Supplementary Cementitious Materials

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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

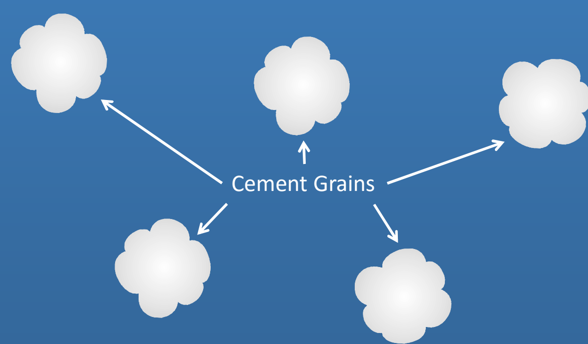
- State highway agencies (SHAs) and others charged with construction and maintenance of roads and bridges expect one key property from concrete: Longevity
- Service demands have increased
  - Use of aggressive deicing chemicals
- Increased expectations for reduced environmental impact and lower initial and lifecycle costs
- SCMs assist meeting these goals

Definitions

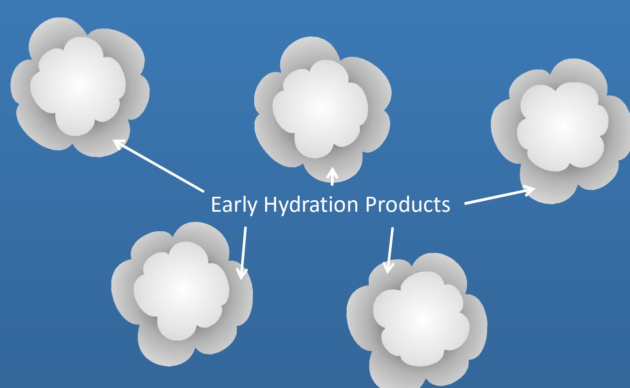
- **cementitious material, supplementary, (SCM)** - an inorganic material that contributes to the properties of a cementitious mixture through **hydraulic** or **pozzolanic** activity, or both
  - *DISCUSSION—Some examples of supplementary cementitious materials are fly ash, silica fume, slag cement, 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…

Water



Hydration Reactions Example: Portland Cement



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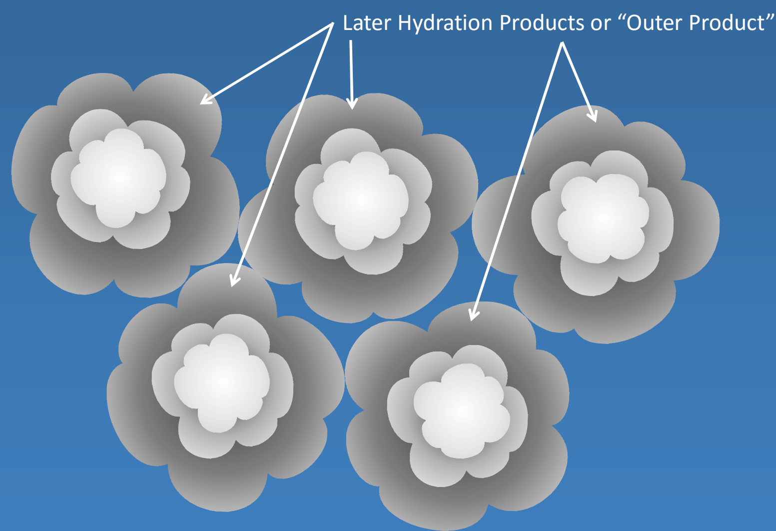
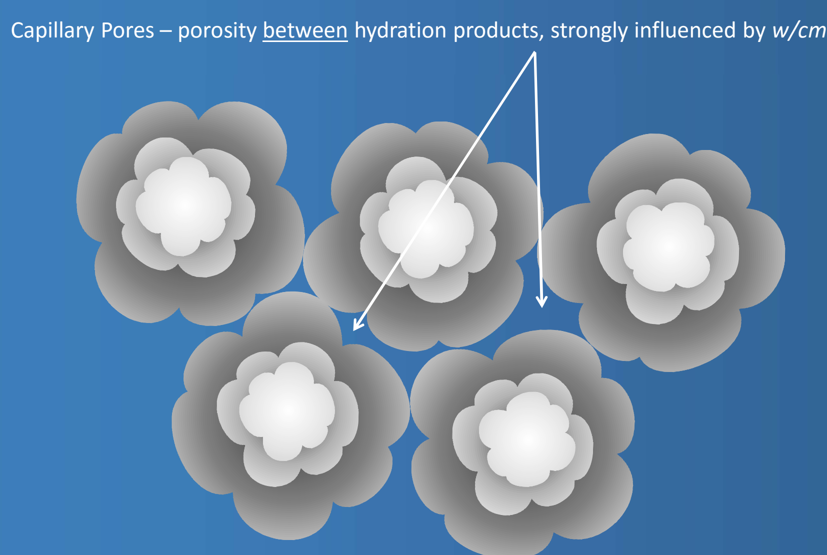
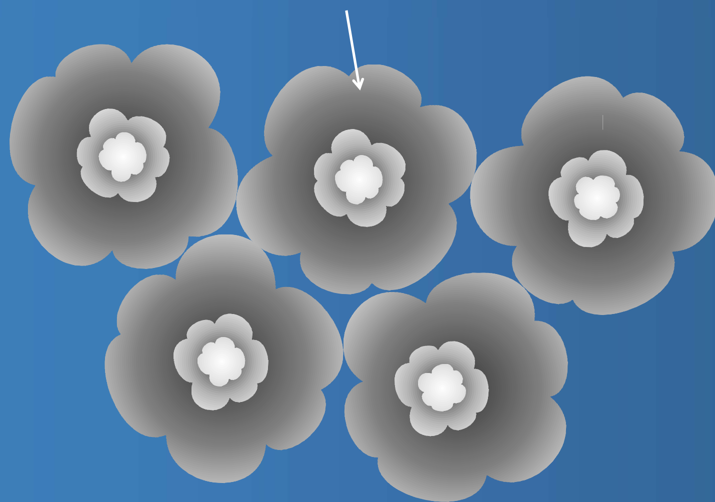


