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Class C and Class F Fly Ash: Comparisons, Applications, and Performance

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Acknowledgements

NCHRP Report 749

Methods for Evaluating Fly Ash for Use in Highway Concrete

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Objective - recommend potential improvements to specifications and test protocols to determine the acceptability of fly ash for use in highway concrete

NCHRP Report 749

- Characterization Study – evaluate over 100 sources, compare to data base of over 300, select 30 for detailed analysis (17 Class F, 13 Class C)
- Strength Test Study – investigate test methods for characterizing the strength activity of ash
- Carbon Effects on Air Entrainment Study – develop test methods for characterizing the adsorption properties of residual carbon in CFA
- ASR Mitigation Study – examine test methods to evaluate use of ash to mitigate ASR in concrete

Laboratory Study for Comparison of
Class C vs. Class F Fly Ash
for Concrete Pavement

Report 0092-12-04

Sponsored by the Wisconsin Highway Research Program

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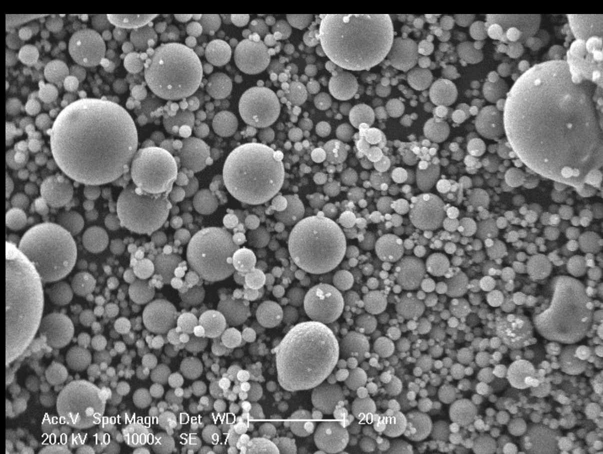
Objectives

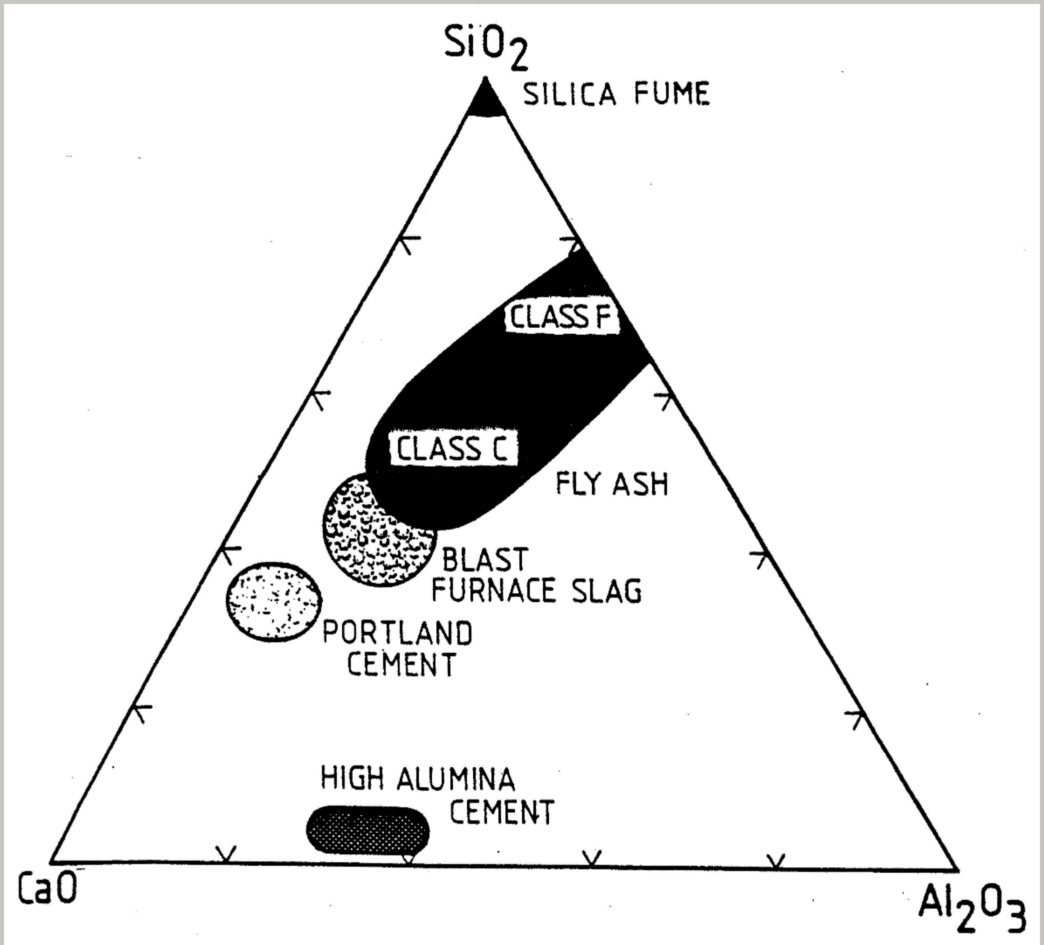
- Evaluate several locally available Class F fly ash sources in comparison with Class C fly ash for impact on:
  - F-T performance
  - Strength
  - Maturity
- Provide mixture design guidance based on statistical analysis of over 40 different mixture designs

Topics for Today

- Comparisons of Class C & Class F
- Performance
- Quality Tests
- The Future of Fly Ash


Acc.V Spot Magn Det WD 20 µm
20.0 kV 1.0 1000x SE 9.7

SCM Composition



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ASTM C618 (AASHTO M 295)

TABLE 1 Chemical Requirements

	Class		
	N	F	C
Silicon dioxide (SiO_2) plus aluminum oxide (Al_2O_3) plus iron oxide (Fe_2O_3), min, %	70.0	70.0	50.0
Sulfur trioxide (SO_3), max, %	4.0	5.0	5.0
Moisture content, max, %	3.0	3.0	3.0
Loss on ignition, max, %	10.0	6.0[A]	6.0

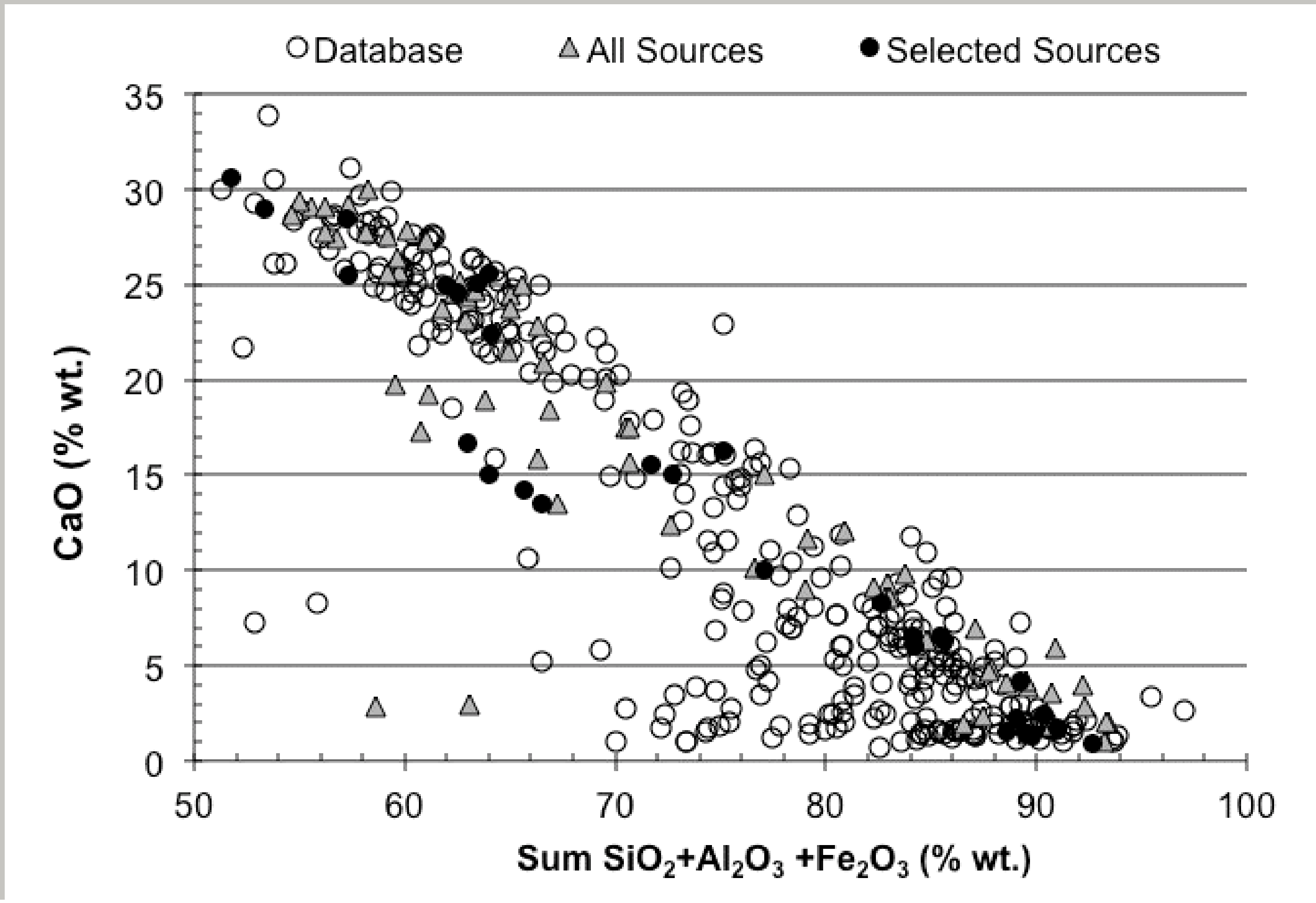
[A] The use of Class F pozzolan containing up to 12.0 % loss on ignition may be approved by the user if either acceptable performance records or laboratory test results are made available.

- Class C – $SiO_2 + Al_2O_3 + Fe_2O_3 \geq 50\%$
- Class F – $SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70\%$
- So… Every Class F is a Class C….. ???

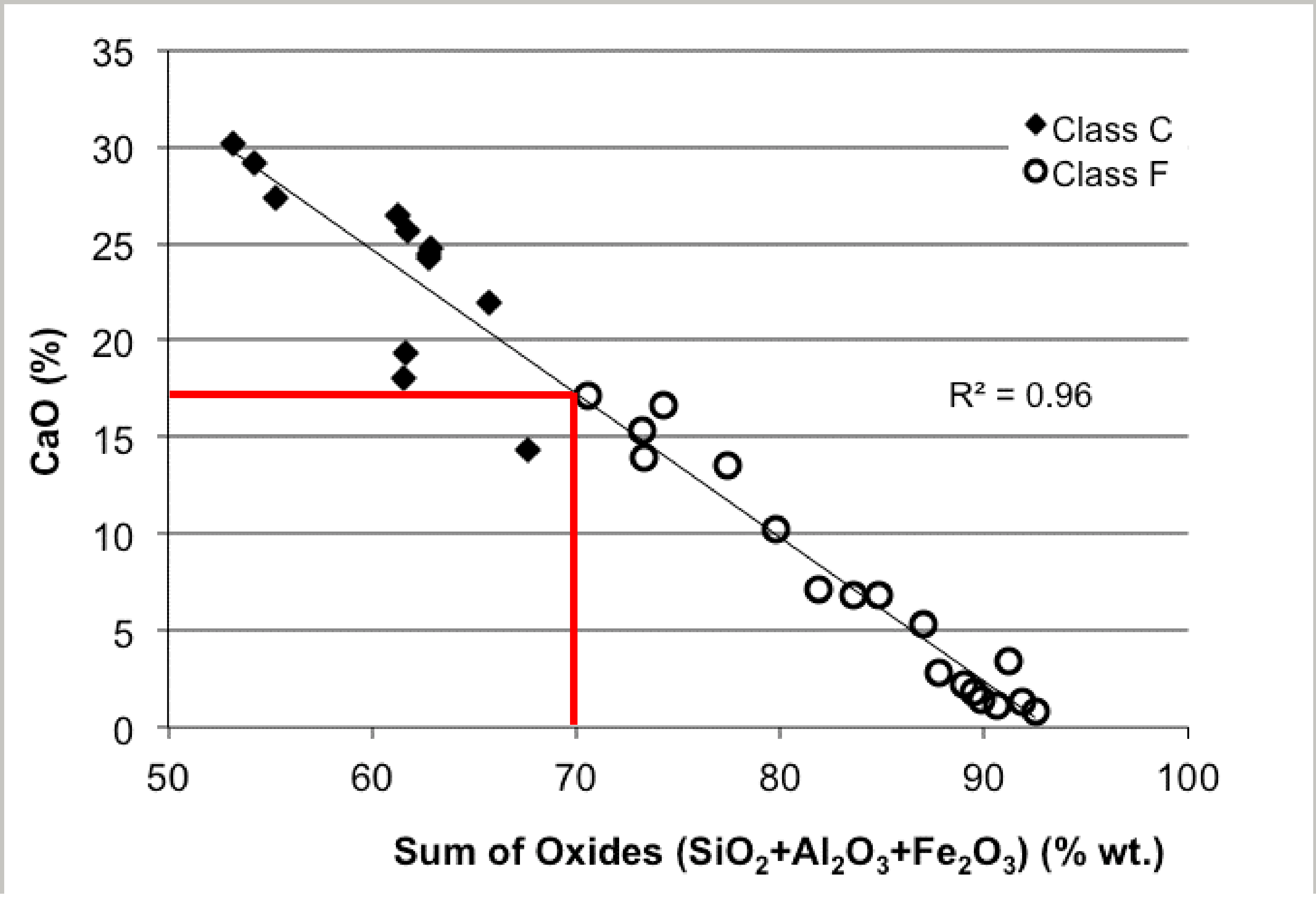
ASTM C618 (AASHTO M 295)

- Big difference in ash characteristics at the far extremes of the classification related to CaO
- **Class C** *(cementitious)*
  - More $CaSO_4$, free lime, C_3A, calcium-rich glass, MgO
- **Class F** *(pozzolanic)*
  - More glass, alumino silicate glass, quartz
- No difference at the margin

Chemical Classification



Chemical Classification



ASTM C618 (AASHTO M 295)

- Big difference in ash characteristics at the far extremes of the classification related to CaO
- **Class C** *(cementitious, hydraulic)*
  - More $CaSO_4$, free lime, C_3A, calcium-rich glass, MgO
- **Class F** *(pozzolanic)*
  - More glass, alumino-silicate glass, quartz
- No difference at the margin

Pozzolan

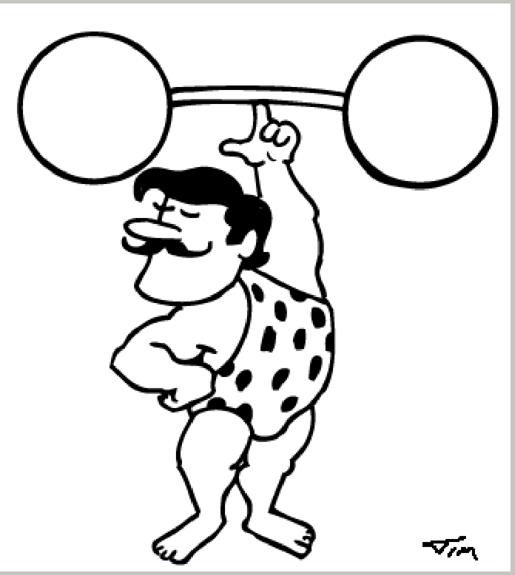
- *pozzolan* - named after a volcanic ash mined at Pozzuoli, Italy

pozzolan - a siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form and in the presence of water, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties.

