Ash formation and deposition during oxy-coal combustion in a 100kW laboratory combustor with various flue gas recycle options

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Abstract

Fouling and slagging processes are important in oxy-coal combustion processes because they greatly influence heat transfer and boiler performance. Ash partitioning processes are precursors to deposition processes and so in order to predict the latter one must have a good understanding of the former. This work involves a 100 kW rated down-fired oxy-fuel combustor outfitted with sophisticated ash aerosol and ash deposit sampling equipment. The work differs from that previously published, in that here we focus on the effects of changes in the composition and amounts of actual recycled flue gas (RFG) streams used in oxy-coal combustion, not using once-through CO₂, as before. Conditions examined here included oxy-coal combustion with three different RFG cleanup options and two different RFG amounts, and results consist of size segregated compositions of the ash aerosol and spatially resolved compositions within the deposits. In general, results suggested that oxy-combustion conditions did not cause *major* changes in ash partitioning, fouling and slagging. There are, however, changes in both the compositions of the ultrafine particles and in that of the inner layer of the deposits, and these were due to higher flame temperatures, when these occurred. These results are discussed and interpreted in detail.

Keywords: oxy-coal combustion; ash; aerosol; deposition; recycled flue gas.

1. Introduction

CO₂, one of the main contributors to climate change [1], attracts more and more attention. As a major source of CO₂ emissions, the pulverized coal combustion power generation industry is likely to have to confront CO₂ capture and sequestration in the foreseeable future. Oxy-coal combustion, which yields a CO₂ rich exhaust gas suitable for sequestration, burns coal in a mixture of pure oxygen and recycled flue gas (RFG), rather than in air. It is a promising option for retrofit to existing, or slightly modified, coal fired power plants. Numerous studies have been conducted to evaluate this technology and have been summarized in several comprehensive reviews [2-7].

Ash formation is an important concern in coal combustion due to the formation of slagging deposits, fouling deposits and particulate matter emissions [8, 9]. Slagging deposition is made up of the fused ash that sticks on the furnace walls in the radiation zone, while fouling deposition is the friable ash that adheres to heat transfer tubes in the convection zone. These ash deposits (slagging and fouling) on furnace walls would produce changes to radiative heat transfer in the radiation zone and increased resistance to heat transfer in the convection zone. They can cause corrosion and even accidents [8]. Particulate matter is the fine ash aerosol, a portion of which can penetrate the ash collection system, causing a hazardous air pollutant emission into the atmosphere. Therefore, knowledge of ash

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formation and ash deposition during oxy-coal combustion is required to evaluate the impact of this technology when retrofitting existing units from air to oxy-firing.

Ash formation during coal combustion is a complex process of mineral transformations, which include fragmentation, vaporization, coalescence, condensation, reaction, nucleation and coagulation [9]. The ash aerosol will then deposit to form slagging, fouling deposits and airborne particulate matter. Information on the ash aerosols, therefore, is essential to help understand and alleviate deposition consequences.

Currently, few studies are reported on both ash aerosol and ash deposit formation during oxy-coal combustion. As far as ash aerosol research is concerned, tests [10-12] conducted on bench-scale facilities show consistent results, namely, compared to air combustion, oxy-coal combustion with the same input O_2 concentration shifts the peak of ultrafine vaporization mode ash aerosol to a smaller size. Increasing the inlet O_2 concentration, moves the peak of the ultrafine vaporization mode to a larger size. Its concentration also increases. The effect of inlet O_2 concentration on ash aerosol formation is due largely to the effect of differences in combustion temperature. Higher combustion temperature from the higher inlet O_2 concentration case, vaporizes more ash in the ultrafine vaporization mode, increasing coagulation rates and moving the peak of the ultrafine vaporization mode to a larger size. However, the research [13, 14] performed on pilot-scale facilities exhibit inconsistent results. Under a similar furnace temperature profile for air and oxy-coal combustion, Yu [14] suggests insignificant differences in both ash aerosol particle size distribution (PSD) and chemical composition, while Li [13] shows that oxy-coal combustion produces more fine ash aerosol. For ash deposition, contradictions also exist in the literature for both ash deposition rates [13-18] and deposits chemistries [14, 16, 18, 19]. These have been summarized in our previous study [20] and might be due to variations in coals, combustion conditions, sampling parameters, as well as insufficient spatial resolution of mineral concentrations within the deposits [20].

