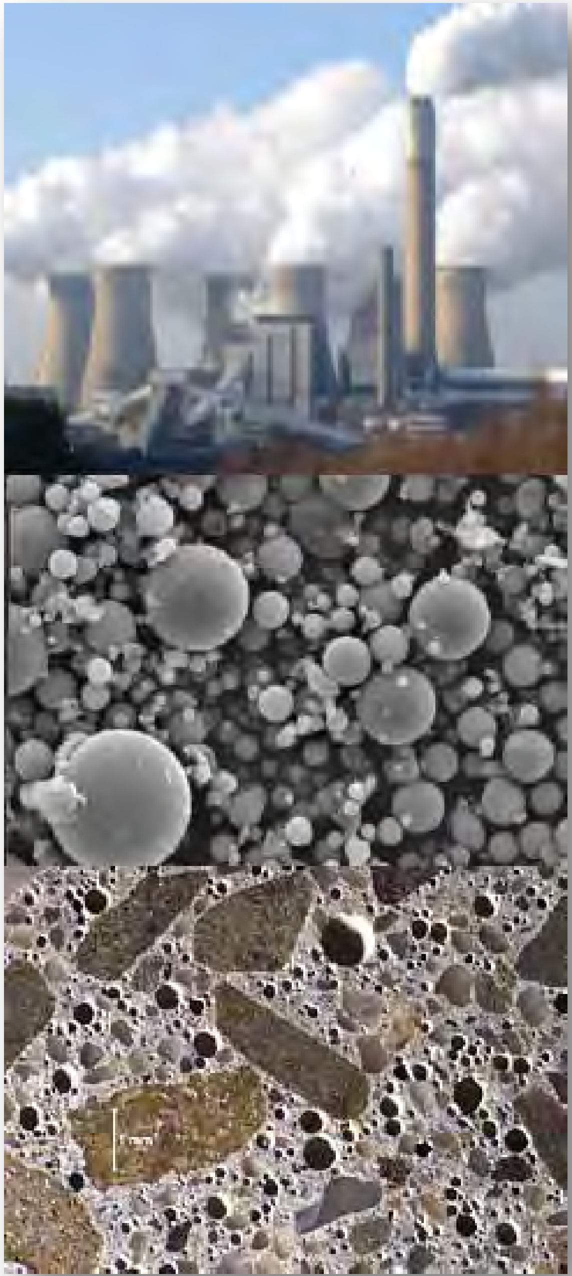
REINHOLD ENVIRONMENTAL Ltd.

# 2016 APC-Wastewater Round Table & Expo Presentation

July 18 & 19, 2016 in Dearborn, MI / Hosted by DTE Energy

BREEN®
SMART SCIENCE • CLEANER ENERGY



# Improving Flyash Quality in a MATS/CPP World


Presented by: Cal Lockert


Presented to: 2016 Reinhold PCUG
July 19, 2016
Dearborn, MI

# Topics for Discussion:

- **What is Flyash?**
- **How can it be “Beneficially Used”?**
- **What Effects do MATS and CPP Regulations have on Beneficial Reuse**
- **What Can be done?**

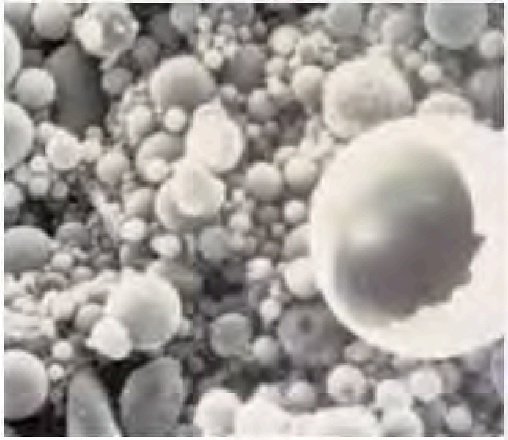
# What Is Flyash?

# Classification of Flyash

**ASTM – C 618-93 categorizes natural pozzolans and fly ashes into the following three categories:-**

1. **Class N Fly ash:**
2. **Class F Fly ash:**
3. **Class C Fly ash:**

A **pozzolan** is a siliceous or aluminosiliceous material that, in finely divided form and in the presence of moisture, chemically reacts with the calcium hydroxide released by the hydration of portland cement to form calcium silicate hydrate and other cementitious compounds.



# Characterization of Flyash

**Requirements for fly ash and natural pozzolans for use as a mineral admixture in Portland cement concrete as per ASTM C 618-93.**

| Requirements | Fly Ash Classification | | |
|---|---|---|---|
| | **N** | **F** | **C** |
| **Chemical Requirements** | | | |
| $SiO_2 + Al_2O_3 + Fe_2O_3$, min % | 70.0 | 70.0 | 50.0 |
| $SO_3$, max % | 4.0 | 5.0 | 5.0 |
| Moisture content, max % | 3.0 | 3.0 | 3.0 |
| Loss on ignition, max % | 10.0 | 6.0 | 6.0 |

# Flyash vs. Cement

BREEN
SMART SCIENCE • CLEANER ENERGY

**COMPARISON OF CHEMICAL AND PHYSICAL CHARACTERISTICS — PORTLAND CEMENT, FLY ASH, SLAG CEMENT, AND SILICA FUME**

*Note that these are approximate values. Values for a specific material may vary from what is shown. (Note 1)*

| PROPERTY | PORTLAND CEMENT | CLASS F FLY ASH | CLASS C FLY ASH | SLAG CEMENT | SILICA FUME |
|---|---|---|---|---|---|
| $SiO_2$ content, % | 21 | 52 | 35 | 35 | 85 to 97 |
| $Al_2O_3$ content, % | 5 | 23 | 18 | 12 | |
| $Fe_2O_3$ content, % | 3 | 11 | 6 | 1 | |
| CaO content, % | 62 | 5 | 21 | 40 | < 1 |
| Fineness as surface area, $m^2/kg$ (Note 2) | 370 | 420 | 420 | 400 | 15,000 to 30,000 |
| Specific gravity | 3.15 | 2.38 | 2.65 | 2.94 | 2.22 |
| General use in concrete | Primary binder | Cement replacement | Cement replacement | Cement replacement | Property enhancer |

