In-boiler modification of fly ash
From an uncontrolled byproduct to an optimized SCM to enable maximum clinker substitution

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Macro trend: Growing demand for Green cement and power

Global cement clinker production (tonnes)

- 2010: 3.3bn
- 2013: 3.6bn

Coal ash produced: 1.2 billion tonnes/year
Coal Ash used: 300-350 million tonnes/year (30%)

Use of all coal ash would bring clinker production back to 2006 levels.

Cement as it is today:
- most widely used building material
- cement is blamed for 5% of global CO2 emissions (2.3bn tons/year)
- Annual portland cement production roughly 3.6 billion tonnes in 2010

Energy generation as it is today:
- Coal dominates – and increasing
- Not enough natural gas, oil, nuclear by a long shot
- Emerging technologies slow and still expensive

Coal ash is the only SCM available in large enough quantity to potentially enable 50% and higher clinker replacement (along with slag, limestone, rice hull ash etc)
## MARKET DATA

<table>
<thead>
<tr>
<th></th>
<th>CHINA</th>
<th>INDIA</th>
<th>US</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cement Consumption</strong></td>
<td>1,600 M ton/yr</td>
<td>265 M tons/yr</td>
<td>95 M tons/yr</td>
</tr>
<tr>
<td><strong>Cement market price</strong></td>
<td>US$45/ton</td>
<td>US$110</td>
<td>US$90/ton</td>
</tr>
<tr>
<td><strong>Share of coal in power generation</strong></td>
<td>80%</td>
<td>70%</td>
<td>48%</td>
</tr>
<tr>
<td><strong>Amount of ash produced</strong></td>
<td>425 M tons/yr</td>
<td>175 M tons/yr</td>
<td>85 M tons/yr</td>
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<tr>
<td><strong>Current use of ash produced</strong></td>
<td>30%</td>
<td>30%</td>
<td>43%</td>
</tr>
<tr>
<td><strong>Ash content in coal</strong></td>
<td>25%-45%</td>
<td>35%-45%</td>
<td>6%-15%</td>
</tr>
<tr>
<td><strong>Average ash disposal cost</strong></td>
<td>n/a</td>
<td>US$21/ton</td>
<td>US$15-20/ton</td>
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<tr>
<td><strong>Ash production annual growth rate</strong></td>
<td>15%</td>
<td>9%</td>
<td>1%</td>
</tr>
<tr>
<td><strong>Government mandated re-use of ash</strong></td>
<td>n/a</td>
<td>100% by 2014</td>
<td>n/a</td>
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Macro need - Coal ash: a three decade long debate …

Current Waste stream and disposal of coal ash

COAL FIRED PLANT

Unused ash (includes bottom ash)

60% (~720M tons)

Beneficially used ash

LANDFILL / STORAGE POND

With no viable ash enhancement technology available, over 700 million tons of coal ash are landfilled in the world every year.

Why is 60% of coal ash unused?
- Variability, poor early age performance, carbon, durability, color……
- Existing beneficiation technologies expensive
… leading to a global Environmental catastrophe

The US, India and China produce over 900 million tons of coal ash every year. All three have embarked on regulating disposal, requiring a substantial increase in coal ash utilization.

<table>
<thead>
<tr>
<th>Coal as % of Power Generation</th>
<th>Ash Generated (tons/yr)</th>
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</thead>
<tbody>
<tr>
<td>US 48%</td>
<td>85 M tons/yr</td>
</tr>
<tr>
<td>India 70%</td>
<td>175 M tons/yr</td>
</tr>
<tr>
<td>China 80%</td>
<td>700 M tons/yr</td>
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</table>

December 2008 ash spillage in Kingston, TN - USA

“The size of the Kingston disaster is 48 times bigger than the 1989 Exxon Valdez Oil spill” (Greenpeace)

Ash slurry overflow from the NTPC's Simhadri plant in Devada village in Vishakhapatnam, India in June 2010

Shentou Number 2 Power Plan and ash pond and “ash storm”, Shuozhou, Shanxi province, China

Ash contamination sites and coal plants in the US
In-Boiler Manufactured SCM: a novel process that eliminates waste ash, creates low cost, high value cement substitute

The In-Boiler beneficiation process at the Coal Fired Power Plant

Our process converts a coal-fired plant into a manufacturing plant for a value added cement substitute
In-Boiler beneficiation: Flexible, “green” AND cost effective

How is In-Boiler beneficiation different from other clean technology solutions?

