Supplementary Cementitious Materials

BEST PRACTICES WORKSHOP
Outline

• Why are we here?

➢ Describe common supplementary cementitious materials (SCMs)

➢ Highlight their benefits and drawbacks when used in concrete for highway applications

➢ Discuss recent trends that may affect the use of SCMs during the foreseeable future
**Background**

- State highway agencies (SHAs) and others charged with construction and maintenance of roads and bridges expect one key property from concrete: Longevity

- Service demands have increased
  - Use of aggressive deicing chemicals

- Increased expectations for reduced environmental impact and lower initial and lifecycle costs

- SCMs assist meeting these goals
Definitions

- **cementitious material, supplementary, (SCM)** - an inorganic material that contributes to the properties of a cementitious mixture through **hydraulic** or **pozzolanic** activity, or both

  - **DISCUSSION**—Some examples of supplementary cementitious materials are fly ash, silica fume, slag cement, rice husk ash, and natural pozzolans. In practice, these materials are used in combination with portland cement. (ASTM C125)

- **cementitious material (hydraulic)** - an inorganic material or a mixture of inorganic materials that sets and develops strength by chemical reaction with water by formation of hydrates and is capable of doing so under water (ASTM C125)
A brief review of hydration...
Hydration Reactions Example: Portland Cement

Early Hydration Products
Hydration Reactions Example: Portland Cement

Later Hydration Products or “Outer Product”
Hydration Reactions Example: Portland Cement

Capillary Pores – porosity between hydration products, strongly influenced by w/cm
Hydration Reactions Example: Portland Cement

Gel Pores – porosity **within** hydration products causing permeability at a nano-scale
Hydration Reactions Example: Portland Cement

As hydration proceeds water must diffuse through the outer product to hydrate the cement within, forming “Inner Product”. This diffusion slows the hydration process.
Hydration Reactions Example: Portland Cement

- Inner Product
- Capillary Pores
- Unhydrated Cement
- Later Hydration Products or “Outer Product”
Hydration Reactions Example: Portland Cement

Entrained Air Voids
Hydration Reaction

- Reaction of hydraulic cementitious materials with water results in production of calcium silicate hydrates (C-S-H) and calcium hydroxide (CH), also ettringite and other hydrated aluminate phases (C-A-H)

  - Examples: portland cement, slag cement, Class C fly ash

- Hydraulic Reaction:

  Hydraulic Cement + Water \(\rightarrow\) C-S-H + C-A-H + CH

- C-S-H provides strength – desirable product

- CH provides little strength and is soluble, also is a reactant in many MRD mechanisms – undesirable product
Definitions

• cementitious material, supplementary, (SCM) - an inorganic material that contributes to the properties of a cementitious mixture through hydraulic or pozzolanic activity, or both

- DISCUSSION—Some examples of supplementary cementitious materials are fly ash, silica fume, slag cement, rice husk ash, and natural pozzolans. In practice, these materials are used in combination with portland cement. (ASTM C125)

• pozzolan - a siliceous or siliceous and aluminous material that in itself possesses little or no cementitious value but will, in finely divided form and in the presence of water, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties (ASTM C125)
Pozzolanic Reaction

• SCMs consume CH through the pozzolanic reaction
  - Improves strength
  - Increases paste density
  - Reduces alkali (ASR mitigation)
  - Reduces rate of heat evolution due to hydration reaction
  - Slower strength evolution

- Pozzolanic Reaction:

\[
\text{Cement} + \text{Water} \rightarrow \text{C-S-H} + \text{CH}
\]

\[
\text{Pozzolan} + \text{CH} + \text{Water} \rightarrow \text{C-S-H}
\]
General Characteristics - Composition

- Coal Fly Ash
- Slag Cement
- Silica Fume

Increasing silica
Low calcium oxide
Pozzolanic

Increasing calcium oxide
Moderate Silica
Hydraulic
General Characteristics – Particle Size & Shape