# Beneficial Reuse?

# Accepted Beneficial Reuse Areas

BREEN
SMART SCIENCE • CLEANER ENERGY

American Coal Ash Association
38800 Country Club Drive
Farmington Hills, MI 48331
Email: info@acaa-usa.org
Phone: 720-870-7897
Fax: 720-870-7889
Internet: www.ACAA-USA.org

## 2014 Coal Combustion Product (CCP) Production & Use Survey Report

Beneficial Utilization versus Production Totals (Short Tons)

| 2014 CCP Categories | Fly Ash | Bottom Ash | Boiler Slag | FGD Gypsum | FGD Material Wet Scrubbers | FGD Material Dry Scrubbers | FGD Other | FBC Ash | CCP Production / Utilization Totals |
|---|---|---|---|---|---|---|---|---|---|
| Total CCPs Produced by Category | 50,422,238 | 12,478,705 | 2,694,056 | 34,123,820 | 12,596,231 | 1,255,775 | 344,551 | 15,768,766 | 129,684,142 |
| Total CCPs Used by Category | 23,181,723 | 6,063,028 | 1,706,621 | 16,750,990 | 1,163,434 | 275,999 | 0 | 13,285,766 | 62,427,561 |
| 1. Concrete/Concrete Products /Grout | 13,126,930 | 609,558 | 0 | 423,613 | 0 | 0 | 0 | 0 | 14,160,100 |
| 2. Blended Cement/ Feed for Clinker | 3,391,272 | 1,197,398 | 0 | 1,308,208 | 120,509 | 0 | 0 | 0 | 6,017,388 |
| 3. Flowable Fill | 84,734 | 2,672 | 0 | 0 | 0 | 0 | 0 | 0 | 87,406 |
| 4. Structural Fills/Embankments | 2,805,515 | 1,928,492 | 51,659 | 1,586,234 | 311,183 | 0 | 0 | 0 | 6,683,084 |
| 5. Road Base/Sub-base | 365,868 | 306,936 | 12,992 | 0 | 0 | 0 | 0 | 0 | 685,796 |
| 6. Soil Modification/Stabilization | 176,112 | 720,791 | 0 | 0 | 0 | 0 | 0 | 0 | 896,903 |
| 7. Mineral Filler in Asphalt | 68,707 | 0 | 9,758 | 5,197 | 0 | 0 | 0 | 0 | 83,662 |
| 8. Snow and Ice Control | 0 | 736,397 | 101,359 | 0 | 0 | 0 | 0 | 0 | 837,756 |
| 9. Blasting Grit/Roofing Granules | 0 | 127,114 | 1,530,853 | 0 | 0 | 0 | 0 | 0 | 1,657,968 |
| 10. Mining Applications | 1,392,935 | 41,330 | 0 | 813,419 | 578,244 | 229,766 | 0 | 13,151,161 | 16,206,855 |
| 11. Gypsum Panel Products | 0 | 0 | 0 | 11,221,836 | 0 | 0 | 0 | 0 | 11,221,836 |
| 12. Waste Stabilization/Solidification | 279,323 | 475 | 0 | 16,390 | 0 | 0 | 0 | 134,605 | 430,794 |
| 13. Agriculture | 62 | 10 | 0 | 1,332,708 | 0 | 0 | 0 | 0 | 1,332,781 |
| 14. Aggregate | 0 | 181,107 | 0 | 0 | 0 | 0 | 0 | 0 | 181,107 |
| 15. Oil/Gas Field Services | 512,100 | 4,708 | 0 | 0 | 0 | 46,233 | 0 | 0 | 563,041 |
| 16. Miscellaneous/Other | 978,165 | 206,039 | 0 | 43,384 | 153,498 | 0 | 0 | 0 | 1,381,086 |

Summary Utilization to Production Rate

| CCP Categories | Fly Ash | Bottom Ash | Boiler Slag | FGD Gypsum | FGD Material Wet Scrubbers | FGD Material Dry Scrubbers | FGD Other | FBC Ash | CCP Utilization Total |
|---|---|---|---|---|---|---|---|---|---|
| Totals by CCP Type/Application | 23,181,723 | 6,063,028 | 1,706,621 | 16,750,990 | 1,163,434 | 275,999 | 0 | 13,285,766 | 62,427,561 |
| Category Use to Production Rate (%) | 46% | 49% | 63% | 49% | 9% | 22% | 0% | 84% | 48% |
| 2014 Cenospheres Sold (Pounds) | 4,862,361 | Data in this survey represents 189 GWs of Name Plate rating of the total industry wide approximate 302 GW capacity based on EIA's July 2015 Electric Power Monthly. | | | | | | | |

# Uses and Association

BREEN
SMART SCIENCE • CLEANER ENERGY

| | |
|---|---|
| 1. Concrete/Concrete Products /Grout | 13,126,930 |
| 2. Blended Cement/ Feed for Clinker | 3,391,272 |
| 3. Flowable Fill | 84,734 |
| 4. Structural Fills/Embankments | 2,805,515 |
| 5. Road Base/Sub-base | 365,868 |
| 6. Soil Modification/Stabilization | 176,112 |
| 7. Mineral Filler in Asphalt | 88,707 |
| 8. Snow and Ice Control | 0 |
| 9. Blasting Grit/Roofing Granules | 0 |
| 10. Mining Applications | 1,392,935 |
| 11. Gypsum Panel Products | 0 |
| 12. Waste Stabilization/Solidification | 279,323 |
| 13. Agriculture | 62 |
| 14. Aggregate | 0 |
| 15. Oil/Gas Field Services | 512,100 |
| 16. Miscellaneous/Other | 978,165 |

