

A Brief History of Hydraulic Cement

in Construction



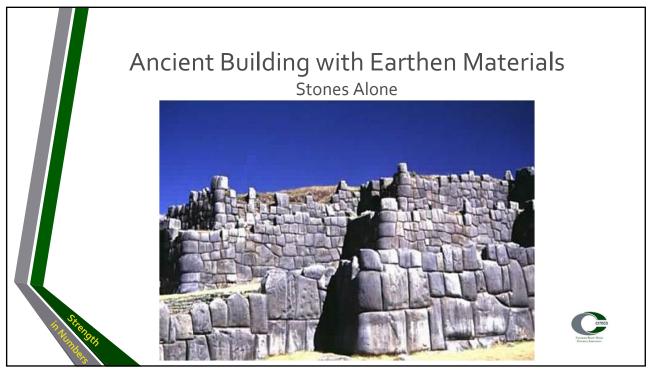
COLORADO READY MIXED CONCRETE ASSOCIATION

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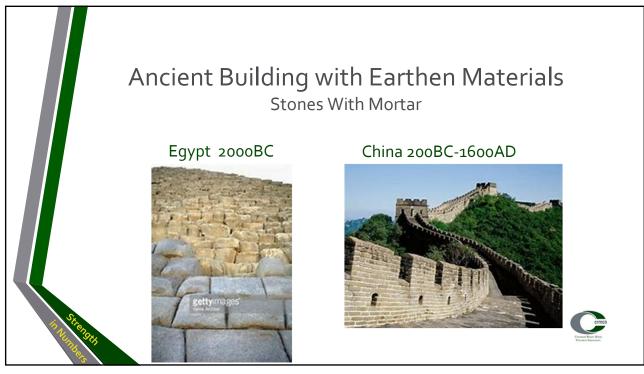


- Definition (ACI) A binding material that sets and hardens by chemical reaction with water and is capable of doing so underwater.
 - Portland cement.
 - Natural cement.
 - Slag cement.
 - Class C fly ash.
 - Plaster of Paris









Ancient Building with Earthen Materials Stones With Mortar

Egypt 2000 BC

- Some of the stones were found to be bedded with calcined gypsum (300C).
- Modern day term for this is Plaster of Paris.
- Controversy surrounds all the theories of pyramid construction.

China 200BC - 1600 AD

- Methods varied with age.
- Ming Dynasty construction included use of Plaster of Paris with a "rice pectin" admixture, one of few documented organic admixtures



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Ancient Building with Earthen Materials Concrete and Mortar

- Roman Structures (Pantheon / Colosseum and many others)
- Built with calcined Limestone (84oC-90oC) ground up and mixed with about 85% volcanic ash from Mount Vesuvius, from near Puzzuoli. Ash became known as "pozzolana".
- Combination was later called "Natural Cement"



Ancient Building with Earthen Materials Concrete and Mortar

Crete



Santorini



- Greeks used calcined lime and Santorin Earth, a volcanic tuff from major modern eruptions on Thera.
- They also ground up ceramics to use as pozzolan



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The Advent of Portland Cement

Eddystone Rock Lighthouse

- In 1756 the third of 4 lighthouses built in this location was completed. Although it later was undermined, it was never totally removed.
- John Smeaton experimented with production of lime by including some clay in the feed – and found it improved its strength properties.
- Trass (Rhine region volcanic material) was combined with the Smeaton cement.
- In spite of Smeaton's experiment, not much improvement was made to his lime for about 100 years.





The Advent of Portland Cement

- In 1842, Joseph Aspdin patented Portland Cement.
- He calcined limestone, broke it up and mixed it with clay and water, calcined it yet again and ground it up.
- It is called Portland Cement because of Aspdin's observation that the hardened cement resembled stone bluffs surrounding the Isle of Portland.
- This new product did not take off quickly. Aspdin's son took over its promotion. A man named Charles Johnson noticed that when some of the clinkers were "over burned", they made excellent cement when ground up. Modern day cement is calcined at about 1450C.

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The Use of Portland Cement in the Past 150 Years

- People started putting stones and sand in mortar.
- Germany formed their own "Portland Cement Assn." in about 1870.
- The world started to be more scientific in its development better tools and more scientific understanding.
 - Petrography was instrumental in understanding the Bogue reactive component composition of cement (C₃S,C₂S,C₃A,C₄AF)
 - Thermal analyses became a useful tools.
- ASCE began formulating test methods to assess it.
- ASTM formed Committee C1 on Cement.



Early Standards

- British Standard for Portland Cement 1904
- First ASTM standard for Portland Cement 1904
- ASTM Standard for Natural Cement (C10) 1904
- First ASTM Standard C150 for Portland Cement 1940
- Carnegie Institute, US Bureau of Standards, and (after 1926) the Portland Cement Institute did a lot of study and research on Portland Cement during the first part of the 20th Century.
- The British "Cement and Concrete Association was formed after WWII



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Advent of GGBFS (Slag Cement)

- By-product of iron production.
- Mixed with calcined lime in the 1700's to make mortar
- Iron ore is heated to 1500 °C to separate iron from the ore.
- Molten slag is granulated by guenching when dumped from the furnaces.
- Thus, we get "ground, granulated blast-furnace slag"
 - Now called "SLAG CEMENT"



Advent of Fly Ash

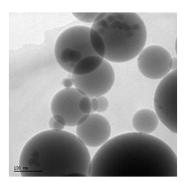
- Not as old as natural pozzolans.
- It gained attention in the 1950's and 1960's as powerplants became more sophisticated and the ash was cleaner and finer.
- USBR, COE, TVA all used it in water resource, hydraulic power and/or flood control structures in the mid 1900's.
- Originally Class F ash was used. The Class C ash was later as the Powder River Basin and similar lignite/sub-bituminous coals were mined for power plants.



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Advent of Silica Fume

- First tested in 1952
- Mostly not collected until the 1970's.
- By-product of the silicon chip production process.
- Extremely fine in comparison to other pozzolans. (100 times finer than most)
- It became commonly used in the 1980's.
- There is a limited supply.





Advent of Metakaolin

- Just a natural pozzolan on steroids.
- Kaolin clay calcined to 700 °C ±50?
- Ground very fine, finer than cement, not as fine as silica fume.
- Used in high performance concrete.
- I remember it first becoming available in the 1970's.
- No separate ASTM specification for it was ever published.



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ACAA Mission

 The mission of the American Coal Ash Association is to encourage beneficial use of CCP in ways that are



- environmentally responsible,
- technically sound,
- commercially competitive,
- supportive of a sustainable global community.



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What is the state of supply today and why?

