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1. Title

Ash aerosol formation from oxy-coal combustion and its relation to ash deposit chemistry

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Figure 4: 522 words $[(219+10) \times 2.2 \times 1 + 18]$

Figure 5: 308 words $[(55+10) \times 2.2 \times 2 + 22]$

Abstract

Ash aerosol and ash deposit formation during oxy-coal combustion were explored through experiments in a self-sustained 100 kW rated down-fired oxy-fuel combustor. Inlet oxidant conditions consisted of 50% inlet oxygen with CO₂ (hereafter denoted as OXY50 conditions). A Berner low pressure impactor (BLPI), a scanning mobility particle sizer (SMPS), and an aerodynamic particle sizer (APS) were used to obtain size segregated ash aerosol samples and to determine the particle size distributions (PSD). A novel surface temperature controlled ash deposition probe system that allowed inside and outside deposits to be separated was used to collect the ash deposits. The ash aerosol PSDs given by the BLPI and those produced by SMPS/APS were consistent with each other. Data suggested that oxy-coal combustion under these conditions did not change the formation mechanisms controlling the bulk ash aerosol composition, but it did increase the formation of ultra-fine particles initially formed through metal vaporization, due to increased vaporization of silicon at the higher combustion temperature. The smaller particles contained within the deposits had higher Si and lower Na and S concentrations under OXY50 conditions than for air combustion. Moreover, the ash aerosol composition for particle sizes less than 2.4 μm was related to the composition of the inside deposits. A higher Na in the ash aerosol resulted in higher Na in inside deposits with comparable absolute Na concentrations in both those aerosol particles and those inside deposits particles. The contribution of S and Si to the inside deposits showed that S in the vaporization modes together with Si in the ultrafine vaporization mode, contributed significantly to the composition of the inside deposits. These results provided direct evidence that prediction of the chemistry of the initial deposit layer (but not of the bulk deposits) required knowledge of the size segregated chemistry of the ash aerosol.

Keywords: Oxy-coal combustion; Ash aerosol; Ash deposition; Particle size distribution

1. Introduction

Climate change is a challenging issue for humans, eliciting much attention on CO₂ emission control from coal combustion sources [1-2]. Oxy-coal combustion, using pure oxygen and recycled flue gas (RFG) instead of air to react with coal is an auspicious technology to allow retrofit of existing coal combustion power plants to enable the capture and subsequent sequestration of the CO₂ produced. Numerous studies [3-5] have been conducted to evaluate furnace performance when converting from air combustion to oxy-coal combustion. This paper is concerned with the effects of retrofit on both the fly ash produced and the fouling deposits laid down on heat transfer surfaces.

The ash aerosol from coal combustion is an important issue because of the following aspects. First, it affects the performance of precipitators used to remove the larger particles and also influences the emission of fine particulate matter (PM_{2.5}), which contaminates the environment and harms the health of humans, animals, and plants [6]. Second, the ash aerosol is the precursor to forming ash deposits on heat transfer surfaces, thus determining the rates of deposit formation, as well as the chemical and physical properties of the deposits [7]. Ash deposition on heat-exchanger surface will cause problems with heat transfer, and lead to increased corrosion, accidents, or even boiler shutdowns [8]. Thus, in order to predict the impact of retrofit from air to oxy-coal combustion it is essential to predict how the ash aerosol may be altered and how the ash deposition characteristics may change. Furthermore, it would be valuable to determine the relationship between the airborne ash aerosol composition and that of the deposits created from that ash, since this would ultimately lead to models that follow the creation of the ash aerosol, the prediction of its size segregated composition, and its subsequent deposition and possible reaction on heat transfer surfaces. This work presented here follows our previous study [9] in which experimental methods were developed and tested, and is but an early step to achieve that goal. The focus is on deposits normally denoted as “fouling” (loosely bound deposits normally found on

superheater tubes) rather than “slagging” (fused deposits formed near the burner in the radiant zone of the furnace).