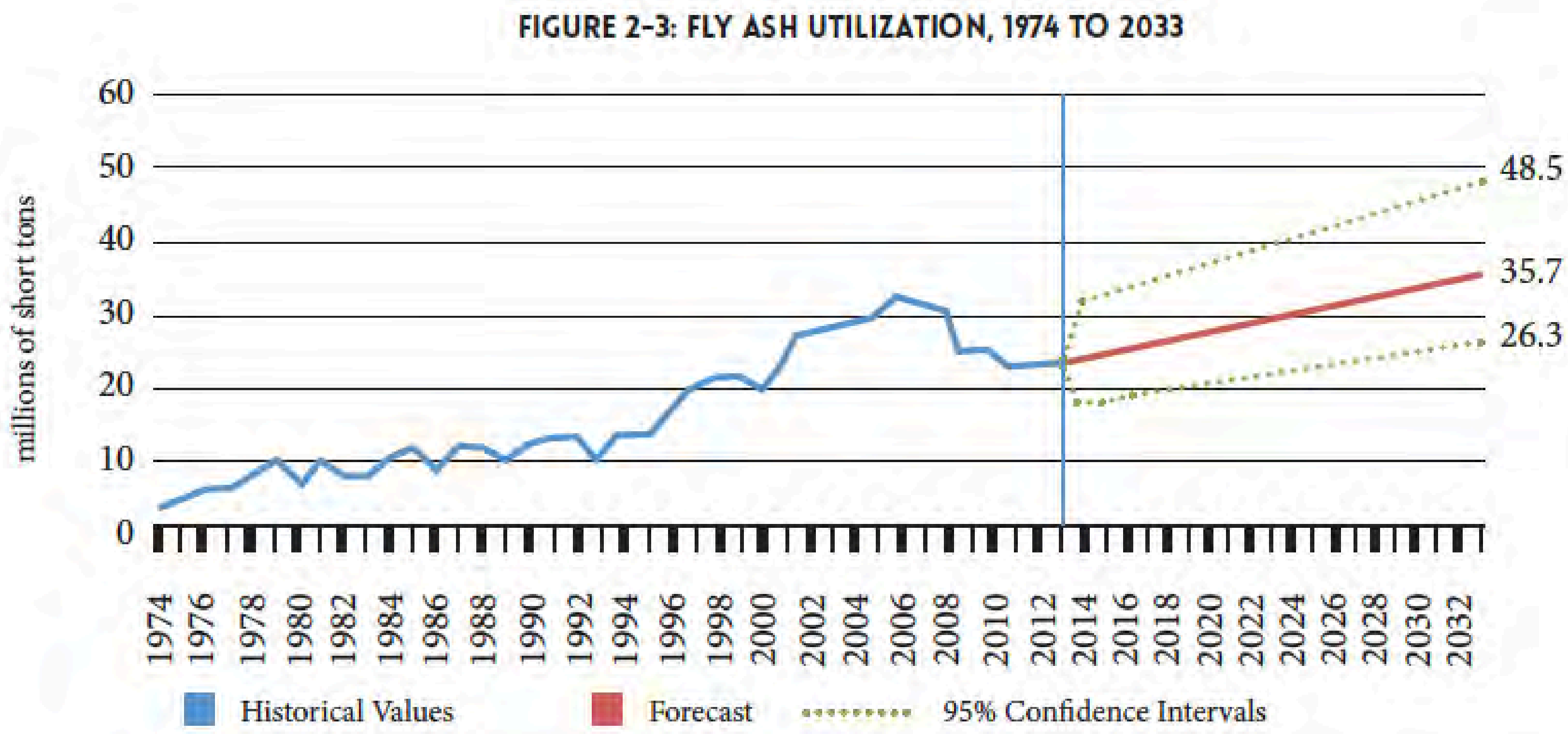
| 2014 CCP Categories | Fly Ash |
|---|---|
| Total CCPs Produced by Category | 50,422,238 |
| Total CCPs Used by Category | 23,181,723 |

| CCP Categories | Fly Ash |
|---|---|
| Totals by CCP Type/Application | 23,181,723 |
| Category Use to Production Rate (%) | 46% |
| 2014 Cenospheres Sold (Pounds) | 4,862,361 |

American Coal Ash Association
38800 Country Club Drive
Farmington Hills, MI 48331
Email: info@acaa-usa.org