- On a national level, some regions are experiencing a significant gap between supply and demand.
- Primary reason for this gap: demand has been increasing while coal-fueled generation has been decreasing
- About 6 years ago, coal fueled about 50% of the generation of electricity
- Today, coal accounts for 20% to 25% of generation
- Base-load generation has declined
- Coal plants are now running mostly in very hot and very cold weather conditions



State of Supply - continued

- 2009: U.S. Environmental Protection Agency (EPA) started an attempt to regulate fly ash and other coal combustion products (CCP) as a hazardous waste.
- Many older coal-fueled plants began to hit retirement age or became uneconomical to retrofit to meet increasingly stringent EPA standards
- Combustion stream injections made some fly ash unsuitable for use in concrete
- Fracking caused a rapid increase in supplies of natural gas
- As natural supplies increased, gas prices decreased dramatically
- Fossil fuels became a primary target of environmental activists

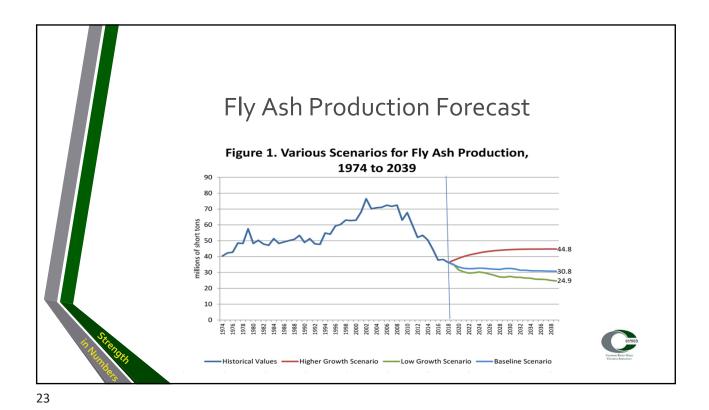


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There is fly ash not in use

- Each year millions of tons of fly ash produced goes to disposal rather than into beneficial use.
- Primary Reason #1 Dislocation
- Primary Reason #2 Quality
- 2015 to 2019 185.9 m tons of fly ash produced
- 2015 to 2019 108.7 m tons of fly ash used in all beneficial uses
- 2015 to 2019 69.4 m tons of fly ash used in concrete
- 2015 to 2019 77.2 m tons of fly ash not used





Fly Ash Production Forecast 2018 to 2039 Table 1. Fly Ash Forecast Scenarios (in millions short tons) Projected Total Projected Avg. Annual Volume Projected **Growth Rate** 2018 Volume 2039 Change Fly Ash Production Baseline Forecast 36.2 30.8 -14.9% -0.8% 1.0% High Growth Scenario 36.2 44.8 23.8% Low Growth Scenario 36.2 24.9 -31.2% -1.8% Fly Ash Utilization 20.1 27.8 38.3% 1.6%

What is "harvesting"?

- "Harvesting" is the term selected by consensus to describe to process of removing coal ash from disposal – dry and wet – for beneficial uses.
- Why "harvesting??
- Disposal of coal ash occurs in landfills and surface impoundments (a.k.a. ponds)
- Coal ash comingled with other materials is likely not to be a candidate for processing for concrete manufacture
- Coal ash in monofills is the target
- Over 2.5 billion tons in disposal in the U.S.



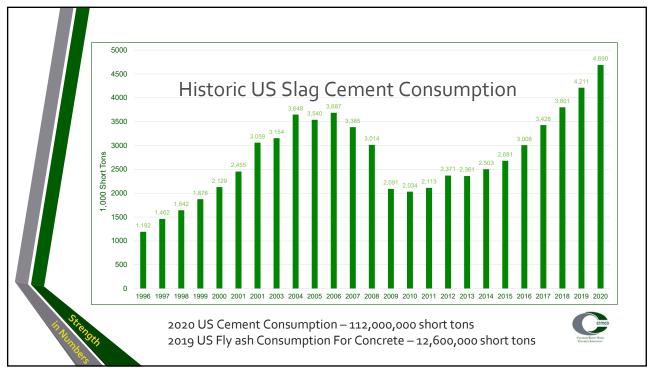
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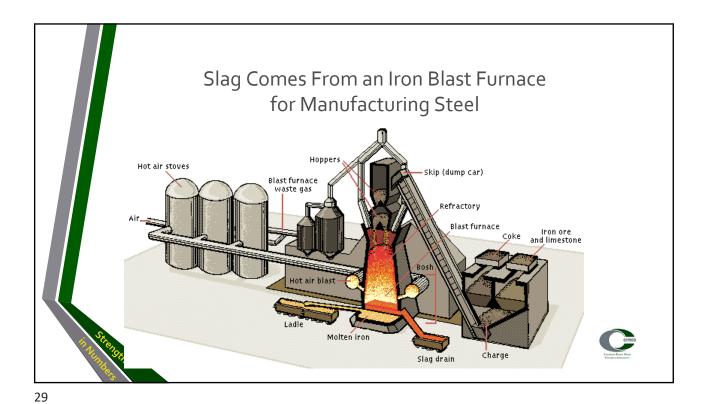
Summary

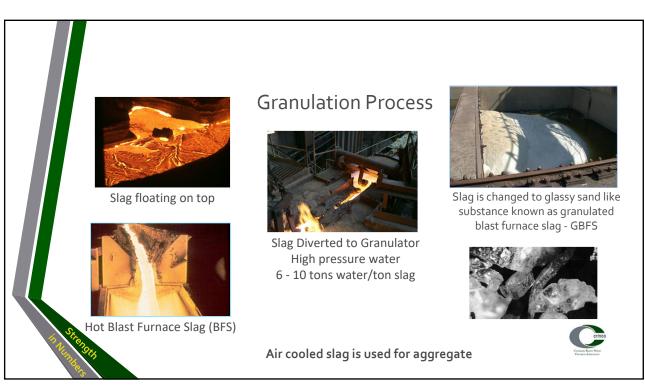
- There are millions of tons of fly ash being produced annually that are not being used
- Fly ash production is expected to remain fairly constant for the next 15 to 20 years.
- Harvesting will close or eliminate the gap between supply and demand in some regional markets.
- Specification changes can assist with alleviating shortages in some markets.
- Beneficiation technologies are available but can be costly.