Hydration Reactions Example: Portland Cement



Hydration Reactions Example: Portland Cement

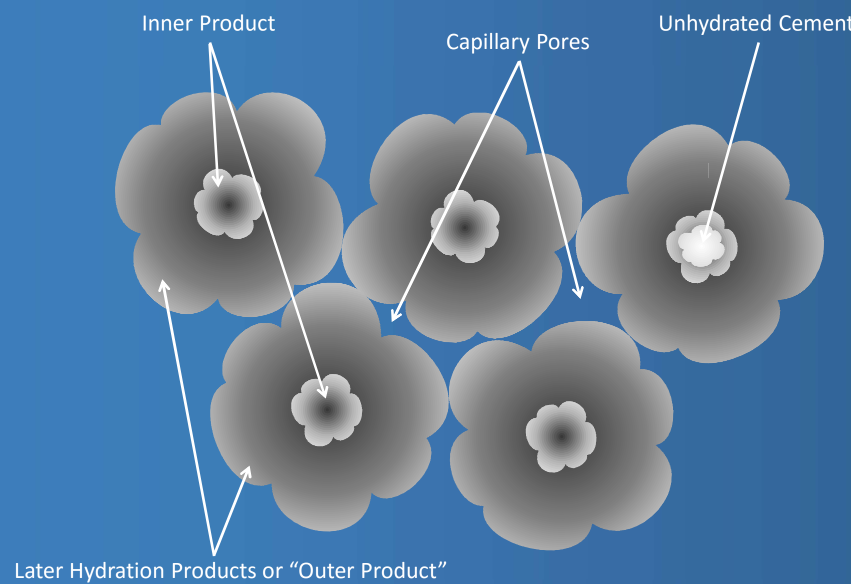
Gel Pores – porosity within hydration products causing permeability at a nano-scale



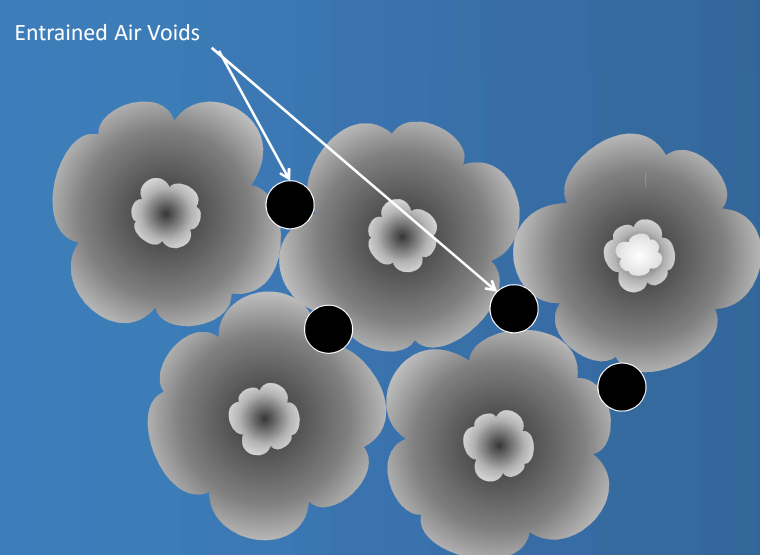
Hydration Reactions Example: Portland Cement