Phone: 720-870-7897
Fax: 720-870-7889
Internet: www.ACAA-USA.org

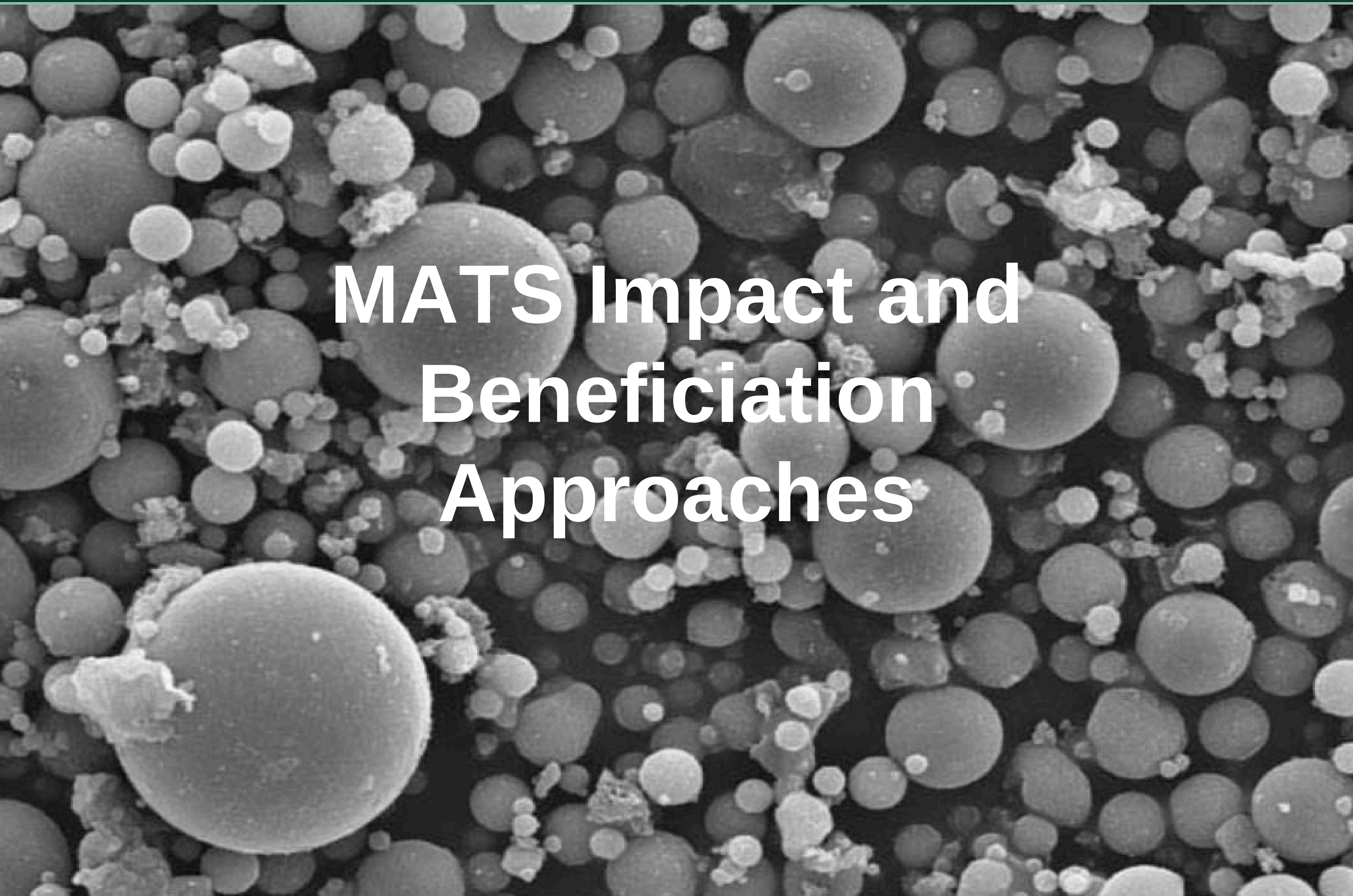
# Flyash Usage Forecast - ARTBA



# MATS and Obstacles to Reuse?

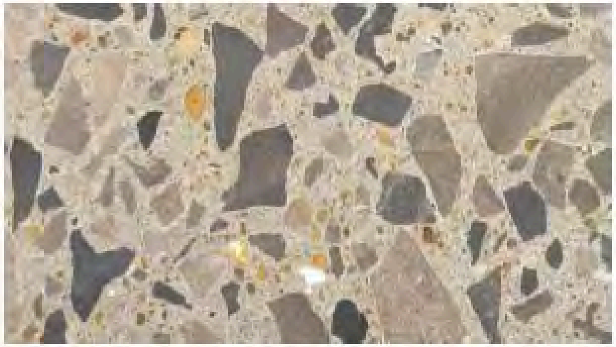
- **Carbon Content vs. Air Entrainment Agent**
  - Activated Carbon Use is Increasing
- **Sulfate Content**
  - Hydrated Lime and Trona for SO3 Control
- **Alkali Silica Reaction**
  - Sodium creates issues in some areas

# MATS Impact and Beneficiation Approaches



# Ready Mix Concrete Needs

**Concrete** ***Is a composite material made of stone and sand bonded together by a hydraulic binder.***

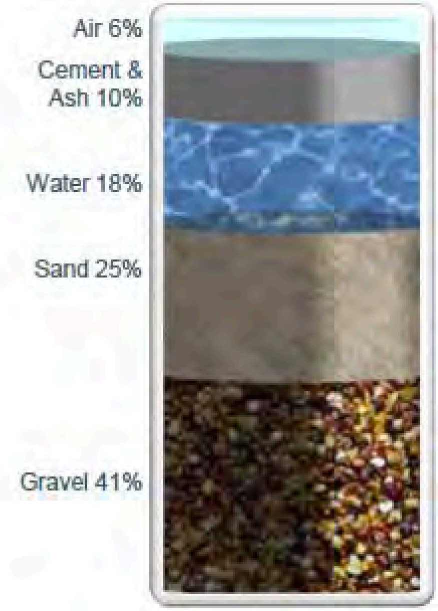


**The binder consists of cement, fly ash, water and chemical admixtures.**

**Fly ash is considered a supplementary cementitious material (SCM) a.k.a "mineral admixture" used to enhance the rheology of fresh concrete and the strength and durability of hardened concrete.**

# Flyash in Concrete

## *Portland Cement & Fly Ash in Concrete*




Fly ash in concrete reacts with calcium hydroxide and other alkalis released during cement hydration:

- consuming those reactive alkalis (durable concrete) &
- forming additional binder products (stronger concrete)

Water reducing benefits (ball bearing effect) and particle packing during concrete placement also contribute to denser & less permeable concrete (added strength and durability)

Cement Hydration: $2Ca_3SiO_5 + 7H_2O \rightarrow 3(CaO)\cdot 2(SiO_2)\cdot 4(H_2O) + 3Ca(OH)_2$