What the hell does that mean?

Pozzolans

- Back up a step...
- If you combine portland cement and water you basically form two things (combined we call hardened cement)
- Calcium Silicate Hydrate (CSH)
  - Strength of hardened cement



Pozzolans

- Back up a step...
- If you combine portland cement and water you basically form two things (combined we call hardened cement)

- Calcium Hydroxide(CH)
  - Weak link in hardened cement

Pozzolans

- A pozzolan eats CH with water and *"excretes"* CSH
- Two-step process:
- **Portland Cement Reaction**

Cement + Water -> **CSH** + CH

- **Pozzolanic Reaction**

CH + Pozzolan + Water -> **CSH**

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Fly Ash Basics

- So...
- Using a fly ash (pozzolan) consumes calcium hydroxide (CH: the weak link) and other free hydroxides (-OH) to form more calcium silicate hydrate (CSH: Strength)
- **Fly ash can increase strength**
- But…

Fly Ash Basics

- It takes time...
- **Portland Cement Reaction**

Cement + Water -> **CSH** + CH

- **Pozzolanic Reaction**

CH + Pozzolan -> **CSH**

Fly Ash Basics

- Using a fly ash (pozzolan) consumes calcium hydroxide (CH: the weak link) to form more calcium silicate hydrate (CSH: Strength)
- Fly ash can increase strength
- **Strength gain happens slower with a pozzolanic (Class F) vs. Class C ash**

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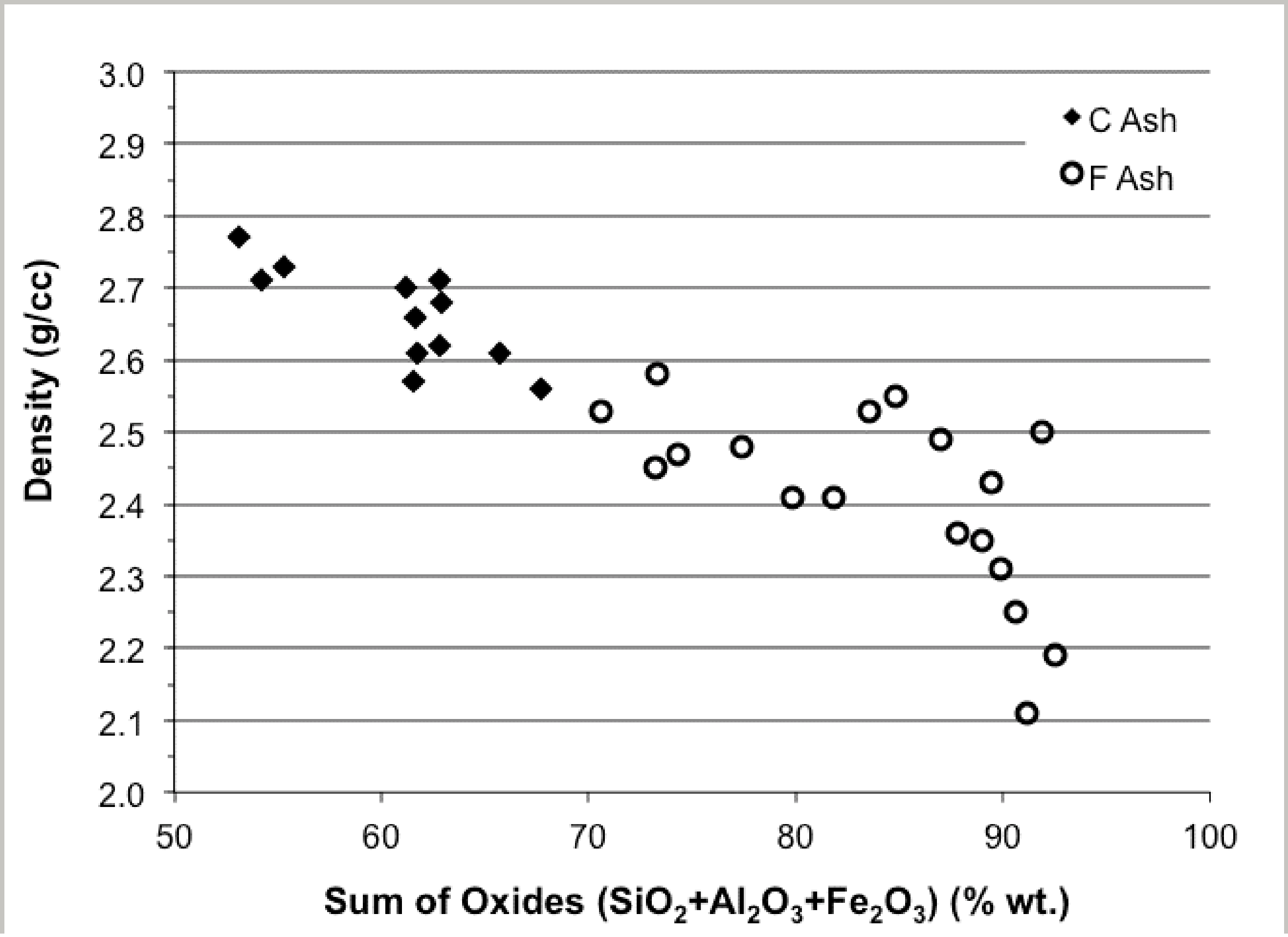
Fly Ash Basics

- Using a fly ash (pozzolan) consumes calcium hydroxide (CH: the weak link) to form more calcium silicate hydrate (CSH: Strength)

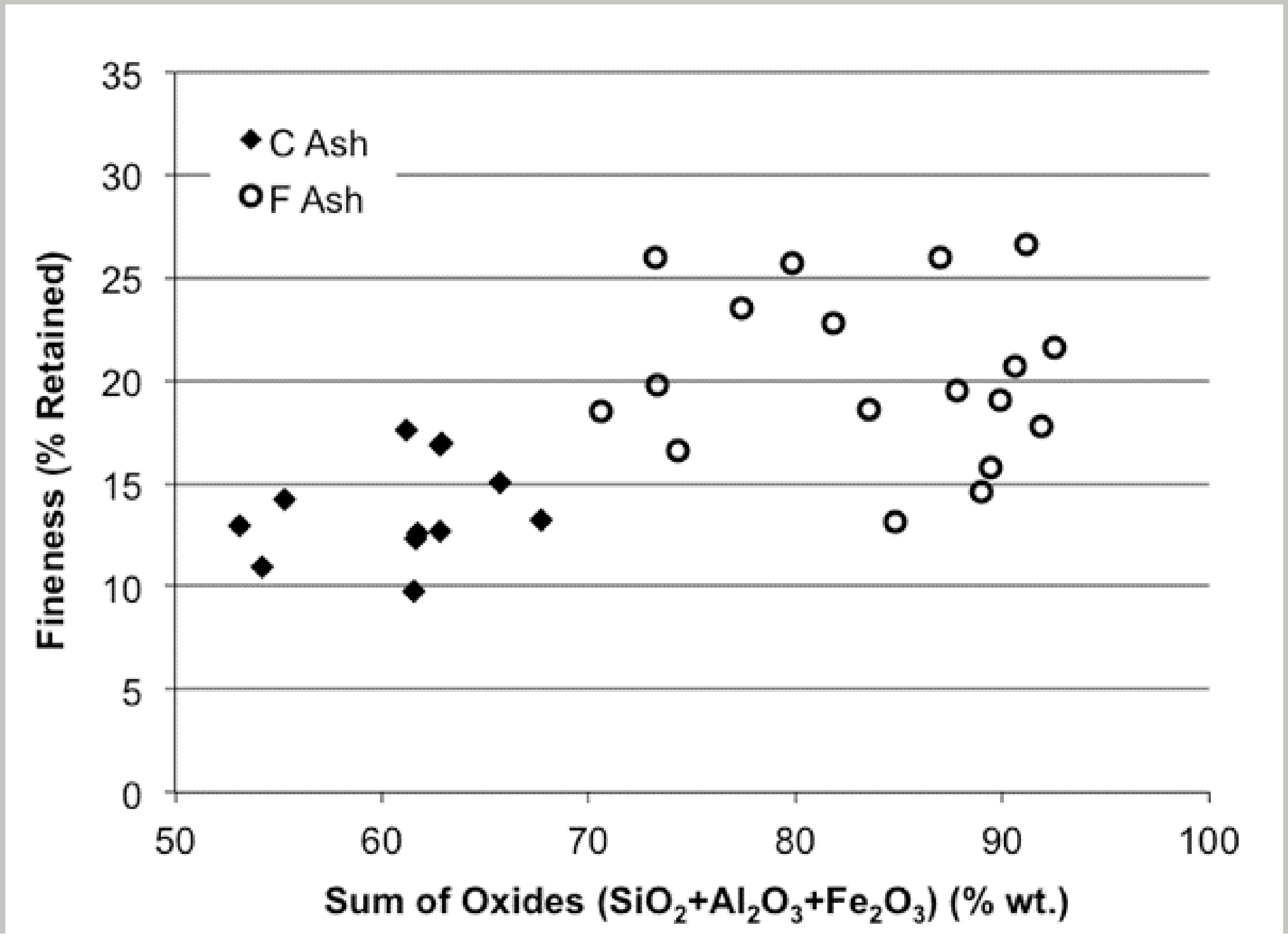
- Fly ash can decrease permeability

- **Forming more CSH fills gel pores; consuming CH decreases dissolution**

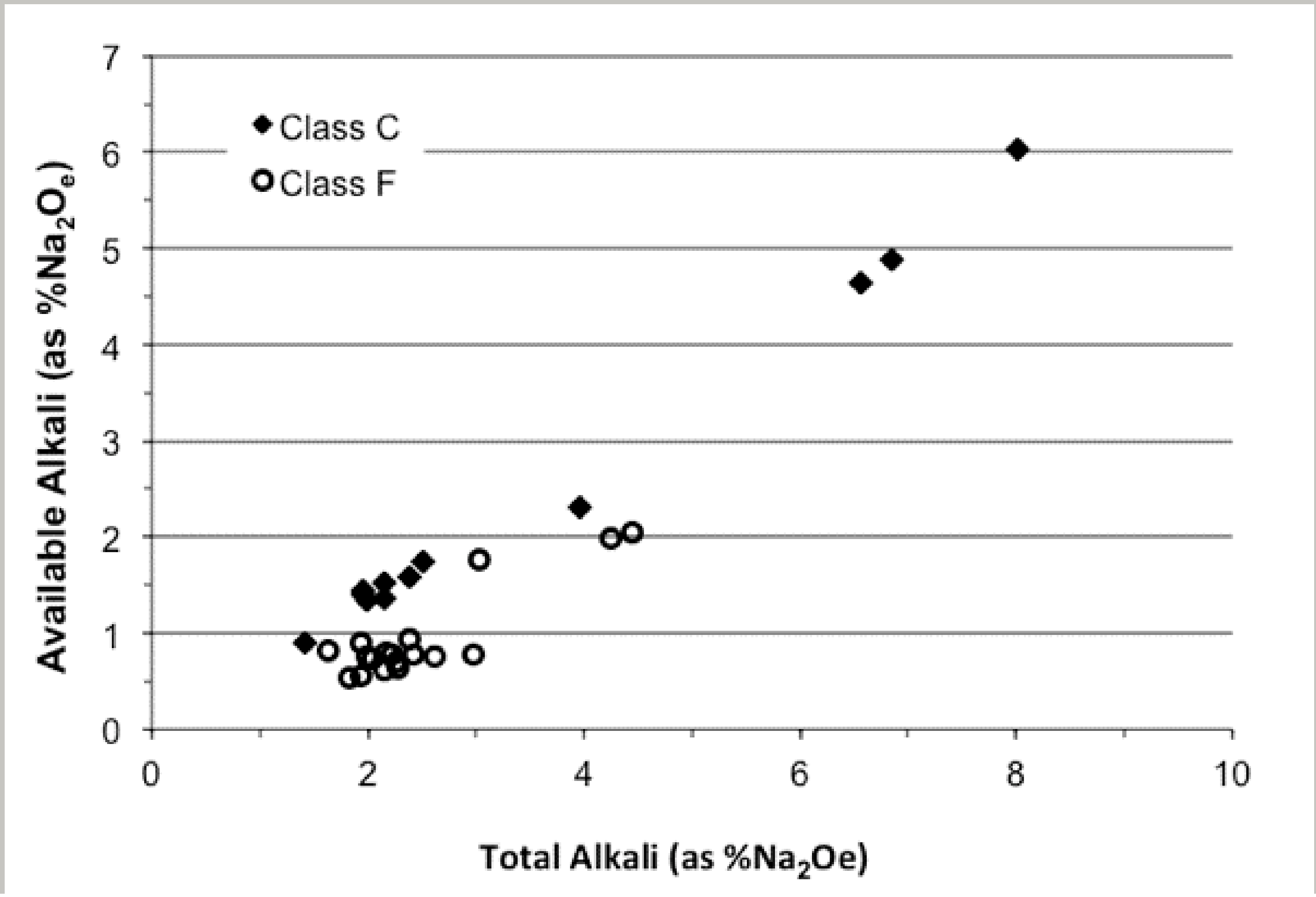
Other Differences - Density



Other Differences – Fineness (45 microns)