Using a novel deposition probe we demonstrated that it was important to spatially segregate ash deposits into initial and outer deposit layers [20]. Then, the size segregated composition of the ash aerosol was related to that of initial layer of the deposits [21]. The results suggested that initial layer deposits consisted of the vaporization mode ash aerosol transported to the surface by thermophoresis. The previous work, however, focused on oxy-coal combustion experiments with pure once through CO_2 as the diluent for oxygen. This did not allow for variations in SO_2 , water, and ash content in the recycle stream. The current work reported here builds on the previous work [20, 21] but extends it to oxy-coal combustion with actual recycled flue gases, of various compositions and in various amounts. The objective was to explore the impact of various practically realizable RFG cleanup options on the resulting ash aerosol and deposit. Other work from our laboratory dealt with total (not spatially resolved) ash deposits on uncooled ceramic surfaces, also with once through CO_2 [14]. Other published work [22] using actual RFG focused only on the ash aerosol, and not simultaneously on the ash deposit, as did this work. The relationship between the size segregated composition of the ash aerosol from a given coal and the composition of the segregated inside fouling deposits, is an important feature of this work. Additional focus here is also on the uncooled slagging deposits obtained in the radiation zone, where all experiments described below were performed using actual RFG, not once through CO_2 as the diluent.

2. Material and Methods

2.1 Oxy-fuel Combustor (OFC) with Flue Gas Recycle (FGR) System

A pilot-scale Oxy-Fuel Combustor (OFC) with an FGR system was used in this work. The OFC allows systematic controlled tests, but still represents combustion conditions of commercial-scale units, especially in terms of temperatures, particle concentration and mixing. More details about OFC can be found elsewhere [20, 23].

A bag house system, installed after convection zone, was used for fly ash removal [24], as shown in Figure 1(a). It utilizes six fabric filters [0.14 × 0.79 m (diameter × length)], which are made of nomex cloth and could operate at temperatures as high as 473 K. A gas-injected pulse system is designed to prevent ash particle buildup on the filters. Either CO₂ from a CO₂ tank donated by Praxair (for oxy-coal combustion) or compressed air (for air combustion) could be injected into the bag house to shake off the ash particles. The pulse interval is set at 300 seconds and each pulse lasts for 999 milliseconds. The filters could be removed for experiments employing FGR without particle removal (dirty recycle).

A condenser, as shown in Figure 1(b), was used to remove the moisture in the flue gas [24]. To reduce air leaking in as much as possible in oxy-coal combustion with RFG, pressure resistance in the RFG stream needs to be minimized. Therefore, the condenser is designed to be a two-stage direct contact heat exchanger, with water as the cooling medium. The first stage is that flue gas enters from the bottom of the condenser and bubbles up through the water. The second stage is the spray of cold water from the top of the condenser, while the flue gas flows up and exits from the top of the condenser. This process could help cool down the flue gas to below 43°C with little pressure drop. When the cooling water contains dissolved (and suspended) lime(CaO),the condenser acts as both condenser and scrubber to remove both H₂O and SO₂ from the flue gas. The condenser is located downstreamof the bag house and could be bypassed by manually disconnecting it.

Two blowers, as shown in Figure 2, were used for the RFG stream [24]. One is a small size blower, which could produce high pressure (25 kPa) recycle, but is functional only for clean low temperature flue gas. The other is a very much oversized blower, which produces only low pressures (5 kPa) and could work for high temperature (505 K) and particle laden flue gas. The large oversized blower is used only for particle laden recycle (dirty recycle) case, and only 5% of the gas recycled in that blower is drawn off for the dirty RFG stream. The remainder 95% is recycled through the blower, in order to allow it to operate at its design capacity, which is necessary, in order for it to handle particle laden gases. This facet of the design had ramifications as noted in the results section below. The oversized blower with “internal” 95% recycle is used for RFG of dirty flue gas, while the small blower is used for all the other FGR cases.