Portland Cement

Slag Cement

Fly Ash

Silica Fume
<table>
<thead>
<tr>
<th>Property</th>
<th>Fly ash</th>
<th>Slag</th>
<th>Silica fume</th>
<th>Natural Pozzolan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strength Gain</td>
<td>↓</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Abrasion Resistance</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Freeze-Thaw and Deicer-Scaling</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Resistance</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drying Shrinkage and Creep</td>
<td></td>
<td></td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Permeability</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Alkali-Silica Reactivity</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Chemical Resistance</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Carbonation</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Concrete Color</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
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</tr>
</tbody>
</table>
Coal Fly Ash

- The finely divided residue that results from the process of combustion of ground or powdered coal and that is transported by flue gasses (ASTM 2015)
- Produced from pulverized coal fuel

- Fuel stream may have other components such as limestone, trona, other additives for pollution control
Coal Fly Ash Production

- Airborne residue from coal combustion processes collected from the flue gases by a variety of means
  - Electrostatic precipitators
  - Fabric filters (baghouse)
Coal Fly Ash Production

• Quality and consistency depends in part on burning conditions and fuel sources

• An important characteristic of coal combustion fly ash is the presence of residual carbon intermixed with the fly ash
  ➢ Natural product of combustion – more prevalent in Class F ash
  ➢ Powder activated carbon (PAC) added to achieve pollution control goals

• Not all ash produced is acceptable for use in concrete

• Non-spec ash may be useful for other construction applications
  ➢ CLSM (flowable fill)
  ➢ Subgrade stabilization
**Fly Ash Specification**

- Fly ash is specified under ASTM C618 (AASHTO M 295) *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*

- **Chemical Requirements**
  - Classified based on the “sum of the oxides” (SUM)
    
    $$\text{SUM (wt.\%) = } \% \text{ SiO}_2 + \% \text{ Al}_2\text{O}_3 + \% \text{ Fe}_2\text{O}_3$$
    
  - **Class F** ➔ SUM ≥ 70% (low calcium oxide)
  - **Class C** ➔ SUM ≥ 50% (high calcium oxide)
  - **Class N** ➔ SUM ≥ 70% (natural pozzolan source only)
### Fly Ash Specification

**ASTM C618 / AASHTO M 295**

**Other Chemical Requirements**

<table>
<thead>
<tr>
<th></th>
<th>Class F</th>
<th>Class C</th>
<th>Class N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur trioxide (SO$_3$), max, %</td>
<td>4.0</td>
<td>4.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Moisture content, max, %</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Loss on ignition, max, %</td>
<td>6.0</td>
<td>6.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Available alkali, max %,</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

(Optional in AASHTO M 295 only)
**Fly Ash Specification**

• Key Physical Requirements
  - Fineness – amount retained on 325 mesh sieve
    - Limit of 34% all classes
  - Strength Activity Index (SAI) – relative strength of a mortar with 80% portland, 20% fly ash compared to control (100% portland cement)
    - Limit of 75% of control, all classes at 7 or 28 days

• Other Physical Requirements
  - Water requirement (based on flow attained in SAI test)
  - Soundness (autoclave expansion)
  - Uniformity (density, fineness only)
Fly Ash Specification

• Supplementary Optional Physical Requirements
  ➢ Increase in Drying Shrinkage
  ➢ Uniformity Requirements
    - Air content, AEA required to achieve 18 % air
  ➢ Effectiveness in Controlling Alkali-Silica Reaction
    - Based on ASTM C441 (Pyrex Glass Bead Test)
  ➢ Effectiveness in Contributing to Sulfate Resistance
    - Based on ASTM C1012
Coal Fly Ash Characteristics

• Benefits
  ➢ Improved workability
  ➢ Decreased heat of hydration
  ➢ Reduced cost
  ➢ Potential increased sulfate resistance and alkali-silica reaction (ASR) mitigation
  ➢ Increased late strength, and decreased shrinkage and permeability

• Concerns
  ➢ Air-entraining admixture adsorption by residual carbon in the fly ash
  ➢ ASR-accentuated at pessimism replacement levels
  ➢ Slow initial strength gain
  ➢ Fly ash variability
Coal Fly Ash Specification

Class C

Class F

$R^2 = 0.96$

Sum of Oxides ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) (% wt.)