Only a few studies [10-19] have focused on ash aerosol and ash deposition formation during oxy-coal combustion. Bench-scale experiments [10-12] on a drop tube furnace (DTF) have probed the effects of combustion conditions and oxygen proportions in O_2/CO_2 combustion on the ash aerosol. Suriyawong et al. [10] concluded that oxy-combustion decreased the geometric mean size of the ultrafine aerosol. However, as the inlet O_2 increased the mean size of the ultrafine mode increased, probably due to increased metal vaporization and subsequent increased rate of coagulation at the higher flame temperatures. Similar results were obtained by Sheng et al. [11] who showed that, when compared to air combustion, oxy-combustion with the same O_2 concentration shifted the peak of ultrafine mode aerosol to a smaller size and decreased the fraction of ultrafine mode aerosol. However, this difference diminished as the O_2 ratio increased. Jia et al. [12] studied ash particulate formation during oxy-coal combustion in a DTF operated at oxygen concentrations of 21% and 31.5% and with three coals. They found three particle modes below $20\mu m$ and the mass concentrations of ultrafine mode aerosol ($<0.1\mu m$) increased with increased temperature. In general, the bench-scale experimental results [10-12] were comparatively consistent with each other. However, pilot-scale studies [13, 14] on ash aerosol formation during oxy-coal combustion showed inconsistent results. Yu et al. [13] investigated ash aerosol formation in a self-sustained oxy-fuel combustor, investigating air combustion, as well as oxy-combustion with 27% and 32% O_2/CO_2 oxy-coal combustion. Their results suggested that oxy-coal combustion had no significant effects on either the tri-modal particle size distribution (PSD) or the size segregated particle compositions. However, the study of Li and co-workers' [14] on a self-sustained one-dimensional down-fired coal combustor, suggested the production of increased amounts of fine ash aerosol under oxy-coal combustion conditions, than under air combustion conditions with similar furnace temperature profiles. Differences between bench-scale and pilot-scale studies [10-14] may be

attributed to many factors, such as differences in coal types, furnace temperatures, combustion conditions, and, especially, particle concentrations.

As far as ash deposition is concerned, some studies [13-19] for oxy-coal combustion have raised disparate conclusions, due to variations in experimental equipment, deposition probe conditions, combustion conditions, and coal types. Required is an experimental system in which both combustion conditions and collection devices for deposits are systematically controlled. To this end, the deposit collection system developed and tested in previous work [9] was applied to the present work.

One would expect that deposit chemistry would be related to the size segregated composition of the ash aerosol. Yet, even though multiple discrepancies exist in ash aerosol studies and in deposit studies [10-19] for oxy-coal combustion conditions, and there have been no attempts to directly relate particle size resolved details of the ash aerosol to temporal details of how the ash deposits were formed. Therefore, in this study size segregated aerosol composition data, PSD data and temporally resolved deposit composition data were obtained, and connections between all of these factors were inferred. To the best of the authors' knowledge, this study is among the first to ascertain the relationship between the detailed ash aerosol chemistry and the ash deposit chemistry in oxy-coal combustion.

2. Material and methods

2.1 *Oxy-fuel combustor (OFC)*

Experiments were conducted on a nominal 100 kW, laboratory down-fired oxy-fuel combustor (OFC). This rig allows combustion to be self-sustaining with temperatures, particle concentrations, and mixing comparable to those of full-scale units. It nevertheless allows for systematic control of inlet flow rates and wall temperatures, and of other experimental conditions. As shown in Fig. 1, the OFC contains nine pairs of sampling and observation ports along its vertical section, denoted as P1-P9 in Fig. 1. In this research, the ash aerosol was sampled at Port 9 and deposits were collected at Port 6, using a unique,

wall temperature controlled deposit sampling probe described in detail in previous work [9]. It is hypothesized that not much happens to the ash aerosol composition between Port 6 (1200K), where the deposits are collected, and Port 9 (960K-1060K), where the ash aerosol sample is withdrawn, and this is supported by (HSC) equilibrium calculations that showed negligible differences in the equilibrium condensed mineral concentrations between these ports. Additional details about OFC can be found elsewhere [9, 20]. The burner for this study was the swirl burner used previously [20]. Oxy-fuel combustion with 50% inlet O₂ and once through CO₂, to simulate the fully cleaned RFG, was compared to results from air firing. Although the combustion temperature in the ignition zone was higher in OXY50 than in air, temperatures were almost the same at Port 6 where deposits were collected.