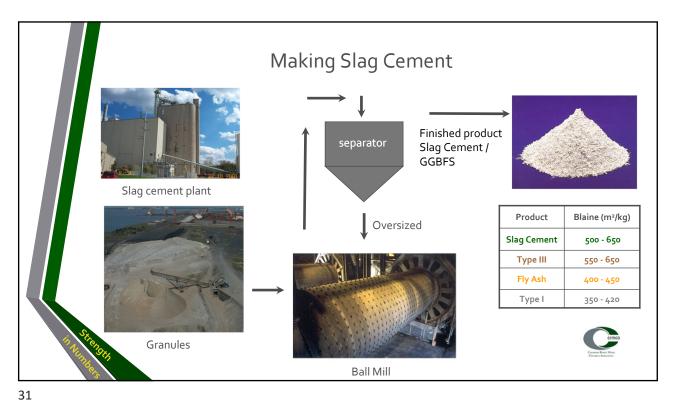


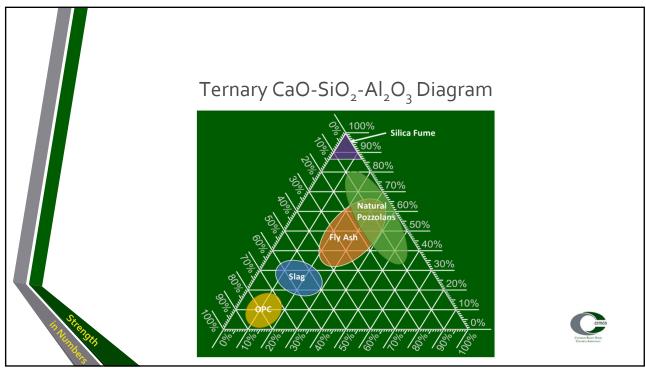


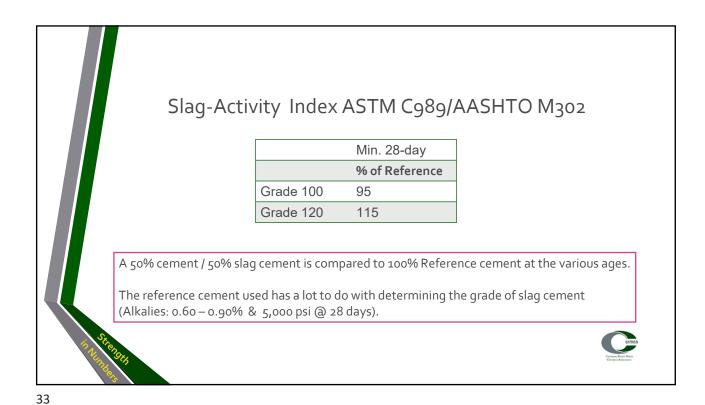






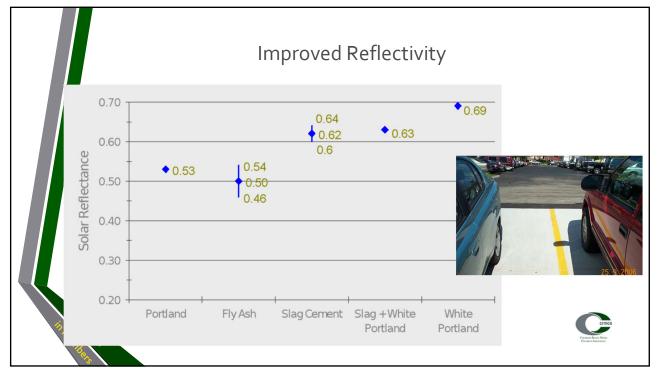






Slag Cement's Effect on Concrete Properties **General Concrete Properties Hardened Concrete Fresh Concrete Reduces Water Demand Lower Early Strength** Improves Workability 1 Much Higher Later Age Strength $\uparrow \uparrow$ $\Psi\Psi$ **Much Lower Permeability Slower Bleeding** 1 $\overline{\Psi}$ Ψ **Lowers Chloride Ingress** Slightly Lower Air Content **Lower Heat of Hydration Mass Concrete** $\Psi\Psi$ $\Psi\Psi$ **Greatly Reduces ASR Potential** Ψ **Slower Setting Time Greatly Increases Sulfate Resistance** ተተ Improves Finishability lackNo Difference Freeze Thaw Resistance **←→** Improves Pumpability No Difference Abrasion Resistance \leftrightarrow 1 No Difference Plastic Shrinkage No Difference Drying Shrinkage

Analisation	Class	. C	Application	Slag Cemer
Application	Slag	Cement %	Masonry/Pavers	20 – 50 %
Concrete paving	2	5 – 50 %	ICF	25 – 60 %
Exterior flatwork not exposed to deicer salts	posed	20 – 35 %	High strength	25 – 50 %
		20-35 /0	Tilt-up panels	25 – 50 %
Exterior flatwork exposed to deicer salts with (w/cm < 0.45)		.0 – 15 %	ASR mitigation	25 – 50 %
	(0.45)	10 – 15 %	Lower permeability	25 – 50 %
Interior flatwork	2	5 – 50 %	Mass concrete	25 – 70 %
Footings	,	0 – 65 %	Sulfate Resistance	
	3	30 - 05 70	Type II equivalence	25 – 50 %
			Type V equivalence	35 - 65 %



Greening

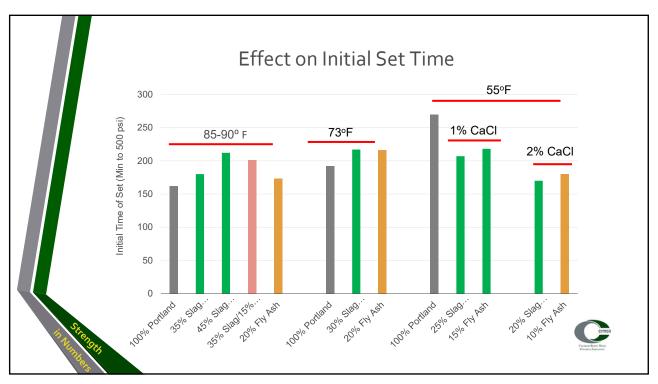


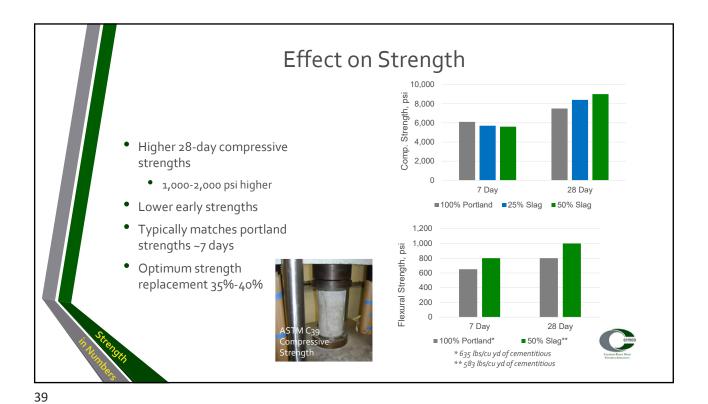


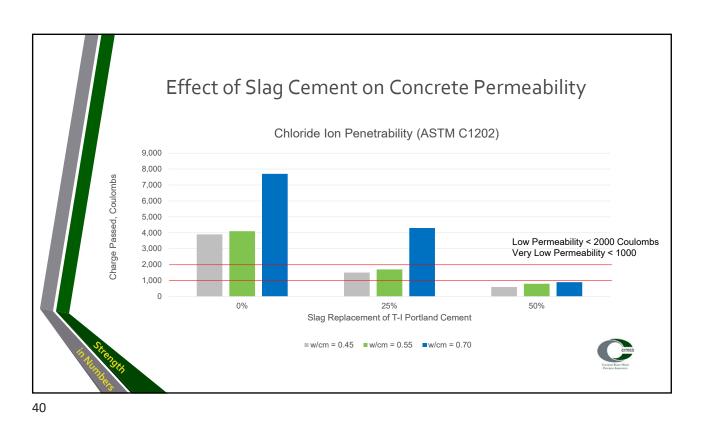
- "Greening" is a temporary blue-green color showing on the surface of concrete containing slag in the first few days after placement
- Occurs in small percentage of concrete made with slag, disappears within a week of exposure to air and sunlight (oxidizes)