Figure 1. (a) bag house system and (b) moisture/sulfur removal system.

Figure 2. OFC with RFG system.

2.2 Sampling Systems

A Berner low pressure impactor (BLPI), a scanning mobility particle sizer (SMPS, model 3080; with Model 3081 long differential mobility analyzer (DMA)) and an aerodynamic particle sizer (APS, model 3321) were used for size segregated ash aerosol samples and PSD measurements extracted from port 9. The BLPI has a 50% aerodynamic cutoff diameters of 15.7, 7.33, 3.77, 1.98, 0.973, 0.535, 0.337, 0.168, 0.0926, 0.0636, and 0.0324 μm . Cellulose acetate membranes were used as substrates to collect ash aerosol samples for subsequent chemistry analysis. Aluminum substrates coated with Apiezon grease were used to determine gravimetric PSD's, together with a high-quality Mettler Toledo balance with a precision of 0.1 μg . The SMPS and APS provided PSD's in the size ranges of 0.0143 μm $\sim$ 0.6732 μm and 0.532 μm $\sim$ 20 μm respectively. The SMPS and APS data were merged and plotted together. Details of the aerosol sampling systems could be found elsewhere [21]. Collection of *fouling* deposit samples was achieved using a novel surface temperature controlled ash deposition probe system that allowed theseparation of fouling deposits into inside, outside, vertical and side deposits, as described in a previous paper [20]. The probe surface temperature was kept at 923 K with a holding time of one hour and location of port 6 [20], where the flue gas temperature is similar to those around the superheaters in full scale units. In addition to this, an *uncooled ceramic* tube [0.03 $\times$ 0.12 m (diameter $\times$ length)], attached to the end of a water-cooled stainless probe, was used to collect *slagging* deposits (as opposed to *fouling* deposits). The slagging deposits on the ceramics tube were scraped off for further analysis. The slagging deposits were collected at port 4 [20] right off the flame in the radiation zone, with a holding time of two hours.

2.3 Experimental Conditions and Analysis Methods

Ash aerosols and ash deposition data were obtained from cases of oxy-coal combustion with three different RFG cleanup options and two different RFG amounts. The three different RFG cleanup options are:

- 1) RFG with ash removed, which means recycling the flue gas right after the bag house.

- 2) RFG with ash and moisture removed, which means recycling the flue gas right after the condenser.
- 3) RFG with ash, moisture and sulfur removed, which means recycling the flue gas right after the scrubber.

The two different RFG amounts are:

- 1) 27 vol. % O₂ / 73 vol. % RFG (overall) in oxy-coal combustion.
- 2) 50 vol. % O₂ / 50 vol. % RFG (overall) in oxy-coal combustion.

The first condition represents that in which radiant heat fluxes between oxy and air firing are matched [5]. Previous data [14] has shown no significant difference between 27% inlet O₂ and 32% inlet O₂, which matches adiabatic flame temperatures. The second condition allows large changes in RFG amount to be investigated. The measured flame temperatures were 1334 ± 20 K and 1441 ± 10 K for OXY27 cases and OXY50 cases, respectively. These were measured using a bare, unshielded K-type thermocouple and so these reported temperatures are lower than the true temperatures, although they may demonstrate relative values for comparison purposes. Although a shielded suction thermometer would have provided more accurate measured temperatures under hot flue gas conditions, it could not be used at the current combustor scale because it would withdraw too large a volume of flue gas from the furnace. That reported higher K-type thermocouple values correctly correlate with higher combustion temperatures when these occur, is also supported by the low values of loss on ignition (LOI) under those conditions.[24].

