The Effect of Low-Level Sodium Concentrations on the Use of Fly Ash as a Cement Replacement in Concrete

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http://www.flyash.info/
Fly Ash Overview

54 Million tons of fly ash produced (2013)
  • 24 Million tons re-used
  • About 50% re-use in concrete (SCMs)

Benefits of fly as a SCM are many
  • Improved workability & reduced permeability
  • Reduced segregation & heat of hydration
  • Reduced susceptibility to ASR
  • Enhanced sulfate resistance

Challenges to re-use exist
  • Fly ash production down 25% (from as recently as 2008)
  • Reduced base-load operation (composition variability)
  • Higher contaminant levels (LOI, alkali & SO₃)
Potential Sodium Impacts

Increasing use of sodium-containing reagents
- $SO_3$ control (opacity “blue plume”)
- $SO_2$ control (MATS compliance)

Excessive levels of alkali & sulfate can be problematic
- Expansion & damage of hardened concrete
- ASTM C 618 formerly limited alkalis to < 1.5%
- $SO_3$ limited to 5% (Class F & Class C)

Modest alkali levels may not always be cause for concern
- Compositions of fly ash, cement & aggregate must be considered
- Other factors include end use, location & cost
- Generalization is counterproductive
Agenda

01 Overview of SBS Injection™ process
   • Process characteristics relevant to fly ash re-use

02 Summary of Boral testing
   • Objectives
   • Sample collection & preparation
   • Test results

03 Conclusions & recommendations
Visible Emissions

Sulfuric acid emissions can become visible at around 5 ppm
Sulfuric Acid Impacts

- Equipment Corrosion
- Air Heater Reliability
- Mercury Capture
- NO\(_x\) Removal
- Heat Rate
- CO\(_2\) Emissions
SBS Injection – Process Description

Features
• Patented technology
• Sodium-based reagent
• Liquid solution injection
• Dual-fluid atomization
• Selective reactions
• High SO₃ removal efficiencies
• Low reagent injection rates
• Product collected with ash

Benefits
• Opacity elimination
• Corrosion reduction
• ESP enhancement
• HCl & Se removal
• Enhanced heat recovery
• SCR/SNCR flexibility
• Enhanced mercury capture
• CO₂ emissions reduction

Maximum Benefits with “Upstream” Injection
How Does SBS Injection Affect Fly Ash?

Low reagent injection rates minimize contaminants in the fly ash
- Sodium: 0.75 – 3.0% (as Na$_2$O)
- Sulfate: 0.95 – 3.8% (as SO$_3$)

Reagent addition controlled based on load & SO$_3$ molar flow
- Avoids over-injection of reagent
- Sodium & sulfate levels are more consistent

Applied on units firing bituminous coals
- Class F fly ashes effective in suppressing ASR
- Modest levels of alkali more easily tolerated
Test Objectives & Procedures

Perform key chemical & physical testing on actual samples

Samples collected from a station using SBS technology
  • Included ash w/wo SBS
  • Samples collected from 1st & 2nd ESP fields
  • Composited to mimic “total” ash stream
  • Some of the samples without SBS “spiked” with sodium sulfate

Samples included in the testing:
  • Baseline ash (no SBS)
  • Baseline ash with sodium sulfate - 1% & 2% added (as Na₂O)
  • Two samples with SBS in service
Testing Performed by Boral

Particle size distribution

Chemical analyses of fly ash for major species, water & LOI

Concrete samples prepared with 25% cement replacement

Measured fresh concrete properties

• Slump, entrained air, density, initial & final set times

Measured compressive strength of hardened concrete (up to 56 days)

Measured susceptibility to ASR (ASTM C 1260/1567 AMBT)
Particle Size Distribution Results

21 to 28% Retained (ASTM C-618 Specification is 34% Max)
## Fly Ash Sample Composition

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Baseline Fly Ash (No SBS)</th>
<th>Baseline Ash with 1% Na$_2$O Spike</th>
<th>Baseline Ash with 2% Na$_2$O Spike</th>
<th>Fly Ash with SBS #1</th>
<th>Fly Ash with SBS #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon Dioxide (SiO$_2$), %</td>
<td>50.51</td>
<td>49.24</td>
<td>47.75</td>
<td>50.13</td>
<td>50.33</td>
</tr>
<tr>
<td>Aluminum Oxide (Al$_2$O$_3$), %</td>
<td>20.10</td>
<td>19.77</td>
<td>19.04</td>
<td>19.82</td>
<td>20.21</td>
</tr>
<tr>
<td>Iron Oxide (Fe$_2$O$_3$), %</td>
<td>16.44</td>
<td>16.10</td>
<td>15.79</td>
<td>16.29</td>
<td>16.13</td>
</tr>
<tr>
<td>Sum of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, %</td>
<td>87.05</td>
<td>85.11</td>
<td>82.58</td>
<td>86.24</td>
<td>86.67</td>
</tr>
<tr>
<td>Calcium Oxide (CaO), %</td>
<td>1.81</td>
<td>1.74</td>
<td>1.74</td>
<td>1.64</td>
<td>1.66</td>
</tr>
<tr>
<td>Magnesium Oxide (MgO), %</td>
<td>0.77</td>
<td>0.79</td>
<td>0.76</td>
<td>0.79</td>
<td>0.82</td>
</tr>
<tr>
<td>Sulfur Trioxide (SO$_3$), %</td>
<td>0.50</td>
<td>1.47</td>
<td>3.02</td>
<td>1.30</td>
<td>0.95</td>
</tr>
<tr>
<td>Sodium Oxide (Na$_2$O), %</td>
<td>0.94</td>
<td>1.80</td>
<td>3.06</td>
<td>2.18</td>
<td>2.03</td>
</tr>
<tr>
<td>Potassium Oxide (K$_2$O), %</td>
<td>2.67</td>
<td>2.57</td>
<td>2.49</td>
<td>2.51</td>
<td>2.59</td>
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<tr>
<td>Total Alkalies (as Na$_2$O), %</td>
<td>2.70</td>
<td>3.49</td>
<td>4.70</td>
<td>3.83</td>
<td>3.73</td>
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<tr>
<td>Moisture, %</td>
<td>0.25</td>
<td>0.21</td>
<td>0.23</td>
<td>0.14</td>
<td>0.18</td>
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<tr>
<td>Loss on Ignition, %</td>
<td>5.04</td>
<td>5.35</td>
<td>5.22</td>
<td>4.20</td>
<td>4.09</td>
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</table>
## Concrete Samples – Physical Test Results