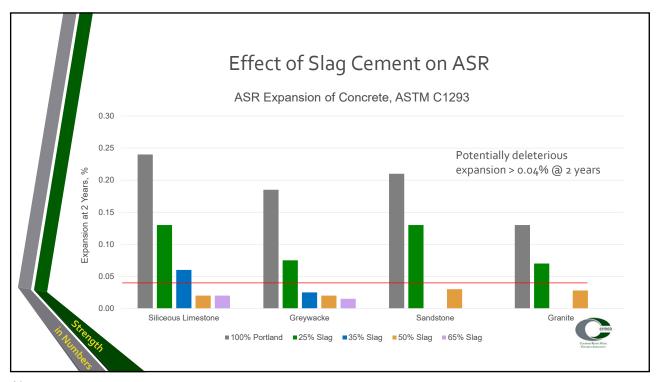
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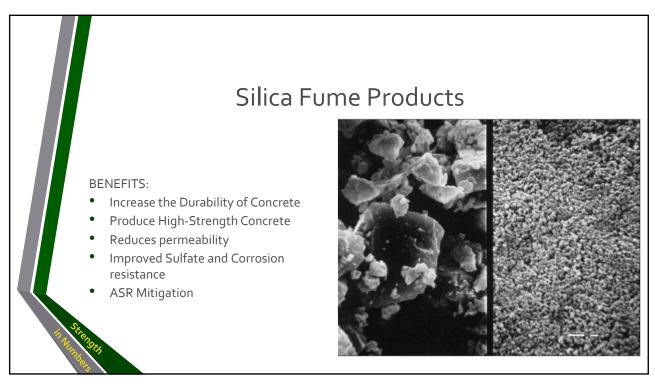


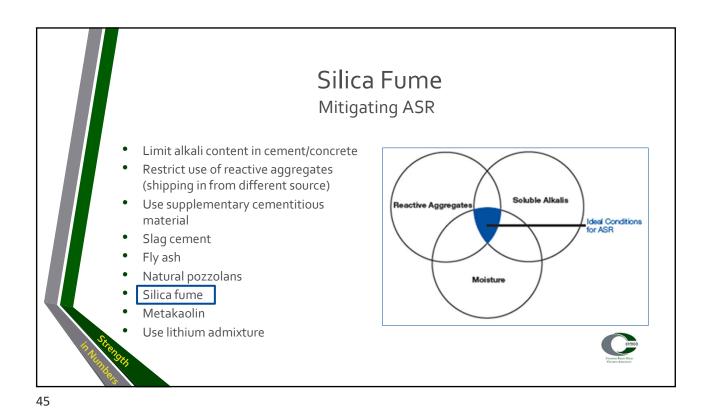
Ash an Expert...
A Prelude to Alternative SMCs



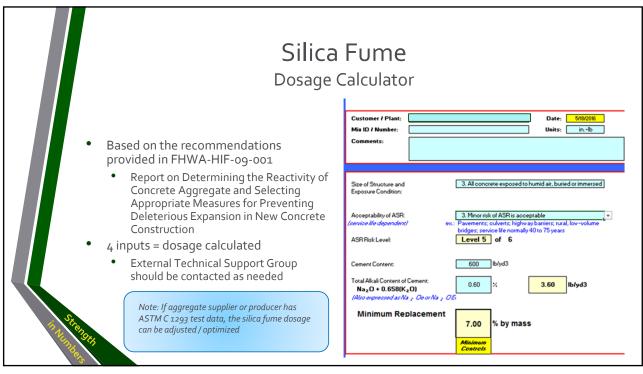


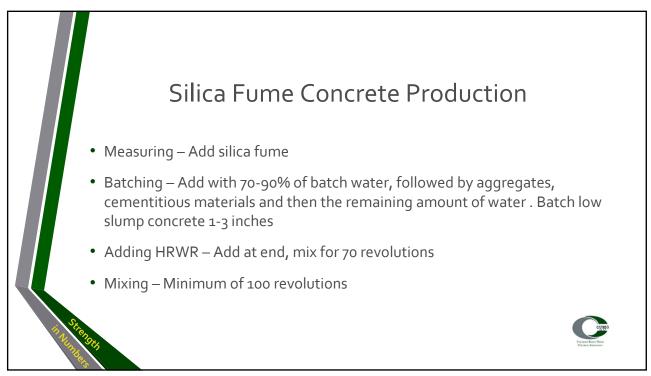


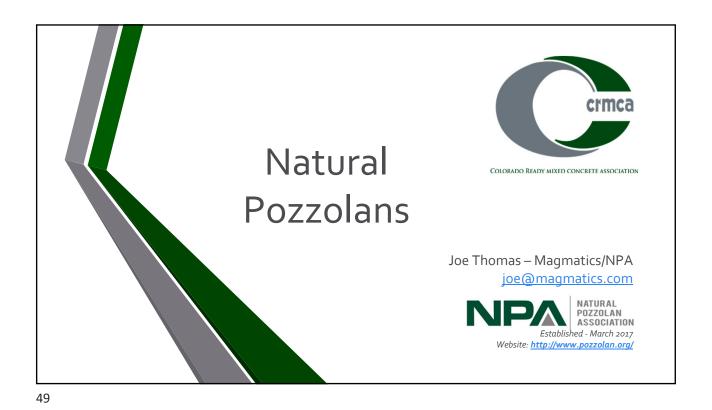


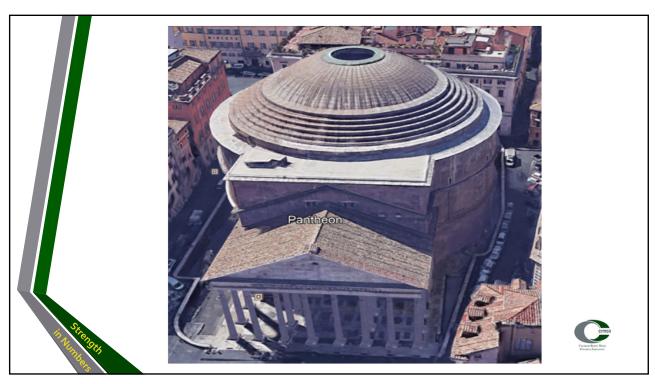


Silica Fume Mitigating ASR Silica fume is a highly efficient pozzolan Combines rapidly with alkalies in pore 0% CSF Incorporates alkalies as substitutes for calcium in the hydrated cement gel Reduces diffusion rate of alkalies through the pores of concrete 0.10 Reactive 5% CSF 10% CSF TIME, months Sufficient Sufficient