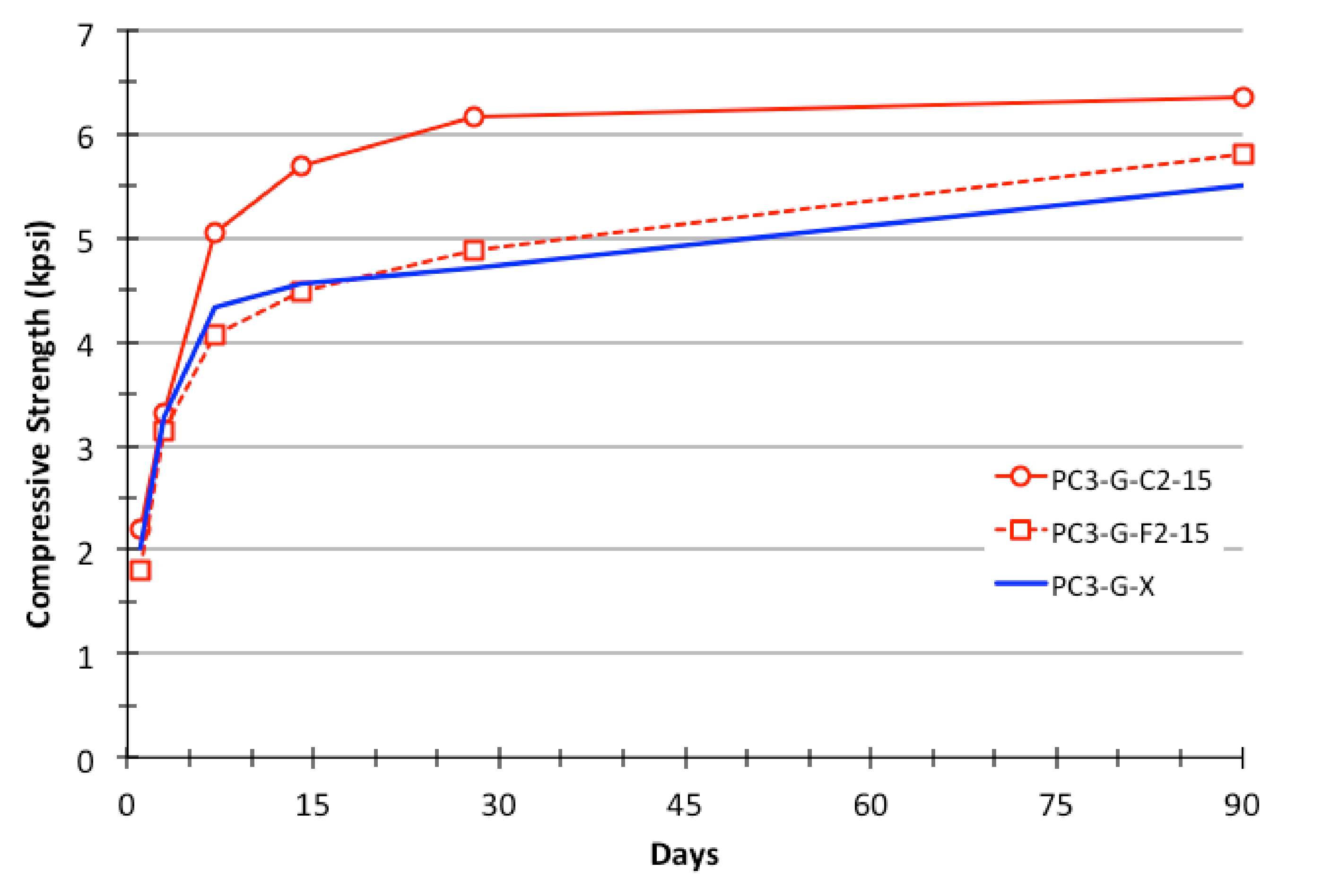
Other Differences – Alkali



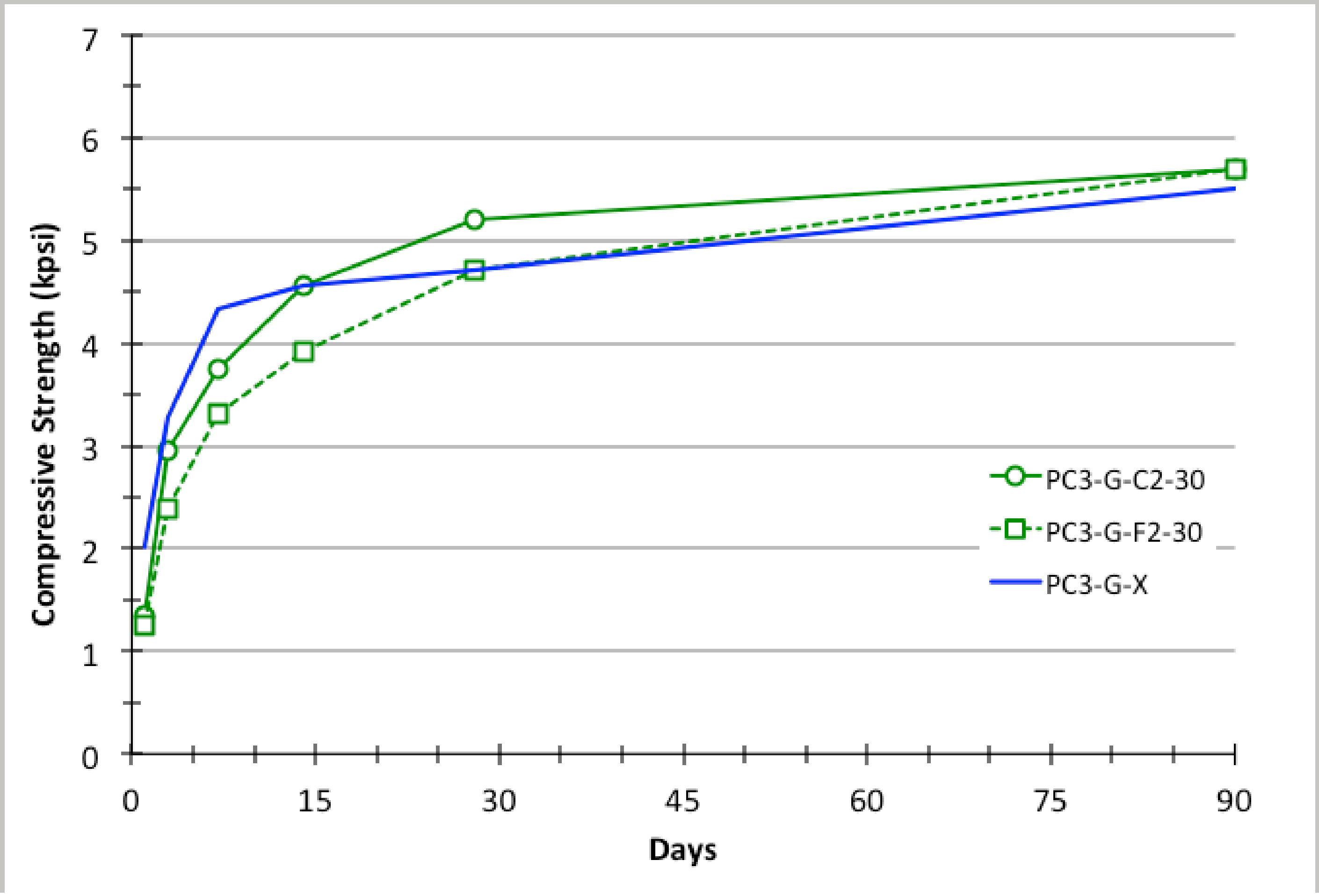
How Does All This Affect Performance?

- The combination of pozzolanic and cementitious reactions – determined by fly ash composition – affects:
  - Concrete Strength
  - Heat Evolution in Concrete Mixtures
  - Ability to Mitigate ASR and Sulfate Attack