All these cases are labelled as shown in Table 1. A dirty recycle case (RFG with nothing removed) was also attempted for the OXY27 case. However, the operation did not yield reasonable results in that the data obtained suggested that recycling dirty flue gases without particulate removal yielded lower particle concentrations in the exhaust, rather than higher, as would be expected. We now believe that the internal recycle around the oversized blower that was used for RFG in these tests, removed these particles with condensed water within the piping. Therefore, the dirty recycle case with the oversized blower and internal recycle and no baghouse, is not further discussed in this work. It might be noted that this newly uncovered problem calls into question some of the results of Morris et al [22], who showed, using a similar system, that dirty recycle appeared to remove exhaust soot, a process that was then attributed to reburning, but might in fact have removed the soot physically in the internal recycle loop.

Table 1. Experimental cases abbreviation and description.

Case abbreviation	Description
OXY50-Ash	oxy-coal combustion with 50% inlet O ₂ and RFG after bag house
OXY27-Ash	oxy-coal combustion with 27% inlet O ₂ and RFG after bag house
OXY50-Ash-H ₂ O	oxy-coal combustion with 50% inlet O ₂ and RFG after condenser
OXY27-Ash-H ₂ O	oxy-coal combustion with 27% inlet O ₂ and RFG after condenser
OXY50-Ash-H ₂ O-S	oxy-coal combustion with 50% inlet O ₂ and RFG after scrubber
OXY27-Ash-H ₂ O-S	oxy-coal combustion with 27% inlet O ₂ and RFG after scrubber

A Powder River Basin (PRB) coal was the only coal used in the research presented here. Future work will present results from other coals. PRB coal is a sub-bituminous coal, with high moisture content (23.69 wt. %), low ash and low sulfur. Its proximate analysis, ultimate analysis and ash composition data are shown in Table 2 and Table 3 [21].

Table 2. PRB coal analysis (as-received basis).

C	H	N	S	O (diff)	H ₂ O	Ash	V	FC	HHV
(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(BTU/lb)
53.72	6.22	0.78	0.23	34.11	23.69	4.94	33.36	38.01	9078

Table 3. 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

O₂ and CO₂ (for baghouse pulse) needed in the combustion were supplied by the Praxair O₂ and CO₂ storage tanks. No pure CO₂ was injected into the combustion system for oxy-coal combustion cases with RFG. The furnace wall temperature at the ignition zone was set at 1283 K (1850 F). The coal feed rate was set at 4.54 kg/h (10 lb/h). Excess oxygen in the exhaust was fixed at 3 vol. % (dry). CO₂ concentrations in flue gas for all these cases were between 88-95 vol.% (dry). The OFC was always at a slightly positive inside pressure to prevent air leakage.

We experienced some problems due to limitations of the OFC during actual furnace operation under these conditions. First, it is difficult to prevent some moisture condensation in the recirculated flue gas. That is because the RFG temperature is limited by the maximum working temperature (377 K) of the smaller FGR blower. At the OFC scale the high surface to volume ratio in the pipe downstream of the blower exacerbates the flue gas cooling rate. Furthermore, the moisture removal system did not remove the moisture completely (for this high moisture PRB coal) and so the flue gas leaving the scrubber is saturated at temperatures of about 316 K for OXY27 cases and 303 K for OXY50 cases. The saturated vapor pressures of water removed cases are 11.7 kPa and 6.6 kPa for OXY27 and OXY50 respectively, while those of water contained cases are 20 kPa and 17.3 kPa for OXY27 and OXY50 respectively.

3. Results and Discussion

3.1 Ash Aerosol PSD

Ash aerosol PSD's were measured gravimetrically by BLPI and through electric mobility and light scattering through SMPS/APS. Results are shown in Figure 3 (gravimetric PSD's) and Figure 4 (electric mobility and light scattering PSD's) for all the runs listed on Table 1. Figure 3(a) is volume based ash aerosol PSD, that is, aerosol mass per unit volume of flue gas ($\mu\text{g}/\text{m}^3$) versus particle size (μm). It contains the information on ash aerosol concentrations, showing that ash aerosol concentrations in the OXY50 cases are higher in all size ranges, when compared to the OXY27 cases. Figure 3(b) is based on the aerosol mass *per unit input ash* ($\mu\text{g}/\text{g}$) versus particle size (μm). It accounts for the changes in flue gas volume, and shows that the OXY50 cases actually produce more ash aerosol in the submicron particle size range. Figure 4 compares the BLPI data of Figure 3 to the analogous SMPS/APS data. The latter has a finer particle size resolution and potentially can uncover finer detail regarding PSD modes and consequently different particle formation mechanisms. In general, the two PSD measuring technologies show consistent results even though there is an apparent discrepancy at around 0.6 μm which is at the upper limit of accuracy of the SMPS and the lower limit of accuracy of the APS. Nevertheless, both the gravimetric and the electric mobility/light scattering technique show two PSD modes in the submicron region, at the same locations. The SMPS data shows them more clearly because of the increased resolution.

