The Future of Fly Ash: Dystopia or Hysteria?

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Background

- We 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

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Definitions

- cementitious material, supplementary, (SCM) an inorganic material that contributes to the properties of a cementitious mixture through <u>hydraulic</u> or <u>pozzolanic</u> 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)

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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 + CH

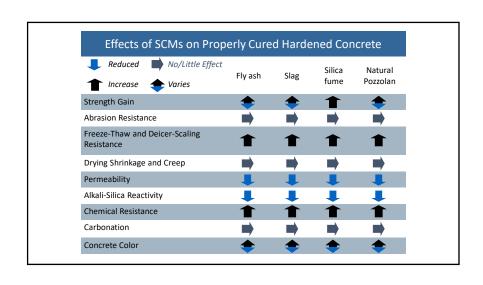
- C-S-H provides strength <u>desirable</u> product
- CH provides little strength and is soluble, also is a reactant in many MRD mechanisms – undesirable product

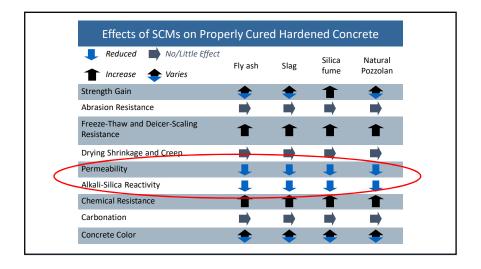


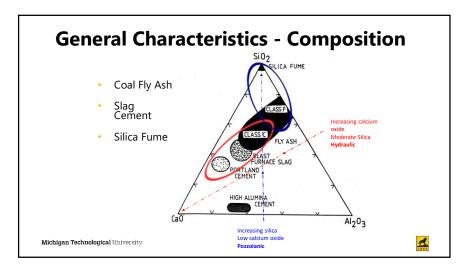
Pozzolanic Reaction • SCMs consume CH through the pozzolanic reaction • Improves strength • Increases paste density • Reduces alkali (ASR mitigation) • Reduces rate of heat evolution due to hydration reaction • Slower strength development Hydration Reaction: Cement + Water C-S-H + CH Pozzolanic Reaction: Pozzolan + CH + Water C-S-H

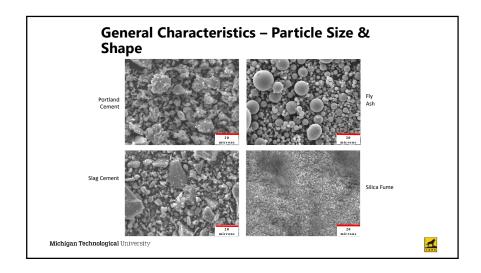
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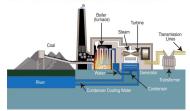


Coal Fly Ash

- 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

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Airborne residue from coal combustion processes collected from the flue gases by a variety of means Electrostatic precipitators Fabric filters (baghouse) Michigan Technological University

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

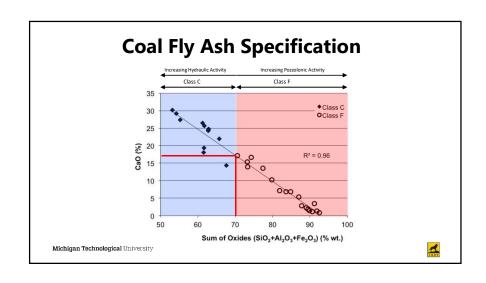


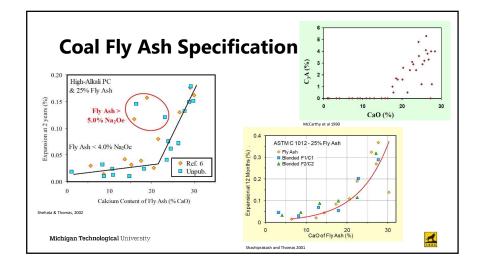
Fly Ash Specification

- 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) RECENT CHANGE
 SUM (wt.%) = % SiO₂ + % Al₂O₃ + % Fe₂O₃
 - Class F and Class C → SUM ≥ 50%
 - Class F → CaO ≤ 18% (low calcium oxide)
 - Class C → CaO > 18% (high calcium oxide)
 - Class N → SUM ≥ 70% (natural pozzolan source only)