CaO (%)
Coal Fly Ash Specification

Increasing Pozzolonic Activity

Increasing Hydraulic Activity

CaO (%)

Sum of Oxides (SiO₂+Al₂O₃+Fe₂O₃) (% wt.)

Class C
Class F

R² = 0.96
Coal Fly Ash Specification

![Graph showing the relationship between CaO (%) and Sum of Oxides (SiO₂+Al₂O₃+Fe₂O₃) (% wt.).]

- **Class C**
- **Class F**

$R^2 = 0.96$
Strength Activity Index

75% Specification Limit

Sum of Oxides ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) (% wt.)

Strength Activity Index (% of control)
**Strength Activity Index**

- Strength Activity Index is questioned as it allows inert materials to pass.

- Experiments performed with non-pozzolanic quartz filler – all pass the SAI.

<table>
<thead>
<tr>
<th>Cement Type</th>
<th>Age (days)</th>
<th>100% Cement</th>
<th>20% Replacement</th>
<th>35% Replacement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Strength (psi)</td>
<td>Strength (psi)</td>
<td>SAI</td>
</tr>
<tr>
<td>PC-1</td>
<td>7</td>
<td>4554</td>
<td>3829</td>
<td>84</td>
</tr>
<tr>
<td>PC-2</td>
<td>7</td>
<td>4293</td>
<td>3408</td>
<td>79</td>
</tr>
<tr>
<td>PC-3</td>
<td>7</td>
<td>4090</td>
<td>3539</td>
<td>87</td>
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<tr>
<td>PC-1</td>
<td>28</td>
<td>5715</td>
<td>4815</td>
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<tr>
<td>PC-2</td>
<td>28</td>
<td>5526</td>
<td>4235</td>
<td>77</td>
</tr>
<tr>
<td>PC-3</td>
<td>28</td>
<td>5134</td>
<td>4351</td>
<td>85</td>
</tr>
</tbody>
</table>
Strength Activity Index

Effect of Cement & Fly Ash on Strength Activity Index

Strength Activity Index vs. Compressive Strength (kpsi)

PC1-F-7d
PC1-C-7d
PC2-F-7d
PC2-C-7d
PC3-F-7d
PC3-C-7d
PC1-F-56d
PC1-C-56d
PC2-F-56d
PC2-C-56d
PC3-F-56d
PC3-C-56d
## Changes to Concrete Mixture Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Class C Replacement</th>
<th>Class F Replacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Set</td>
<td>Delayed</td>
<td>Delayed</td>
</tr>
<tr>
<td>Rate of Strength Gain</td>
<td>Same or higher</td>
<td>Slower</td>
</tr>
<tr>
<td>Heat of Hydration</td>
<td>Lower</td>
<td>Significantly lower</td>
</tr>
<tr>
<td>Early Strength (3-7 days)</td>
<td>Higher</td>
<td>Lower</td>
</tr>
<tr>
<td>Late Strength (28-56 days)</td>
<td>Same or higher</td>
<td>Same or higher</td>
</tr>
<tr>
<td>ASR Mitigation Potential</td>
<td>Only at high</td>
<td>Significant mitigation above pessimism replacement levels</td>
</tr>
<tr>
<td></td>
<td>replacements</td>
<td>replacement levels</td>
</tr>
</tbody>
</table>
Fly Ash Carbon Affect on Air Entrainment

• Air entraining admixtures (AEAs)
  ➢ organic compounds used to entrain a controlled amount of air

• AEAs typically contain ionic and non-ionic surfactants made of natural sources such as wood resins, tall oil, or synthetic chemicals

Schematic view of AEA molecule

- Non-ionic: Little or no attraction to water (*hydrophobic*)
- Ionic portion: Strong attraction to water (*hydrophilic*)
Fly Ash Carbon Affect on Air Entrainment

• For sufficient air entrainment two conditions must be satisfied:
  
  ➢ The AEA molecule should be adsorbed on the solid particles with their non-polar ends pointing toward the water to give hydrophobic character to the cement particles and make them adhere to the air bubbles