CSH Gel

Excess Lime

Reacts with aluminosilicate of fly ash

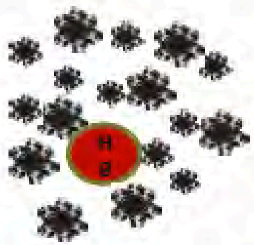
more CSH Gel

# Challenges Facing Ash Utilization

BREEN
SMART SCIENCE • CLEANER ENERGY

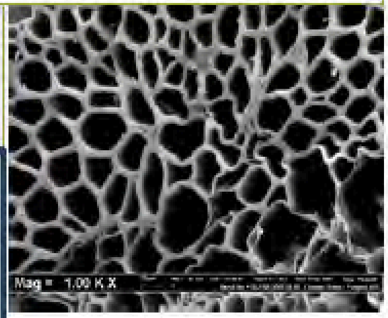
- **Fly Ash Quality**
  - PAC for Hg Control
  - Lime, Trona, Ammonia Use for SO3 Control
- **Resource Availability**
  - Plant Closures are leading to localized supply issues
  - Natural Gas availability and pricing are reducing ash quantity
- **Changing Ash Characteristics**
  - Fuel Switching from CAPP to PRB and ILB changing localized ash constituents

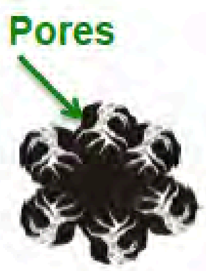
# Issues with PAC



Mercury in coal flue gas is ~ 9 parts per billion.
PAC is injected (1~3 lb/ million acf) to capture Hg.

The mercury is sequestered in very small portions of the carbon structure.




There are ample pores and surface areas available to adsorb other compounds including:

**Hydrophobic substances such as surfactants (AEA's)**.

**Air Entrainment Agents (AEA's) prefer activated carbon over air.**

Activated carbon in ash is expected to be at less than 1% by weight.
@ this rate, PAC ~ 1pound per cubic yard of concrete

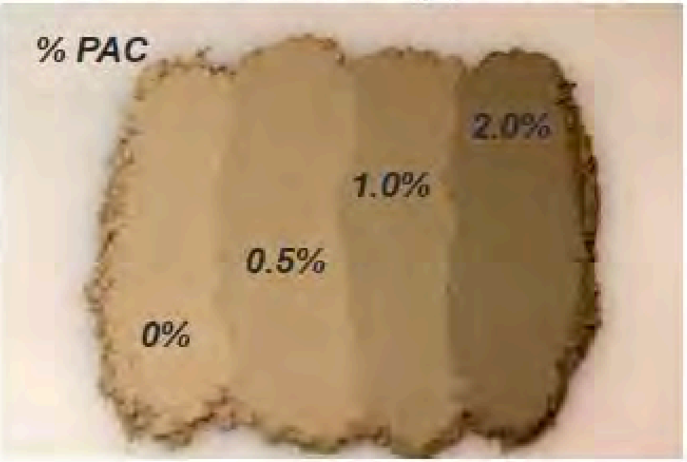
AEA's dosage is typically 6 to 18 fl oz per cubic yard of concrete.

# Activated Carbon in Ash

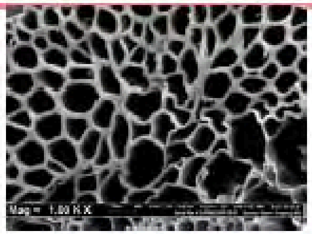
Impact on fly ash quality for concrete use:

- No impact on concrete set time or strength.
- No direct impact on concrete durability (unless it interferes with AEA's)
- Color sensitive applications

<table>
<tr><th></th><th>Unburned Carbon %</th><th>Activated Carbon %</th><th>BET (m²/g)</th></tr>
<tr><td>F-Ash</td><td>0.0</td><td>-</td><td>0.35</td></tr>
<tr><td>F-Ash</td><td>1.0</td><td>-</td><td>0.75</td></tr>
<tr><td>C-ash</td><td>0.9</td><td>-</td><td>2.91</td></tr>
<tr><td>F-Ash</td><td>6.8</td><td>-</td><td>5.72</td></tr>
<tr><td>C-Ash</td><td colspan="2">0.5</td><td>6.84</td></tr>
<tr><td>C-Ash</td><td colspan="2">2.4</td><td>10.41</td></tr>
</table>




**Activated Carbon is much more adsorptive than unburned coal.**

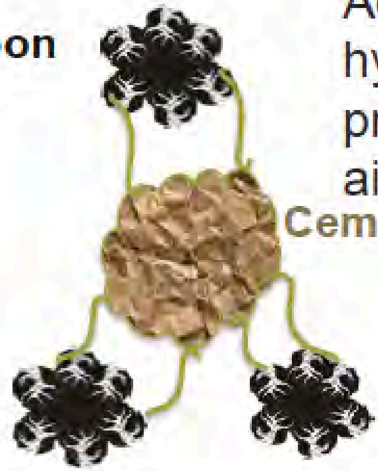


*Activated Carbon*

*Unburned Carbon*

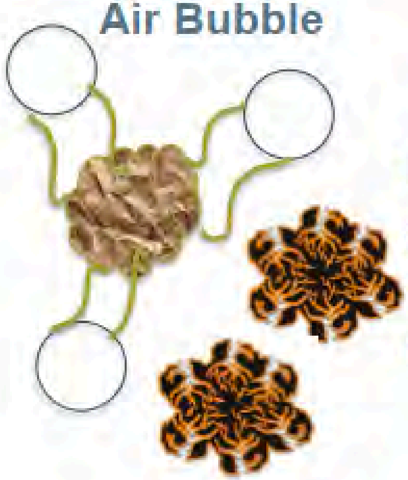
*Activated Carbon has a very high affinity to adsorb Air Entraining Agents.*

# Chemical Passivation




Activated carbon in concrete attracts the hydrophobic end of AEA's molecule and prevent it from collecting and entraining air.