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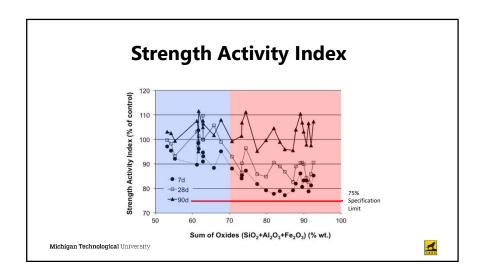




Coal Fly Ash Specification

- 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 day





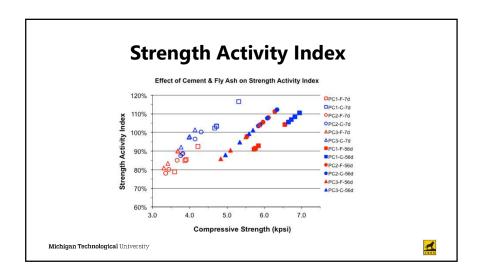
Strength Activity Index

- Strength Activity Index is questioned as it allows inert materials to pass
- Experiments performed with non-pozzolanic quartz filler at 20% replacement they all pass the SAI
- · Need a new test to measure SCM reactivity

	Age (days)	Strength (psi)	20% Replacement		35% Replacement	
Cement Type			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

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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
 - · Slow initial strength gain (Class F)
 - Fly ash variability
 - · How reactive is it?



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



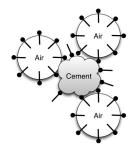
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Non-ionic (has no charge) Little or no attraction to water (hydrophobic) lonic portion (has a charge) Strong attraction to water (hydrophilic)

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Fly Ash Carbon Affect on Air Entrainment

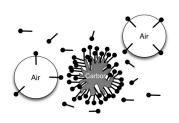


- Hydrophilic, anionic polar groups (i.e. head) sorb strongly to the ionic cement particles
- Hydrophobic, non-polar end of the surfactants (i.e. tail) orient towards the solution
- Stabilize (entrain) air bubbles, prevent coalescing into larger bubbles

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Fly Ash Carbon Affect on Air Entrainment



- Carbon in fly ash adsorbs AEA from the concrete mix water
- Reduces the amount of AEA remaining in the water to a point where the AEA is no longer able to stabilize the required volume of air bubbles

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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)





Designation: C1827 - 20

Standard Test Method for Determination of the Air-Entraining Admixture Demand of a Cementitious Mixture¹

This standard is issued under the fixed designation C1827; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (e) indicates an editorial change since the last revision or reapproval.

- 1.1 This test method is for the determination of the airentraining admixture (AEA) demand of a mixture of cementitious materials, AEA, and water.
- 1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this
- 1.3 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the

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- 3.1.1 For definitions of terms used in this test method, refer to Terminology C125.
- 3.2 Definitions of Terms Specific to This Standard:
- 3.2.1 absolute volume of AEA, n—the air-entraining admixture demand expressed as volume of un-diluted air-entraining admixture to produce a stable foam.
- 3.2.2 air-entraining admixture demand, n-the quantity of air-entraining admixture required to produce a stable foam for a specific mixture of cementitious materials, air-entraining admixture, and water,



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

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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 all tests are empirical, which means they are based on experience and observation
- An empirical test only means something if you do it the same way when testing, as you did when you made the observation and created the test

