PONDED COAL ASH AS A SUPPLEMENTARY CEMENTITIOUS MATERIAL: PRODUCTIVE REUSE INCLUDING CHEMI-MECHANICAL BENEFICIATION

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CREATING THE NEXT®
Fly ash is a byproduct of coal combustion and is currently the most widely utilized supplementary cementitious material in the world.

- Provides improvements to compressive strength, workability, heat of hydration, and resistance to chemical/weather damage.
- Based on its status as an industrial byproduct blending fly ash provide improvements to embodied CO$_2$ emissions and cost.

An industry wide shift away from coal combustion as a source of power (in favor of Natural gas and renewables) is leading to shortages in fly ash supply.

The construction Industry highly depends on fly ash in order to reduce cost and improve quality.

A new, large supply of supplementary cementitious materials is needed in order to compensate for this drop in supply.

Source: U.S. Energy Information Administration, Monthly Energy Review

https://www.eia.gov/todayinenergy/detail.php?id=40013
WHAT IS THE SOLUTION?

• Only approximately half of all fly ash produced is beneficially utilized
• Waste coal ash is placed in wet storage (ponds) or in dry storage (landfills)
• The ACAA estimates that there is >2 billions tons of ponded ash stored around the country
• The majority of coal ash ponds are unlined (~95%) and contaminate groundwater sources exceeding federal levels (~90%)
• 2015 EPA regulations require the relocation or closure of the majority of these ponds
• May utilize the material as an SCM instead of relocating it

https://earthjustice.org/features/map-coal-ash-contaminated-sites

Coal Ash = Fly Ash + Bottom Ash + Flue Gas Gypsum

Liner status of 738 coal ash ponds in 43 states
13 Ashes were collected from 4 power plants
All ashes were derived from eastern bituminous coal
PM ashes were taken from depths: 0.5 – 5 ft and are less than 10 years old
  • PM ashes historically do not consistently meet ASTM C618 standards
PW ashes were taken from depths: 0.5 – 3 ft
  • PW ashes are typically stored due to a lack of market demand
V ashes were collected from depths: 10 – 15 ft and are less than 20 years old
Y ash was collected at shallow depths below phreatic surface using a hydraulic excavator
  • Plant Y possesses no dry collection capacity
## RECLAIMED ASH OXIDE COMPOSITION: XRF

<table>
<thead>
<tr>
<th>Wt.%</th>
<th>Class F Ash</th>
<th>PM1</th>
<th>PM2</th>
<th>PM3</th>
<th>PM4</th>
<th>PM5</th>
<th>PW3</th>
<th>PW6</th>
<th>PW8</th>
<th>PW9</th>
<th>PW10</th>
<th>Y1</th>
<th>V1</th>
<th>V2</th>
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<td>2.0</td>
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<td>8.9</td>
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<td>D₅₀ (μm)</td>
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<td>45.7</td>
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<td>23.4</td>
<td>27.6</td>
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<td>17.9</td>
</tr>
<tr>
<td>Fineness (%)</td>
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<td>50.1</td>
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<td>14.7</td>
<td>21.8</td>
<td>38.6</td>
<td>13.6</td>
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</tbody>
</table>
PARTICLE SIZE DISTRIBUTIONS: LASER PSA

Particle Size Distribution

Percent Passing (%)

0 25 50 75 100

0.1 1 10 100 1000 10000

Particle Size (μm)

PM
PW
Y
V
Class F Ash

CREATING THE NEXT®
TESTING PLAN

• Compressive Strength 2” Mortar Cubes (Strength Activity Index)
  • In accordance with ASTM C109
  • 20% replacement at a constant W/B ratio 0.48
• Isothermal Calorimetry
  • 20% replacement at a W/B Ratio of 0.4
  • Held at 25 °C for 48 hours
• ASR Expansion
  • ASTM C1567 measured up to 14 days
  • 20% Replacement and a W/B = 0.47

https://civilarc.com/compressive-strength-mortar-cubes/
https://www.globalgilson.com/1x1x10inch-single-prism-mold
• Ashes possessing an LOI greater than 8% frequently fail SAI requirements
• Failing ashes also possess larger quantities of hydrated phases
Four of the 13 ashes fail compressive strength Requirements
Two additional ashes fail requirements for LOI and fineness
A total of six ashes fail ASTM C618 Requirements