2.2 Ash deposition collection system

A novel temperature-controlled ash deposition probe system was used for collection of ash deposits [9]. This system allows the probe surface temperature to be controlled. The laminar flow in the OFC at Port 6 allows thermophoretic deposition on the probe vertical surface to be isolated without complications caused by inertial impaction. It has been shown [9] that this vertical layer is similar to the sticky inner deposits on the horizontal surface of the probe. “Outer” and “inner” deposits on the horizontal surface (see Fig. 2) of deposit probe are separated manually through judicious tapping of the probe. For the present work, the major focus is to determine the relationship between ash aerosol chemistry and the chemistry of the ‘inside’ or sticky ash deposits, and how these vary between air and oxy-combustion. Future work will explore the effects on the “outside” ash deposits. The rate and mechanisms of deposition of the vertical deposits are reported in Reference [9].

2.3 Ash aerosol sampling systems

For detailed ash aerosol information, two groups of instruments were utilized: a Berner Low Pressure Impactor (BLPI) [13] and a Scanning Mobility Particle Sizer (SMPS, TSI model 3080) coupled with an

Aerosol Particle Sizer (APS, TSI model 3321, hereafter refers to as SMPS/APS). Cellulose acetate membranes were used to collect ash aerosol samples for subsequent composition and morphology analyses. Aluminum filters coated with Apiezon grease were used for gravimetric PSDs, together with a high-quality Mettler Toledo balance with a precision of 0.1 μg . The SMPS produces PSD's in real time, in the size ranges of 0.0143 μm to 0.6732 μm , with the APS measuring in the size ranges of 0.532 μm to 20 μm . The SMPS and APS data are combined and shown in the same figure. As shown in Fig. 1, the BLPI sampling system includes a water-cooled, nitrogen-quenched isokinetic sampling probe, a cyclone, a BLPI, a vacuum pump, a nitrogen gas cylinder, and a flow meter. The SMPS/APS sampling system includes the same water-cooled, nitrogen-quenched isokinetic sampling probe, a nitrogen gas cylinder, a flow meter, clean compressed air, an orifice, SMPS, APS, and a dilution manifold. The SMPS/APS sampling system, with a total dilution ratio of about 200 to 400 to 1, uses two-stage dilutions to prevent further interactions between particles.

Sampling was as isokinetic as possible for both air and oxy cases, based on calculated furnace flue gas rates and measured sampling flow rates, which were adjusted for air and oxy conditions through changes in the dilution N_2 flow rate.

2.4 Experimental conditions and analysis methods

A Power River Basin (PRB) coal was used in this research, and its composition is shown in Tables 1 and 2.

To identify PRB coal ash formation characteristics in oxy-coal combustion and ascertain the relationship between ash aerosol chemistry and ash deposits chemistry, experiments on air and OXY50 combustion were conducted on the OFC. Details about combustion conditions could be found elsewhere [9].

Ash aerosol PSDs were obtained by both BLPI (gravimetric) and SMPS/APS (electric mobility and light scattering). The ash aerosol particles on cellulose acetate membranes were analyzed by scanning electron microscopy–energy-dispersive X-ray spectrometry (SEM–EDS) for elemental composition analysis. The collected deposits, on the other hand, were analyzed using computer-controlled scanning electron microscopy and SEM (CCSEM). In this work, the chemistry of the deposits rather than their deposition rate are of interest.