The BLPI offers a fairly narrow size range PSD (0.0324 μm ~ 7.33 μm), and is able to show three modes over its entire particle size range (Figure 3). A distinct ultra-fine vaporization mode at ~0.06 μm for OXY27 and air conditions and a fine vaporization mode at ~0.17 μm for OXY50 conditions. These are followed by a fragmentation mode at ~2 μm . The SMPS/APS combination offers a wider size range PSD (0.0143 μm ~ 20 μm), and exhibits four modes, where the first three modes roughly overlap the three modes uncovered by the BLPI, and the largest particle mode lies at ~10 μm . One can identify modes at a particle size smaller than 0.1 μm as an ultra-fine particle vaporization

mode (probably due to nucleation in the probe), whereas the modes centered at a particle diameter of $0.5 \mu\text{m}$ is the typical accumulation mode resulting from nucleation and significant coagulation prior to sampling. It is also a vaporization mode. A fine fragmentation mode is centered at around $2.5 \mu\text{m}$ and the coarse fragmentation mode centered at around $10 \mu\text{m}$ [25]. The similar PSD's between the air case and all the OXY27 cases, suggest that switching from air combustion to oxy-coal combustion at 27% inlet O_2 to match radiant heat flux[5], may not greatly affect the ash aerosol formation mechanisms, even with different RFG cleanup options applied. However, decreasing the RFG amounts (50% O_2 in the inlet oxidant versus 27% O_2) leads to an increased load of ultra-fine particulates, most probably due to the increased flame temperature. The shift of the vaporization mode from $0.06 \mu\text{m}$ (for OXY27) to $0.17 \mu\text{m}$ (for OXY50) is likely due to the increased concentration of ultrafines in the OXY50 case to allow more rapid coagulation and hence cause the ultrafine mode to shift to the right[26, 27]. This change in ultrafine and fine particle concentrations may impact deposition rates, since the ultrafine and fine particles are the ones that form the initial sticky layer, which is critical to the ultimate rate of fouling[21]. Although different RFG amounts have an apparent effect on vaporization mode particle formation, the RFG's with different cleanup options seem to have insignificant effect on ash aerosol formation, at least in the pilot combustor used here. This is discussed in more detail below.

Figure 3. PSD from BLPI: (a) volume based; (b) input ash based.

Figure 4. Ash based PSD from SMPS/APS and BLPI: (a) OXY27 cases; (b) OXY50 cases.

3.2 Ash Aerosol Elemental Compositions

Size-segregated ash composition data are shown in Figure 5, for S, Si, Na and Ca respectively. Figure 5(a) (c) (e) (g) are the elemental composition for OXY27 and air cases under various RFG cleanup options. Figure 5(b) (d) (f) (h) are the elemental composition for OXY50 cases under various RFG cleanup options.

The partitioning of sulfur is shown in the top panel (Figure 5 (a) (b)). For both OXY27 and OXY50 cases sulfur is concentrated in the vaporization mode particles. However, in order to interpret the sulfur, and to some extent the Na, data, one must consider removal of sulfur (and Na_2SO_4) by water within the piping downstream of the baghouse, which was kept at approximately a constant temperature for all cases. Results for these recycle options are therefore unique to the cooling rates experienced in this equipment, and may not be valid for all full scale systems. Data show that with no water or sulfur removed, but only ash removed, there is less sulfur in the particles for the OXY50 case.