<table>
<thead>
<tr>
<th></th>
<th>ASTM C618 Class F</th>
<th>PM1</th>
<th>PM2</th>
<th>PM3</th>
<th>PM4</th>
<th>PM5</th>
<th>PW3</th>
<th>PW6</th>
<th>PW8</th>
<th>PW9</th>
<th>PW10</th>
<th>Y1</th>
<th>V1</th>
<th>V2</th>
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<tbody>
<tr>
<td>SiO₂ + Al₂O₃ + Fe₂O₃ (%)</td>
<td>&gt;50%</td>
<td>92</td>
<td>91</td>
<td>93</td>
<td>92</td>
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<td>93</td>
<td>92</td>
<td>91</td>
<td>93</td>
<td>90</td>
<td>90</td>
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<tr>
<td>CaO (Report)</td>
<td>&lt;18%</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
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<td>1</td>
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<td>3</td>
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<tr>
<td>SO₃ (%)</td>
<td>&lt;5%</td>
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<td>0</td>
<td>0</td>
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<td>0</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<tr>
<td>LOI (%)</td>
<td>&lt;6%</td>
<td>10</td>
<td>18</td>
<td>4</td>
<td>9</td>
<td>6</td>
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<td>2</td>
<td>4</td>
<td>3</td>
<td>9</td>
<td>13</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Fineness (%)</td>
<td>&lt;34%</td>
<td>50</td>
<td>34</td>
<td>28</td>
<td>30</td>
<td>37</td>
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<td>29</td>
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<td>15</td>
<td>22</td>
<td>39</td>
<td>14</td>
<td>14</td>
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<tr>
<td>SAI 7 Days (%)</td>
<td>≥75%</td>
<td>81</td>
<td>61</td>
<td>88</td>
<td>72</td>
<td>75</td>
<td>78</td>
<td>78</td>
<td>81</td>
<td>83</td>
<td>71</td>
<td>58</td>
<td>75</td>
<td>87</td>
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<tr>
<td>SAI 28 Days (%)</td>
<td>≥75%</td>
<td>90</td>
<td>70</td>
<td>83</td>
<td>68</td>
<td>78</td>
<td>81</td>
<td>83</td>
<td>85</td>
<td>82</td>
<td>69</td>
<td>62</td>
<td>76</td>
<td>85</td>
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<td>Passes C618 (Y/N)</td>
<td></td>
<td>N</td>
<td>N</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td>Y</td>
<td>Y</td>
</tr>
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</table>
ISOTHERMAL CALORIMETRY

Cumulative Heat (J/g)

Time (Hours)

OPC, Quartz, PM, PW, Y, V

PM1, PM2, Y1
• Ashes possessing elevated hydration heats universally possess larger LOI compared to ashes behaving conventionally.
ASR EXPANSION

Reclaimed Fly Ash Expansion ASTM C1567

- OPC
- Class F Fly Ash
- PM
- PW
- Y
- V

PW10
V1, V2, Y1
PW6, PW3
For low CaO content ashes the ASR mitigation depends on the ratio of primary oxides. With high iron contents aggravating the ASR reaction.
Common problems with ponded ashes:
- High LOI
- Large Iron Contents
- Large PSD
- Low reactivity
- Dewatering

Potential Problem:
- Flue Gas Gypsum

THOUGHTS

Fails C618

Passes C618

<table>
<thead>
<tr>
<th>LOI (%)</th>
<th>Fineness (%)</th>
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<tr>
<td>0</td>
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</tr>
<tr>
<td>5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
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<tr>
<td>15</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

- Passes SAI Requirements
- Fails SAI Requirements
Utilizing chemi-mechanical grinding via ball mill possesses the potential to mitigate a number of these problems.

Mechanical grinding is typically utilized to lower the particle size of a material.

Each impact possesses the potential to create hot spots with high temperature/pressure of up to ~800 °C.

This process destroys crystalline structures increasing quantity of reactive phases.

High water content ashes may provide additional benefits.

*B A Short communication on this topic is currently under review by Fuel*
FORMATION OF SILANOL GROUPS

• The high heat/pressure creates an environment ideal for forming silanol groups

• Silanol groups form on the surface of siliceous materials via hydrolysis, a chemical reaction with water:

\[ Si_2O + H_2O \rightarrow 2 Si - O - H \]

• Silanol groups behave as reactive sites for the induction of the pozzolanic reaction

• Possess the capability of reacting quickly with Ca(OH)₂

• Speeds up the pozzolanic reaction

Pozzolanic reaction between silanols and calcium hydroxide


https://www.researchgate.net/publication/239046276_Density_of_silanol_groups_on_the_surface_of_silica_precipitated_from_a_hydrothermal_solution
Ashes which failed compressive strength requirements were beneficiated: PM2, PM4, PW10, and Y1

These ashes were mixed with H₂O until they reached a “muddy” consistency.

Ashes were grinded in a Mixer Mill MM400 by Retsch for 1 hr at 25 Hz.

Resulting ashes were analyzed utilizing x-ray diffraction (XRD), scanning electron microscopy (SEM), and attenuated total reflectance (ATR).
## X-RAY DIFFRACTION

- Quantified using 10% LaB$_6$ as a reference material
- Shows an increase in amorphous content of between 5 – 36 percentage points

<table>
<thead>
<tr>
<th>Wt. %</th>
<th>Before Milling</th>
<th>After Milling</th>
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<tbody>
<tr>
<td></td>
<td>PM2</td>
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<td>Quartz</td>
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<td>13.7</td>
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<td>Hematite</td>
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<td>Magnetite</td>
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<tr>
<td>Mullite</td>
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<td>Calcite</td>
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<td>Ettringite</td>
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<tr>
<td>Amorphous</td>
<td>59.2</td>
<td>51.6</td>
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</table>
Scanning electron microscopy was conducted on samples PM2 before and after grinding.

Hitachi SU 8230 with a 5 kV acceleration voltage.

Samples were observed between 20 – 50 μm magnification range.

https://www.britannica.com/technology/scanning-electron-microscope
• Attenuated total reflectance were collected for each sample before and after milling

• Nicolet 8700 equipped with a Smart iTR Attenuated Total Reflectance sample accessory

• 64 scans with a resolution of 4 cm$^{-1}$

Work performed by Giada Innocenti

ATR (CONT.)

- A) PM2
- B) PM4
- C) PW10
- D) Y1
Fixes:

- Particle size/fineness Issues
- Increases Reactivity (Change amorphous content and silanol groups)
- Can be performed with a high water content/ reduces dewatering cost
- Resulting product will perform more consistently

Other:

- Workability will not improve
- May not affect LOI