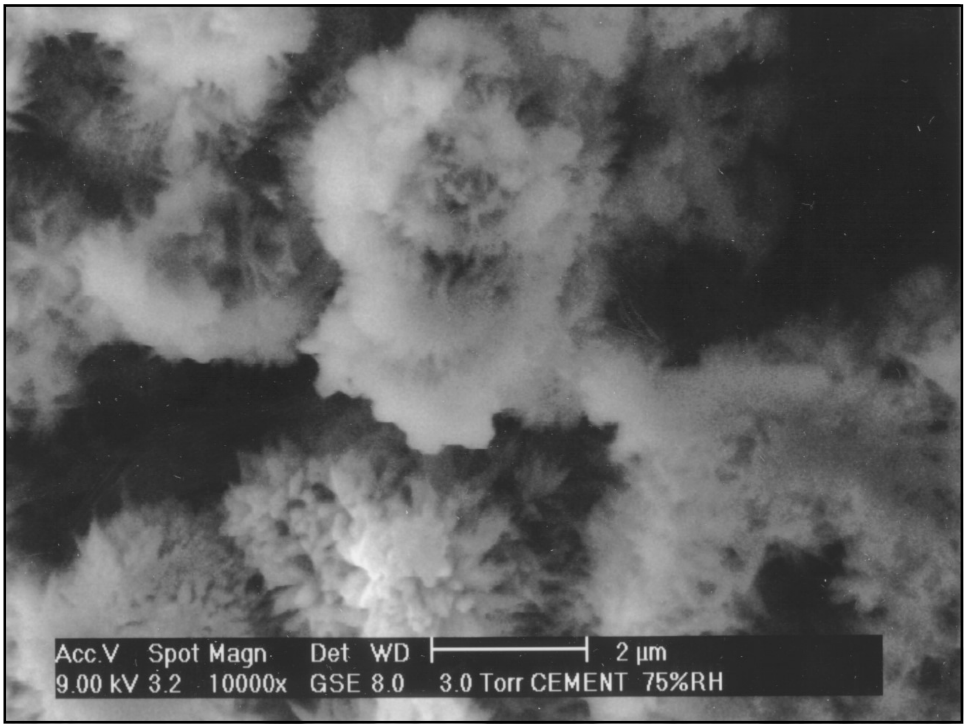
As hydration proceeds water must diffuse through the outer product to hydrate the cement within, forming "Inner Product". This diffusion slows the hydration process.

Hydration Reactions Example: Portland Cement



Hydration Reactions Example: Portland Cement





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 ⟶ 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

Pozzolanic Reaction

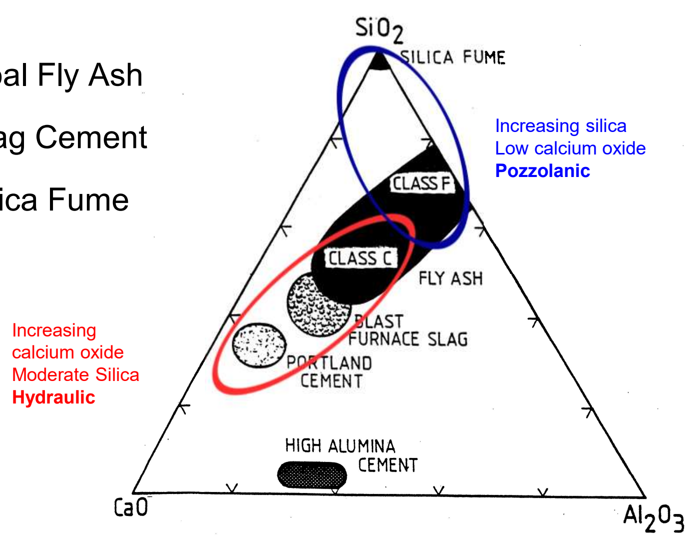
- SCMs consume CH through the pozzolanic reaction
  - Improves strength
  - Increases paste density
  - Reduces alkali (ASR mitigation)
  - Reduces rate of heat evolution due to hydration reaction
  - Slower strength development
  - **Pozzolanic Reaction:**