  ➢ The cement mixture must maintain a high enough liquid phase concentration of AEA to entrain air during mixing

Fly Ash Carbon Affect on Air Entrainment

- Hydrophilic, anionic polar groups (i.e., head) sorb strongly to the ionic cement particles
- Hydrophobic, non-polar end of the surfactants (i.e., tail) orient towards the solution
- Stabilize (entrain) air bubbles, prevent coalescing into larger bubbles

Illustration: Larry Sutter, MIT
Fly Ash Carbon Affect on Air Entrainment

- Carbon in fly ash adsorbs AEA from the concrete mixture
- Reduces the aqueous phase concentration of AEA to a point where the AEA is no longer able to stabilize the required volume of air bubbles

Illustration: Larry Sutter, MIT
Fly Ash Carbon Affect on Air Entrainment

- Non-polar surfaces of carbon provide active adsorption sites and the AEA adsorbed onto the carbon surfaces do not participate in air entrainment for two reasons:

  - The hydrophobic tail can be adsorbed on to the carbon and will therefore not be in contact with the air/water interface
  - AEAs may be adsorbed at depth within surface cracks or pores on the carbon particle and sheltered from the air/water interface
Fly Ash Carbon Affect on Air Entrainment

• Carbon content in fly ash is estimated by the loss on ignition (LOI) test
  ➢ Determines the total volatile materials, not just carbon
  ➢ Test does not characterize the adsorption capacity of the carbon - most important

• Two ashes can have the same LOI content but affect air entrainment very differently

• Newly developed tests, such as the foam index test, iodine number test, and direct adsorption isotherm test, provide different approaches to measuring ash adsorption (NCHRP 749)
Fly Ash Carbon Affect on Air Entrainment

• An emerging issue is the use of powdered-activated carbon (PAC) as an additive in the coal combustion process to adsorb mercury from flue gases
  ➢ PAC is highly adsorptive
  ➢ A small amount may not significantly affect the LOI value but can drastically affect the ash adsorption properties

• As PAC is more commonly included in coal fly ash, the need for adsorption-based tests and specifications will increase
ASR Mitigation with Fly Ash

- Class F ash (pozzolanic) best at ASR mitigation
  - Pozzolanic materials consume CH, reducing hydroxyl ions in pore water, leads to ASR mitigation
- Because of the variability in ash properties, it is important to verify an ash’s mitigation potential
- Testing Fly Ash Mitigation
  - ASTM C1293
  - ASTM C1567
ASR Mitigation with Fly Ash

• ASTM C1293 Concrete Prism Test
  
  ➢ Currently the most reliable test available – not infallible
  
  ➢ Not quick – one year minimum – two years when validating SCM replacement
  
  ➢ Known drawbacks include alkali leaching that can lead to errors in estimating the alkali threshold need for ASR to occur
ASR Mitigation with Fly Ash

- ASTM C1567
  - Accelerated Mortar Bar Test
  - Based on ASTM C1260
  - Cannot be used unless there is a reasonable correlation between C1260 and C1293 for the aggregate in question

ASTM C1293 Data

The diagram shows the prism expansion at 24 months for different percentages of cement replacement with fly ash. The x-axis represents the percent replacement of cement with fly ash (% wt), ranging from 20 to 40. The y-axis represents the prism expansion at 24 months (%). The graph includes data points for various fly ash types, indicated by different colors and patterns:

- FA-H
- FA-M
- FA-O
- FA-Q
- FA-U
- FA-X
- FA-ZA
- FA-ZC

The data points are shown for each percentage replacement, with a horizontal line indicating the 0.141% expansion for the control at 24 months.
ASTM C1567 Data – 14 day (standard)
ASTM C1567 Data – 28 day (non-standard)
Slag Cement

- Produced from blast-furnace slag (reduction of iron ore) in a blast furnace
- Predominately glassy structure with a composition very similar to OPC.
- Slag cement is hydraulic and produces calcium silicate hydrate (CSH) as a hydration product

Images: Used with permission from the Slag Cement Association
**Slag Cement - Hydration**