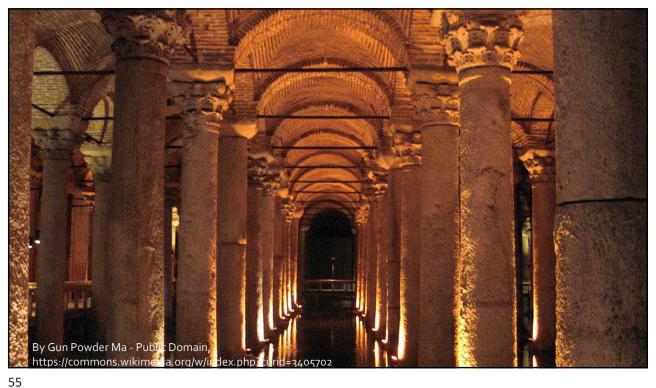


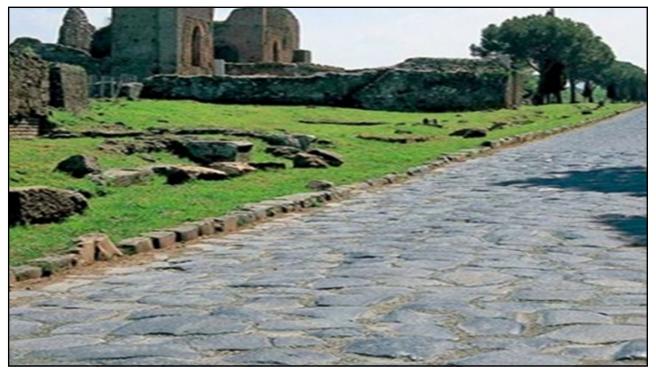


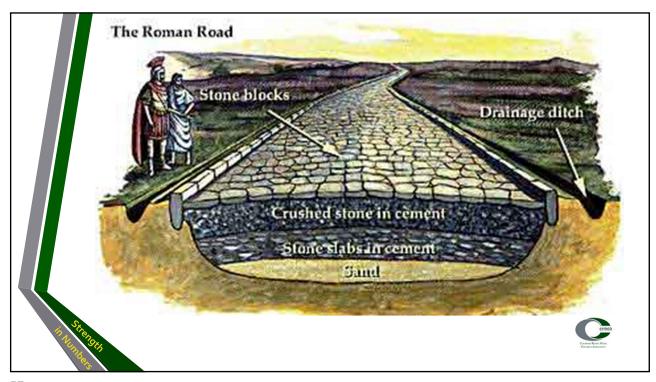












Natural Pozzolans

The word most associated with Roman Concrete is:
 Durability

 Concrete that lasts, often in pristine condition, for thousands of years, as opposed to 40 or 60 if we're lucky....so, what is this stuff made of?



Natural Pozzolans

There are 2 types of Natural Pozzolans (NP):

- Raw NP (Volcanic ejecta-based materials pumice, pumicite, volcanic ash, etc. Pre-calcined by Mother Nature)
- Calcined NP (such as MetaKaolin)



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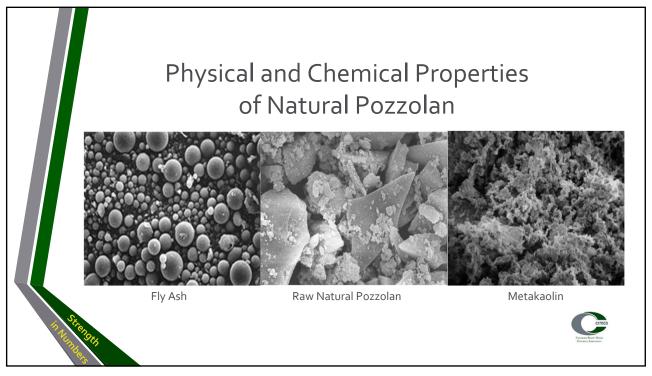




• Roman Concrete: "It's the most durable building material in human history, and I say that as an engineer not prone to hyperbole," Roman monument expert Phillip Brune told the Washington Post. July 4, 2017, Washington Post

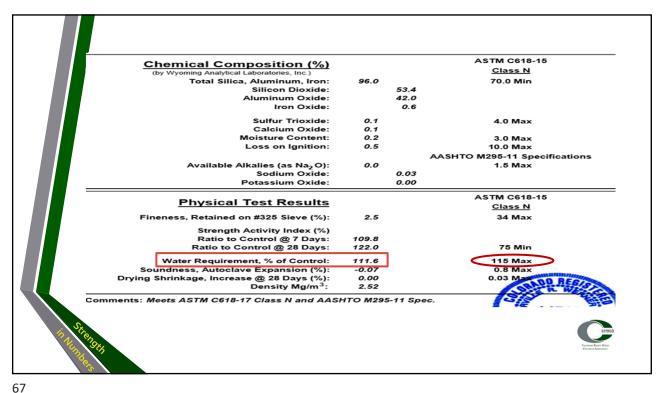


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	Chemical Analysis		ASTM / AAS Class F	SHTO Limits Class C	ASTM Test Method	
	Chemical Analysis	No. Const.	Class F	Class C	Method	
	Silicon Dioxide (SiO2)	59.73 %				
	Aluminum Oxide (Al2O3)	23.01 %				
	Iron Oxide (Fe2O3)	4.47 %				
	Sum of Constituents	87.21 %	70.0% min	50.0% min	D4326	
	Sulfur Trioxide (SO3)	0.37 %	5.0% max	5.0% max	D4326	
	Calcium Oxide (CaO)	4.84 %			D4326	
	Moisture	0.05 %	3.0% max	3.0% max	C311	
	Loss on Ignition	0.85%	6.0% max 5.0% max	6.0% max 5.0% max	C311 AASHTO M295	
	Available Alkalies, as Na2Oe When required by purchaser	1.36 %	not re 1.5% max	quired 1.5% max	C311 AASHTO M295	
	Physical Analysis	_				
	Fineness, % retained on #325	17.13%	34% max	34% max	C311, C430	
	Strength Activity Index - 7 or 28 day r 7 day, % of control	equirement 84 %	75% min	75% min	C311, C109	
	28 day, % of control	84%	75% min	75% min		
	Water Requirement, % control	95 %	105% max	105% max		
S	Autoclave Soundness	0.00 %	0.8% max	0.8% max	C311, C151	
A Manger	Density	2.25			C604	Course Rase Mass Concess Associates

Chemical Composition (%)			ASTM C618-15
(by Wyoming Analytical Laboratories, Inc.)			Class N
Total Silica, Aluminum, Iron:	86.6		70.0 Min
Silicon Dioxide:		72.5	
Aluminum Oxide:		13.2	
Iron Oxide:		0.9	
Sulfur Trioxide:	0.1		4.0 Max
Calcium Oxide:	1.3		
Molsture Content:	1.5		3.0 Max
Loss on Ignition:	4.1		10.0 Max
			AASHTO M295-11 Specifications
Available Alkalles (as Na ₂ O):	1.5		1.5 Max
Sodium Oxide:		0.76	
Potassium Oxide:		1.12	
Physical Test Results			ASTM C618-15
rifysical rest flesuits			Class N
Fineness, Retained on #325 Sieve (%):	5.7		34 Max
Strength Activity Index (%)			
Ratio to Control @ 7 Days:	89.6		
Ratio to Control @ 28 Days:	95.4	_	75 Min
Water Requirement, % of Control:	99.2		115 Max
Soundness, Autoclave Expansion (%):	-0.03	•	0.8 Max
Drying Shrinkage, Increase @ 28 Days (%):	0.02		0.03 Max 00 REGIO
Density Mg/m ³ :	2.40		N. W.
comments: Meets ASTM C618-15/ AASHTO M295-1	1 Type N.	Retest	ed SAI.
2			
Viz.			
1 170.			Committee



How does Natural Pozzolan enhance and protect concrete?

