% PRB blend coal and are shown in Figure 4. For the OXY27 tests, results for two RFG cleanup conditions are reported, namely with only the ash removed in a bag house, and then with ash, sulfur, and water removed in a SO₂ scrubber.

These data were obtained using simple EDX, that is, without sample planarization. Thus the compositions tend to emphasize the surface compositions of the particles. Careful examination of these data shows that while the difference in (mainly particle surface) compositions between inside deposits (left column) and outside deposits (right column) is small for the PRB coal (top row panels), it is significant for the Illinois and Blend coals (middle and lower row panels). This is not inconsistent with our argument that the inside layer was constituted primarily of vaporization mode ash aerosols, while the outside deposits were composed primarily by super-micron ash aerosols.

For PRB coal, compared to air, oxy-combustion conditions led to decreased sulfur and increased calcium concentrations for both inner and outer deposits (as measured by simple EDX). It seemed to make little difference whether ash only or ash together with sulfur and water were removed from the recycle stream.

For Illinois coal the simple EDX analyses showed that, compared to air, oxy-combustion led to decreased Si and increased Fe in the inner deposits, with no change in Si and a larger increase in Fe in the outer deposits. The 60% Illinois/40% PRB blend appeared to follow the Illinois results, rather than those for PRB or a calculated average for the two coals.

The OXY27 runs for each of the three coals investigated did not show significant differences in either their temperature profiles and nor in their particle size distributions [13], and are not shown here.

3.2 Ash aerosol characteristics and deposit compositions for air and oxy-combustion with 50% inlet O₂ (OXY50, PRB coal only) and their relationship to one another

Major differences were observed between AIR and OXY50 cases for the PRB coal for both ash aerosol characteristics and ash deposit characteristics. We believe this is because the OXY50 run occurred at furnace measured temperature profiles with a substantially higher peak than that for AIR but, serendipitously, with similar temperatures at the deposit probe insertion location [5]. Therefore these conditions are useful for investigating the relationship between the size segregated composition of the ash aerosol and the spatially resolved ash deposit composition. From these data one can explore how changes in the ash aerosol affect both inner and outer deposit compositions.

Figures 5, 6 and 7 have been taken from Ref [4] but are included here because they show the key differences in ash aerosol and ash deposit characteristics between AIR combustion and OXY50 combustion for the PRB coal, and these characteristics play important roles when differences in *deposition rates* are discussed below. Figure 5 shows a complete set of particle size distribution (PSD) data for combustion of the PRB coal with air, and with 50% O₂ and 50% CO₂. Data were obtained using a) the Berner Low Pressure Impactor (BLPI) and gravimetric measurements using a pico-balance; b) the SMPS and c) the APS. Remarkably, data from all three, completely different, methods of measuring particle size, agreed very well.

The left panel presents data on a differential concentration basis that is, in terms of differential mass per standard m³ of flue gas, while the right panel takes account of the diminished flue gas rate for OXY50 conditions and presents the data in terms of differential kg particles per kg ash. The differential ordinate allows the amount of particles between two particle sizes to be calculated by the area under the curve between those two particle diameters.

Important results are that OXY50 produces greater amounts (and higher concentrations) of vaporization mode particles with two modes, one at 0.1 μm, the other at 0.3 μm, with the modes being shifted slightly to the right (consistent with increased coagulation due to increased concentrations). The two modes at 1 μm and above represent the fine and coarse fragmentation modes previously identified by Linak et al [8]. The increased vaporization for OXY50 compared to AIR is almost certainly a result of the increased flame temperature. This will have additional ramifications as described below.

A sample of the size segregated composition data of the ash aerosol is shown on Figure 6, which compares results for air combustion and for oxy-combustion of PRB coal with 50% O₂/50%CO₂ in the inlet oxidant, with the

PSD's shown on Figure 5. Note that OXY50 had a significantly higher flame temperature than did the case for AIR combustion.

The four elements depicted (Na, S, Si, and Fe) show significant differences in their compositions between AIR and OXY50, especially in the submicron range. Recall that Figure 6 shows that OXY50 had much greater amounts of sub-micron sized aerosol. OXY50 shows less sodium, less sulfur, greater silicon and less iron in the vaporization mode particles. Net sodium vaporization decreased at the higher temperature because of increased scavenging of sodium vapor by alumino-silicates at high temperature [14, 15]. Sulfur was diminished because of the lower amounts of sodium with which to react [1]. Silicon vaporization increased at the higher OXY50 temperature, and also possibly, because of the increased levels of CO [16]. Iron in the submicron mode decreased under OXY50 conditions presumably because of increased iron in the glass (presumably in larger particles) under oxy-firing conditions [17]. The important item to note is that both the compositions of sub-micron particles for Air and OXY50 are quite different from each other (Figure 6), as well as their concentrations in the flue gas (Figure 5).