- Slag cement is hydraulic and produces calcium silicate hydrate (C-S-H) as a hydration product.
- Slag cement reacts slower than portland cement.
  - Hydration of portland cement produces C-S-H and CH.
  - CH reacts with the slag cement, breaking down the glass phases and causing the material to react with water and form C-S-H.
- Slag cement is not pozzolanic.
  - It does consume CH by binding alkalis in its hydration products.
  - Provides the benefits of a pozzolan.
**Slag Cement - Specification**

- ASTM C989 (AASHTO M 302) *Standard Specification for Slag Cement for Use in Concrete and Mortars*
- Classifies the material under three categories: Grade 80, Grade 100, and Grade 120
- The grade classification refers to the relative strength of mortar cubes using the SAI test with a 50% replacement of OPC
  - Uses standard reference cement
  - 75% of the Control 28-day strength = Grade 80
  - 95% of the Control 28-day strength = Grade 100
  - 115% of the Control 28-day strength = Grade 120
Slag Cement

- Because slag cement is slower to react, setting time can be increased significantly compared to OPC concrete.

- Curing is always essential for achieving a quality product; it is even more critical with slag-cement-based concrete.

- The slower reaction rate, especially at lower temperatures, is often overlooked, and this can lead to durability issues such as scaling when not properly cured.

- A slower reaction rate and associated lower heat evolution makes slag cement an ideal ingredient for mass concrete placement where control of internal temperatures is critical to achieving durability.

- Up to 80% replacement of OPC with slag cement is used for mass concrete.
Slag Cement

• Slag cement is effective at mitigating ASR
  ➢ Requires higher replacement rates than Class F ash (e.g., > 50%)

• The ASR mitigation stems from a number of mechanisms
  ➢ Slag cement binds alkalis in C-S-H reaction products
  ➢ CH is consumed by the hydration of slag cement
  ➢ Increased hardened cement paste density
    - Lower permeability
    - Improves resistance to ASR and external sulfate attack
Silica Fume

- Produced in arc furnaces during the production of silicon alloys

- Extremely fine particle size (i.e., particle size averaging 0.1 to 0.2 micron in diameter)

- 100% Amorphous silica that is highly pozzolanic

Image: © 2012 BMI Cementitious Materials, Part of the Lafarge Group
SCMs – Particle Size & Shape

Portland Cement

Slag Cement

Fly Ash

Silica Fume
Silica Fume – Particle Size & Shape

ACMAL 5.0kV 12.4mm x50.0k SE(U) 1 micron
Silica Fume

• Other amorphous silica products are available
  ➢ Fumed silica
  ➢ Precipitated silica
  ➢ Colloidal silica

• These materials may provide benefits when included in a concrete mixture

• Should not be assumed to be equivalent to silica fume

• Verify performance of these materials through concrete testing
Silica Fume

- Silica fume is specified under ASTM C1240 (AASHTO M 307) *Standard Specification for Silica Fume Used in Cementitious Mixtures*

- Chemical Requirements
  - $\text{SiO}_2$ content of 85% (minimum)
  - Moisture content and LOI

- Physical requirements
  - 10% retained on a 45 micron sieve
  - Accelerated pozzolanic strength activity index of 105% of control (minimum) at 7 days using a 10% replacement of OPC with silica fume
Silica Fume

• The accelerated pozzolanic strength activity index differs from the SAI test in two ways

• First, the test requires a constant flow and the $w/cm$ ratio must be maintained between the test and the control samples

  ➢ High-range water reducer (HRWR) is permitted

• Second, after 24 hours of moist curing at room temperature, the test samples are further cured at $65^\circ C (150^\circ F)$ for an additional 6 days, thereby accelerating the pozzolanic reaction
Silica Fume

• Because of the fine particle size, silica fume results in an increased water demand
  ➢ HRWRs used to maintain or decrease \( w/cm \)

• Silica fume accelerates the hydration of OPC by providing nucleation sites for the formation of OPC hydration products

• This is generally accompanied by an increased heat of hydration, particularly at early ages