Roman Concrete utilized a balanced cement paste – virtually all of the Calcium Hydroxide was consumed based on the recipe shared by Vitruvius.

Note: Calcium Hydroxide (free lime) in concrete, which is not converted to C-S-H, becomes a volatile, bad actor in concrete...upwards of 25% of free lime is released into the concrete matrix, by weight of cement, as a byproduct of the hydraulic reaction.



How does Natural Pozzolan enhance and protect concrete?

- If 20~30% of cement is replaced with NP, the Portland cement system, like the ageless Roman cement, is now better balanced.
- In other words, much of that 20~25% free-ranging lime by-product in the concrete is consumed, over time in a reaction with the NP to form additional C-S-H, the binder in concrete thus densifying the concrete.



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How does Natural Pozzolan enhance and protect concrete?

• By converting the free-lime into additional C-S-H, a concrete using NP at a 20~25% replacement of cement will have greater compressive strength than a 100% cement mix design - up to 140% SAI of the straight cement mixes at 1 year.



How does Natural Pozzolan enhance and protect concrete?

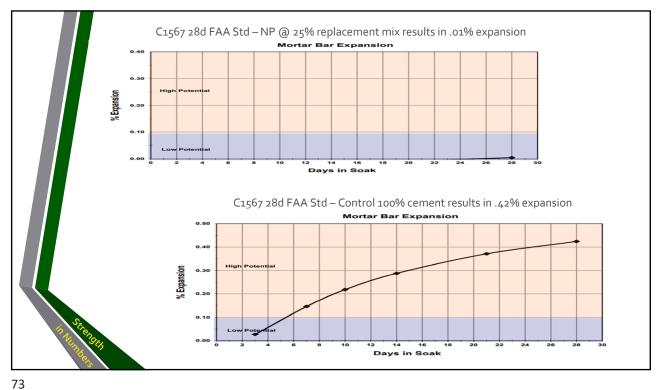
- All or most of the free-lime will be converted to C-S-H, providing enhanced strength, reduced permeability, and fortifying the concrete against chemical attack, such as ASR and Sulfate attack.
- The NP converts a bad actor into a good actor, and your concrete will be inoculated from common concrete diseases, giving your customer's concrete a very long service life....



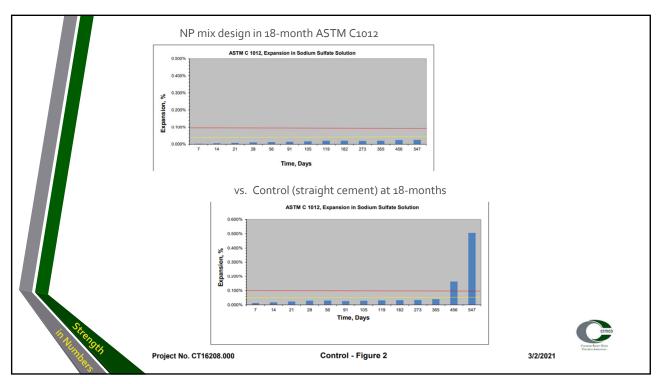
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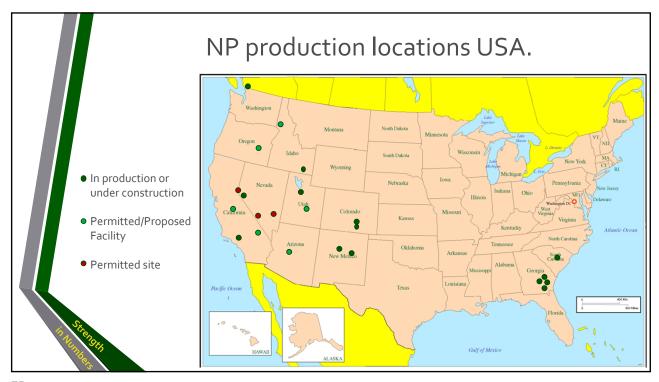
Benefits of Natural Pozzolans

- **1.** Product consistency: No need to continually adjust your mix design based on product variability.
- 2. Reduce Carbon Footprint: Almost a pound for pound reduction of embodied carbon for every pound of cement replaced for raw NP and more than ½ pound for calcined NPs.
- 3. Reduced Heat of Hydration (HOH): Up to 25% or more reduction in HOH based on mix design.
- 4. Mitigate Chemical Attack: NPs are very effective at mitigating ASR and Sulfate attack, as well as Efflorescence.
- 5. Reduce Permeability: NPs densify and strengthen concrete. This increases durability & strength and reduces chloride ingress protecting reinforcement.
- Air Entrainment Consistency: NPs do not cause variability in air entrainment. LOI in NP is measured bound water, not carbon content.