Cement + Water ⟶ C-S-H + CH

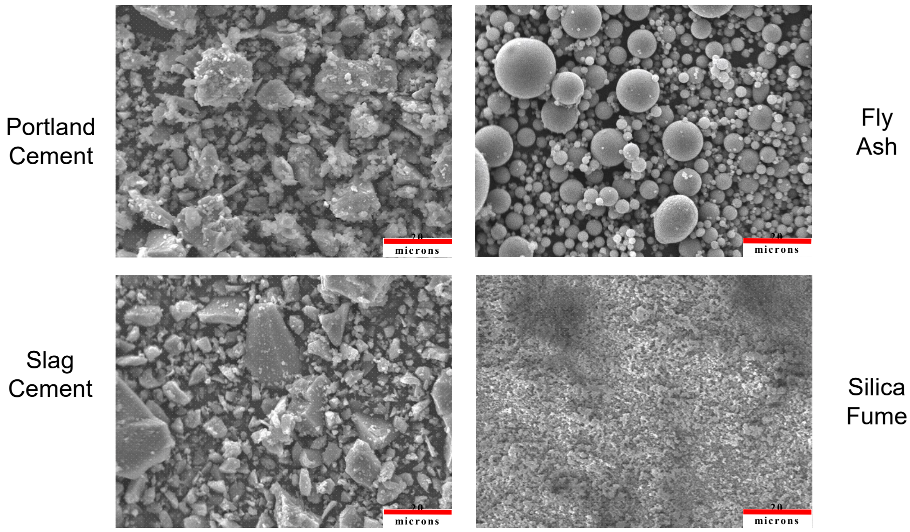
Pozzolan + CH + Water ⟶ C-S-H

General Characteristics - Composition

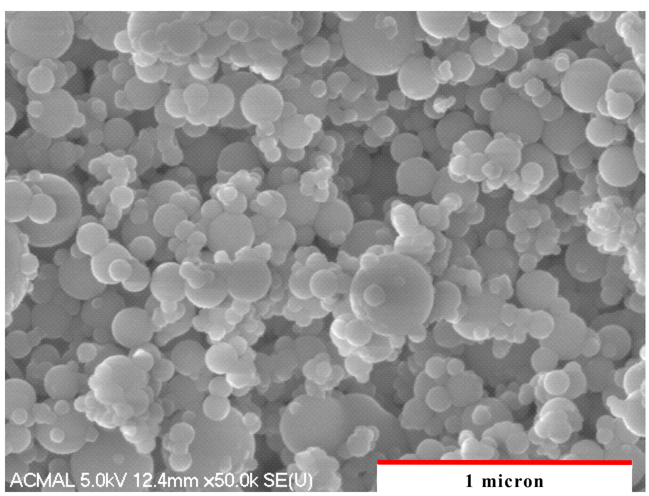
- Coal Fly Ash
- Slag Cement
- Silica Fume



General Characteristics – Particle Size & Shape



Silica Fume – Particle Size & Shape



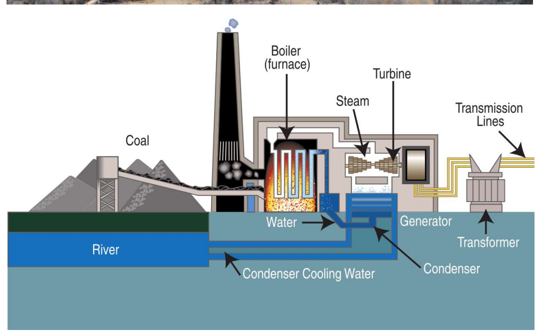
Effects of SCMs on Properly Cured Hardened Concrete

⬇ *Reduced* ➡ *No/Little Effect* ⬆ *Increase* ⬍ *Varies*

	Fly ash	Slag	Silica fume	Natural Pozzolan
Strength Gain	⬍	⬍	⬆	⬍
Abrasion Resistance	➡	➡	➡	➡
Freeze-Thaw and Deicer-Scaling Resistance	⬆	⬆	⬆	⬆
Drying Shrinkage and Creep	➡	➡	➡	➡
Permeability	⬇	⬇	⬇	⬇
Alkali-Silica Reactivity	⬇	⬇	⬇	⬇
Chemical Resistance	⬆	⬆	⬆	⬆
Carbonation	➡	➡	➡	➡
Concrete Color	⬍	⬍	⬍	⬍