Air Entrainment Agents (AEA's) prefer activated carbon over air.




RestoreAir® saturates the activated carbon surfaces with a sacrificial agent to prevent the carbon from attracting the AEA's.

# Headwaters RestoreAir

BREEN SMART SCIENCE • CLEANER ENERGY

*Based on the original carbon passivation technology developed over 15 years ago*

1. A reformulated reagent:
   - ✓ Improved dispersion and greater affinity to adsorb on activated carbon.

2. An improved reagent injection system:
   - ✓ Provides accurate/uniform distribution of reagent in ash.

3. A new ash activity sensor (SorbSensor):
   - ✓ Can be used for QA or QC to determine treatment dosage.

***RestoreAir®*** *is customized to match site needs. RestoreAir Systems:*

**10 – Completed**

**4 - Scheduled for spring/summer 2016**

**+12 others in evaluation/design stage**

# SDA Ash?

SDA is a semi-dry $SO_2$ control technology that consists of injecting lime slurry in the flue gas prior to particulate capture. The material produced by SDA systems consists of:

Fly Ash: 10% to 30%

Calcium Sulfite: 10% to 40%

Calcium Sulfate: 5% to 15%

Un-reacted lime: 10% to 30%

Others: Calcium carbonate, calcium Chloride, etc.

**SDA Material is not suitable for concrete.**

## Potential Use Applications:

- Mine reclamation
- Waste solidification
- Flowable fill
- Synthetic aggregates (requires capex)
- Soil stabilization (requires site specific testing)
- Agriculture applications
- Other limited uses (limited masonry applications)

# Sodium for $SO_2$ Ash

BREEN
SMART SCIENCE • CLEANER ENERGY

Sodium based DSI systems:

- Contribute water soluble compounds to fly ash
- Increase alkalis content in ash
- Increase sulfur content in ash
- Increase in the leachability of some trace elements, such as: Se, As, and Cr.

| Example (PRB fired Unit) | Baseline Ash | Ash w/ trona | Ash w/ trona & AC |
|---|---|---|---|
| Solubility | *2.5%* | *15.9%* | *13.7%* |
| Total Alkalis (as **$Na_2O$**) | *8.2%* | *22.47%* | *13.2%* |
| **$SO_3$** | *3.1%* | *16.0%* | *8.9%* |
| **$SiO_2 + Al_2O_3$** | *59.2%* | *37.0%* | *46.9%* |

The pozzolan component of the ash is proportionally reduced by dilution.

**These high levels make the fly ash not suitable for concrete.**

Some low levels of Trona injection (ESP enhancement or minor $SO_3$ control) might result in acceptable fly ash for use in conventional portland cement concrete.



Not acceptable for pre-stressed concrete applications

# Trona DSI Leachability

BREEN
SMART SCIENCE • CLEANER ENERGY

| Parameter | Unit | Baseline Ash | Ash/Trona/AC | CaO added to Ash/Trona/AC 25/75 blend |
|---|---|---|---|---|
| Arsenic, As | mg/l | 0.0147 | 0.681 | 0.0188 |
| Barium, Ba | mg/l | 2.23 | 0.845 | 2.83 |
| Cadmium, Cd | mg/l | .00052 | U | .00051 |
| Chromium, Cr | mg/l | 0.315 | 0.761 | 0.257 |
| Lead, Pb | mg/l | .00119 | 0.001 | .00112 |
| Selenium, Se | mg/l | 0.334 | 1.10 | 0.267 |
| Silver, Ag | mg/l | U | U | U |
| Mercury, Hg | mg/l | U | U | U |

SPLP with 4:1 liquid to solid ratio L/S.

- Increased leachability of As, Cr, Se in trona containing fly ash.
- Amending the trona/ash with CaO reduced the leachability.

# DSI and Carbon Passivation

BREEN
SMART SCIENCE • CLEANER ENERGY

- The injection of PAC upstream of the particulate collection system can result in fly ash quality deterioration.
- Carbon in ash used in concrete interferes with the concrete admixture ability to entrain air for freeze/thaw durability.
- The RestoreAir® technology has been effective in mitigating the impact of activated carbon in ash for use in concrete.

Moderate amount of calcium based DSI byproducts could be tolerated in the ash, if the ash continues to pass the 5% limit for $SO_3$ (per ASTM C618)

All other DSI and SDA derived materials must be evaluated on a case by case basis for beneficial use applications.

Several flyash marketers offer competitive chemical treatments similar to RestoreAir. Boral, Waste Management and SEFA to name a few.