• Because of its fine particle size, silica fume improves the packing density of the solids and leads to a higher density HCP
• Another important factor that leads to increased concrete strength and durability is that silica fume is able to pack around aggregate particles effectively, consume CH at the aggregate-paste interfacial zone, and greatly improve the strength and impermeability of the interfacial transition zone.
Silica Fume

• Silica fume is a very effective at mitigating ASR and sulfate attack
  ➢ Highly pozzolanic
  ➢ Significant decrease in permeability

• Regarding ASR, it is very important to achieve good dispersion of the silica fume in the concrete mixture

• Clumps of silica fume can act like an expansive aggregate and actually contribute to ASR

• Silica fume is more expensive than other SCMs, limiting its use to a few key areas
Natural Pozzolans

• With issues of availability for other SCMs, natural pozzolans and ASCMs are attracting interest within the industry

• Natural pozzolans have been used in varying degrees for many years, dating back to Roman times

• The first large-scale construction projects that used natural pozzolans was the Los Angeles aqueduct, constructed from 1910 to 1912

• Numerous other large projects have been constructed using natural pozzolans
Natural Pozzolans

Monolith Cement Plant built by the city of Los Angeles for the Aqueduct project 1909

1912 Fairmont Tufa Quarry – Drying the rhyolite by burning wood before grinding
Natural Pozzolans

A MUNICIPAL CEMENT MILL

Owned and Operated by the City of Los Angeles, Calif., for Furnishing Cement for the City's
Aqueduct-Engineering of the Mill—Manufacture of Tufa Cement

By BURT A. HEINLY

City of the third side issues in the construction of the Los Angeles aqueduct has been the building and operation of a municipal cement mill. With the work completion of the aqueduct now in view, the Board of Public Works has practically decided upon its site if a location can be found and the Council is accordable.

Vernon is given a detailed description of the plan, a brief account of the new enterprise into municipal cement-making.

The first and most important element in the United States, however, is the ability to make large quantities and introduce tufa cement to the American builder, and already, some of the machines are in the manufacture of the material.

In 1905, Los Angeles has in recent months $52,000 in increased cement-making properties. The reasons leading up to the large expenditure were these:

When the plans to build the $400,000 of stock and convert aqueduct was first proposed, the Pacific Coast

Tufa cement is obtained from the bottom of the East and West canyons, by the baking which is done at the mill.

The tufa is shipped by rail and at mills, with every ordinary convenience, and the tufa cement is of the highest quality.

The cement is mixed with water to form the desired consistency, and the tufa cement is then ready for use. The plant is located at Vernon.
Natural Pozzolans

“Tufa cement consists of equal amounts by volume or Portland cement and ground tufa reground to a fineness of not less than 90 per cent. passing a 200-mesh screen.

In the tests, straight Portland for the first seven days shows to best advantage, but after the first week the tufa cement surpasses it in breaking strength. At the end of one year it exceeds Portland by about 20 per cent. Comparative breakage tests of 60 briquettes a day show Portland breaking in 28 days at 315 pounds average, and at 345 pounds in 90 days.”
Natural Pozzolans

• Examples of natural pozzolans include
  ➢ Some diatomaceous earths
  ➢ Opaline cherts and shale
  ➢ Tuffs
  ➢ Volcanic ashes
  ➢ Pumicite
  ➢ Various calcined clays and shales

• Some natural pozzolans can be used as mined
• Most require processing such as drying, calcining, or grinding
Natural pozzolanic materials

- Global distribution: natural pozzolans vs. volcanics
Natural Pozzolans

- Natural pozzolans are specified under ASTM C618 (AASHTO M 295)
- When considering the use of natural pozzolans, concrete testing should be performed as the pozzolanic properties can vary significantly from other materials such as fly ash
Alternative SCMs

• Inorganic materials that react, pozzolanically or hydraulically, and beneficially contribute to the strength, durability, workability, or other characteristics of concrete, and do not meet ASTM specifications C618, C989, and C1240

• Examples include some slags or fly ash from co-combustion processes such as coal with biomass

• Used in limited applications in some markets

• ASTM C1709 Standard Guide for Evaluation of Alternative Supplementary Cementitious Materials (ASCM) for Use in Concrete was developed to provide a clear methodology for evaluating these materials
Ternary Mixtures