- Better cost position:
  - No separate treatment facility:
  - No inter-facility shipment cost
  - No large capital outlay
  - No costly chemical treatment

- Better market acceptance:
  - Can tailor additions so that treated product falls into existing standards
  - Does not require concrete producers to change the way they operate
  - Yields a consistent product manufactured under controlled production

In-boiler beneficiation does not change the way concrete is produced today, and does not carry the burden of heavy capital investments or transportation costs.
How it works: Chemical & physical / thermal activation

Chemistry

Many industrial “waste” materials and natural deposits (limestone, clays etc) have the right chemistry at low cost.

Physical

Smaller the better – surface area is critical for activation as well as nucleation of cement hydrates in concrete.

Thermal

Similar to kaoline – even an incomplete conversion yields improved performance.

Process

Improved combustion – less carbon, smaller and more reactive fly ash particles. Surface activation.

Example: Targeting faster strength development to allow higher clinker substitution without lower early strength.
**How it works:** In-boiler additions changes the ash to a manufactured material with desired properties

**Inputs:** Each Coal source / boiler combination will have different viable options for adjustments in:

- Raw material selection / dosages
- Injection points (temperature)
- Raw material particle sizes

**End Product:** We control production of a high performance cement substitute, made to desired specifications:

- Target specific performance attributes (strength, durability, LOI)
- Control consistency of end material
- Manufactured product fits into existing standards
  - Geopolymers (Ceratech, Zeobond, etc.) don’t.
Experimental: Sub scale boiler test pilot plant in Wyoming

Details of materials added to the coal fired furnace

<table>
<thead>
<tr>
<th>Raw material addition</th>
<th>Average particle size, μm</th>
<th>Elemental composition mass % by XRF</th>
<th>Details of Portland cement and un-modified fly ash</th>
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<tr>
<td></td>
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<td>SO₃</td>
<td>Na₂O eqv</td>
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<tr>
<td>Limestone</td>
<td>80</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A</td>
<td>8</td>
<td>1.7</td>
<td>0.5</td>
</tr>
<tr>
<td>B</td>
<td>200</td>
<td>0.7</td>
<td>3.9</td>
</tr>
<tr>
<td>C</td>
<td>3</td>
<td>0</td>
<td>0.3</td>
</tr>
<tr>
<td>D</td>
<td>100</td>
<td>0.1</td>
<td>13.3</td>
</tr>
<tr>
<td>E</td>
<td>20</td>
<td>0.3</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Materials:
- Portland Cement “A”
- Portland Cement “B”
- Portland Cement “C”
- ASTM class C fly ash
- ASTM class F fly ash

Elemental composition mass % by XRF:

<table>
<thead>
<tr>
<th>Material</th>
<th>Average particle size, μm</th>
<th>SO₃</th>
<th>Na₂O eqv</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
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<tr>
<td>Portland Cement “A”</td>
<td>18</td>
<td>3.9</td>
<td>0.7</td>
<td>62</td>
<td>20</td>
<td>4.7</td>
<td>3.0</td>
<td>2.6</td>
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<tr>
<td>Portland Cement “B”</td>
<td>23</td>
<td>3.3</td>
<td>0.8</td>
<td>64</td>
<td>19</td>
<td>5.4</td>
<td>2.6</td>
<td>1.1</td>
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<tr>
<td>Portland Cement “C”</td>
<td>24</td>
<td>3.1</td>
<td>0.5</td>
<td>63</td>
<td>21</td>
<td>4.4</td>
<td>3.6</td>
<td>0.7</td>
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<td>ASTM class C fly ash</td>
<td>12</td>
<td>4.7</td>
<td>2.6</td>
<td>30</td>
<td>27</td>
<td>18</td>
<td>6.3</td>
<td>6.7</td>
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<tr>
<td>ASTM class F fly ash</td>
<td>14</td>
<td>2.6</td>
<td>1.8</td>
<td>5</td>
<td>52</td>
<td>20</td>
<td>9.7</td>
<td>2.0</td>
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</table>
Calorimetry: In-boiler modifications improve early hydration of C ash

Effect of additions on reactivity of a 60% high calcium ash - 40% Portland cement blend at 23 C

Untreated ash: Uncontrolled aluminate reaction – Poor strength gain.

In-boiler modified ash: Normal hydration peaks, characteristic of controlled hydration and strength gain.

CleanCem material (red, blue, light blue and black curves) shows favorable early hydration pattern, with heat curves that are similar to Portland Cement.