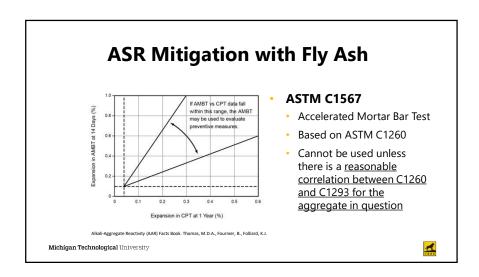
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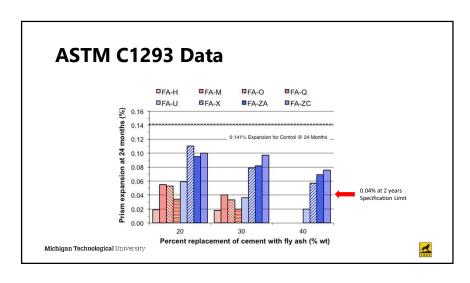


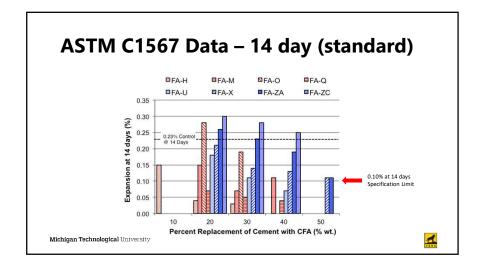
ASR Mitigation with Fly Ash

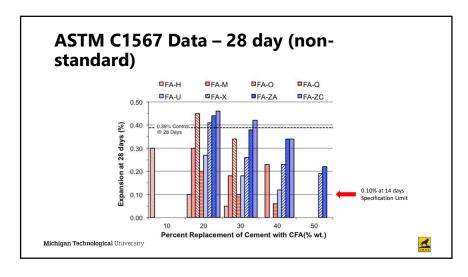
- ASTM C1293 Concrete Prism Test
 - Currently the most reliable test available not infallible
 - Not quick one year minimum two years when validating SCM replacement
 - Known drawbacks include alkali leaching that can lead to errors in estimating the alkali threshold need for ASR to occur











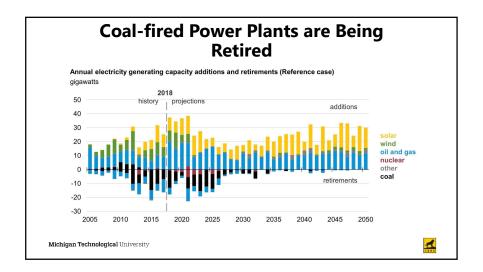


The Problem

- Fly ash supplies are challenged by plant closures and conversions to natural gas
- Fly ash spot shortages have been reported in many U.S. markets
- Concerns center on the fact that no other material is available with the reserves that fly ash historically has provided

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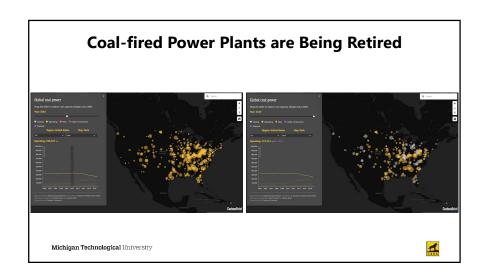


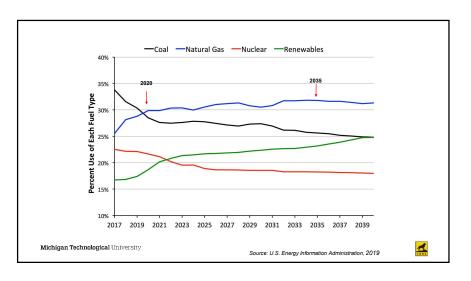
Navajo Generating Station

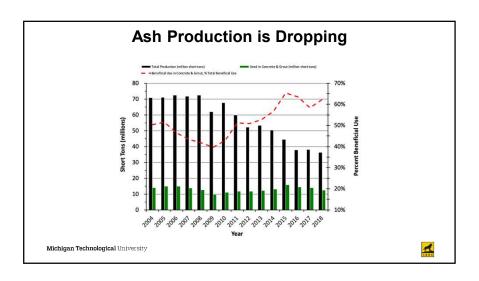
- 2250 megawatt net coalfired powerplant
- Largest coal fired electrical generating station west of the Mississippi
- Produces approximately 500,000 tons a year of Class F fly ash
- Closed 2020











So What's Up With Fly Ash?