Figure 7 shows compositions of inside deposits (left panel) and outside deposits (right panel) for Air and OXY50, as analyzed by CCSEM (that provided a better estimate of particle bulk rather than surface particle compositions), rather than by simple EDX as shown on Figure 4. These data clearly show very large differences between the composition of the inside layer and the composition of the outside layer. Furthermore the data show that oxy-combustion (OXY50) results in differences in composition of the inside layer. Finally, on comparing Figure 5 and Figure 7, one can see that differences between AIR and OXY50 firing in the submicron ash aerosol are reflected in similar concentration differences in the inside layer. For example, compared to AIR, OXY50 leads to a large increase in Si in the sub-micron aerosol range and also in the composition of the inside deposits. Likewise, OXY50 results in lower Na, S and Fe in the sub-micron ash aerosol and in the inside deposits.

These correlations between aerosol composition and deposits compositions do not hold for the super-micron and the outside deposit, neither of which is significantly affected by OXY50 conditions. In all these results, it is the increase in flame temperature in OXY50 that has the largest effect on sub-micron aerosol formation (Figure 5) and the consequent changes in the composition of the inside, but not the outside deposit layers.

4. Results and Discussion II: Deposition Rates

Deposition rates were measured by measuring the mass of ash deposited as tight sticky deposits and as loose outer deposits at times of 1 hour and 4 hours. By necessity, the measurement of loose outer deposits is not precise because of possible re-entrainment effects and the like.

Measurements, shown on Figure 8 suggest that deposit rates are indistinguishable between the AIR and OXY27 cases. However, for OXY50 there is a significant increase (compared to AIR) in the rates of deposition of the inside deposit, and a slight increase in the rate of deposition of the outside deposit. These data suggest that flame temperature, but not so much flue gas composition, is an important variable in determining deposition rates. This effect is mainly because of the effect of flame temperature on the inner deposits, and this is relevant to field units because the inner deposits are formed primarily by thermophoresis, which occurs similarly in both test and field units, rather than by particle impaction, which is not well simulated in our tests because our flue gas flow is laminar.

The fact that for one coal, the PRB coal, differences in AIR and OXY50 are to be found in the sub-micron particle composition and concentration in the flue gas, and that these are the only cases in which significant differences in inside deposition rates were observed suggests that it might be the sub-micron particle concentration in the flue gas that controls the formation of inner, tight deposits is the small particle concentration, and this might be the case no matter how or from what, or with what composition the sub-micron particles are formed. It is therefore advantageous to correlate all the available deposition data, for all three coals, and all oxidant mixtures (OXY27 and OXY50) with PM_1 and so this was attempted as shown on Figure 9.

It should be noted that the correlation on Figure 9 is for the deposition rate of the inside deposits only. The data correlate well, even though the composition of the OXY50 submicron particles was significantly different than that of the submicron particles from AIR combustion – see Figure 6. Indeed the higher deposition rates are from aerosols with lower sodium concentrations in the sub-micron range, and this is at variance with accepted theories on what constitutes the “glue” to enable firm deposits to be formed [1]. The outside deposits did not correlate at all. Note also that these were very difficult to measure precisely just because they were so loosely bound. It should also be noted that the inside deposition rate also correlated with $PM_{2.5}$ because $PM_{2.5}$ was proportional to PM_1 in these tests, suggesting that either the changes in peak flame temperature or of changes in the flue gas flow rate caused proportional changes in PM_1 and $PM_{2.5}$.

It is important to realize that in all these tests, $PM_{2.5}$ constituted the dominant portion of PM_{10} and PM_{10} was always less than 10% of the total ash formed during coal combustion. There was no correlation whatsoever between inside layer deposition rate and the total ash concentration as shown on Figure 10.

5. Conclusions

The results presented here should aid in the development of deposition models to be used in oxy-coal combustion simulations, which is a critical component controlling the validation of those models.

For all coals and all oxidant conditions investigated, fouling ash deposits form a tight, sticky inside layer that is removed only by scraping and a much more loosely bound outer layer. Mechanisms of formation of these layers can be systematically experimentally explored using a 100 kW down fired combustion rig and a specially designed wall temperature controlled deposit probe.