- Concrete mixtures that contain OPC and two other materials in the binder fraction
  - The binder materials may be combined at the batch plant, or obtained as a pre-blended product

- In general, ternary mixtures perform in a manner that can be predicted by knowing the characteristics of the individual ingredients

- One benefit of ternary mixtures is that negative properties of one SCM can be offset by positive properties of another
Trends in Power Production

Coal Fly Ash Use
Recovered Ash

- With diminishing production, ash marketers are turning to landfills & ash ponds to recover fly ash
  - Most recovered sources are Class F ash
  - Limited research to date on performance of recovered ash
- All recovered sources will require processing
  - Drying
  - Sizing
  - Blending
  - Could lead to more uniformity or less, depending upon source and degree of processing
Recovered Ash

• Concerns

➢ Uniformity – ash in ponds will stratify based on density and strata in land fills/ponds will represent different coal sources and burning conditions

➢ Weathering – Does storage alter the chemical or physical nature of the ash?

➢ Adulteration – many land fills/ponds hold bottom ash, scrubber residue, and other wastes in addition to ash

➢ Infiltration – clays and other materials may infiltrate and co-deposit

➢ Testing – do current specifications provide tests & limits that will adequately screen recovered ash?
Recovered Ash

• Concerns (continued)
  ➢ Current federal and state regulations create pressure to close disposal ponds quickly, leaving insufficient time to recover and use the ash
  ➢ Power producers have little to no incentive to use ash beneficially under current regulations.

• Benefits
  ➢ Well over a billion tons of ash in disposal
  ➢ Proper processing could provide a more uniform product
  ➢ Significant reserves could help limit cost increases although processing will add costs
**Trends in Specifications**

- Overall inconsistent performance & recovered ash use have caused ASTM & AASHTO to re-evaluate specifications
- Items under consideration
  - Revise classification
    - Use CaO instead of SUM
    - CaO more predictive of key properties
  - Move to ASTM C1567 for assessing ASR mitigation
  - Consider modifications to SAI
    - Use constant volume rather than mass replacement of ash
  - Particle size – need better test
  - Adsorption potential
    - Use adsorption based tests rather than LOI
Summary

• SCMs are essential to concrete durability

• Key materials
  ➢ Fly Ash
  ➢ Slag cement
  ➢ Silica fume

• Emerging Materials
  ➢ Natural pozzolans
  ➢ Alternative SCMs
Summary

• All SCMs are expected to favorably affect the following but each does so in varying degrees
  ➢ Strength
  ➢ Permeability
  ➢ Heat of hydration
  ➢ ASR and Sulfate attack mitigation

• SCMs may or may not favorably affect the following
  ➢ Early strength
  ➢ Rate of strength gain
  ➢ Cost
Summary

- Each material has general strengths and weaknesses

<table>
<thead>
<tr>
<th>Material</th>
<th>Strength</th>
<th>Weakness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly Ash</td>
<td>Most experience with Low cost (currently)</td>
<td>Inconsistency</td>
</tr>
<tr>
<td></td>
<td>Largest reserves</td>
<td>Diminishing supplies</td>
</tr>
<tr>
<td></td>
<td>Best availability (though variable)</td>
<td></td>
</tr>
<tr>
<td>Slag Cement</td>
<td>Consistent performance</td>
<td>Geographically limited supply</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Requires more attention to curing</td>
</tr>
<tr>
<td>Silica Fume</td>
<td>Highly pozzolanic</td>
<td>Cost</td>
</tr>
<tr>
<td>Natural Pozzolan</td>
<td>Consistent performance for a source</td>
<td>Limited experience with use</td>
</tr>
<tr>
<td></td>
<td>Cost competitive with fly ash</td>
<td>Geographically limited supply</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Range of performance</td>
</tr>
</tbody>
</table>
Summary

• Availability and use of SCMs is changing

• Trends will be towards more ternary mixtures where blends of SCMs will be used

• Traditional material supplies will be challenged

• New materials will enter the market place

• Testing of all materials and verification of performance in concrete will become more important moving forward
Questions?