- Domestic fly ash production (new production) will be gradually decreasing over the next 20 years and beyond
 - Domestic production is predicted to stabilize (next 5 years) reductions in coal–fired power will plateau (EIA 2019)
 - · Fewer plants, running at a higher percentage of capacity
 - Suppliers believe that although total reserves may decrease, the volume of quality ash as a percentage of total production will increase due to dry handling – no more ponding
- Harvested ash from landfills/ponds will become a significant fraction of the total reserves



So What Else is Up With Fly Ash?

- Other Challenges
 - Pollution control measures will affect "fresh" ash
 - · Powdered Activated Carbon
 - Trona
 - · Competing with other markets for the material
 - Lower supply consider ash once rejected?
 - Harvested Ash A New Frontier

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Options

- · What will replace fly ash if needed?
 - * Slag cement (existing solution)
 - * Harvested fly ash (emerging solution)
 - * Ash Imports (emerging solution)
 - Natural pozzolans (existing solution)
 - · Lower quality fly ash (last resort)
 - · New Materials (colloidal silica, ground glass)
 - · Straight cement

Are existing tests and specifications adequate?

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Slag Cement



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- 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 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

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Slag Cement

- · Because slag cement reacts slow:
 - Setting time can be increased significantly compared to OPC concrete
 - Has lower heat evolution making slag cement ideal for mass concrete placement where control of internal temperatures is critical - up to 80% replacement of OPC with slag cement is used for mass concrete
- Curing is essential for all concrete; 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 scaling when not properly cured
- · Slag cement is effective at mitigating ASR
 - Requires higher replacement rates than Class F ash (e.g., > 50%)

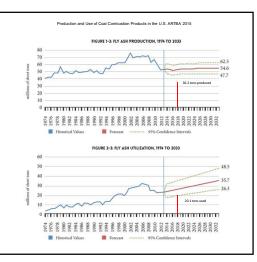
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Harvested Ash

- Significant volumes of highquality fly ash have been disposed
 - Approximately 2000 million short tons produced 1974 -2013
 - Approximately 650 million short tons used 1974 – 2013
 - ~33% utilization 1350 million short tons disposed
- Not all is recoverable, but a large fraction is

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Harvested Ash

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



Harvested 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 harvested ash?

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Harvested Ash

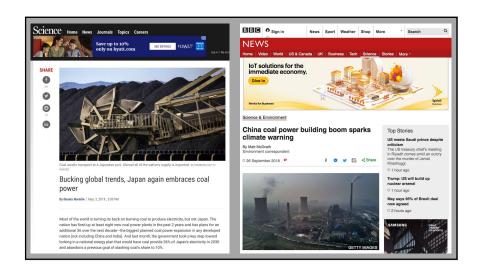
- Concerns (continued)
 - Current federal and state regulations require near-term closure of disposal ponds, leaving insufficient time to recover and use all available ash
 - Power producers have little to no incentive to use ash beneficially, closure (cap-in-place) is the lowest cost option.
- Benefits of landfilled ash
 - · 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

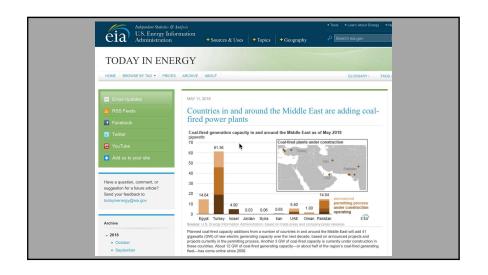
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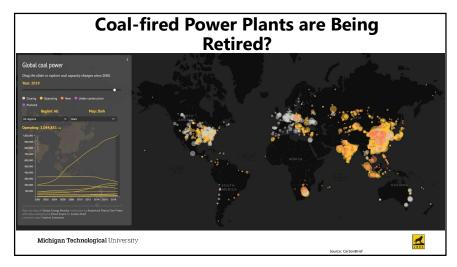


