THE USE OF AL-SI ADDITIVES TO IMPROVE MELTING AND DEPOSITION BEHAVIOUR OF BIOMASS ASH

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Supervisors: Prof. Jenny Jones, Prof. William Gale, Prof. Alan Williams, Dr. Patrick Mason

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## Introduction

<table>
<thead>
<tr>
<th>Ash Component</th>
<th>Kaolin (%)</th>
<th>Coal PFA (%)</th>
<th>Olive Cake Ash (%)</th>
<th>White Wood Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash Content</td>
<td>-</td>
<td>-</td>
<td>8.5</td>
<td>1.1</td>
</tr>
<tr>
<td>SiO₂</td>
<td>48.3</td>
<td>58.2</td>
<td>11.2</td>
<td>27.1</td>
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<tr>
<td>Al₂O₃</td>
<td>36.4</td>
<td>20.8</td>
<td>1.2</td>
<td>4.6</td>
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<tr>
<td>Fe₂O₃</td>
<td>0.9</td>
<td>9.3</td>
<td>0.9</td>
<td>2.3</td>
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<tr>
<td>CaO</td>
<td>0.04</td>
<td>2.9</td>
<td>10.3</td>
<td>24.8</td>
</tr>
<tr>
<td>MgO</td>
<td>0.4</td>
<td>1.4</td>
<td>3.0</td>
<td>4.7</td>
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<tr>
<td>Na₂O</td>
<td>0.06</td>
<td>2.3</td>
<td>0.6</td>
<td>1.5</td>
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<tr>
<td>K₂O</td>
<td>2.6</td>
<td>1.70</td>
<td>32.3</td>
<td>9.2</td>
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<tr>
<td>P₂O₅</td>
<td>-</td>
<td>0.2</td>
<td>5.0</td>
<td>2.0</td>
</tr>
<tr>
<td>SO₃</td>
<td>-</td>
<td>0.9</td>
<td>2.4</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Introduction

• High potassium biomass often contains KCl and potassium silicates

• Al-Si additives have shown strong ability to convert KCl and potassium silicates into potassium aluminosilicates
Experiments

• Ash Fusion Testing
  • Indicates effect of additive upon flow temperature of biomass ash

• Sinter Strength Testing
  • To investigate regions of initial particle stickiness/melting (700°C+)
Experiments

- Ash Fusion Testing
  - Indicates effect of additive upon flow temperature of biomass ash
Ash Fusion Testing

White Wood Ash - 900°C

- White Wood Ash w/ 15% coal PFA
- White Wood Ash w/ 5% coal PFA
- White Wood Ash w/ 25% coal PFA
- 100 %White Wood Ash
Ash Characterisation

White Wood Ash - 1280°C

- White Wood Ash w/ 15% coal PFA
- 100% White Wood Ash
- White Wood Ash w/ 5% coal PFA
- White Wood Ash w/ 25% coal PFA
Ash Fusion Testing

Biomass Ashes - Comparison

Thermograms showing ash fusion temperatures:
- 1025-1115°C for WWA
- 915-945°C for OCA
Experiments

• Ash Fusion Testing
  • Indicates effect of additive upon flow temperature of biomass ash

• Sinter Strength Testing
  • To investigate regions of initial particle stickiness/melting (700°C+)

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Experiments

• **Sinter Strength Testing**
  • To investigate regions of initial particle stickiness/melting (700°C+)
1. **Pelletising** - 1.37 MPa used to best simulate deposit formation [1]

2. **Exposure to Heat** - 5°C/min heating rate to avoid thermal shock, 3 hour hold time

3. **Sinter Strength Test** - Pressure applied gradually: arm extension of 5mm/s

Sinter Strength Testing

Ideal Compression Profile - Pellet crumbles under initial application of pressure
Sinter Strength Testing

Ideal Compression Profile - Pressure increases at constant rate, clean fracture
Non-ideal sinter strength!
Sinter Strength & AFT Comparison

Olive Cake Ash
Worst case scenario - Pellet compresses under pressure, rather than fracture - False sinter strength readings, indicates sootblower removal will fail
OCA @ 950°C - XRD

Counts

Position [°2 Theta]

KCl Peak
OCA @ 950°C - SEM-XRF

Electron Image 1

K Kα1

Cl Kα1

100μm
Sinter Strength Pellets
Sinter Strength & AFT Comparison

Olive Cake Ash - 5% PFA addition
Sinter Strength Testing

Counts

Position [°2 Theta]