Figure 5. Elemental mass PSD of ash aerosols from BLPI: Na, S, Si and Ca.

than in the OXY27 case. This is because, in the OXY50 case, more sulfur is removed in the piping downstream of the baghouse, at the lower RFG flow rates and longer (post baghouse) residence times. Therefore, when the water in the RFG is removed for the OXY50 case, there is a large *increase* of S in the ultrafines. Removal of sulfur by SO_2 scrubbing from the RFG lowers the concentration of S in the vaporization mode particles for both OXY27 and OXY50, as is to be expected. The higher sulfur content in the ultrafines for OXY27 compared to OXY50 (except for ash and water removed case) is consistent with the results also reported by Sheng [12] who shows higher S concentration in OXY20 compared to OXY40 case. This is associated with the fate of Na, the reaction between Na and Si and the reaction between Na and S, as discussed in greater detail below.

Comparison of Figure 5 (c) and (d) suggest that with only ash removed in the FGR the partitioning of Na in the ultrafines is higher for OXY27 cases than for OXY50. This is maybe due to the effect of increasing temperature on increasing the reaction rate of the scavenging reaction between Na and silica or alumina-silicate particles[28]. Note that for OXY50 the Na (Figure 5d) very roughly tracks the Si (Figure 5f), whereas for OXY27 it does not (Figure 5c,e). HSC equilibrium calculations, as shown in Figure 6, show that sodium silicates are stable at high temperatures 1000-1500K. Gallagher et al [28] conclusively showed that the reactive scavenging of sodium vapor by large alumino-silicate particles increased with increasing temperatures, due to increased reaction rates. The current data support these conclusions. Unlike the silicates, calcium sulfates are not stable at the higher temperatures. The effect of different RFG cleanup options on Na for the OXY50 cases is consistent with the hypothesis that Na_2SO_4 is removed by condensing water in the piping downstream of the baghouse. The highest Na content is found in all particle sizes when water and ash but not sulfur are removed. Without sulfur, there can be no formation of sulfate in the pipe, and without water any sulfate particles formed are not removed. Most of the sodium, however is bound with the silicon, which it tracks. Only a small fraction of Na is sulfated in the piping, leading to the trend observed in Figure 5d).

Figure 6. Species equilibrium calculated by HSC. The various RFG cleanup options show insignificant effect on ash composition, therefore, only the equilibrium results of OXY27-Ash-H₂O-S (OXY27 in this plot) and OXY50-Ash-H₂O-S (OXY50 in this plot) cases were shown here. To specify the Na-Si and Ca-S species, only abundant species of Na-Si and Ca-S were shown in this plot. Stable species are shown as a function of temperature, with no significant difference between OXY27 and OXY50.

Si is rich in both ultrafine vaporization mode and fine fragmentation mode for OXY50 cases, while merely rich in fine fragmentation mode for OXY27 cases. It roughly tracks Na for OXY50 but not for OXY27. Both effects can be explained by the higher temperatures for OXY50, which vaporize more silicon and enhance the reaction rate of silicon and sodium in the combustor. Quantitative conclusions based on correlations between elements are reached with difficulty because interactions between Na and Si (in the combustor) and Na and S (in the cool flue gas), and the effect of condensed water in the pipe downstream of the baghouse, all complicate interpretations of apparent correlations between the size segregated concentrations of Si, Na, and S. Comparison of the size segregated distribution of Ca in OXY27 (Figure 5g) to that in OXY50 (Figure 5h) suggests that increased temperature (in the OXY50 case) yields increased amounts of Ca in the smaller particles. The effect of various RFG cleanup options (H₂O and S) on Si and Ca transformation is negligible suggesting that Ca and Si did not interact with S or H₂O in the piping downstream of the baghouse, and in this respect differed from Na.

3.3 Relationship among Ash Aerosols, Fouling and Slagging Deposition Chemistry

Figure 7. Elemental mass fraction of inside deposit from RFG cases: S, Si, Na and Ca.