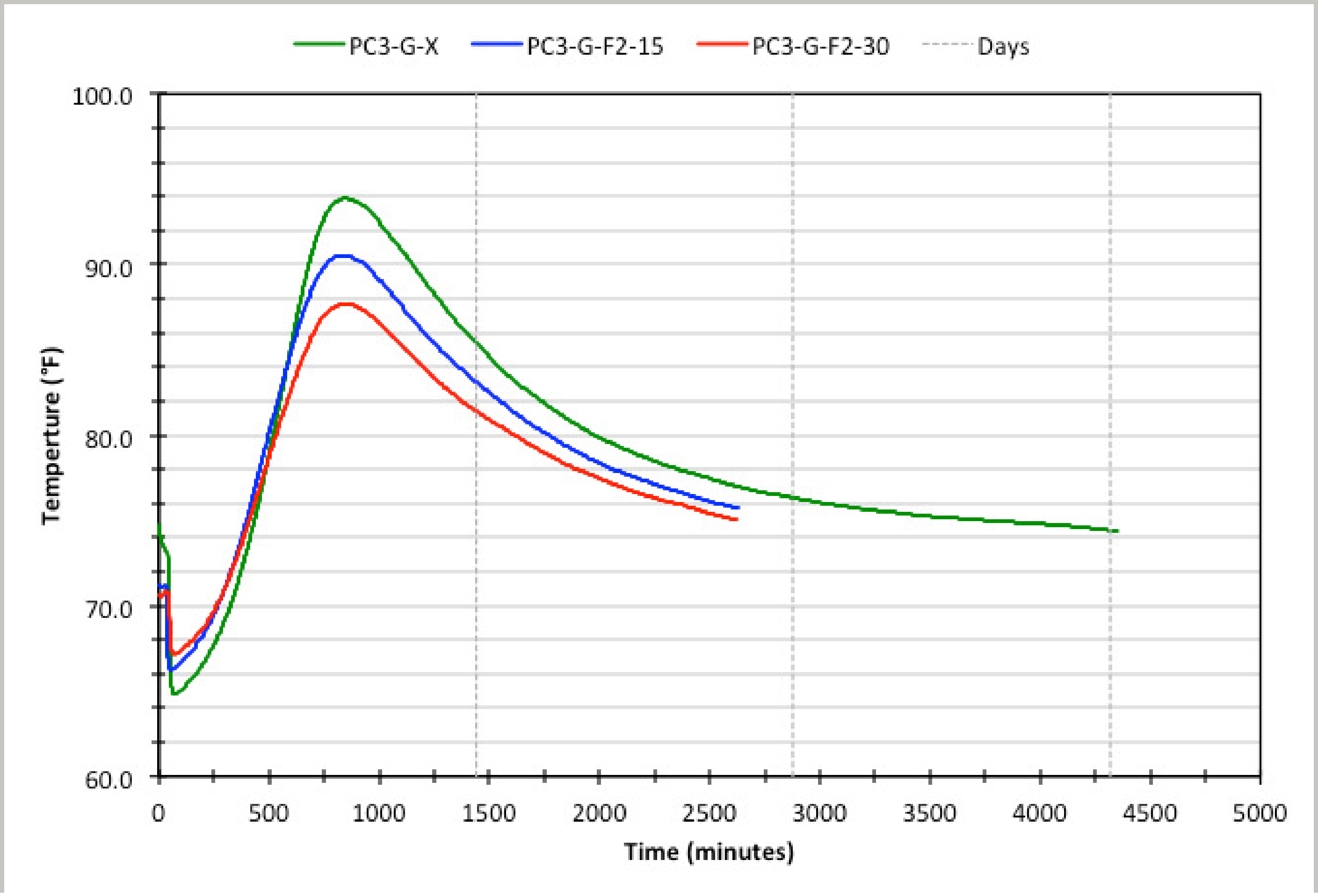
Compressive Strength



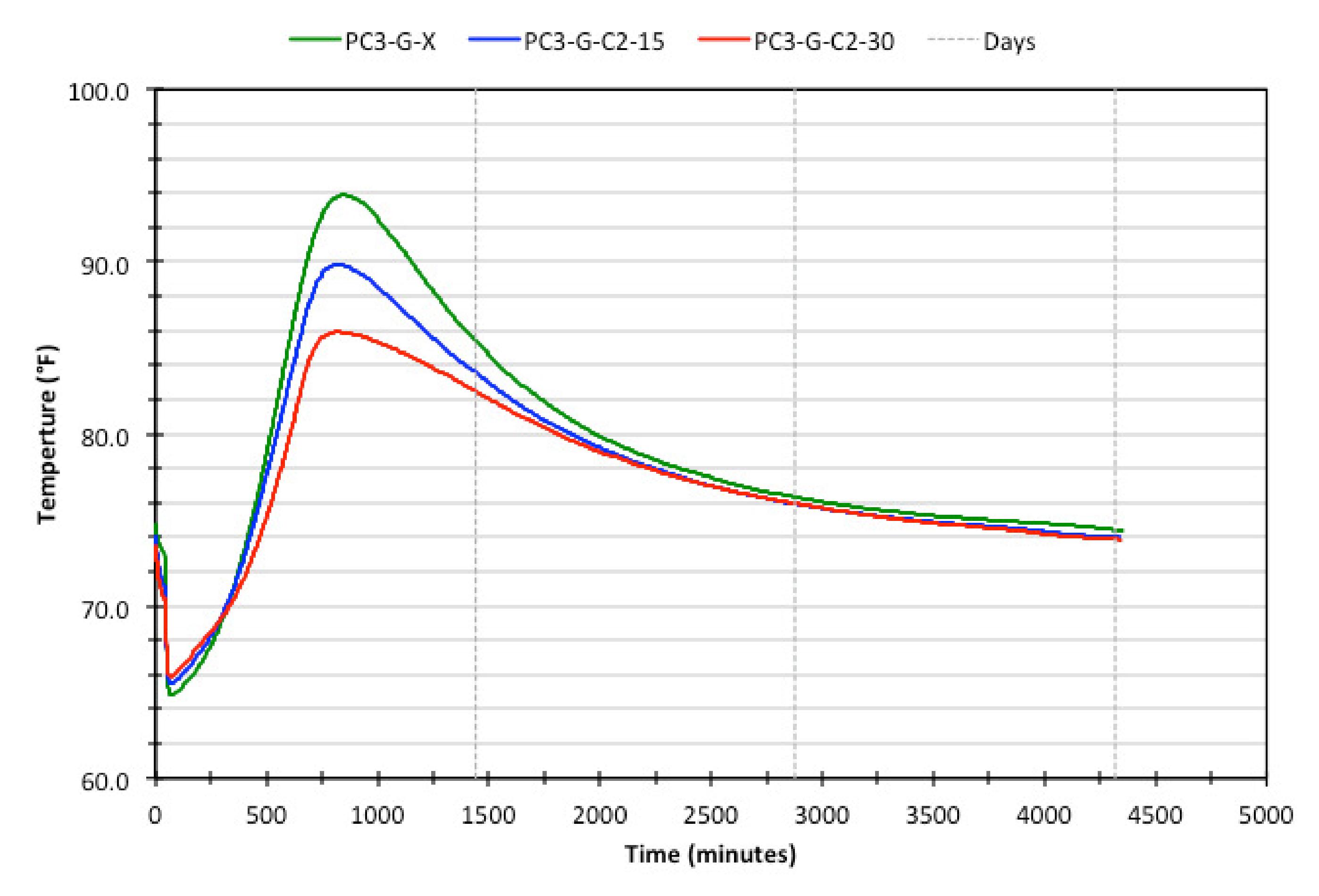
Compressive Strength



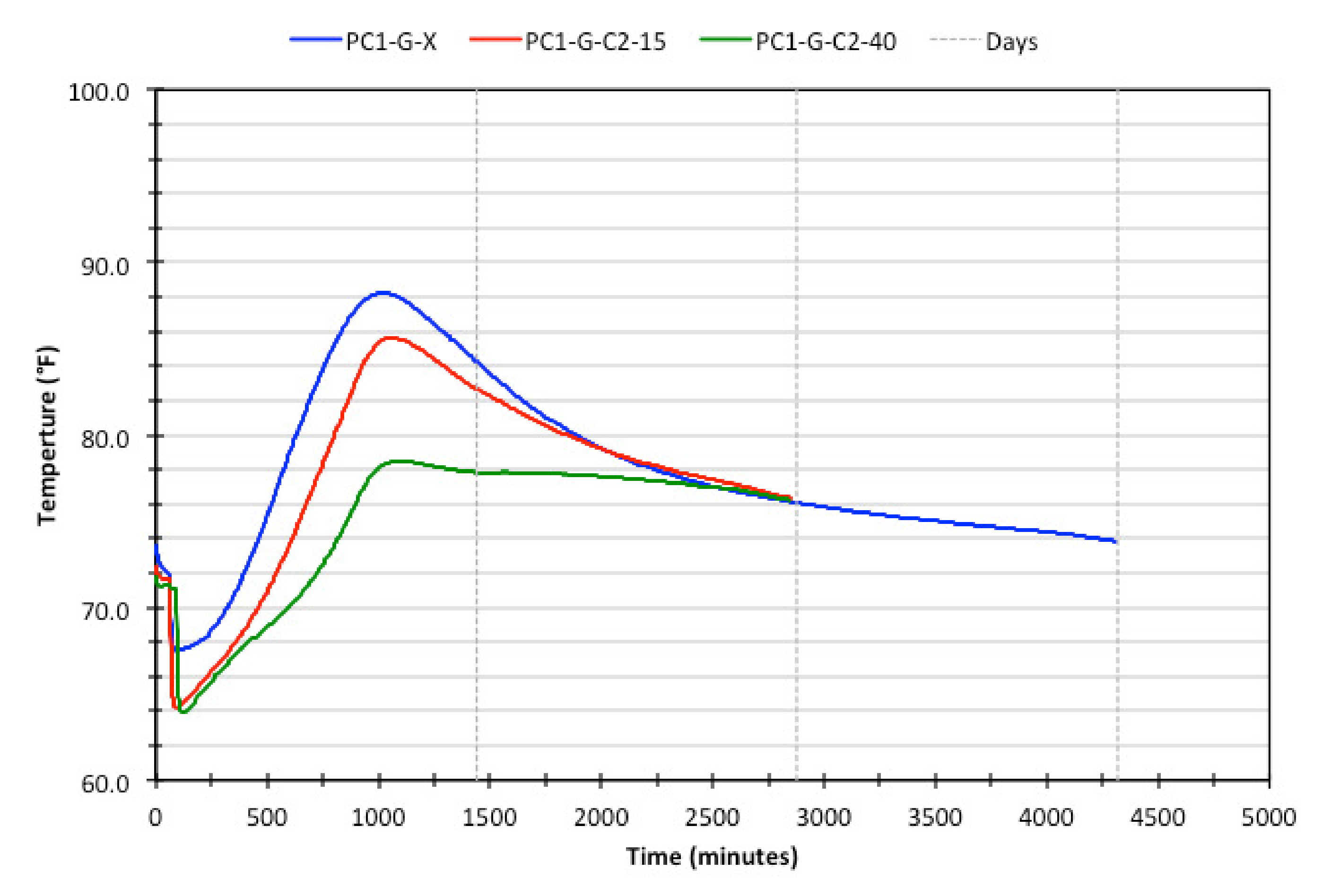
Heat of Hydration



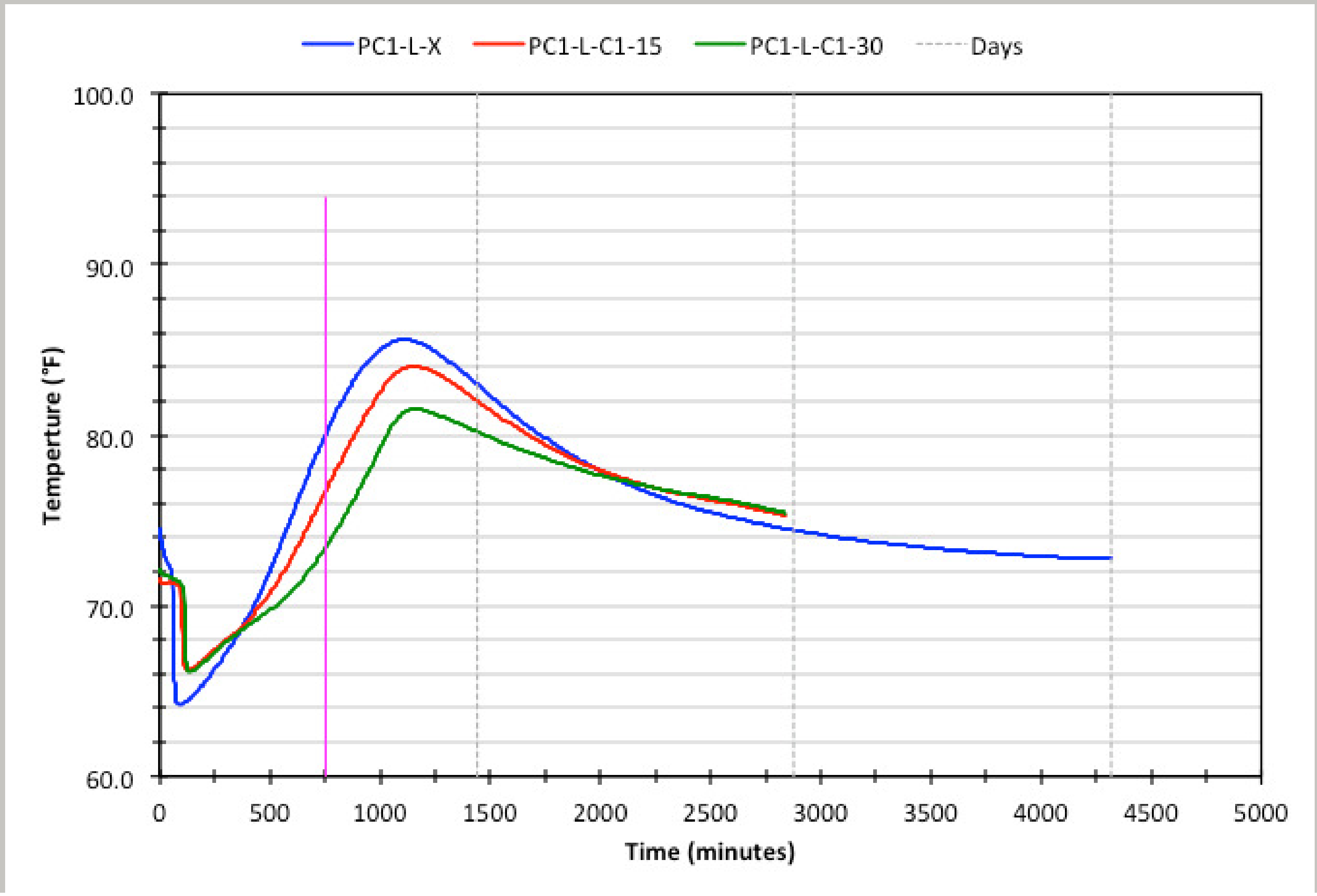
Heat of Hydration



Heat of Hydration



Heat of Hydration



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What Does Ash "Class" Tell us About Performance?

- Not much… except at the extremes…
- Compressive & flexural strength are concrete properties and cannot be clearly associated with fly ash Class – <u>not constant for a given Class</u>
- ASTM C618 specifies "Strength Activity" that is often erroneously correlated to concrete strength

Strength Activity Index

TABLE 2 Physical Requirements

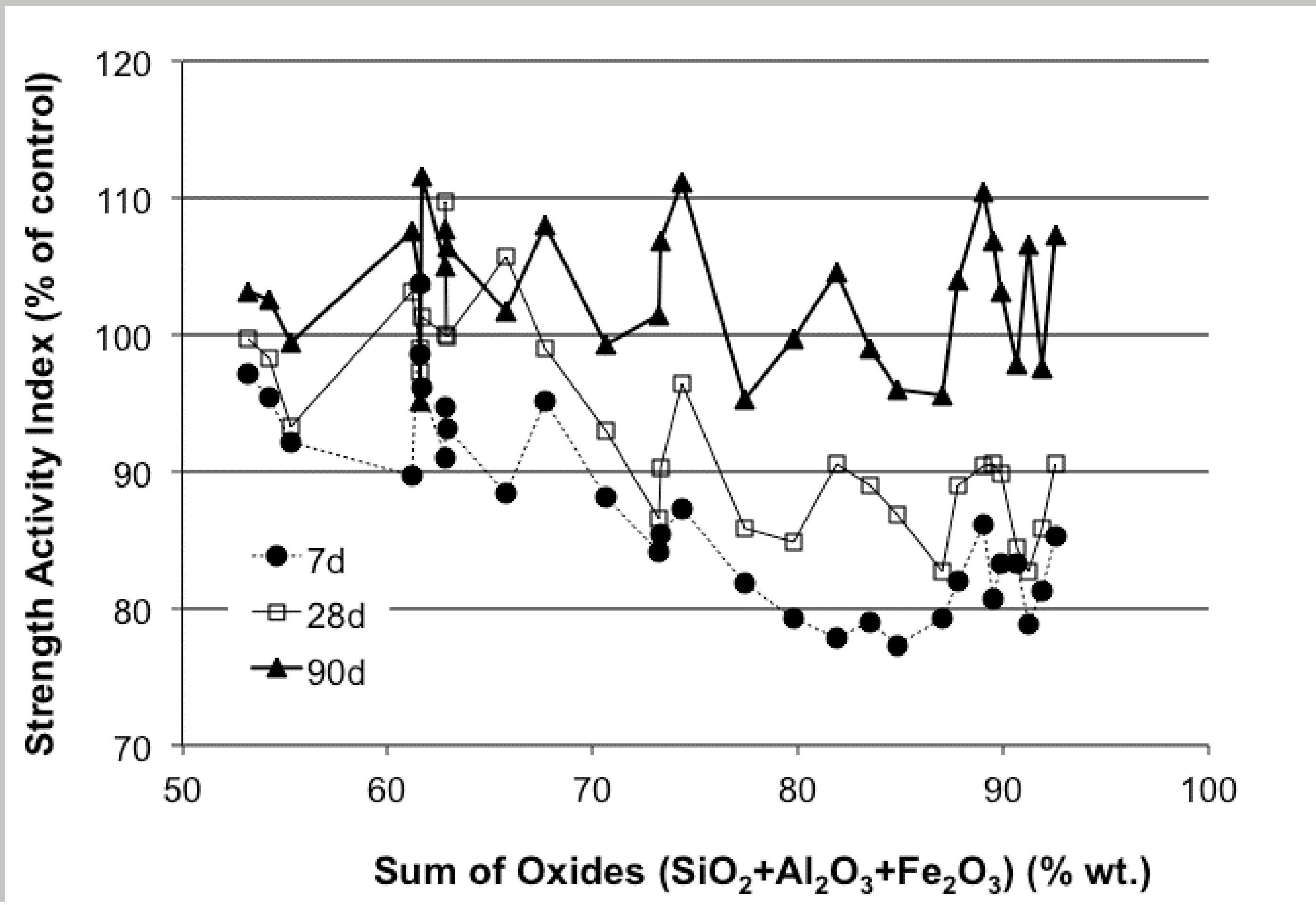
	Class		
	N	F	C
Fineness:			
Amount retained when wet-sieved on 45 µm (No. 325) sieve, max, %	34	34	34
Strength activity index: [A]			
With portland cement, at 7 days, min, percent of control	75[B]	75[B]	75[B]
With portland cement, at 28 days, min, percent of control	75[B]	75[B]	75[B]
Water requirement, max, percent of control	115	105	105
Soundness: [C]			
Autoclave expansion or contraction, max, %	0.8	0.8	0.8
Uniformity requirements:			
The density and fineness of individual samples shall not vary from the average established by the ten preceding tests, or by all preceding tests if the number is less than ten, by more than:			
Density, max variation from average, %	5	5	5
Percent retained on 45-µm (No. 325), max variation, percentage points from average	5	5	5

[A] The *strength* activity index with portland cement is not to be considered a measure of the compressive strength of concrete containing the fly ash or natural pozzolan. The mass of fly ash or natural pozzolan specified for the test to determine the *strength* activity index with portland cement is not considered to be the proportion recommended for the concrete to be used in the work. The optimum amount of fly ash or natural pozzolan for any specific project is determined by the required properties of the concrete and other constituents of the concrete and is to be established by testing. *Strength* activity index with portland cement is a measure of reactivity with a given cement and is subject to variation depending on the source of both the fly ash or natural pozzolan and the cement.