KAlSi Peak

KCl Peak

OCA5PFA 950

OCA 950
Sinter Strength Testing
Sinter Strength Testing
Sinter Strength & AFT Comparison

Olive Cake Ash - 5% KAO addition

![Graph comparison of sinter strength and AFT for Olive Cake Ash with 5% KAO addition. The graph plots temperature (°C) against sinter strength (MPa) and pellet height (cm). Three curves are shown: OCA, OCA5P, and OCA5K.]
Sinter Strength Testing
Sinter Strength & AFT Comparison

White Wood Ash

![Graph showing sinter strength and pellet height comparison](image-url)
Sinter Strength & AFT Comparison

White Wood Ash - 5% PFA Addition
Sinter Strength & AFT Comparison

White Wood Ash - 5% KAO Addition
## Kaolinite Transformations

<table>
<thead>
<tr>
<th>Temperature Range</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>500-925°C</td>
<td>$\text{Al}_2\text{O}_3\cdot2\text{SiO}_2\cdot2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{O} + \text{Al}_2\text{O}_3\cdot2\text{SiO}_2$</td>
</tr>
<tr>
<td>925-1100°C</td>
<td>$2(\text{Al}_2\text{O}_3\cdot2\text{SiO}_2) \rightarrow \text{SiO}_2 + 2\text{Al}_2\text{O}_3\cdot3\text{SiO}_2$</td>
</tr>
<tr>
<td>&gt;1100°C</td>
<td>$2\text{Al}_2\text{O}_3\cdot3\text{SiO}_2 \rightarrow \text{SiO}_2 + 2(\text{Al}_2\text{O}_3\cdot\text{SiO}_2)$</td>
</tr>
<tr>
<td>&gt;1400°C</td>
<td>$3(\text{Al}_2\text{O}_3\cdot\text{SiO}_2) \rightarrow 3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2 + \text{SiO}_2$</td>
</tr>
</tbody>
</table>

Formation of amorphous phase metakaolinite and silica: known sintering mechanism

High melting T mullite (>1800°C) only created above 1100°C
Sinter Strength & AFT Comparison

5% KAO Addition
Kaolinite Transformations

500-925°C  \[ \text{Al}_2\text{O}_3\cdot2\text{SiO}_2\cdot2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{O} + \text{Al}_2\text{O}_3\cdot2\text{SiO}_2 \]

925-1100°C  \[ 2(\text{Al}_2\text{O}_3\cdot2\text{SiO}_2) \rightarrow \text{SiO}_2 + 2\text{Al}_2\text{O}_3\cdot3\text{SiO}_2 \]

>1100°C  \[ 2\text{Al}_2\text{O}_3\cdot3\text{SiO}_2 \rightarrow \text{SiO}_2 + 2(\text{Al}_2\text{O}_3\cdot\text{SiO}_2) \]

>1400°C  \[ 3(\text{Al}_2\text{O}_3\cdot\text{SiO}_2) \rightarrow 3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2 + \text{SiO}_2 \]

KCl release occurs ~ 800°C, before formation of amorphous phases occurs
Higher melting T KAlSi formed instead
Sinter Strength Testing

![Graph showing sinter strength testing results for different materials and temperatures. The graph compares compression strength (MPa) at 800°C, 850°C, 900°C, and 950°C for materials labeled WWA, WWA5P, WWA15P, WWA25P, WWA5K, WWA15K, and WWA25K. The graph highlights a trend indicating increased strength with higher temperatures.]
Sinter Strength Testing

Counts

Position [°2 Theta]

Fe₂O₃

SiO₂

WWA900C

WWA 5% PFA 900°C
Sinter Strength Testing

Electron Image 9

Al Kα1

Fe Lα1,2

100μm

100μm
Sinter Strength Testing

Counts

Position [°2 Theta]

WWA 5% PFA 900°C

WWA 5%KAO 900°C
Sinter Strength Testing

Electron Image 26

Si Kα1

Al Kα1

100µm

100µm
Further Testing

• High temperature viscometry - to determine viscosity temperature relationship for OCA-5% KAO

• Pilot-scale testing - to determine how effectively lab scale tests reflect boiler operation
Summary

• PFA and Kaolin mechanisms are different, despite similar composition
• Kaolin is extremely effective at reducing KCl release - much less effective for other K species
• Coal PFA improves OCA behaviour to lesser extent
• Induces sintering in WWA, although lower concentrations may improve results
Acknowledgements

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Additional Results
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