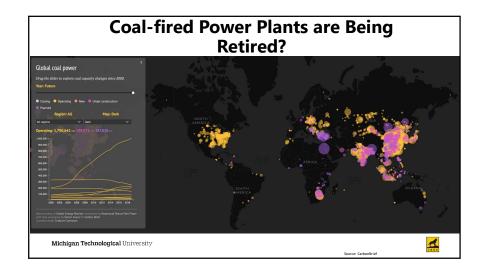
Imported Ash







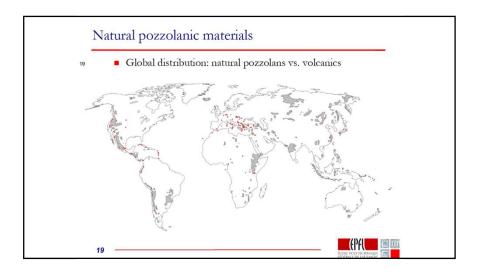




Imports

- Certainly in the near term, and potentially long term, imports will become a significant source
- Imports are already a significant contributor in some markets
- China is COMMITTED to keeping shipping costs low, making imports cost effective (i.e., producing a large number of ocean-going cargo ships at a fraction of the cost of western countries)
- For imports, issues of quality must be considered TESTING





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 TESTING

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Lower Quality - Increased Need for Testing

- So called "off-spec" ash is being considered
 - Note: Existing ash specifications do not address performance (i.e., meeting the specification does not guarantee performance)
- If performance of a material can be demonstrated use it
- Common off-spec issues
 - LOI
 - Fineness
- Materials that are not coal fly ash are not off-spec; they are simply not fly ash – but they may work
- Verify reserves

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New Materials - Ground Glass

- Total Production (~ 11 million tons/year in U.S.)
 - · Container Glass (~ 3 million tons/year in U.S.)
 - E-Glass (100,000 lbs/year in U.S.)
 - Recycling capacity exceeds generation (U.S. EPA)
- Primary Processing Grinding
 - -325 mesh
 - Composition is uniform





Standard Specification for Ground-Glass Pozzolan for Use in Concrete¹

This standard is issued under the fixed designation C1866/C1866M; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproxal. A superscript epsilon (or indicates an editorical changes since the last revision or reapproxal).

1. Scope

- 1.1 This specification covers ground-glass pozzolans for use in concrete where pozzolanic action is desired. This specification applies to ground glass from sources that consist of container glass, plate glass, or E-glass.
- 1.2 The standard references notes and footnotes that provide explanatory material. These notes and footnotes (excluding those in tables and figures) shall not be considered as requirements of the standard.

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- C109/C109M Test Method for Compressive Com
- C125 Terminology Relating to Concrete and Concrete Ag-
- C150/C150M Specification for Portland Cement
 C204 Test Methods for Fineness of Hydraulic Cement by
 Air-Permeability Apparatus
- C311/C311M Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement



Nominal Glass Composition

		E-Glass			
	Bottle Glass	Plate Glass	Display Glass	E-Glass	
SiO ₂	71	71	63	60	
Al ₂ O ₃	1.8	0.4	18	12.5	
Fe ₂ O ₃	0.6	0.4	0.0	0.4	
B_2O_3	0.01	0.02	2.0	0.0	
MgO	0.90	3.9	2.5	2.9	
CaO	11	9.3	0.1	21	
Na ₂ O	13	13	13	0.75	
K ₂ O	0.5	0.05	0.0	0.06	

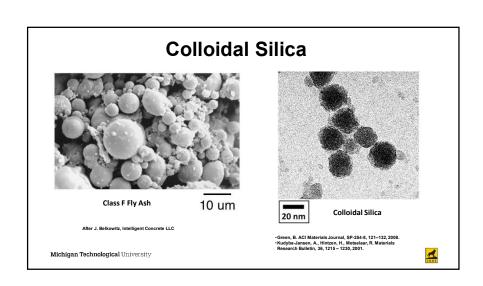
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Bottom Ash

- ASTM is discussing a "Class B" for bottom ash
- Mimics the properties of the fly ash from the same coal but attributes are subdued, relative to the fly ash
 - Contributes to concrete properties
 - Mitigates ASR
- Angular increased water demand
- Commonly comingled with fly ash in harvested materials





Alternative SCMs

- Inorganic materials that react, as a pozzolan or hydraulic cement, 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

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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

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Straight Cement?

