Ash Aerosol Partitioning and Deposit Ash Compositions during Oxy-Coal Combustion under High Inlet $O_2$ Conditions

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Research Objectives and Motivation

**Overall objectives**
- Understand mechanisms of ash deposit formation and determine effects of oxy firing on ash deposit formation mechanisms

**Motivation**
- Deposits on heat transfer surfaces play a major role on coal fired boiler performance
  - In practice, deposits must be removed by soot blowing
  - Understanding of ash deposition mechanism allows prediction of soot-blowing locations and frequency
- Need to predict how retrofit from air firing to oxy-firing affects boiler performance
  - Hence need to predict how conversion from air to oxy-firing affects ash deposit formation
Specific objectives

- Compare ash aerosol partitioning for PRB coal under air-firing and under oxy-firing with 50% inlet O₂ in once-through CO₂.
  - 100kW oxy-fuel combustor
  - Aerosol sample dilution probe
  - Particle size distributions (PSD’s) using Scanning Mobility and Light Scattering Particle Sizers (SMPS/APS)
  - Size segregated particle compositions using Berner Low Pressure Impactor (BLPI). Also PSD using pico-balance for weight measurements.

- Compare ash deposit chemistry under air-firing and under oxy-firing with 50% inlet O₂ in once-through CO₂.
  - Specially designed controlled deposit probe
    - Early deposits
    - Late deposits

- Relate ash aerosol characteristics to deposit characteristics under air firing and oxy-firing with 50% inlet O₂ in once through CO₂.
Advantages
1. Temperatures, particle and species concentrations similar to practical units.
2. Aerosol dynamics (coagulation, condensation etc) similar to those in practical units.
3. Simulates practical units but allows lower cost and better control.

Aerosol, bulk ash sampling port

slagging deposits collection port (un-cooled probe)

fouling deposits collection ports (cooled probe)
Ash aerosol sampling and PSD measurement.

![Diagram of ash aerosol sampling and PSD measurement](image-url)
Size segregated ash aerosol composition
In-situ Deposit Collection System (IDCS)

coupon material: stainless steel; probe material: stainless steel; probe outer diameter: 60.3mm; probe length: 632mm.

coupon surface temperature: 200 - 650 °C
Deposits at different surface locations on deposit collection probe

Note: In the OFC the flue gas flow is laminar at deposit probe position. Hence, turbulent deposition which is important in practical units is not a major deposition mechanism here. However, under these gas laminar flow conditions, inertial impaction is likely to dominate deposition on horizontal surface, but will be absent on vertical surface (where diffusion processes dominate). Need models to extrapolate deposition rates measured here to those in practical turbulent flows.
### PRB Coal Analysis (as-received basis)

<table>
<thead>
<tr>
<th>ASH (%)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>S (%)</th>
<th>O (diff) (%)</th>
<th>LOD</th>
<th>V (%)</th>
<th>FC (%)</th>
<th>HHV (BTU/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.94</td>
<td>53.72</td>
<td>6.22</td>
<td>0.78</td>
<td>0.23</td>
<td>34.11</td>
<td>23.69</td>
<td>33.36</td>
<td>38.01</td>
<td>9078</td>
</tr>
</tbody>
</table>

### PRB Coal Ash Analysis

<table>
<thead>
<tr>
<th>Al$_2$O$_3$ (%)</th>
<th>CaO (%)</th>
<th>Fe$_2$O$_3$ (%)</th>
<th>MgO (%)</th>
<th>MnO (%)</th>
<th>P$_2$O$_5$ (%)</th>
<th>K$_2$O (%)</th>
<th>SiO$_2$ (%)</th>
<th>Na$_2$O (%)</th>
<th>SO$_3$ (%)</th>
<th>TiO$_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.78</td>
<td>22.19</td>
<td>5.2</td>
<td>5.17</td>
<td>0.01</td>
<td>1.07</td>
<td>0.35</td>
<td>30.46</td>
<td>1.94</td>
<td>8.83</td>
<td>1.3</td>
</tr>
</tbody>
</table>
## Operating Conditions and Analysis

### Operating Conditions

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal type</td>
<td>PRB (sub-bituminous)</td>
</tr>
<tr>
<td>Coal feeding rate</td>
<td>10 lb/h (4.54 kg/h)</td>
</tr>
<tr>
<td>Wall temperature</td>
<td>1850 F (1283 K)</td>
</tr>
<tr>
<td>O₂ in flue gas</td>
<td>3% (vol.)</td>
</tr>
<tr>
<td>Case 1</td>
<td>50% O₂ in O₂/CO₂ (once through CO₂, to simulate fully cleaned RFG)</td>
</tr>
<tr>
<td>Case 2</td>
<td>Air combustion condition</td>
</tr>
</tbody>
</table>

### Deposit Ash Collection Conditions

<table>
<thead>
<tr>
<th>Sampling Parameters</th>
<th>Case Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposit Probe Surface (skin)</td>
<td></td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>723, 823, 923</td>
</tr>
<tr>
<td>Flue Gas Temperature (K)</td>
<td>P5 (1292), P6 (1199), P7 (1101)</td>
</tr>
<tr>
<td>Holding Time (hour)</td>
<td>0.5, 1, 4, 7</td>
</tr>
<tr>
<td>Analysis Method</td>
<td>CCSEM, SEM, ICP-MS</td>
</tr>
<tr>
<td>Fixed Parameters</td>
<td>P6, 4h</td>
</tr>
<tr>
<td>Variable Parameters</td>
<td>Skin T 923K, 4h</td>
</tr>
<tr>
<td></td>
<td>Skin T 923K, P6</td>
</tr>
</tbody>
</table>
OFC temperature profiles