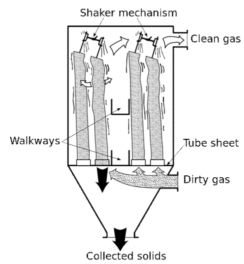
Coal Fly Ash

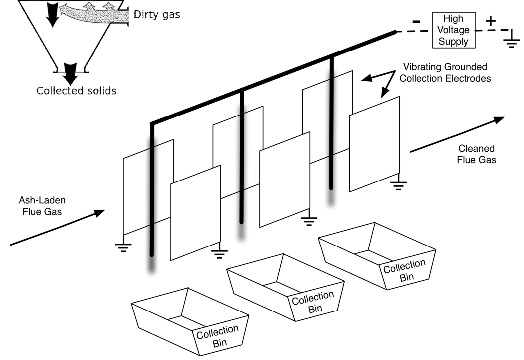
- The finely divided residue that results from the process of combustion of ground or powdered coal and that is transported by flue gasses (ASTM 2015)
- Produced from pulverized coal fuel
  - Fuel stream may have other components such as limestone, trona, other additives for pollution control



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)

    SUM (wt.%) = % SiO_2 + % Al_2O_3 + % Fe_2O_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

	Class F	Class C	Class N
Sulfur trioxide (SO_3), max, %	4.0	4.0	5.0
Moisture content, max, %	3.0	3.0	3.0
Loss on ignition, max, %	6.0	6.0	10.0
Available alkali, max %, (Optional in AASHTO M 295 only)	1.5	1.5	1.5

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)