Elemental mass fraction of inside fouling deposits are shown in **Error! Reference source not found.**, for S, Si, Na and Ca respectively. According to previous research [21], vaporization mode ash aerosol is the mainly contributor to inside layer deposits. Here, the effects of higher concentration of S in vaporization mode ash aerosol for OXY27 cases and higher concentration of Si in vaporization mode ash aerosol for OXY50 cases, are to produce higher concentration of S in inside deposits for OXY27 cases and higher concentration of Si in inside deposits for OXY50 cases, correspondingly. The relationship of Na in ash aerosol and inside fouling deposits is not clear, possibly due to low concentration of Na. Story of Ca is not clear and need further analysis.

Figure 8 shows the elemental mass fraction of slagging deposits, for S, Ca, Na and Si respectively. It can be seen that, OXY27 cases have more S and Ca in slagging deposition, comparing to OXY50 cases. This is most likely due to the decreased stability of sulfur containing compounds at higher combustion temperature for OXY50 cases. Furthermore, the chemical form of S and Ca in slagging deposition in OXY27 cases are presumably to be CaSO_4 . This point is supported by the HSC equilibrium calculation, as shown in Figure 6. At the temperature range of 1000-1500K (the combustion temperature of this work falls in this range), the concentration of main Ca-S species (CaSO_4) decreases rapidly with increasing temperature. The results also show that, concentration of Na and Si in slagging deposition in OXY50 cases is twice as much as in OXY27 cases. These are expected because of higher combustion temperature in OXY50 cases and the scavenging reaction between Na and Si. Higher combustion temperature will increase the vaporization of Si, which then help increase the scavenging reaction rate [28]. The sodium-silicates or sodium-aluminum-silicate formed from the scavenging reaction, normally are sticky and could be easily captured as slagging deposition.

It is further found that, comparing to OXY27 cases, the concentrations of S are always less in OXY50 cases for all three different categories of ash (aerosols, fouling and slagging deposits). It is likely that OXY50 cases have higher S retention in the bulk ash than OXY27 cases due to higher combustion temperature, as reported in previous research [14], while OXY27 cases have higher S deposition (fouling and slagging) tendency.

Figure 8. Elemental mass fraction of slagging deposits from RFG cases: S, Ca, Na and Si.

4. Conclusions

Size segregated ash aerosols and ash deposition (fouling and slagging) data were obtained from oxy-coal combustion conditions, with various RFG cleanup options and RFG amounts. The ash aerosols measured by BLPI and SMPS/APS show similar PSD results, which suggest switching from air combustion to oxy-coal combustion with different RFG cleanup options and RFG amounts may not greatly affect the ash aerosols formation mechanisms. However, the vaporization mode peak shifts from $0.06\mu\text{m}$ to $0.17\mu\text{m}$ when switching from OXY27 to OXY50 due to higher combustion temperature in OXY50 cases. In addition, compared with OXY27 cases, OXY50 cases also increase the formation of vaporization mode particles. That change might lead to a higher ash deposition propensity for OXY50 cases than OXY27 cases. Sulfur is concentrated in vaporization mode. Removal of sulfur by water within the RFG piping stream effects the mass size distribution of sulfur, and simultaneously effects that of sodium. The mass fraction of Na in ash aerosols is slightly higher in OXY27 cases than in OXY50 cases for vaporization modes. This is likely due to the increased reaction rate for the scavenging reaction between Na and silicate or alumina-silicate particles in OXY50 cases because of higher combustion temperature and higher vaporized Si concentrations. Vaporization mode ash aerosol is the mainly contributor to inside layer deposits. For the respect of slagging deposits, OXY27 cases produce more S and Ca, and less Na and Si in slagging deposition, comparing to OXY50 cases. This is most likely due to the decreased stability of sulfur containing compounds and increased scavenging reaction between Na and Si at higher combustion temperature for OXY50 cases.

RFG's with different cleanup options seem to be insignificant effect on ash transformation in oxy-coal combustion, the realistic limitations during RFG operation might diminish the difference of expectation. In addition, it could be inferred that OXY50 cases have higher S retention in the bulk ash than OXY27 cases due to higher combustion temperature, while OXY27 cases have higher S deposition (fouling and slagging) tendency.

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