### Mix Proportions, lb/yd³

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<thead>
<tr>
<th></th>
<th>Capitol</th>
<th>Capitol</th>
<th>Capitol</th>
<th>Capitol</th>
<th>Capitol</th>
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<tbody>
<tr>
<td>Cement Type</td>
<td>517</td>
<td>388</td>
<td>388</td>
<td>388</td>
<td>388</td>
<td>388</td>
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<tr>
<td>Cement Added, lb/yd³</td>
<td>0</td>
<td>129</td>
<td>129</td>
<td>129</td>
<td>129</td>
<td>129</td>
</tr>
<tr>
<td>Fly Ash Type</td>
<td>Control</td>
<td>Baseline</td>
<td>Baseline, 1%</td>
<td>Baseline, 2%</td>
<td>SBS #1</td>
<td>SBS #2</td>
</tr>
<tr>
<td>Fly Ash Type</td>
<td>0</td>
<td>129</td>
<td>129</td>
<td>129</td>
<td>129</td>
<td>129</td>
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<tr>
<td>Fine Aggregate</td>
<td>1442</td>
<td>1414</td>
<td>1414</td>
<td>1414</td>
<td>1414</td>
<td>1414</td>
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<tr>
<td>Coarse Aggregate</td>
<td>1650</td>
<td>1650</td>
<td>1650</td>
<td>1650</td>
<td>1650</td>
<td>1650</td>
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<tr>
<td>Water</td>
<td>308</td>
<td>294</td>
<td>310</td>
<td>279</td>
<td>281</td>
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### Fresh Concrete Properties

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<tr>
<th></th>
<th>3.75</th>
<th>4</th>
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<th>4</th>
<th>3.75</th>
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</thead>
<tbody>
<tr>
<td>Slump, in.</td>
<td>3.75</td>
<td>4</td>
<td>3.75</td>
<td>4</td>
<td>4</td>
<td>3.75</td>
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<tr>
<td>Air, %</td>
<td>1.7</td>
<td>1.5</td>
<td>1.7</td>
<td>1.9</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>Unit Weight, lb/ft³</td>
<td>145.2</td>
<td>145.6</td>
<td>145.2</td>
<td>145.2</td>
<td>146.4</td>
<td>145.6</td>
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<tr>
<td>Temperature, °F</td>
<td>70</td>
<td>69</td>
<td>70</td>
<td>71</td>
<td>70</td>
<td>71</td>
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<tr>
<td>Set Time, Minutes</td>
<td>Initial</td>
<td>287</td>
<td>321</td>
<td>296</td>
<td>280</td>
<td>285</td>
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<tr>
<td></td>
<td>Final</td>
<td>390</td>
<td>461</td>
<td>415</td>
<td>384</td>
<td>402</td>
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</tbody>
</table>

### Hardened Concrete Properties

<table>
<thead>
<tr>
<th>Compressive Strength</th>
<th>1-Day, psi</th>
<th>7-Day, psi</th>
<th>28-Day, psi</th>
<th>56-Day, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Day, psi</td>
<td>1550</td>
<td>3660</td>
<td>5440</td>
<td>6220</td>
</tr>
<tr>
<td>7-Day, psi</td>
<td>1060</td>
<td>3090</td>
<td>4650</td>
<td>5460</td>
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<tr>
<td>28-Day, psi</td>
<td>1340</td>
<td>2900</td>
<td>4140</td>
<td>5470</td>
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<tr>
<td>56-Day, psi</td>
<td>1430</td>
<td>2940</td>
<td>4150</td>
<td>5400</td>
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<tr>
<td>1-Day, psi</td>
<td>1460</td>
<td>3030</td>
<td>4300</td>
<td>5130</td>
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<tr>
<td>7-Day, psi</td>
<td>1470</td>
<td>2900</td>
<td>4390</td>
<td>5400</td>
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</tbody>
</table>
Initial & Final Set Times

- Control Baseline Ash
- Baseline, 1% Spike
- Baseline, 2% Spike
- SBS #1
- SBS #2

Set Time (Minutes)

- Initial
- Final
Compressive Strength

Concrete Strength (psi)

- 1-Day, psi
- 7-Day, psi
- 28-Day, psi
- 56-Day, psi

Legend:
- Control
- Baseline Ash
- Baseline, 1%
- Baseline, 2%
- SBS #1
- SBS #2
ASR (ASTM C 1260/1567 AMBT)

Materials: Capital Type 1 Cement, Varmicon Sand
Conclusions & Recommendations

No significant surprises from the testing
• Fly ash performance consistent with composition
• Minimal effects of sodium noted
  • Reduced set times & improved early strength
  • No impacts in the ASR testing

Similar results for SBS & spiked samples
• Can use spiking procedure to evaluate sodium impacts

Guidelines for sodium alkali
• Minimize added alkali & sulfate
• Limit composition variability
• Modify cement/aggregate properties if necessary/practical
• Perform testing, including longer-term testing if necessary
Thank you
Please contact us for more information

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