[B] Meeting the 7 day or 28 day *strength* activity index will indicate specification compliance.

[C] If the fly ash or natural pozzolan will constitute more than 20 % by mass of the cementitious material in the project mixture, the test specimens for autoclave expansion shall contain that anticipated percentage. Excessive autoclave expansion is highly significant in cases where water to cementitious material ratios are low, for example, in block or shotcrete mixtures.

Strength Activity Index



Strength Test Study

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

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 Test Study

- Evaluated the Keil Hydraulic Index
- Replace an equal percentage of the control sample cement with an inert filler
- Evaluated different fillers, replacement levels, and cements

$$\textit{Keil Hydraulic Index} = \frac{a-c}{b-c} \times 100$$

a = strength of cement/fly ash mixture, replacement level X, time t
b = strength of cement only mixture, time t
c = strength of cement/inert filler mixture, replacement level X, time t

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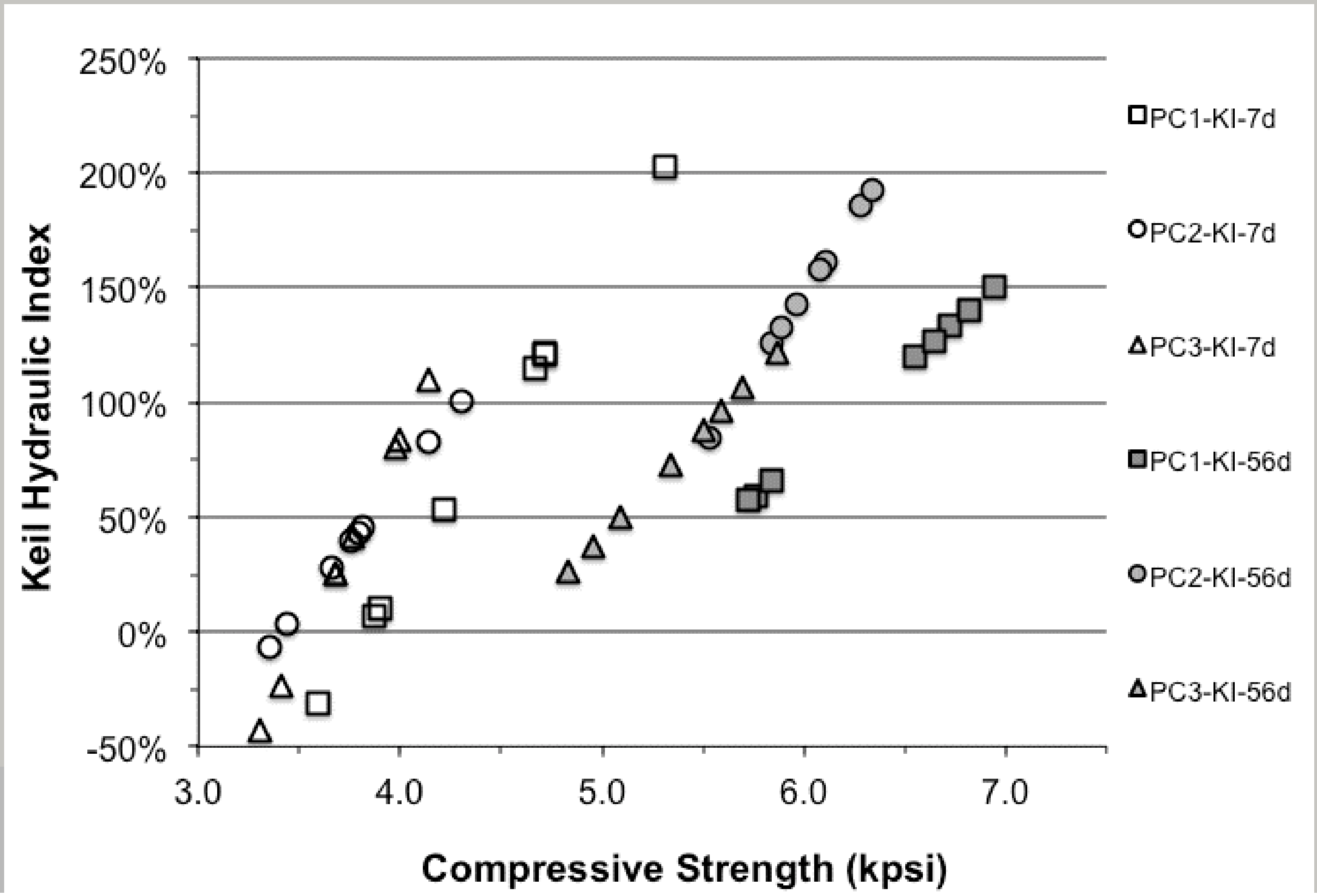
a = strength of cement/fly ash mixture
b = strength of cement only mixture
c = strength of cement/inert filler mixture

100% = a=b
0% = b=c
>100% = a>b
<100%, > 0% = a>c, a<b
<0% = a<c

Keil Hydraulic Index

	KHI - 7 days (%)			KHI - 28 days (%)			KHI - 56 days (%)		
ID-% Replace.	**PC-1**	**PC-2**	**PC-3**	**PC-1**	**PC-2**	**PC-3**	**PC-1**	**PC-2**	**PC-3**
FA-H-20	-31	4	-43	71	91	66	60	162	88
FA-M-20	7	28	26	119	55	34	66	143	50
FA-O-20	10	-6	-24	7	73	39	57	84	26
FA-Q-20	53	44	26	135	102	109	120	185	121
FA-U-20	121	40	84	184	75	171	133	158	73
FA-X-20	115	101	80	96	30	72	127	126	96
FA-ZA-20	122	46	110	184	99	153	150	132	38
FA-ZC-20	203	83	41	138	119	130	140	193	106
FA-U-35	60	21	35	102	44	93	121	102	126
FA-X-35	89	74	110	118	68	94	78	114	82
FA-ZA-35	80	35	63	124	46	114	116	102	101
FA-ZC-35	140	45	39	83	75	82	102	99	96

Keil Hydraulic Index



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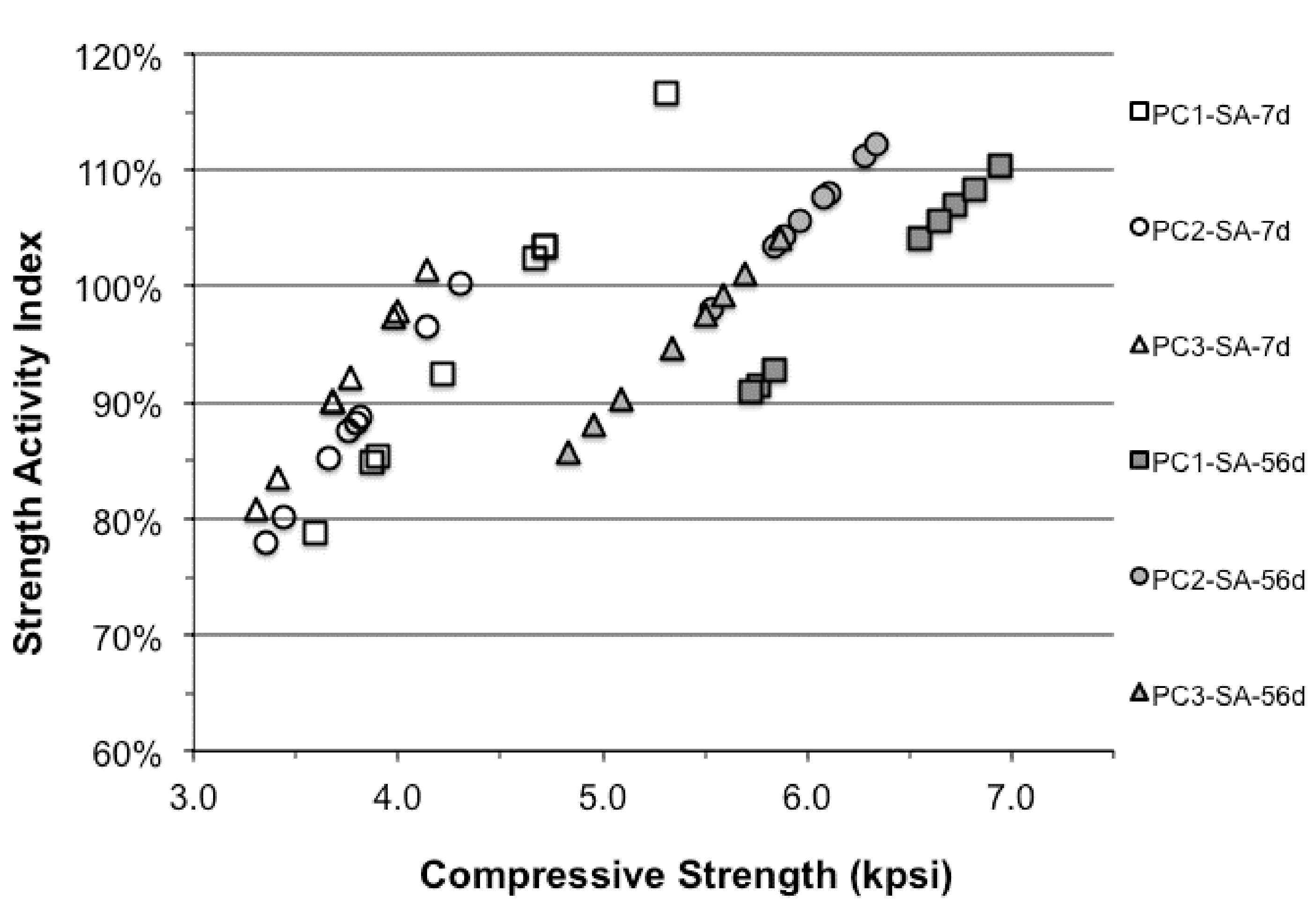
Strength Activity Index



Strength Tests

- *Take Aways*
  - The Strength Activity Index reports strength contribution from "filler" effects as well as pozzolanic or cementitious contributions
  - The test is sensitive to the cement used
  - Evaluations of the existing strength activity index showed increasing the specification limit to 85% eliminated inert materials (filler effect)
  - Need to change the time required for testing to accommodate some Class F ash

Alkali Silica Reaction (ASR)