<table>
<thead>
<tr>
<th>Plot #</th>
<th>Color</th>
<th>Description</th>
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<th>28d psi</th>
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<td>N/A</td>
<td></td>
<td>Plain Portland</td>
<td>3046</td>
<td>5877</td>
</tr>
<tr>
<td>1</td>
<td>green</td>
<td>Plain (unscrubbed) ash</td>
<td>809</td>
<td>3953</td>
</tr>
<tr>
<td>2</td>
<td>yellow</td>
<td>Ash with scrubber</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>3</td>
<td>red</td>
<td>LSSL</td>
<td>n/a</td>
<td>n/a</td>
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<tr>
<td>4</td>
<td>blue</td>
<td>LSRC</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>5</td>
<td>light blue</td>
<td>LSRG</td>
<td>1506</td>
<td>7318</td>
</tr>
<tr>
<td>6</td>
<td>black</td>
<td>LSSLRCRGKSF</td>
<td>2041</td>
<td>10700</td>
</tr>
</tbody>
</table>

Effect of additions on total energy (60% fly ash) as a proxy for potential strength development rate
Effect of additions on reactivity of a 60% low calcium ash - 40% Portland cement blend at 23°C

Effect of additions on total energy (60% fly ash) as a proxy for potential strength development rate

Results from recent full scale field trial in India

- The main target of the trial was to explore if in-boiler modification could reduce un-burned carbon and thereby improve on color
- Approx 2 hrs set acceleration and strength enhancement as well as improved compatibility with PCE seen as secondary improvements.
- Key result was a 50% reduction in un-burned carbon, a lighter colored ash, and a 5% improvement in boiler efficiency

Caution: Many local coal sources in India has very high ash content and are thereby difficult to use to generate good quality ash. We do not expect such drastic performance enhancement for the average US or EU class F-ash
Performance: Sub-bituminous coal: superior compressive strength at 30% replacement …

Strength development of mortar with **30%** In-boiler modified ash vs. untreated ash and pure Cement

![Graph showing compressive strength development](image)

- **30% untreated ash, 70% Portland Cement**
- **100% Portland Cement**
- **30% CleanCem ash, 70% Portland Cement**

Performance Testing made at Clarkson University (NY) and University of Texas, Austin

ANNA MARIA WORKSHOP XII, Concrete for the 21st century, Holmes Beach, FL, Nov 9-11 2011
... and at 60% cement replacement

Strength development of mortar with 60% In-boiler modified ash vs Portland Cement mix and untreated ash.

Performance Testing made at Clarkson University (NY) and University of Texas, Austin.

ANNA MARIA WORKSHOP XII, Concrete for the 21st century, Holmes Beach, FL, Nov 9-11 2011
The CleanCem process: is heat necessary?

Could the Raw Materials used be applied without heat treatment, as a cold blend with ash?

- Untreated ash has insufficient early strength gain (barely sets at 1-day)
- CleanCem treated ash (in boiler) has the best performance, even better than pure Portland Cement
- Ash that is cold-blended with raw materials used in the CleanCem process has a very poor performance across the board

Conclusion: High temperature treatment is essential for the process to work. A raw material- ash blend alone is ineffective, and even detrimental to compressive strength.
Robustness: In-boiler modification yields superior strength across cements: low C3A to high C3A

Curing Ages

Low C3A OPC

High C3A OPC

X-axis: Substitution Level

Y-axis: Compressive strength
Better Durability: ASR testing

ASR Expansion (ASTM C1260)

- Durability of in-boiler modified ash from Sub-bituminous coal (30% substitution) acts similar to OPC
- All in-boiler modified ashes exceed OPC performance at higher substitution rates (40%+)
- Potential to use in-boiler modified ash at higher substitution rate creates advantage over traditional ashes (especially C-ashes)

Drastically improved strength development at 60% substitution allows for much higher replacement levels than today. This in turn results in drastically improved ASR control relative to most untreated C ashes.
Durability: Sulfate resistance

[Graph showing sulfate expansion over time for different concrete mixtures]

- **30% CleanCem (scrubbed)**
- **60% CleanCem (scrubbed)**
- **30% untreated ash (scrubbed)**
Calorimetry tests: Admixture compatibility

Effect of sodium gluconate at 72 F

Effect of sodium gluconate + Calcium nitrate At 72 F
**Ecocrete:** Flowable concrete with less binder

Ecocrete is a low-binder flowable concrete concept developed by Wallevik on Iceland.

### Details of EcoCrete concrete mixture designs tested

<table>
<thead>
<tr>
<th>Materials, kg/m³</th>
<th>Portland mix</th>
<th>Reference ash mix</th>
<th>A-V (modified ash)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland cement &quot;D&quot;</td>
<td>315</td>
<td>215</td>
<td>215</td>
</tr>
<tr>
<td>Reference class F ash</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>A-V in-boiler modified ash</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Water</td>
<td>185</td>
<td>185</td>
<td>185</td>
</tr>
<tr>
<td>Sum binder</td>
<td>315</td>
<td>315</td>
<td>315</td>
</tr>
<tr>
<td>w/c-ratio</td>
<td>0.59</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>Fine aggregate 0-8 mm</td>
<td>1320</td>
<td>1301</td>
<td>1301</td>
</tr>
<tr>
<td>Coarse granite aggregate 8-16 mm</td>
<td>513</td>
<td>506</td>
<td>506</td>
</tr>
</tbody>
</table>