We did not report an overall ash balance because deposits on the wall and large bottom ash particles that are not collected make this impossible for equipment of this scale.

3. Results and discussion

3.1 Ash aerosol PSD

For comparison and validation purposes, both the BLPI and the SMPS/APS were used to measure the PSD of the ash aerosol. The ash aerosol PSDs of both air and OXY50 combustion are shown in Fig. 3. The BLPI and the SMPS/APS PSD's showed excellent agreement, with the latter instruments providing greater resolution. The flue gas flow rate of the OXY50 case ($13.36 \text{ Nm}^3/\text{h}$) is significantly less than that of the air fired case ($30.65 \text{ Nm}^3/\text{h}$). Gas volume-based PSD's are shown on Fig. 3a, whereas PSD's based on the input ash amount (Fig. 3b) account for different dilutions between the air and oxy-firing case. Fig. 3a shows higher ash aerosol concentration in OXY50 for all measured size ranges, these differences are much diminished once dilution effects are taken into account (Fig. 3b).

As shown in Fig. 3, the ash aerosol PSD's contain (at least) three modes for both air and OXY50 combustion. Two of these modes lie within the particle size regime caused by ash vaporization, with one mode less than $0.1 \mu\text{m}$ most probably caused by nucleation of ash constituents in the dilution sampling probe, and the other one, lying between $0.1 \mu\text{m}$ to $1 \mu\text{m}$, being the accumulation mode of coagulated nuclei formed in the combustor. Dilution at the tip of the sampling probe is designed to inhibit

subsequent coagulation there. The modes for particles larger than 1 μm are fragmentation modes, and, following Linak et al [21], may be divided into a fine fragmentation mode ($<2.5\mu\text{m}$) and a coarse fragmentation mode ($\sim 10\mu\text{m}$). Switching from air firing to oxy-firing (OXY50) moves the peak of the first vaporization mode from 0.06 μm to 0.17 μm most probably because of increased vaporization at the higher flame temperatures [22], increased nucleation and subsequent coagulation [23], either before or after the sample probe intake. Taking dilution into account, Fig. 3b shows that for the same amount of input-ash, OXY50 also produces a greater amount of particles in that size range than did air firing. This will be shown below to have implications on deposition of the first, inner layer of deposits. Jia et al. [12] obtained a similar result for the PRB coal, where combustion in a 31.5% oxygen O_2/CO_2 environment yielded smaller amounts of nuclei ($< 0.1\mu\text{m}$) particles than for either air or 20% oxygen O_2/CO_2 environments. The fine resolution data from the SMPS/APS on Fig. 3b showed that OXY50 also yielded a lower mass of particles in the fine fragmentation mode, with the peak in that mode shifted somewhat to the smaller size. The coarse fragmentation mode was essentially unchanged.

3.2 Elemental compositions of ash aerosol

The ash aerosol collected on cellulose acetate membranes on the BLPI plates was analyzed for elemental compositions by EDS. Given the very small amounts of samples on stages 10 and 11, only the ash aerosol on stages 1 to 9 (size ranges of 0.0324 μm to 3.77 μm) were analyzed. The size segregated distributions of the main elements Na, S, Si, and Fe are shown in Fig. 4. These elements comprise a subset of those that were analyzed, and are highlighted here because they show significant differences in their size segregated concentrations between air firing and oxy-firing. It should be noted that the particle aerodynamic diameter used to plot BLPI data is not identical to the visual diameter measured by CCSEM. An aerodynamic diameter of 3.77 μm is equivalent to a geometric visual diameter [24, 25] of 2.36 μm , assuming a particle density of 2.56 g/cm^3 .

The mass fraction of Na is higher in air combustion than in OXY50 for all impactor stages in the range 0.0324 μm to 3.77 μm . This might be due to increased scavenging of Na vapor by larger alumina-silicate particles at the higher combustion temperature in OXY50. Previous studies [26-27] have shown that increased temperatures actually result in a decrease in the sodium sulfate fume, because of increased reaction with aluminum silicates or silicates to form sodium aluminum silicates or sodium silicates, even though more Na might initially be vaporized [28].