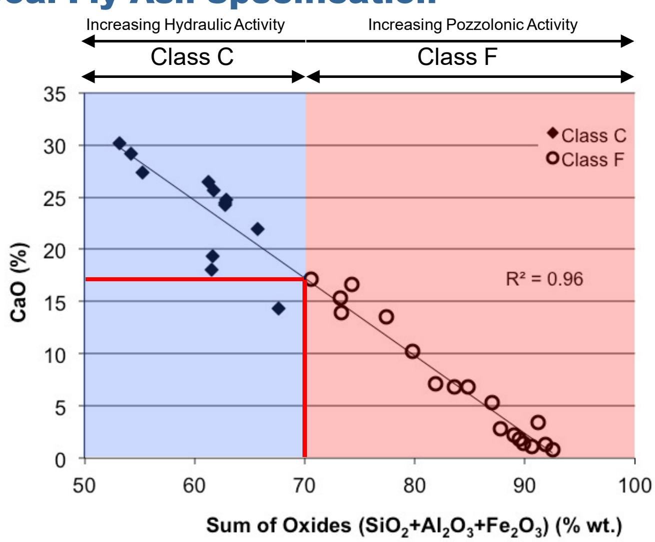
Fly Ash Specification

- 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

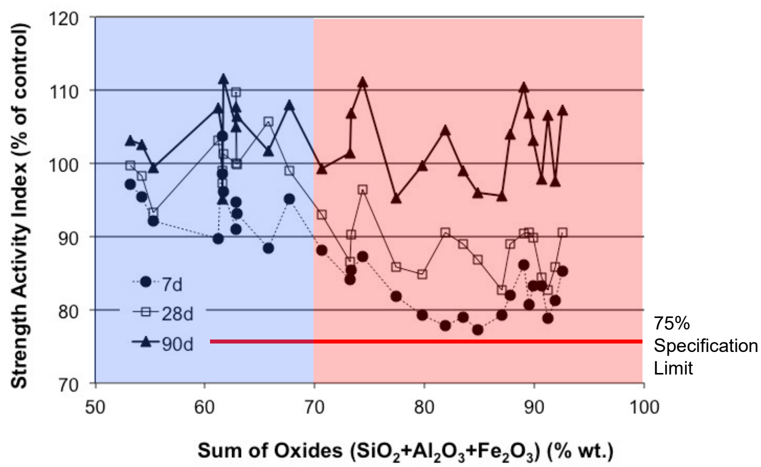
Coal Fly Ash Characteristics

- 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



Strength Activity Index

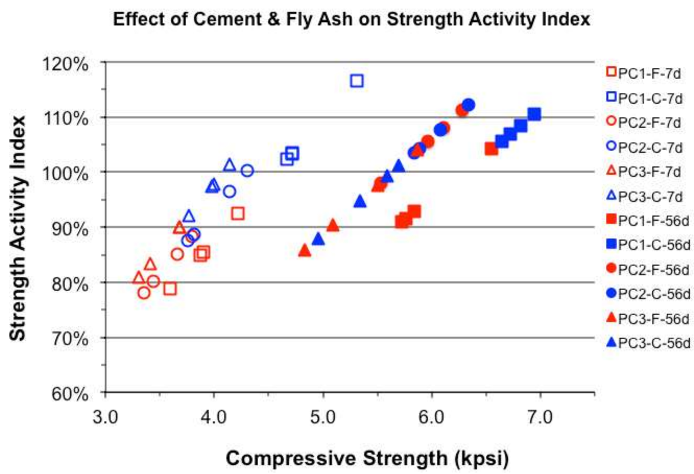


Strength Activity Index

- Strength Activity Index is questioned as it allows inert materials to pass
- Experiments performed with non-pozzolanic quartz filler – all pass the SAI

Cement Type	Age (days)	100% Cement	20% Replacement		35% Replacement	
		Strength (psi)	Strength (psi)	SAI	Strength (psi)	SAI
PC-1	7	4554	3829	84	3075	68
PC-2	7	4293	3408	79	2640	62
PC-3	7	4090	3539	87	2886	71
PC-1	28	5715	4815	84	3945	69
PC-2	28	5526	4235	77	3655	66
PC-3	28	5134	4351	85	3307	64

Strength Activity Index



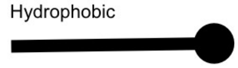
Changes to Concrete Mixture Properties

Property	Class C Replacement	Class F Replacement
Initial Set	Delayed	Delayed
Rate of Strength Gain	Same or higher	Slower
Heat of Hydration	Lower	Significantly lower
Early Strength (3-7 days)	Higher	Lower
Late Strength (28-56 days)	Same or higher	Same or higher
ASR Mitigation Potential	Only at high replacements	Significant mitigation above pessimism replacement levels

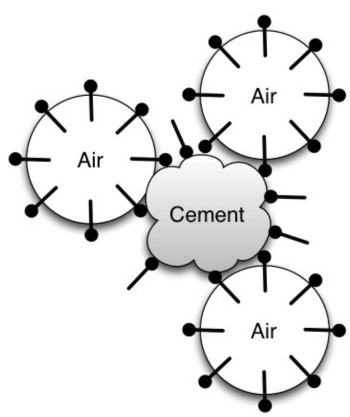
Fly Ash Carbon Affect on Air Entrainment