**Concrete compressive strength development**

- **Portland mix**
- **Reference class F ash**
- **A-V in-boiler modified ash**

**Plastic viscosity**

**Yield value (slump life)**

![Concrete compressive strength development chart](chart.png)
Conclusion: AIT process enables higher substitution rates, cost-effectively

Conclusion – AIT CleanCem is a comprehensive process to:

- Improve reactivity – enables higher cement substitution rates (60% or more)
- Improve durability
- Reduce LOI

... AND ALL THIS IN A COST-EFFECTIVE, LOW CAPITAL WAY

- No separate treatment facility, no added transportation costs
- Sorbents derived from other waste streams
- No new QC requirements – use as you would use ash or cement today
Contact Information:
Ash Improvement Technology Inc.

Paul Sandberg
Vice President, R&D

+1 (617) 207-4030 ext. 30
psandberg@aitcleancem.com
Indian industrial trial: Impact of in-boiler modification process on LOI

Conclusion:

There is a direct relationship between LOI reduction and AIT material dosage. The AIT process brought LOI down from 8.4% to 3.79% as dosage of AIT additives gradually increases.
Boiler efficiency is not affected

In solid fuel incineration processes, boiler efficiency is not affected: boiler temperatures stay constant at equal coal input as materials are added to the boiler.
SOx control is improved

Materials added in the process have a favorable effect on SOx reduction (40% SOx reduction)

SO2 levels, measured with different AIT material additions

Baseline - no sulfur removal

After addition of CleanCem materials
No negative impact on NOx Control

Materials added in the process have a neutral effect on NOx control

NOx levels, measured with different AIT material additions

Baseline with no material addition

After AIT material addition
The impact of in-boiler modification on boiler operations

Operational data was monitored throughout the duration of a full scale industrial trial in India

Main observations:

- There was no statistically significant impact on the boiler draft system as a result of injection of additives
- Air flow to the boiler bed was not a problem
- Flue gas pressure drop across the electrostatic precipitator only increased a 0.5 mm Hg at high injection rates
- Induced Draft fan horsepower increased by a maximum of 4 amps (less than normal variations observed in the absence of AIT additive)

Conclusion: Additions to the boiler did not induce any negative impact on normal boiler operation
A more detailed method to measure the impact on LOI

In order to measure the impact of the AIT process, we have to isolate other variables that influence combustion and LOI.

The lowest LOI is achieved at higher efficiencies. AIT’s process has an impact on LOI and boiler efficiency.

As shown in the graph on the left, boiler efficiency also depends on carbon monoxide (CO) and oxygen (O₂) levels.

Hence, the precise impact of AIT material injection has to be measured at constant CO levels and constant O₂ levels.
Impact of In-boiler modification on average LOI isolating Oxygen levels as an independent variable

Conclusion:
At constant O₂ levels in the boiler flue gases, the injection of AIT materials at target levels (80% to 150% of nominal dosage) consistently lowers LOI by ~3 percentage points.
In-boiler treatment to reduce LOI leads to efficiency gains. Post boiler treatment doesn’t.

Due to the high ash content of Indian coal (46%) unburned carbon in ash has a dramatic impact on boiler efficiency.
How it works: Particle size – Grinding effect

Particle sizes: Raw Materials

Particle sizes: Finished Product

Careful choice of raw material PSD and injection point yields a consistent, finely ground finished product
ASTM C151 soundness results for two in-boiler modified ashes

In boiler modified ashes passes demanding soundness test

<table>
<thead>
<tr>
<th>Sample ID:</th>
<th>Soundness, ASTM C151 Autoclave Expansion (%)</th>
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<tbody>
<tr>
<td>1325-96-003</td>
<td>0.00</td>
</tr>
<tr>
<td>1325-79-006</td>
<td>-0.03</td>
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ASTM C 618-08 Specifications

<table>
<thead>
<tr>
<th>Class</th>
<th>Max</th>
</tr>
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<tbody>
<tr>
<td>Class F</td>
<td>0.8</td>
</tr>
<tr>
<td>Class C</td>
<td>0.8</td>
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</table>
Robustness: Effect of material dosages / injection points

CleanCem efficiency with different material dosages / injection points (30% replacement level)

<table>
<thead>
<tr>
<th>Test #</th>
<th>KA</th>
<th>ST</th>
<th>BE</th>
<th>GL</th>
<th>LE</th>
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</tbody>
</table>

100% Portland Cement – 28-day strength

100% Portland Cement – 7-day strength

100% Portland Cement – 1-day strength

Untreated