Sulfur is enriched in the vaporization modes, most probably occurring by condensation in the probe. Its mass size distribution is similar in both air and OXY50, although its concentration is ostensibly lower throughout the vaporization modes in OXY50. This is consistent with the decrease in sodium vapor produced under OXY50 conditions, and its propensity to form sodium sulfate. Furthermore, the high CO_2 partial pressure in OXY50 combustion may well restrain sulfate formation [29]. Some sulfates will homogeneously nucleate or condense directly onto a cold surface at 1250 K temperature [30, 31]. However, most of the sulfates will condense on the suspended particles, forming sulfate-coated particles. The mixture of the sulfates is molten and sticky between 1157 and 1250 K [31]. Therefore, the sulfur in the vaporization modes may contribute largely to the initial layer deposition at the deposition collection port temperature of 1200 K.

There is a significant difference in the size segregated silicon concentration distribution in particles formed in air and oxy-combustion. The Si concentrations in the ultrafine vaporization mode are much higher under OXY50 conditions, either because of the higher combustion temperature in OXY50 [22] or possibly because of increased CO levels near the particle surface. The size segregated composition of Fe presents the converse picture compared to silicon. Fe concentrations in the ultrafine vaporization mode are lower for OXY50 conditions than for air firing. This is consistent with Sheng [32] who found increased iron present in glass (presumably in larger particles) under oxy-firing conditions. It is unclear whether this is a temperature effect or a CO_2 chemistry effect or both.

3.3 *Ash deposits chemistry and its relationship with ash aerosol*

Fig. 5a and 5b show the composition and morphology of the inside deposits, for all particles observed to be less than $4.6\text{ }\mu\text{m}$ in diameter. Inside deposits after 1 hour exposure and after 7 hours exposure to the flue gas were analyzed. Inside deposits constitute those not easily removed by tapping the deposit probe, and have been shown to be similar to deposits laid down by thermophoresis rather than by impaction [9]. The deposit probe wall temperature was held constant at 923 K. Differences between 1 hour and 7 hours holding times might be due to increasing “dilution” of the early deposit constituents by the bulk ash that arrives later by impaction and sticks. Note that the high Si content of the 1 hour deposit under OXY50 conditions is double that under air firing conditions. This is consistent with the increased ultrafine vaporized silicon rich particles produced under OXY50 conditions (see Fig. 4). Note, also how the 1 hour deposits have lower S and lower Na under oxy-firing than under air firing. This also is consistent with the differences in the vaporized ultrafine aerosol data shown on Fig. 4. It is also noteworthy that the S content in the deposits increases from 1 hour through 7 hours for both air and oxy firing. This suggests that sulfated ash continues to be impacted and to stick on the deposit surface as time proceeds.

It is appropriate to address the issue of particle sizes found by CCSEM in the deposits. The inside deposits appear mainly to consist of particles with geometric sizes less than $4.6\text{ }\mu\text{m}$ [9]. However, the geometric size of the original ash aerosol forming the inside ash deposits is actually much smaller than $4.6\text{ }\mu\text{m}$. The SEM photograph of the inside deposits, shown in Fig. 5b, suggests that some larger particles are formed by agglomeration of groups of small particles with geometric sizes less than $2.5\text{ }\mu\text{m}$. Therefore, the ash aerosol with particle geometric sizes of less than $2.5\text{ }\mu\text{m}$ (equals to about $3.77\text{ }\mu\text{m}$ in aerodynamic size) is the original source of the inside deposits.

Sodium exhibited a straightforward relationship between ash aerosol and inside deposition, that is, compared with OXY50, higher sodium in the ash aerosol of air combustion results in higher sodium in

the inside ash deposition of air combustion. Furthermore, the sodium mass fractions in ash aerosol matched those in inside ash deposition, which are around 5% in air and 3% in OXY50. The results imply that the sodium concentration in the initial layer deposition may be predicted by merely examining ash aerosols. However, the contribution of S and Si to inside deposits seems to be more particle size selective.