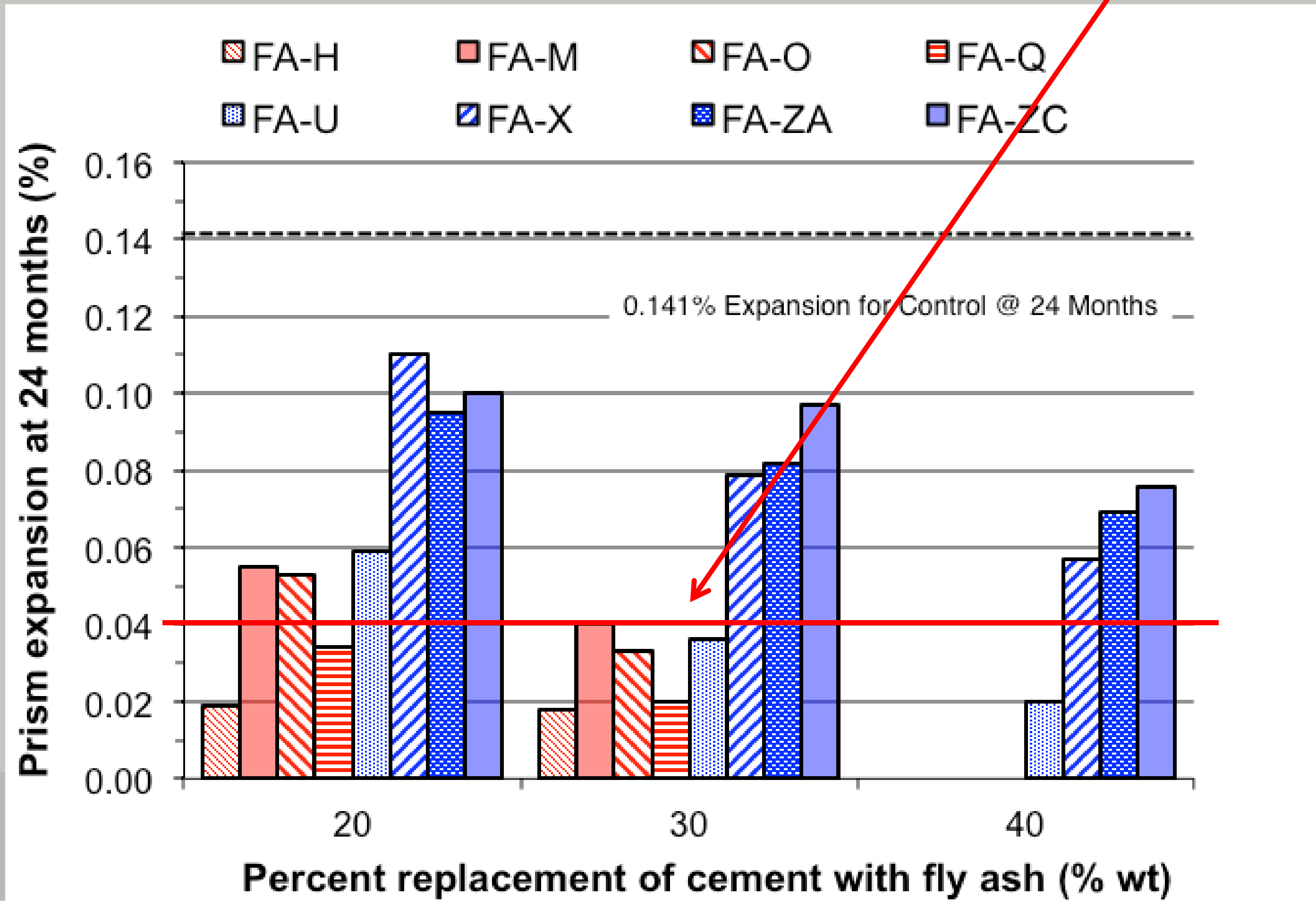
- Biggest single difference between Class F and Class C ash - ability to mitigate ASR (and sulfate attack)
- Class F – first choice for mitigating ASR
  - *Pozzolanic… Consumes –OH (Hydroxide) central to ASR*
- (some) Class C – can also mitigate but much less effective – need higher replacement levels
  - *Cementitious (slightly pozzolanic)*

ASR

- Standard Tests for Assessing ASR Mitigation
  - ASTM C1293 Concrete Prism Test
    - Acceptance criteria: 0.04% expansion at two years
  - ASTM C1567 Accelerated Mortar Bar Test
    - Based on ASTM C1260
    - Acceptance criteria: 0.10% expansion at 14 days
  - “Modified” versions of C1567 are used
    - Cannot modify an empirical test – modified tests are useless

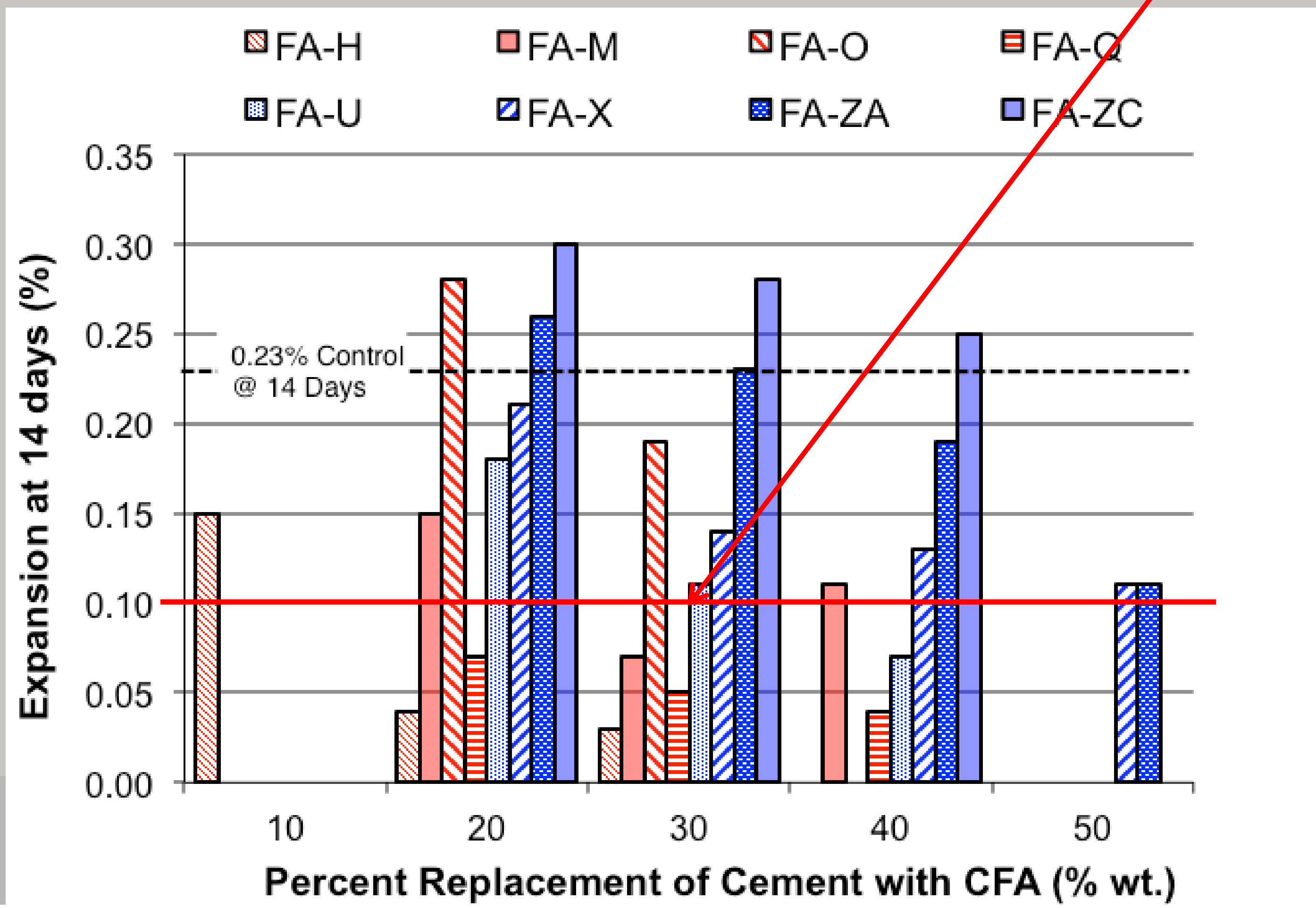
All 4 Mixtures with Class F ash pass as does one mixture with Class C ash

ASTM C1293



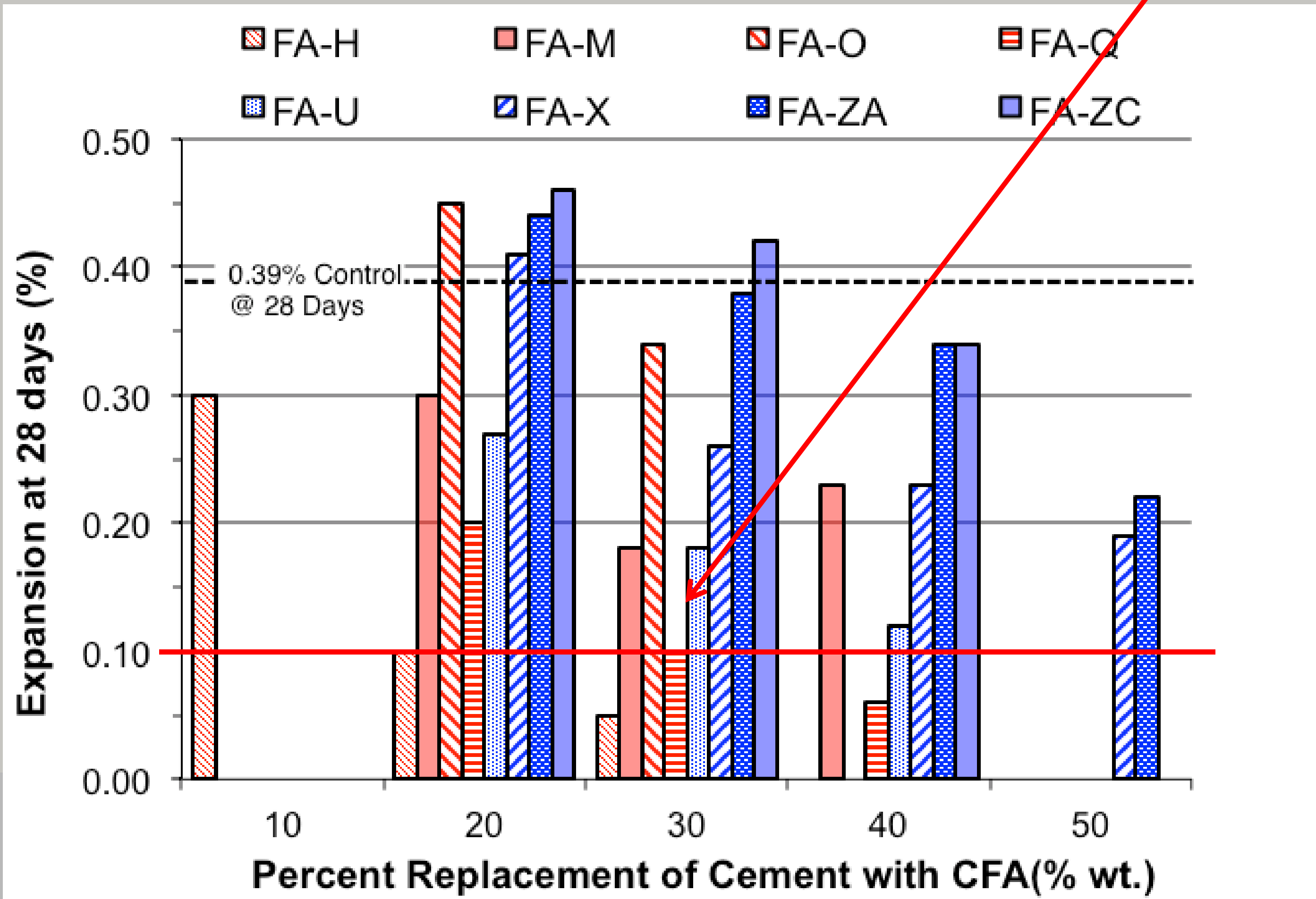
3 of 4 Mixtures with Class F ash pass and the one mixture with Class C ash barely fails – *conservative estimate*

ASTM C1567 – 14 days



3 of 4 Mixtures with Class F ash fail and the one mixture with Class C ash not close – *inaccurate estimate*

ASTM C1567 – 28 days



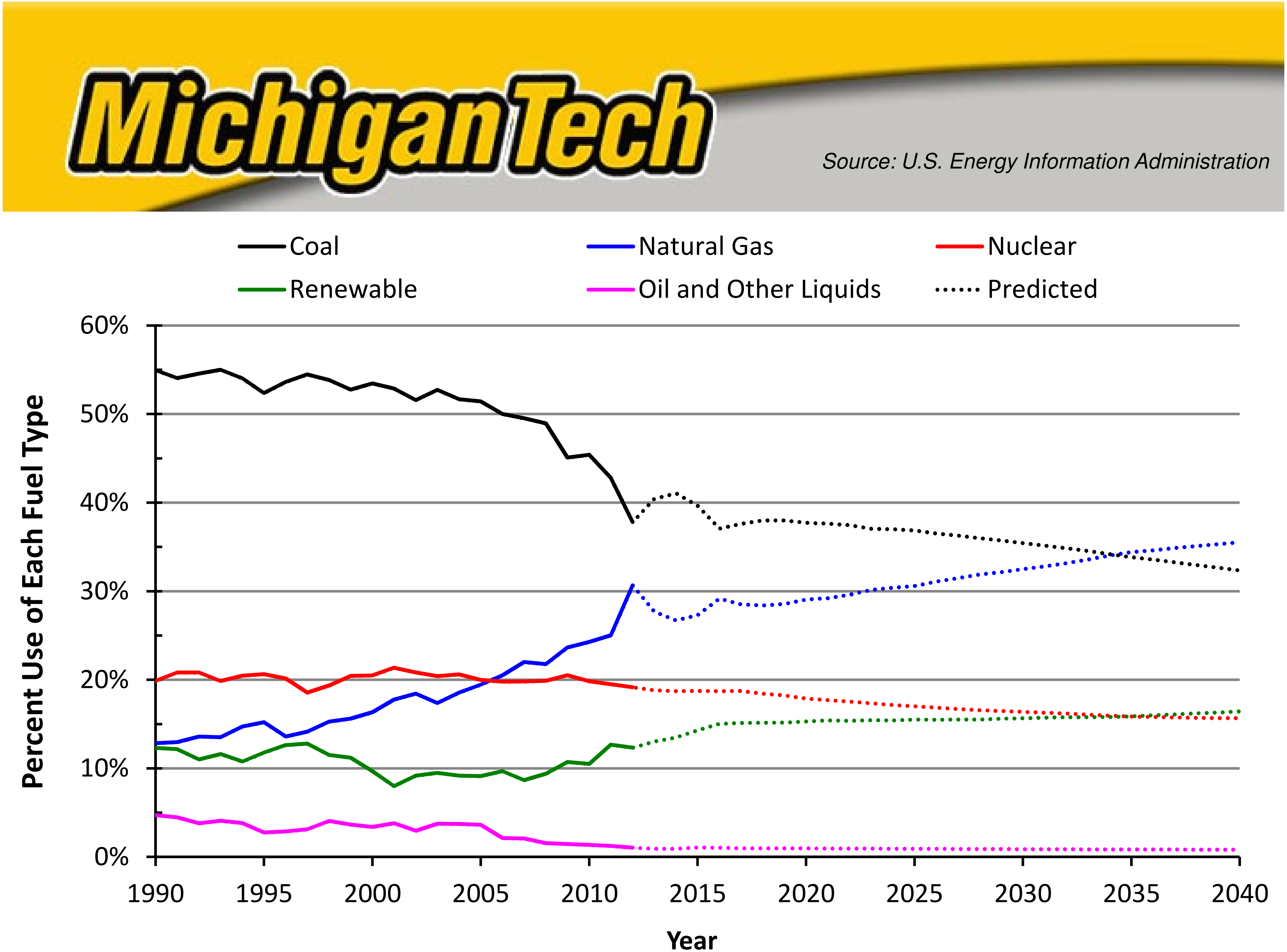
ASR

- *Take Aways*
  - Confirmed the limits of 0.1% expansion @ 14 days for ASTM C1567 as being a good correlation to ASTM C1293
  - Provided data showing a 28-day limit on ASTM C1567 does not correlate with ASTM C1293
  - Increasing mitigation for increasing amounts of all types of ash but Class F (low Ca) is more effective and lower replacement levels are required

So What's the Future of Fly Ash?