- 3:5:6
- Once 3:5:6 doesn't apply (e.g., 6:6:6) the cement replacement advantage is diminished
- Sustainability goals are important <u>only</u> if incentivized
- A higher cement content (low alkali loading) is not out of reality <u>IF</u> the mixture meets performance
 - ASR mitigation
 - Sulfate attack prevention
 - Physical properties

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ASR Risk Mitigation - AASHTO

Standard Practice for

Determining the Reactivity of Concrete Aggregates and Selecting Appropriate Measures for Preventing Deleterious Expansion in New Concrete Construction

AASHTO Designation: R 80-171

Technical Section: 3c, Hardened Concrete



What about tests and specifications?

- Existing tests and specifications provide little information on performance
- As harvested materials and other sources become more common, new tests and specifications are required that relate to performance (i.e., pozzolanic activity, hydraulic activity, particle size, adsorption)
- Need to let go of historic limits/tests established in a completely different concrete world that mean little now (e.g., SAI test, LOI)
- · Specifications need to include blending SCMs
- · Need to get more materials in the market while improving performance and quality

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Trends in Specifications

- Concerns with consistent performance & use of harvested ash have caused ASTM & AASHTO to re-evaluate specifications
- Measure reactivity (done)
 - R3 tests (rapid, reliable, reproducible) measure heat released by isothermal calorimetry or else measure bound water - both for SCM exposed to CH solution
 - · Lime Pozzolanic Activity Test
- Particle size need a better test
- · Consider modifications to SAI
 - · Measure efficiency

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Designation: C1897 - 20

Standard Test Methods for Measuring the Reactivity of Supplementary Cementitious Materials by Isothermal Calorimetry and Bound Water Measurements ¹

This standard is issued under the fixed designation C1897: the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript espita (e) indicates an editorial change since the last revision or reapproval.

1. Scope

- 1.1 These two alternative test methods are used to assess the chemical reactivity of a supplementary cementitious material (SCM) as determined by measurements of cumulative heat release or bound water content of hydrated pastes composed of the SCM, calcium hydroxide, calcium carbonate, potassium sulfate, and potassium hydroxide cured at 40 °C for 3 and 7 days.
- 1.1.1 These two test methods do not distinguish between hydraulic and pozzolanic reactivity.

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2. Referenced Documents

- 2.1 ASTM Standards:3
- C114 Test Methods for Chemical Analysis of Hydraulic Cement
- C125 Terminology Relating to Concrete and Concrete Ag-
- C311/C311M Test Methods for Sampling and Testing Fly
 Ash or Natural Pozzolans for Use in Portland-Cement
 Concrete
- C618 Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete

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Trends in Specifications

- Recently removed the Effectiveness in Controlling ASR test & limits
- Adsorption potential just passed the foam index test at ASTM
- · Use adsorption based tests rather than LOI
- Remove Autoclave soundness nothing fails (pending)
- Remove available alkali test Not required to assess ASR mitigation (pending)
- New natural pozzolan specification (pending)
- New performance-based specification (pending)



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

- Availability and use of SCMs is changing fly ash is in short supply in some markets
- Traditional material supplies will be challenged
- Trends will be towards more ternary mixtures where blends of SCMs will be used
- 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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Summary

- Near term solutions
 - Other SCMs (e.g., slag, ground glass, natural pozzolans)
 - Imports
 - Harvested Ash
 - Straight cement possible durability may suffer if not approached carefully



Questions?

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