Sulfates and sulfate-coated particles are molten and sticky at between 1157 and 1250 K, and thus, could be easily captured on a cooled surface. The flue gas temperature at the deposition collection port is about 1200 K. Therefore, during air combustion, the higher S concentration in the ultrafine and fine vaporization mode ash aerosol indicated more sulfates than under oxy-coal conditions. Consequently deposits contain more sulfur during air combustion than for the OXY50 case. Alternatively, sulfur in the deposits might be replaced by carbon, or sulfate formation might be otherwise diminished, in the high CO₂ partial pressure environment occurring in OXY50, as hypothesized by some studies [29, 33]. Chen et al. [29] noticed that the high CO₂ partial pressure in oxy-fuel furnace had an inhibitory effect on limestone calcination and Zhan et al. [33] reported higher CO₃/SO₄ ratios (measured by XPS) in the bulk ash and deposits from oxy-coal combustion than those from air combustion.

4. Conclusions

Ash aerosol particle size distributions measured by SMPS/APS were consistent with BLPI. The high resolution PSD's measured by the SMPS/APS showed two modes within the vaporization regime and two modes within the fragmentation regime. Oxy-combustion with 50% O₂ in the inlet oxidant (OXY50) increased the size and location of the first vaporization mode, most probably through increased vaporization of silicon at the higher flame temperatures experienced there. Conversely, the fine fragmentation mode decreased under OXY50 conditions, for reasons that are unclear.

The chemistry of the ash deposits collected on a specially designed, controlled deposit probe, were related to the ash aerosol data. The composition of the inside deposits was consistent with the composition of the vaporization mode aerosol. Under OXY50 conditions, the higher Si concentrations in vaporization mode, led to increased concentrations of Si in the early deposits. However, air combustion produced increased S in both the ultrafine aerosol and in the early deposits, compared to OXY50.

In order to elucidate mechanisms of deposit formation two types of data appear to be useful. First, it is important to separate the early deposits that are bound more tightly to the cooled surface from the bulk deposits. Their composition differs from the bulk deposits, and contributes to adhesion mechanisms allowing the bulk deposits to accumulate. Second, one needs the size segregated composition of the ash aerosol, with emphasis on particle sizes in the sub-micron vaporization mode. It is the fine and ultra-fine particles that dominate the early stages of ash deposition.

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Table 1

PRB coal analysis (as-received basis).

Ash (%)	C (%)	H (%)	N (%)	S (%)	O (diff) (%)	LOD	V (%)	FC (%)	HHV (BTU/lb)
4.94	53.72	6.22	0.78	0.23	34.11	23.69	33.36	38.01	9078

LOD: loss on drying.

Table 2
PRB coal ash analysis.

Al ₂ O ₃ (%)	CaO (%)	Fe ₂ O ₃ (%)	MgO (%)	MnO (%)	P ₂ O ₅ (%)	K ₂ O (%)	SiO ₂ (%)	Na ₂ O (%)	SO ₃ (%)	TiO ₂ (%)
14.78	22.19	5.2	5.17	0.01	1.07	0.35	30.46	1.94	8.83	1.3

Fig. 1 Oxy-fuel combustor (OFC) structure, temperature profiles and ash aerosol sampling systems.

Fig. 2 Inside, outside, vertical and side deposits (see also additional details in Reference [9]).

Fig. 3 Ash aerosol PSD measurements by BLPI and SMPS/APS from air and OXY50 combustion: (a) volume-based; (b) input-ash based.

Fig. 4 Size segregated concentrations of Na, S, Si and Fe in the ash aerosol from air and OXY50 combustion.

Fig. 5 (a) Elemental compositions of inside deposits (geometric size less than 4.6 µm) from air and OXY50 combustion; (b) SEM image of inside deposits [9].

Figure captions

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