- Good question!
- Given current trends continuing – domestic sources will cease to be available
  - Environmental Regulations
  - Public Perception of Coal Power
  - Cheap Natural Gas
- But when? **Another Good question!**

Carbon
Tax ?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Source: U.S. Energy Information Administration
Coal
Natural Gas
Nuclear
Renewable
Oil and Other Liquids
Predicted
Percent Use of Each Fuel Type
60%
50%
40%
30%
20%
10%
0%
1990
1995
2000
2005
2010
2015
2020
2025
2030
2035
2040
Year

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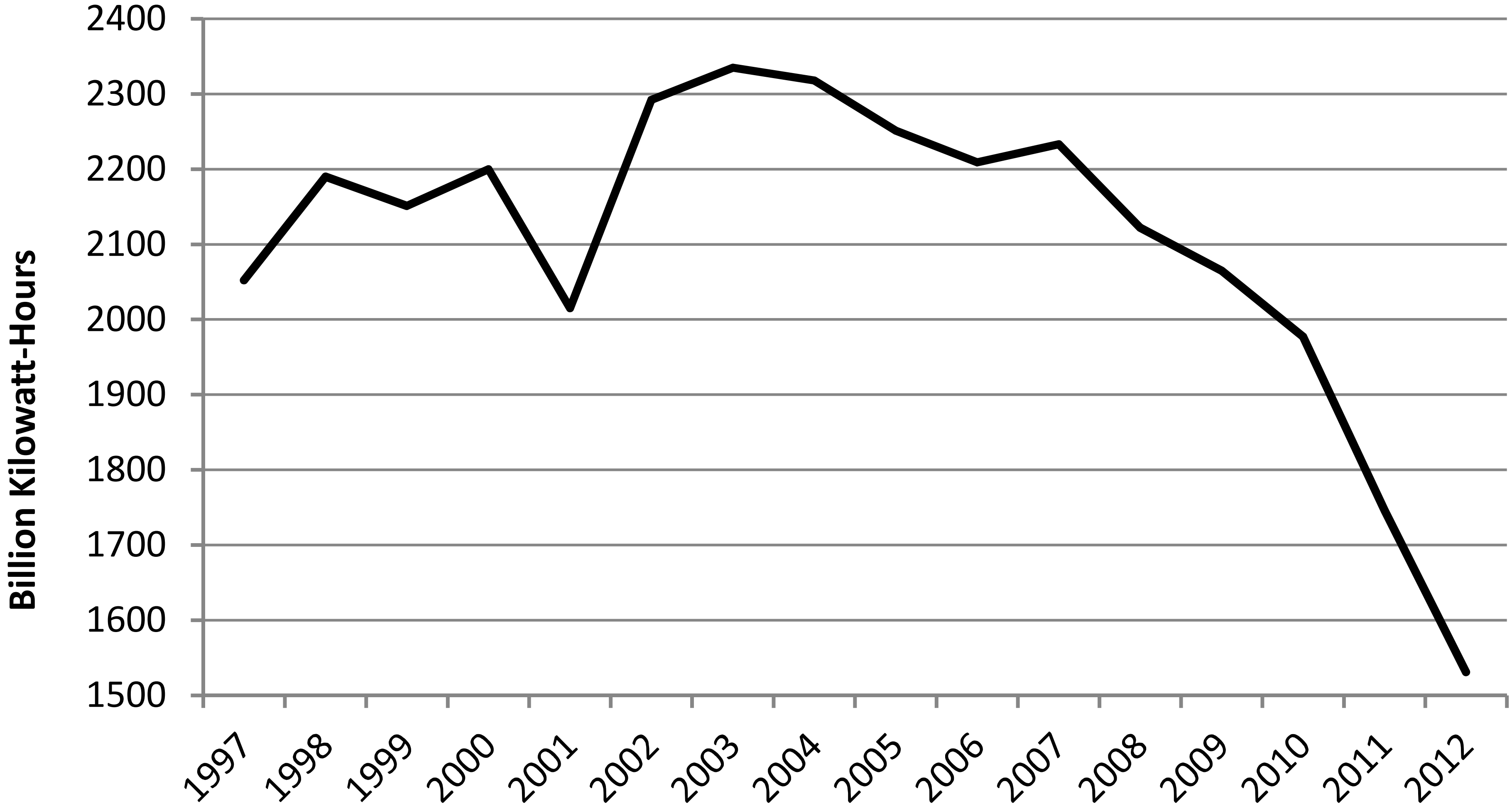
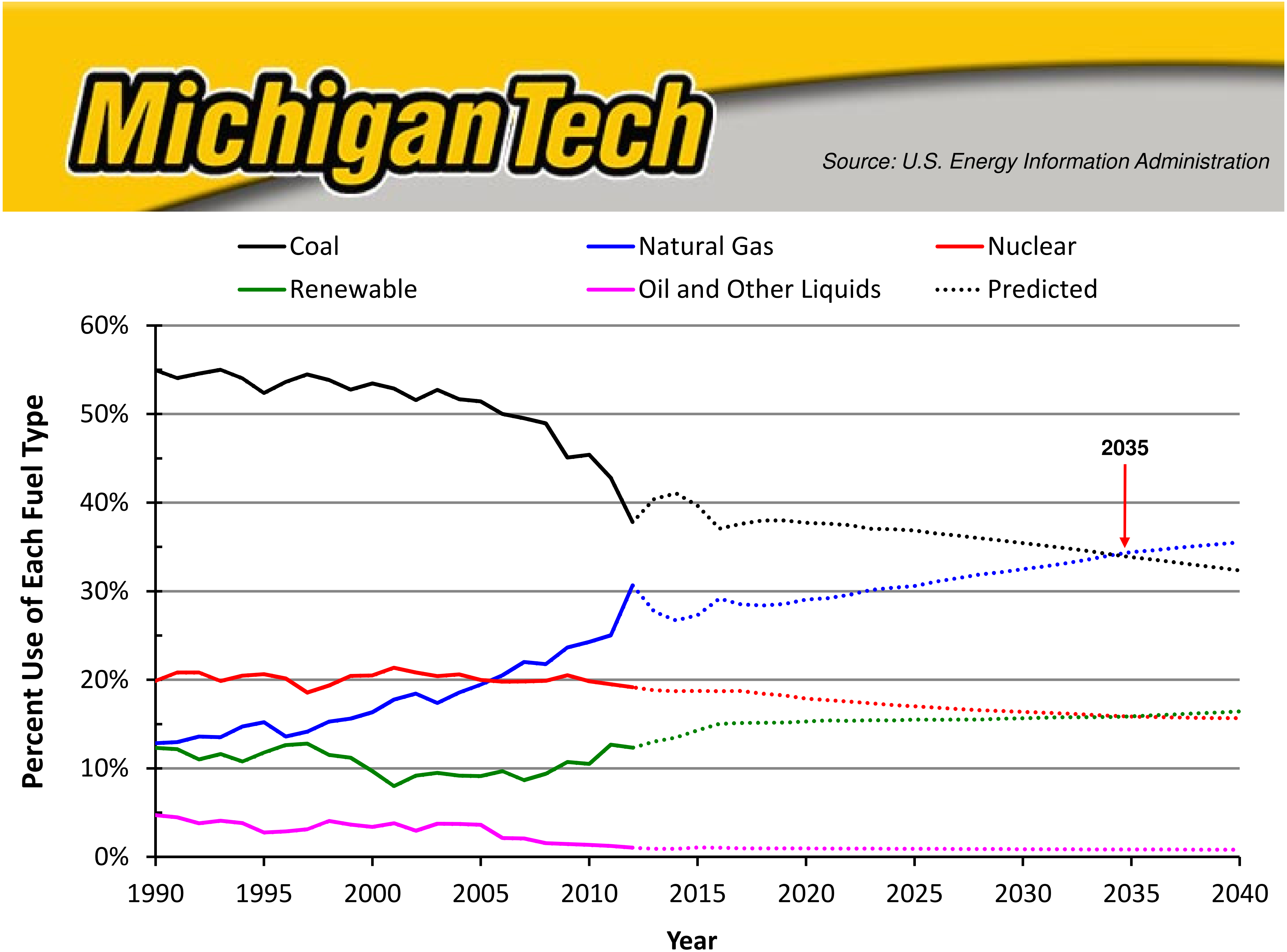
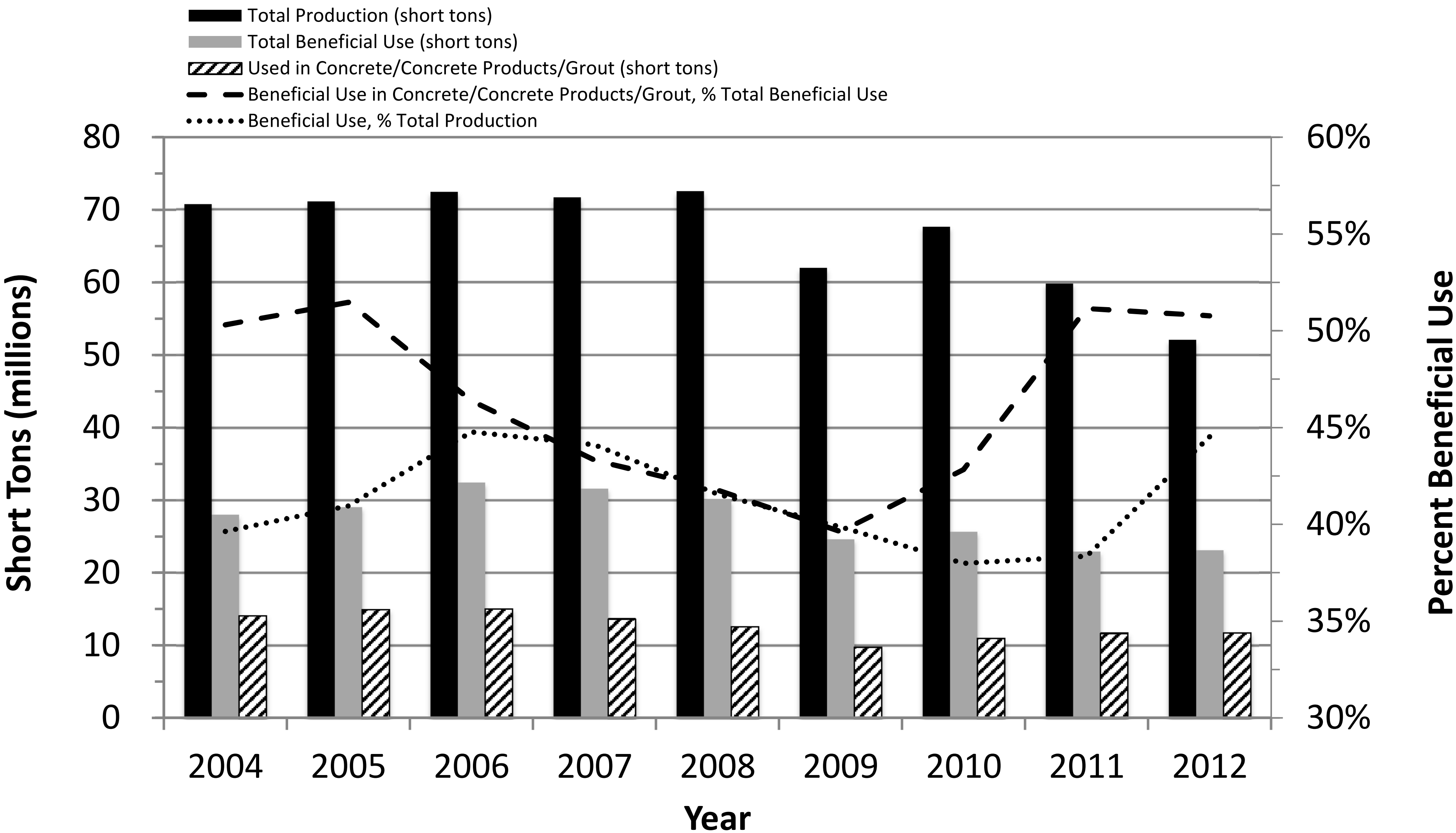
Source: U.S. Energy Information Administration

2015 Predicted Power Production - Coal




Michigan Tech
Source: U.S. Energy Information Administration
Coal
Natural Gas
Nuclear
Renewable
Oil and Other Liquids
Predicted
60%
50%
40%
30%
20%
10%
0%
Percent Use of Each Fuel Type
2035
1990
1995
2000
2005
2010
2015
2020
2025
2030
2035
2040
Year

Source: American Coal Ash Association



So What's the Future?

- Domestic, fresh fly ash supplies will be decreasing over the next 20 years and beyond
- Existing reserves will be *recovered*
  - Likely imported supplies will become more available and likely at a higher cost
- Simultaneously – High quality aggregates are also becoming a challenge to access in some markets
  - Anecdotally there appears to be more concern/occurrence of ASR

So What's the Future?

- What can replace fly ash as our *go-to* tool to mitigate ASR? Or just replace cement?
  – Slag Cement (*current solution*)
  – Natural Pozzolans (*emerging solution*)
  – Ternary blends of SCMs
  – Recovered fly ash (*emerging solution*)
  – Lower quality fly ash (*current solution*)

So What's the Future?