- 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

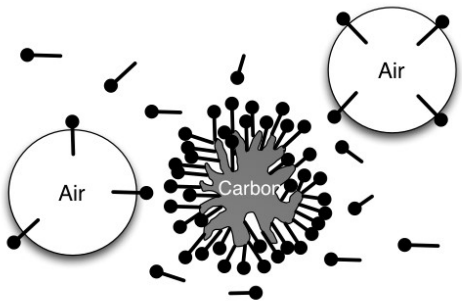


Fly Ash Carbon Affect on Air Entrainment



- 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

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

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

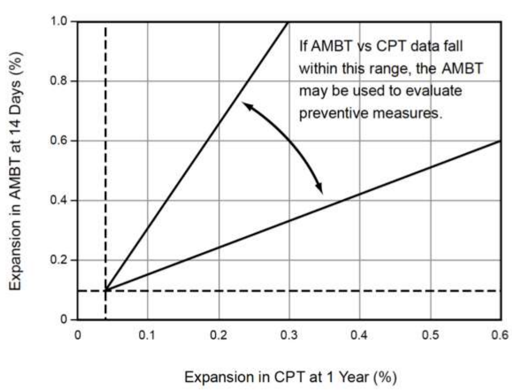
ASR Mitigation with Fly Ash

- 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

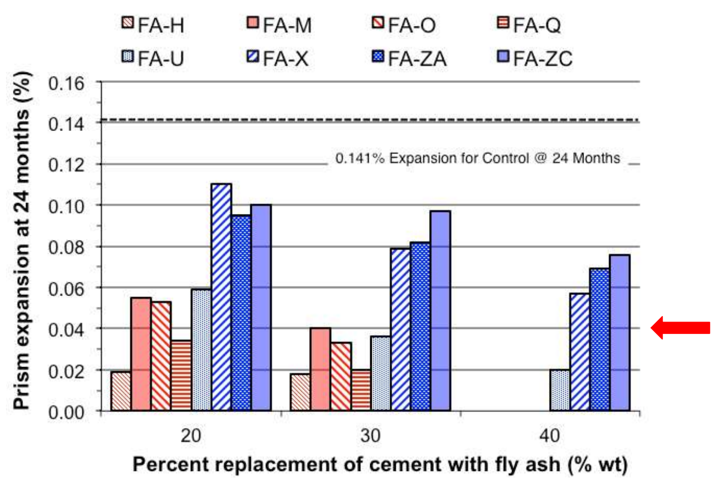
ASR Mitigation with Fly Ash



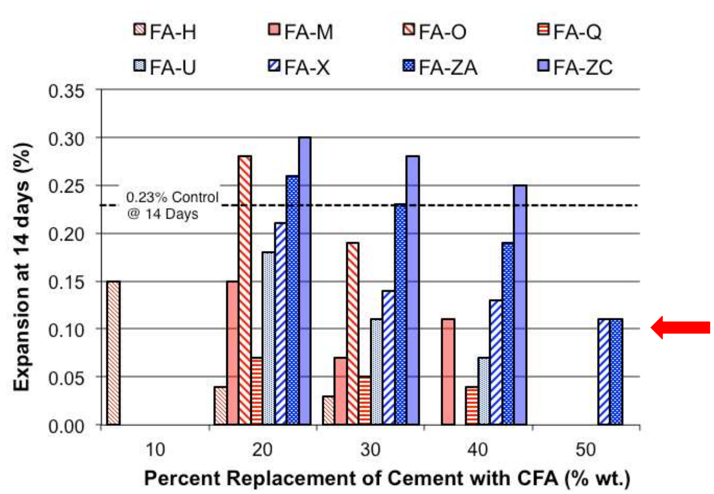
- ASTM C1567
  - Accelerated Mortar Bar Test
  - Based on ASTM C1260
  - Cannot be used unless there is a reasonable correlation between C1260 and C1293 for the aggregate in question

Alkali-Aggregate Reactivity (AAR) Facts Book. Thomas, M.D.A., Fournier, B., Folliard, K.J.

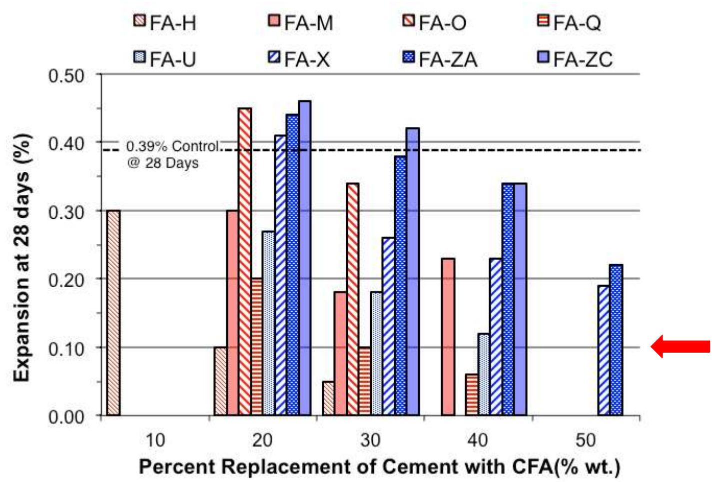
ASTM C1293 Data



ASTM C1567 Data – 14 day (standard)

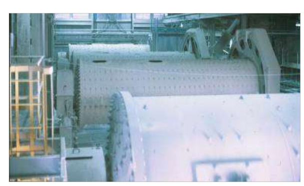


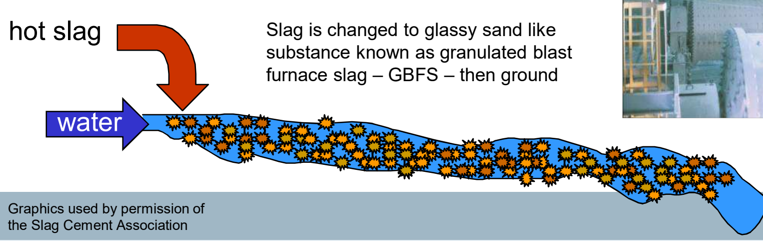
ASTM C1567 Data – 28 day (non-standard)