# Carbon Removal and Ash Reclaim

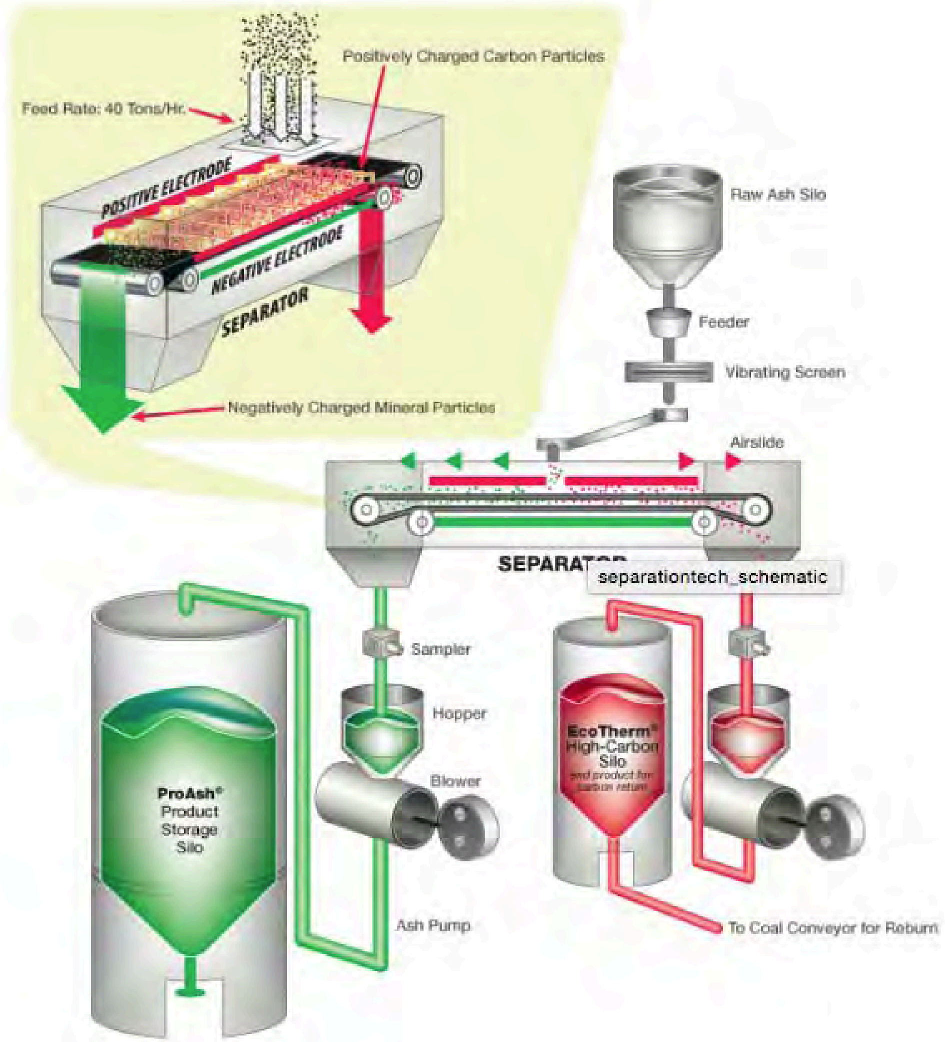
# Beneficiation Technologies

- **Carbon Burnout**
- **Tribo-electrostatic Separation**
- **STAR (Staged Turbulent Air Reactor)**

# Carbon Burnout - PMI

- **Early Technology**
- **Fluidized Bed Reactor**
- **Recycles Heat back to plant**
- **1% Typical LOI product**
- **Throughput is heat input sensitive**

# Tribo-electrostatic STI




**Less Capital Intensive**

**Mechanical Belt drive creates static charge**

**Typical 1%-2% LOI Product**

# STAR – SEFA Group


**Uses ash-carbon as process fuel**

**Has been applied to reclaiming ponded Ash!**

# CPP & Combustion Practices

# The Clean Power Plan

Technical Support Document (TSD) for
Carbon Pollution Guidelines for Existing Power Plants:
Emission Guidelines for Greenhouse Gas Emissions from Existing Stationary Sources:
Electric Utility Generating Units

Docket ID No. EPA-HQ-OAR-2013-0602

## Greenhouse Gas Mitigation Measures

# CPP Heat Rate Initiatives

- **Reduction in $CO_2$ from Heat Rate Improvement**
  - 4%
  - SCR, ESP, FGD Operating Practices
- **Migration of Coal Generation to CCNG**
- **Gas CoFiring**
  - MSL Reduction
  - Fuel Flexibility

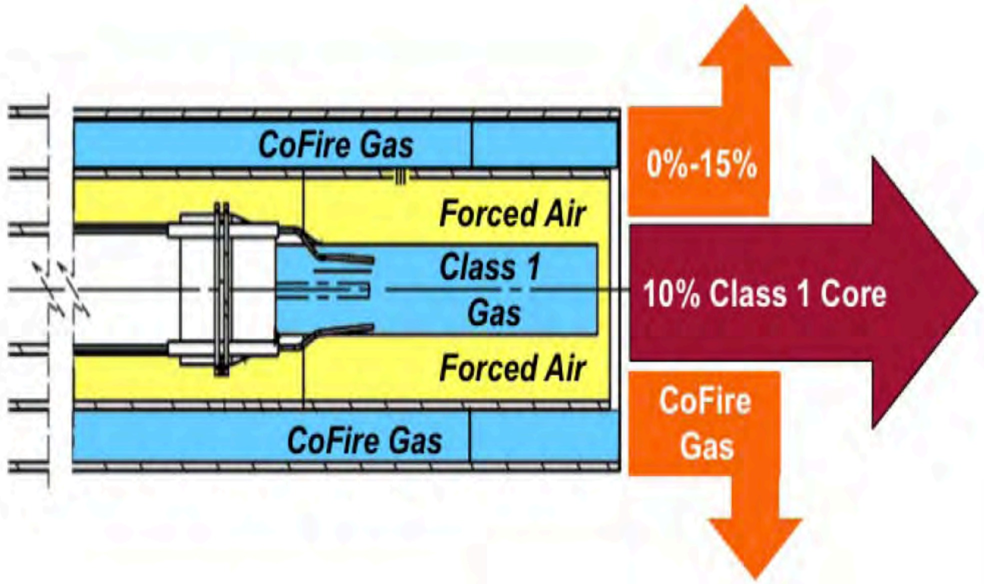
**Of these, CoFiring holds the best promise for improving flyash quality without compromising other plant operations**

# CoFiring Effects

- **Selective placement of natural gas can reduce LOI**
- **Cofiring at levels of 20% - 25% can reduce pulverizer loading leading to better fuel fineness and reduced LOI**
- **Cofiring at levels of 20% - 25% can reduce the particulate loading on the ESP, allowing for improved use of hydrated lime for $SO_2$ ad $SO_3$ capture**

# Wall Fired Design

Maximizes Gas flow while maintaining heat proximity to the furnace walls




Cofire gas comes from a higher area secondary annulus

# Site Installation

System Requires:

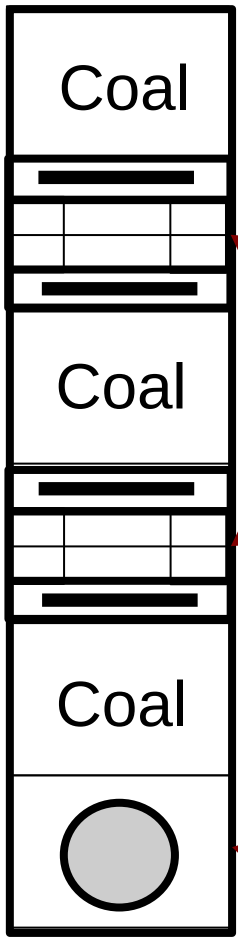
- 80 CFM Forced Combustion Air/Igniter
- Isolation Valve between Core and CoFire sides
- Pressure Control on the Core side

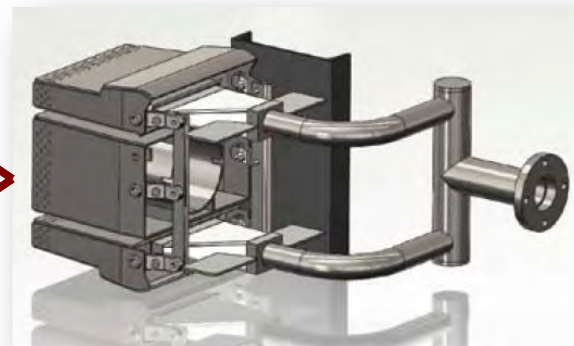
- Additionally we remotely monitored:

- Gas Pressure
- Air Pressure
- Core Flame Stability

# T-Fired Layout

**Total Gas Supplied via Furnace CoFire = 600 mmBTU**

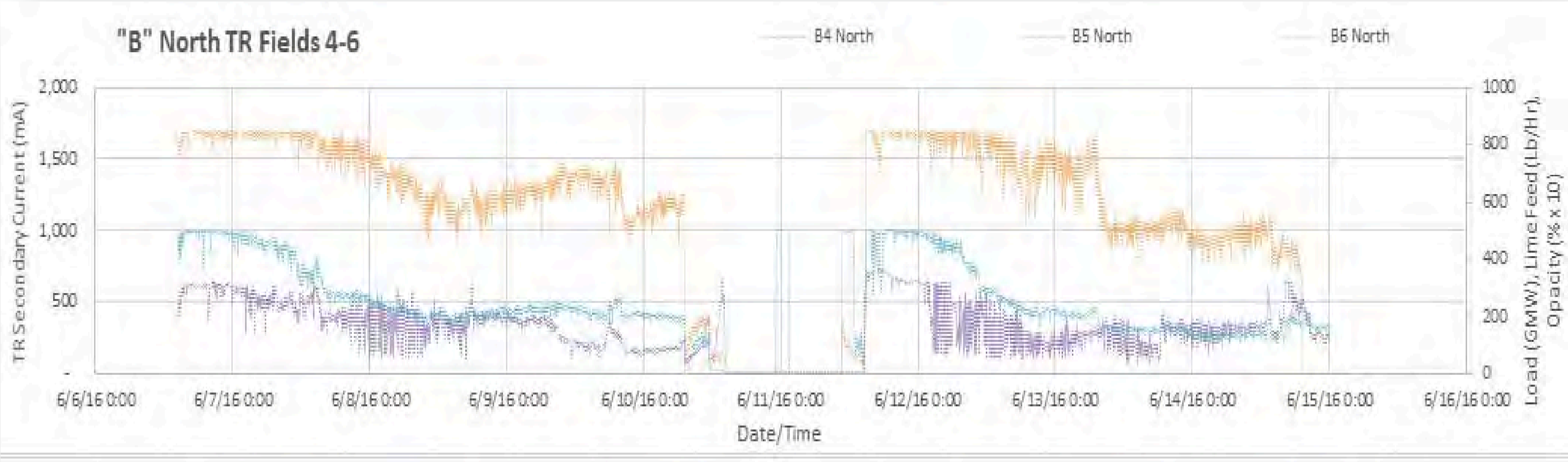


Cofire Spuds - 50 mmBTU//device = 400 mmBTU total

Gas Warm-Up Leave As-is (200 mmBTU)

# Overuse of DSI on ESP




Over injection of DSI can strip the ESP of its conditioning agent. This can happen regardless of sorbent used.

Natural Gas use will:

- Reduce particulate load and $SO_2/SO_3$
- Increase flue gas moisture
- Reduce LOI

# Conclusions

# MATS Conclusions

- **Flyash quality is critical to plant commercial viability. The more you can beneficially reuse, the less you have to landfill**

- **MATS compliance has compromised the ash quality through increased LOI (ACI) and Sulfate.**
- **The Ash Marketing industry has responded with chemical passivation technologies that remove the AEA issues as long as carbon is within spec**

- **New Mechanical Separation approaches allow removal of unwanted carbon from both dry and ponded ash.**

# CPP Conclusions

- **CPP Compliance will place a different type of strain on flyash quality.**

- **Improved combustion practices coupled with enhanced use of gas through Cofiring can provide:**
  - improvements in Ash Quality
  - Reduction in Total Ash created
  - Improvements in plant responsiveness to renewable and CCNG demands

# Special Thanks

- **Special thanks to:**
  - Rafic Minkara – Headwaters
  - Jimmy Knowles – SEFA Group
  - Hollis Walker – Southern Company
  - Terry Peterson – Boral
- **For providing valuable input to this presentation.**

BREEN®

SMART SCIENCE • CLEANER ENERGY

# Improving Flyash Quality in a MATS/CPP World

## Thank You for listening

## Questions?