Flue gas flow rate:
OXY50: 13.36 m³/hr at Port 9
AIR: 30.65 m³/hr at Port 9

Flue gas flow rate in AIR is about 2.3 times as much as in OXY50.
Analyses of Ash Deposits and Ash Aerosol

• Composition
  • Deposits
    • EDX
    • XPS (See Poster Session – looking for carbonates)

• Collected Ash Aerosol
  • EDX
  • ICP-MS (as required)

• Particle size distribution
  • Deposits
    • CCSEM (Courtesy of SKLCC, HUST)

• Ash aerosol
  • SMPS/APS (TSI Scanning mobility particle sizer and aerosol particle sizer)
  • Low pressure impactor (Berner) plus pico-balance (10^{-7}g)
- Excellent agreement between SMPS/APS and BLPI gravimetric PSD’s
- OXY50 substantially higher sub-micron particle concentrations, probably because of increased flame temperatures to enhance vaporization.
Oxy- and air-ash aerosol: Elemental compositions

- OXY50 enhances vaporization of some mineral elements, such as Ca and Si in the nucleation mode.
- Air-firing enhances formation of submicron Na and S compared to OXY50. Increased scavenging of Na by alumino-silicates at higher T?
- This has implications regarding deposit chemistry of sometimes sticky “inside” deposits that arise from transport of metal vapors and/or nano-sized particles to cool heat transfer surface.
Two methods were attempted to gather deposits. Method 1: Use epoxy to fix the deposit on the probe and attempt to keep sample intact for analysis.

This method proved cumbersome and not practical for analyses purposes, but allows us to observe the deposit on the coupon. All the analyses presented hereafter do NOT use epoxy to bind the deposit sample.
Method 2: Using scraped deposit samples

For the horizontal deposits it was possible to divide the sample into “outside” deposits that were loose and fell off easily from the probe when the probe was rotated, and into “inside” deposits that remained stuck to the probe even after the probe was tapped or shaken with some vigor. These samples of “outside” and “inside” deposits consisted of (largely individual) ash particles.
OXY50 Deposits: inside, outside and vertical surfaces

OXY50: skin temp. = 923 K, Port 6, time = 7 hours

(a) Mass fraction (%) of elements:

Vertical and inside deposits:
1) more S, Ca, Na, Mg than in outside;
2) smaller particles size;

outside:
1) more Si and Fe;
2) larger particles size

- Condensation, thermophoresis, chemical reaction;
- Inside deposit might share the same formation mechanism as vertical deposit.
- Inertial impaction.
OXY50 Deposits: vertical, inside and outside surfaces

SEM Morphology

(a) vertical, ×600  
(b) inside, ×600  
(c) outside, ×600  
(d) vertical, ×5000  
(e) inside, ×5000  
(f) outside, ×5000

Vertical and inside samples have morphological similarity (except for a few particles)
apparent differences in elemental compositions at short deposit holding times (< 1 hour) only;

Therefore, separation of deposits into early (inside) and late (outside) samples is important, as opposed to treating all deposits as bulk deposits only.
Horizontal deposits: Effect of holding time >1h on inside and outside deposits

For times greater than 1 hour, compositions of “inside” and “outside” deposits do not change significantly with time;

However, particle size of both “inside” and “outside” deposits grows slightly with time.
The elemental compositions of “inside” deposits obtained from different temperature (1292K, 1199K and 1101K) flue gas shows no significant difference except regarding S;

Their MSD peak shifts to a larger size as flue gas temperature decrease.
Lower collection probe surface temperatures cause a greater temperature gradient at the probe surface, which will enhance the driving force of particle diffusion through particle thermophoresis (as opposed to Brownian motion or molecular diffusion).
Application of deposit probe: Comparison of deposits from oxy- and air-combustion (oxy- at 50% inlet O₂)

- **“inside” deposits from OXY 50 have higher Si and Fe while lower S and Na comparing to that of air combustion;**
- **no significant difference is found for “outside” deposits.**
• Compositions and sizes of particles collected from the vertical deposit are similar to those collected from the inside surface of the horizontal deposits (but not the bulk deposits).

• Therefore, for the current probe/combustor configuration, the vertical deposits represent the early, inside portion of the horizontal deposit, and mechanisms of formation of the vertical deposit (which can be measured separately and thereby segregated from the bulk deposits) represent those applicable to the early horizontal deposits.

• Deposits collected as a function only of surface temperature suggest that vertical (and hence inside (and early) horizontal) deposits are formed largely by thermophoresis, rather than by Brownian particle or Fickian gaseous diffusion.

• Elemental compositions of bulk horizontal deposits are a function of time for small deposition times (less than 1 hour). For times greater than 1h, no significant effect of holding time on compositions of both “inside” and “outside” deposits were found, although their particle size is increases with time.

• No significant differences were found for “outside” deposits from OXY50 and air, however, “inside” deposits from OXY50 have higher Si and Fe while lower S and Na comparing to that of air combustion, and this is related to the ash aerosol composition.
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