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





Slag is changed to glassy sand like substance known as granulated blast furnace slag – GBFS – then ground

Graphics used by permission of 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 Grade120
- 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

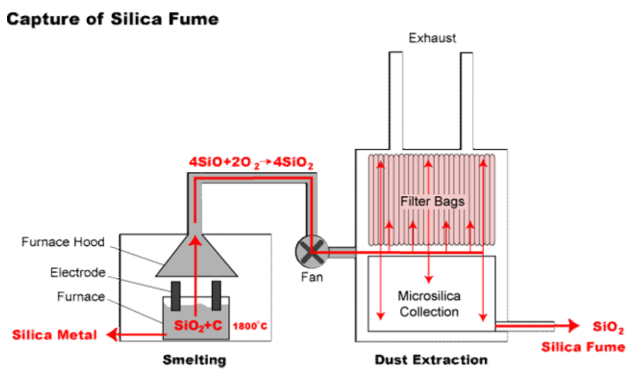
- Because slag cement is slower to react, setting time can be increased significantly compared to OPC concrete
- Curing is always essential for achieving a quality product; it is even more critical with slag-cement-based concrete
- The slower reaction rate, especially at lower temperatures, is often 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 Source: http://www.bulkmaterialsinternational.net/bmi_silica_fume.html

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
  - 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 65º C (150º F)** for an additional 6 days, thereby accelerating the pozzolanic reaction

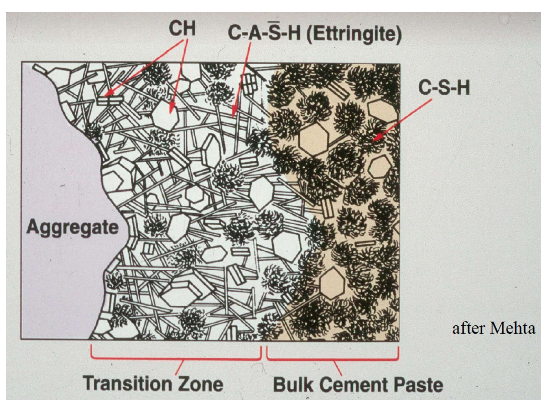
Silica Fume

- 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

Silica Fume

- Another important factor that leads to increased concrete strength and durability is that silica fume is able to <u>pack around aggregate particles</u> effectively, <u>consume CH at the aggregate-paste interfacial zone</u>, and greatly improve the strength and impermeability of the interfacial transition zone

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 pozzolanic materials

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- Global distribution: natural pozzolans vs. volcanics

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ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Natural Pozzolans

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

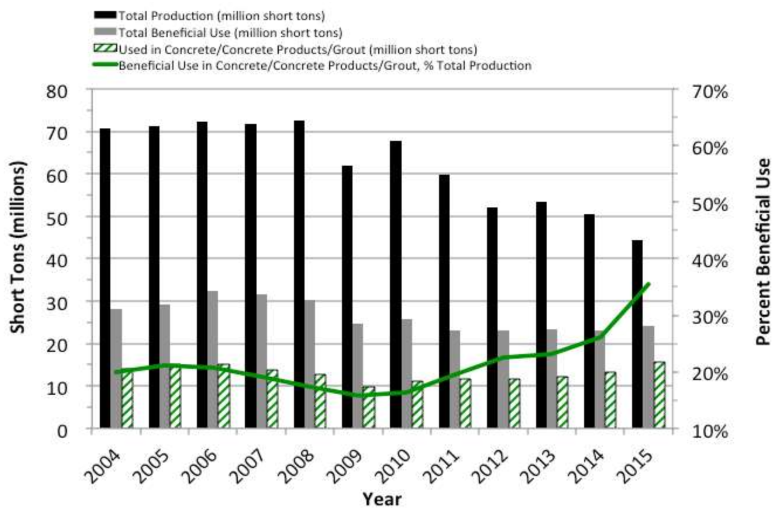
Alternative SCMs

- 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 a one SCM can be offset by positive properties of another

Coal Fly Ash Use



Recovered Ash

- With diminishing production, ash marketers are turning to land fills & 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

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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

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Summary

- Each material has general strengths and weaknesses

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

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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

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Questions?