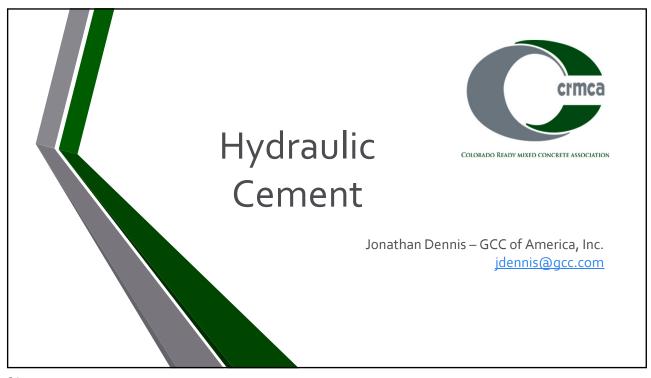


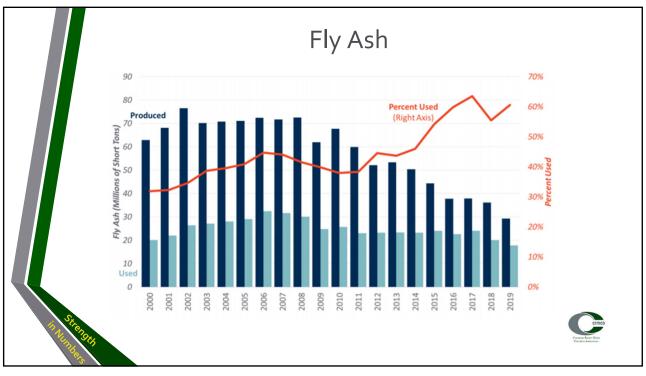


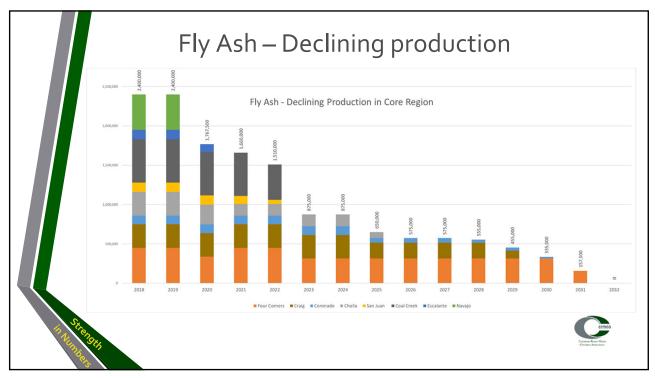


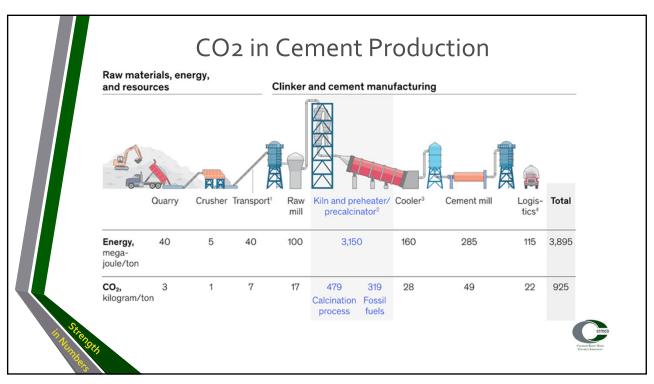


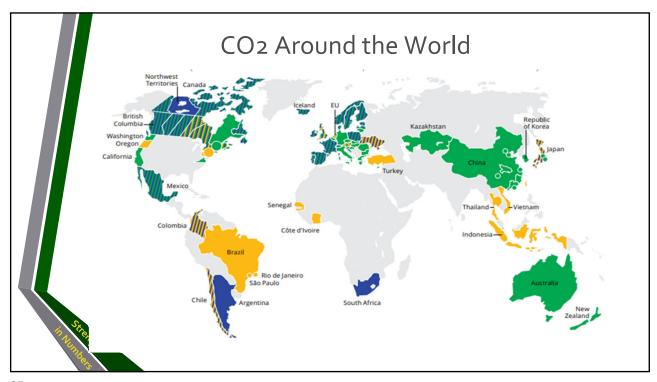


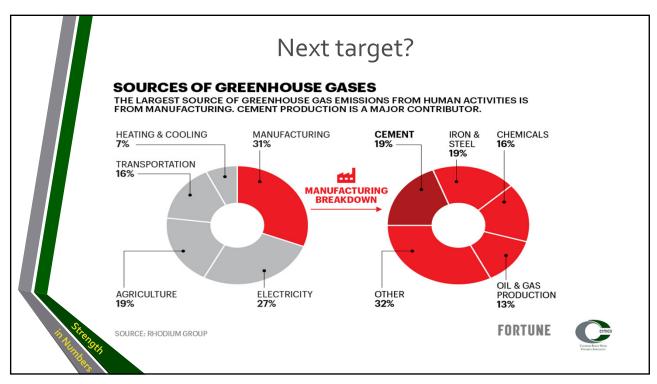


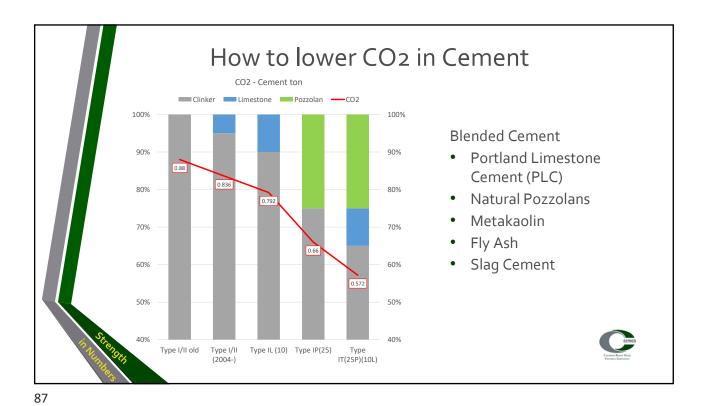












Blended Cement & Specifications Performance Prescriptive **ASTM C1157** ASTM C595 ASTM C₁₅₀ Type GU Type IL Type HE Type I Type IP Type MS Type II Type HS Type IS Type III Type IT Type MH Type V Options A,MS,HS,MH,LH Type LH Options R & A Least Most Flexibility to lower CO₂



Durability and Sustainability CO2 - Cement ton Clinker Limestone Pozzolan —CO2 100% 100% 90% 90% 0.88 0.836 80% 80% 0.792 70% 70% 0.66 60% 60% 0.572 50% 50% 40% Type IT(25P)(10L) Type I/II old Type I/II (2004-) Type IL (10) Type IP(25)



Economics - Supply Transition

- Fly ash has previously been effective, available, and inexpensive. Other SCMs have struggled to compete economically with it for general construction.
 - Shipping (not as many sites for supply) Grinding Drying/Calcining
- Fly ash will continue to be available, but not in excess and for a higher price? Other SCMs are becoming price competitive with fly ash, especially in the West as ASR is a general concern.
- I predict all SCMs will approach and in some cases exceed the cost of Portland cement, so we will see more of them used.

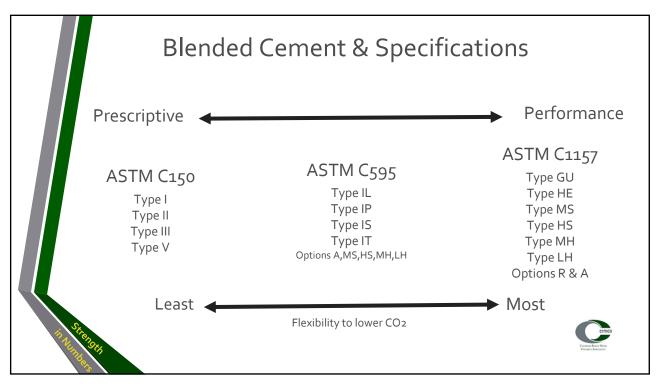


Economics of blended cements

- Advantages
 - Handle one cementitious material at batch plant (especially good for portable plants.)
 - Cement manufacturers can chemically and physically optimize the blends.
 - A blend can be prequalified
 - Multiple SCM's in a blend more friendly to concrete suppliers.
- Disadvantages
 - Can't customize for multiple types of mixes at one plant
 - Some blends may be more expensive to produce. (Duplicate shipping expense)



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What about specs?

- Prescriptive vs. performance
 - It has taken decades for specifiers to understand the nuances of different types of Portland cement.
 - Typical specifiers will not know the difference between a IT(L>P) or IS cement, nor will they know how to specify them. ASTM C-595 will not be particularly useful.
 - ASTM C-1157 offers understandable properties. (Speed of strength gain, sulfate resistance, and heat of hydration potential, and an option for mitigating ASR.) GU, HE, MS, HS, MH, LH, and Option R.
 - However, C-1157 is uncomfortably open ended as to what can be in the cement



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What about specs?

- Specifiers will be required to make dramatic changes to their specification documents.
- These are complicated changes, and many of them will not be comfortable with the change unless given lots of guidance.
- CDOT, larger government agencies, might be the first to make these positive changes. Commercial specifications will take many years, even with lots of help.