Data show that oxy-coal combustion does not change deposit compositions, deposition rates or ash aerosol characteristics from those from air combustion when flame temperatures in the radiant zone are maintained. This is true for all three coals examined, and surprisingly independent of the extent of RFG cleanup, although the extent of RFG was not precisely controlled in these experiments. However, when the peak flame temperature is increased, by increasing the inlet oxygen percentage, both the deposition rates and the sub-micron ash aerosol concentration increase. The composition of both the sub-micron ash and that of the inside deposit layer change similarly.

Clearly, the sub-micron ash aerosol plays a dominant role in determining both the deposition *rates* and the compositions of the inside deposit. All the deposition rate data for the inside deposit, for all coals and for all air and oxy conditions could be simply correlated with PM_1 . We tentatively suggest that the quantity of PM_1 rather than its composition is important in determining the deposition rate of the inside layer. If this is true, and if this should hold up in additional experiments, it suggests that the bonding mechanism is controlled by the small particle size only, not necessarily by the alkali content of these particles. However, the composition of the inside layer closely represents the composition of the PM_1 and that did change with peak flame temperature.

If the correlation depicted on Figure 9 should hold up it in future work, it would appear that deposition rates can be directly correlated with PM_1 and this would allow the rate of deposition of this initial layer to be accurately predicted in real time by measuring the submicron particle density in practical boilers on-line, using SMPS, for example.

Acknowledgments

The authors would like to acknowledge the support from the Illinois Clean Coal Institute (ICCI Project 14/5A-2), from the State of Wyoming under the Clean Coal Research Program (Project 1100-20268) and from the National Science Foundation of China (No. 51376061). We also acknowledge Praxair Inc. for contributing the O₂ and CO₂ supply, and Lawrence E. Bool, III of Praxair for his technical input. We thank Chris Coulter, Mbonisi Sibanda and Brian van Devenner at the University of Utah for their help in experiments and analysis.

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Figure Captions

Figure 1. Outside, inside and vertical deposits on a finite deposit probe inserted into a test furnace.

Figure 2. Relationship between ash aerosol formation mechanisms and ash deposition mechanisms.

Figure 3. Schematic of the Oxy-Fuel Combustor (OFC).

Figure 4. Deposit compositions (as measured by EDX) for air (AIR) and oxy fired with 27% inlet O₂ (OXY27) tests. PRB coal (top panel), Illinois coal (center panel) and Blend (bottom panel). Inside deposits - left column; outside deposits - right column. Each panel shows AIR, OXY27 (RFG, Recirculated Flue Gas, with ash only removed and RFG with ash, sulfur and water removed).

Figure 5. Ash aerosol PSD's (BLPI gravimetric, SMPS/APS) for PRB coal under air fired conditions and OXY50 (50% inlet O₂) conditions. Left: concentration basis; Right: mass basis. Taken from Ref [4].

Figure 6. Size segregated concentrations of Sodium (Na), Sulfur (S), Silicon (Si), and Iron (Fe) for air combustion and OXY50 combustion of PRB coal. Taken from Ref [4].

Figure 7. Composition by CCSEM of inside (left panel) and outside (right panel) deposits for PRB coal burned under air firing and oxy-firing conditions with 50% O₂ (OXY50). Holding times for 1 hour and 7 hours are shown. Taken from Ref [4].

Figure 8. Inside, outside, and total deposition rates (g/(h·m²)) for PRB coal for air firing, oxy-firing with 27% inlet O₂ (OXY27) and oxy-firing with 50% inlet O₂ (OXY50).

Figure 9. Correlation of ALL available deposition rate data of the inside (sticky) deposits with PM₁ (ash aerosol concentration of particles less than 1 μm).

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	Illinois	PRB	Blend		Illinois	PRB	Blend
Coal analysis				Coal ash analysis (wt. % of ash)			
ASH (wt. %)	9.42	4.94	7.63	Al ₂ O ₃	20.18	14.78	18.02
C (wt. %)	63.47	53.72	59.57	CaO	3.22	22.19	10.81
H (wt. %)	5.43	6.22	5.75	Fe ₂ O ₃	16.46	5.2	11.96
N (wt. %)	1.24	0.78	1.06	MgO	0.89	5.17	2.6
S (wt. %)	3.12	0.23	1.96	MnO	0.03	0.01	0.02
O (diff, wt.%)	17.32	34.11	24.04	P ₂ O ₅	0.1	1.07	0.49
LOD (wt. %)	9.64	23.69	15.26	K ₂ O	2.1	0.35	1.4
VM (wt.%)	36.04	33.36	34.97	SiO ₂	51.22	30.46	42.92
FC (wt. %)	44.9	38.01	42.14	Na ₂ O	1.06	1.94	1.41
HHV (BTU/lb.)	11552	9078	10562	SO ₃	2.79	8.83	5.21