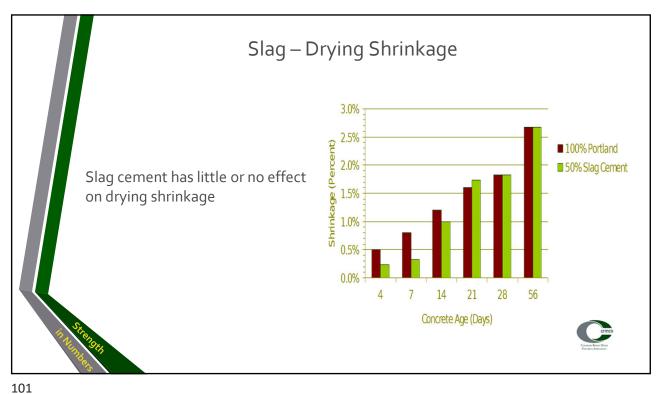


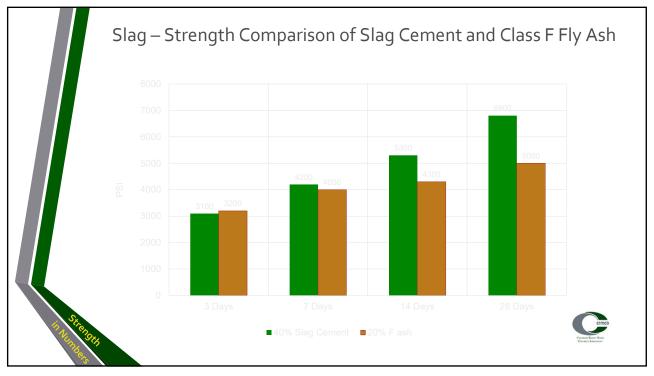


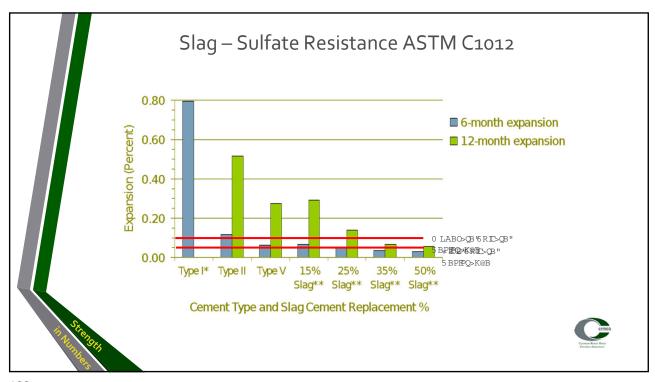


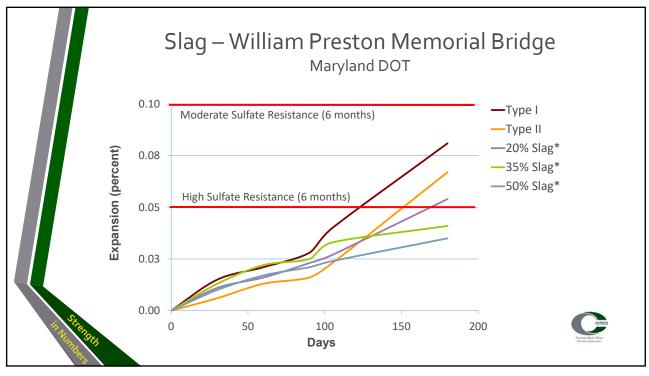


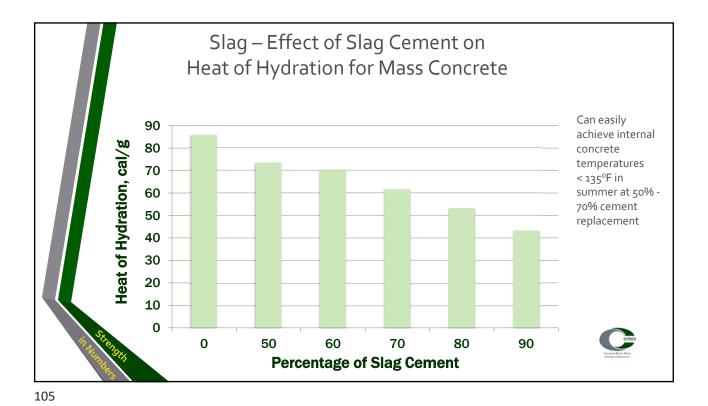
Ash an Expert...
A Prelude to Alternative SMCs











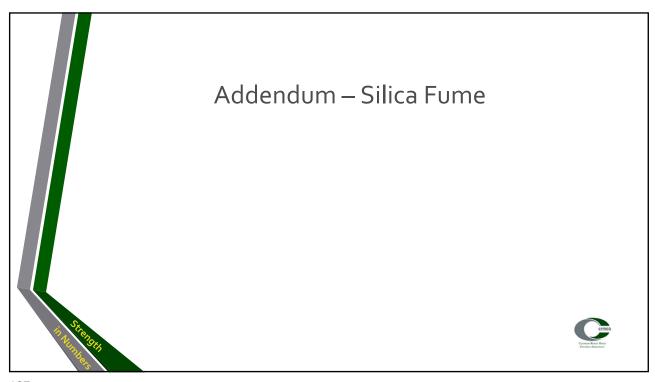
Slag Cement Association website: www.slagcement.org

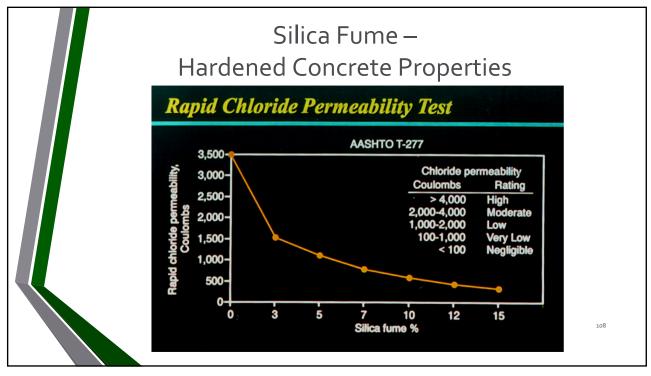
About Slag Cement

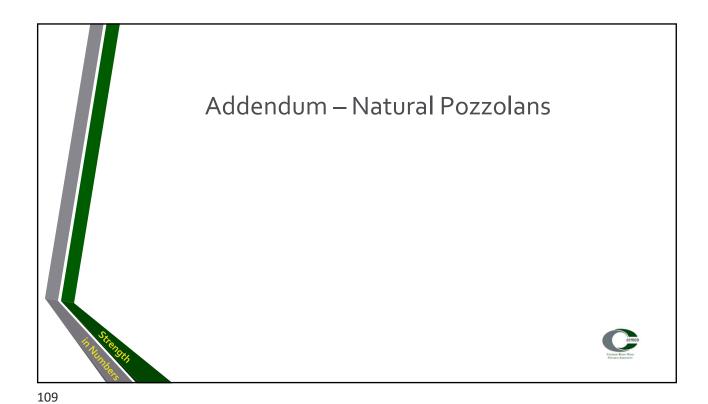
About Slag Cement

What is Slag Cement

Sucrease a particular principle of the sucrease is the sucrease and in case the replace is the sucrease of the sucrease and in case the replace is the sucrease of the sucrease and in case the replace is the sucrease of the sucrease and in case the replace is the sucrease of the sucrease and in the sucr







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