- Slag Cement
  - Currently used, excellent solution
  - Geographically limited
  - Good performance both as a cement replacement and as an ASR mitigator
  - Concerns about scaling – lets start curing concrete again

So What's the Future?

- Natural Pozzolan
  - With decreased fly ash supplies, natural pozzolan reserves once overlooked are being considered – and they should be
  - Similar to Class F ash (low CaO, sum of the oxides > 70%)
  - Examples: Calcined Clay or Shale, Diatomaceous Earth, Volcanic Materials such as Dacite, Rhyolite

So What's Up With Fly Ash?

- Natural Pozzolan
  - Unlike other emerging "alternative supplementary materials" that have no existing specification, natural pozzolans can be specified under ASTM C618 / AASHTO M 295
  - Transportation costs an issue in some cases – needs to be weighed against rising costs for fly ash as supply becomes more difficult

So What's Up With Fly Ash?

- Ash Quality Challenges
  - Competing with other markets for the material
  - Lower supply – may have to consider an ash once rejected
  - Recovered ash
  - Pollution control measures will affect the ash
    - Ammonia
    - Powdered Activated Carbon

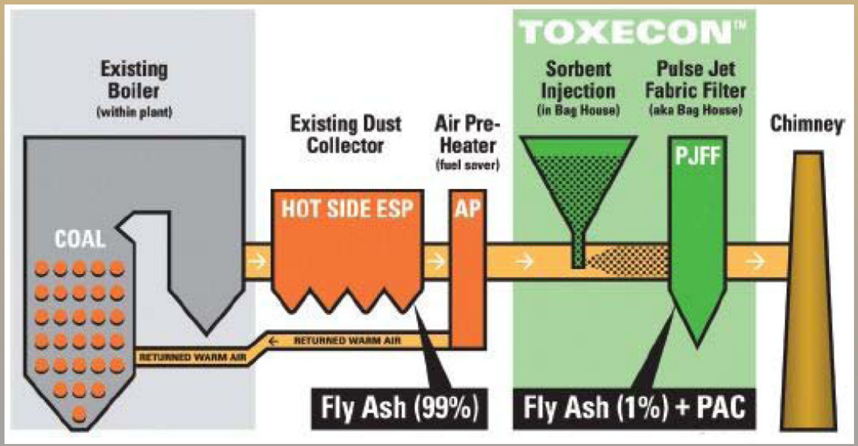
Ammonia

- Product of Selective Catalytic Reduction (SCR) technology to reduce NOx
  - Reduction of NOx to N_2 and H_2O by the reaction of NOx and ammonia (NH_3) within a catalyst (TiO_2, zeolites)
- Product of Selective Non-Catalytic Reduction (SNCR) technology to reduce NOx
  - Converts NOx into molecular N_2 without the use of a catalyst
  - A reducing agent, typically ammonia, is injected into the flue gases and at high temperatures
- Both approaches (primarily SNCR) can lead to "ammonia slip"
  - Health issue – does not affect concrete quality

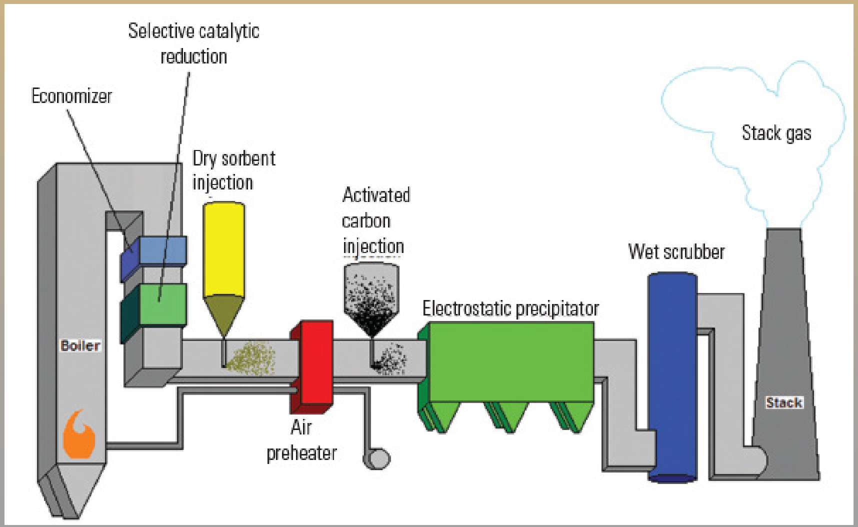
Powdered Activated Carbon (PAC)

- High specific surface
- Used as part of an overall Mercury and Air Toxics Standards (MATS) strategy
- Mercury sorbent

- Can be added before or after ash collection
  - Before more common (capital cost)
- Concern for concrete – impacts air entrainment



Source: We Energies CCP Handbook

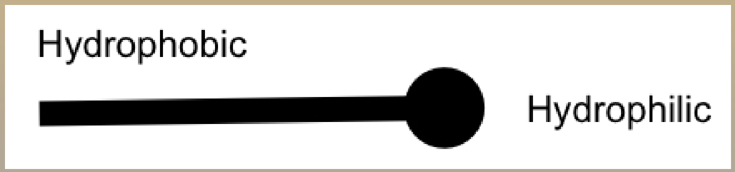


Source: www.powermag.com

Powdered Activated Carbon (PAC)

- 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
- An AEA molecule contains two parts

Schematic view of AEA molecule

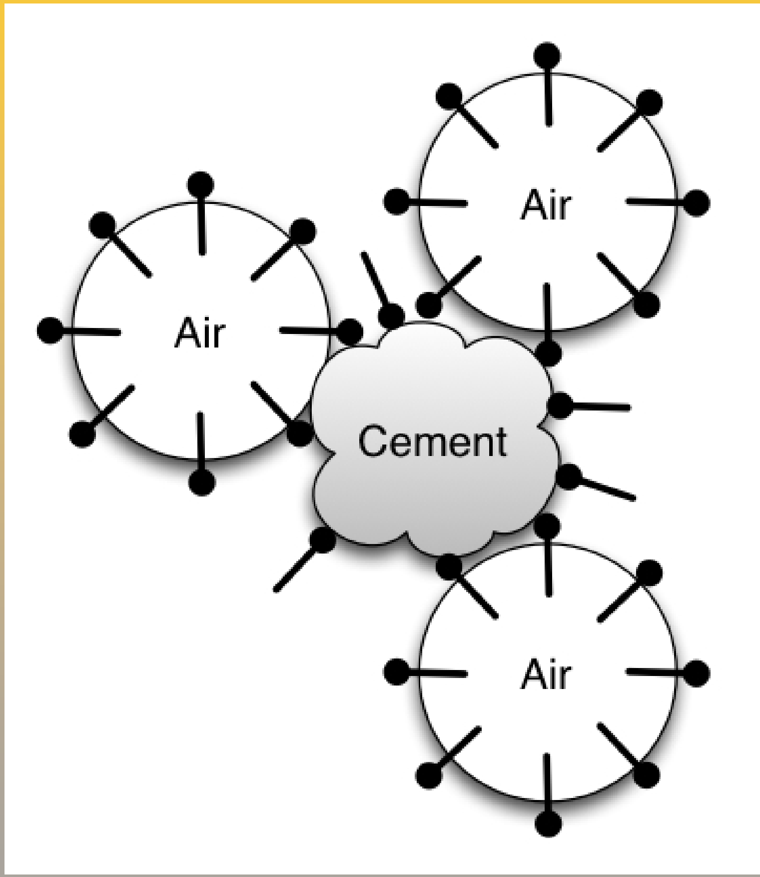


Tail
Non-polar (non-ionic)
Little or no attraction to water
(*hydrophobic*)

Head
Polar (ionic) portion
Strong attraction to water
(*hydrophilic*)

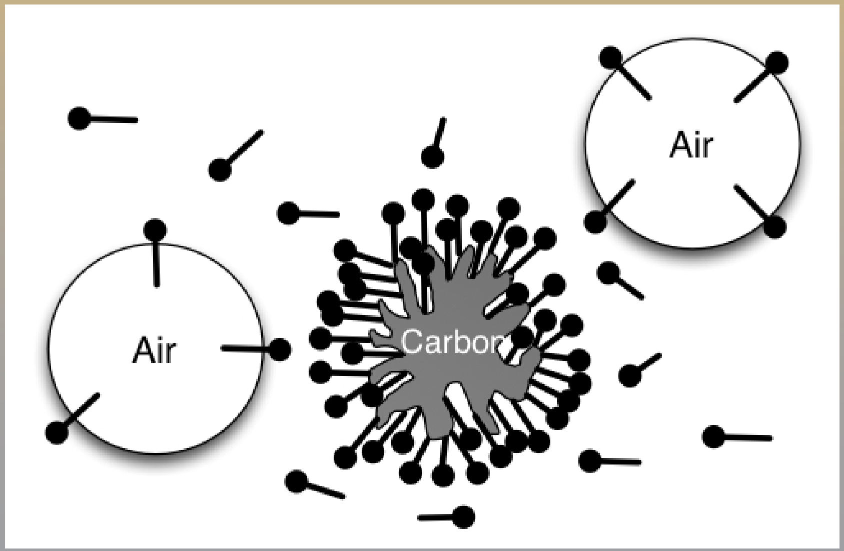
Powdered Activated Carbon (PAC)

- Hydrophilic, anionic polar groups (i.e., head) adsorb 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



Powdered Activated Carbon (PAC)

- AEAs adsorbed on to carbon surfaces do not participate in air entrainment for two reasons:
  - The hydrophobic tail can be adsorbed on to the solid phase 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



Powdered Activated Carbon (PAC)

- PAC can be addressed by post-processing
  - Tribo-electric (electrostatic) separation
  - Carbon burn-out
  - Surface treatment of the PAC
- New tests to measure ash adsorption
- **NCHRP 749**
  - Foam Index
  - Direct Adsorption Isotherm
  - Iodine Number

Foam Index Test

- Evaluated 16 published versions
- Adopted the methodology of Harris with some modifications

Harris, N. J., K. C. Hover, K. J. Folliard, and M. T. Ley. The Use of the Foam Index Test to Predict AEA Dosage in Concrete Containing Fly Ash: Part I-Evaluation of the State of Practice. Journal of ASTM International, Vol. 5, No. 7, 2008.

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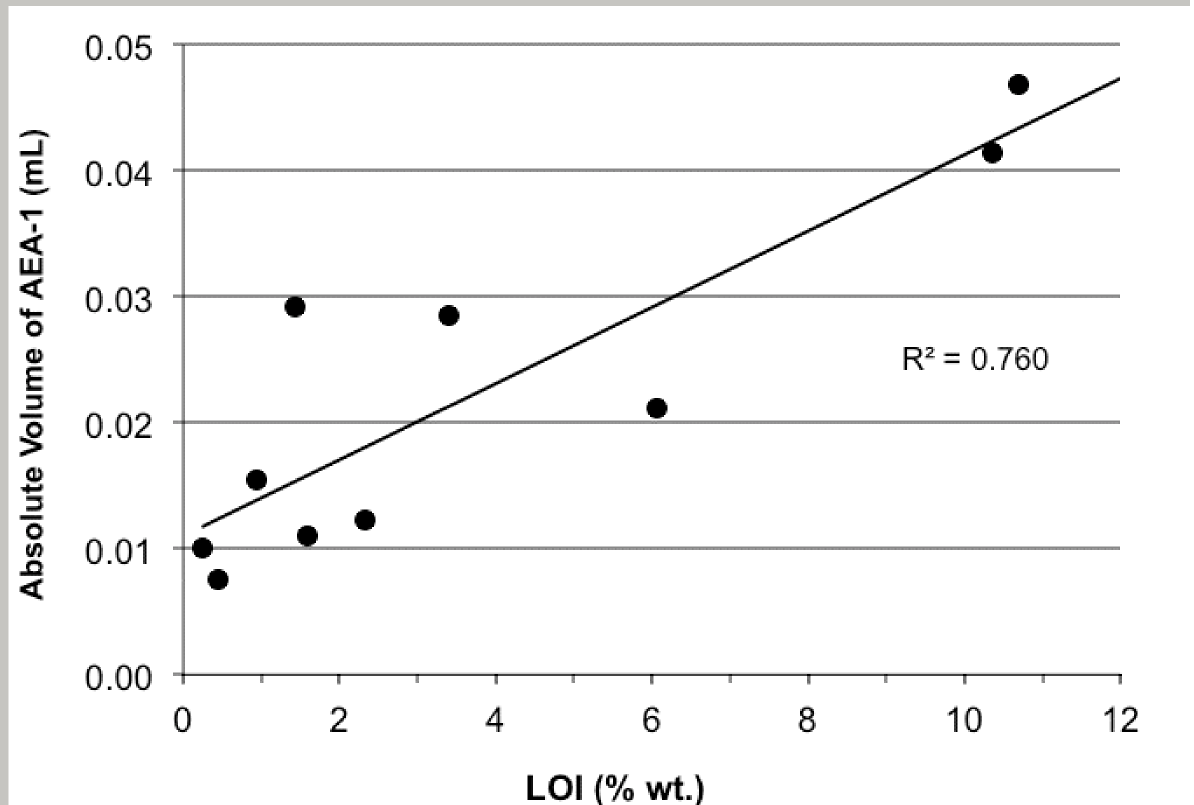
Michigan Tech

Foam Index Test

- 2 g ash, 8 g cement
- 25 mL water
- Add AEA solution drop-wise
  - 5 % vol. AEA / Water solution
  - (0.02 mL/drop)
- Shaken, not stirred
- Look for a stable foam
- Repeat…

Foam Index Test

- Benefits
  - Cheap & Easy
- Issues
  - Not achieving equilibrium
  - Not quantitative
  - Subjective
    - Agitation?
    - What is a stable foam?



Adsorption Based Tests

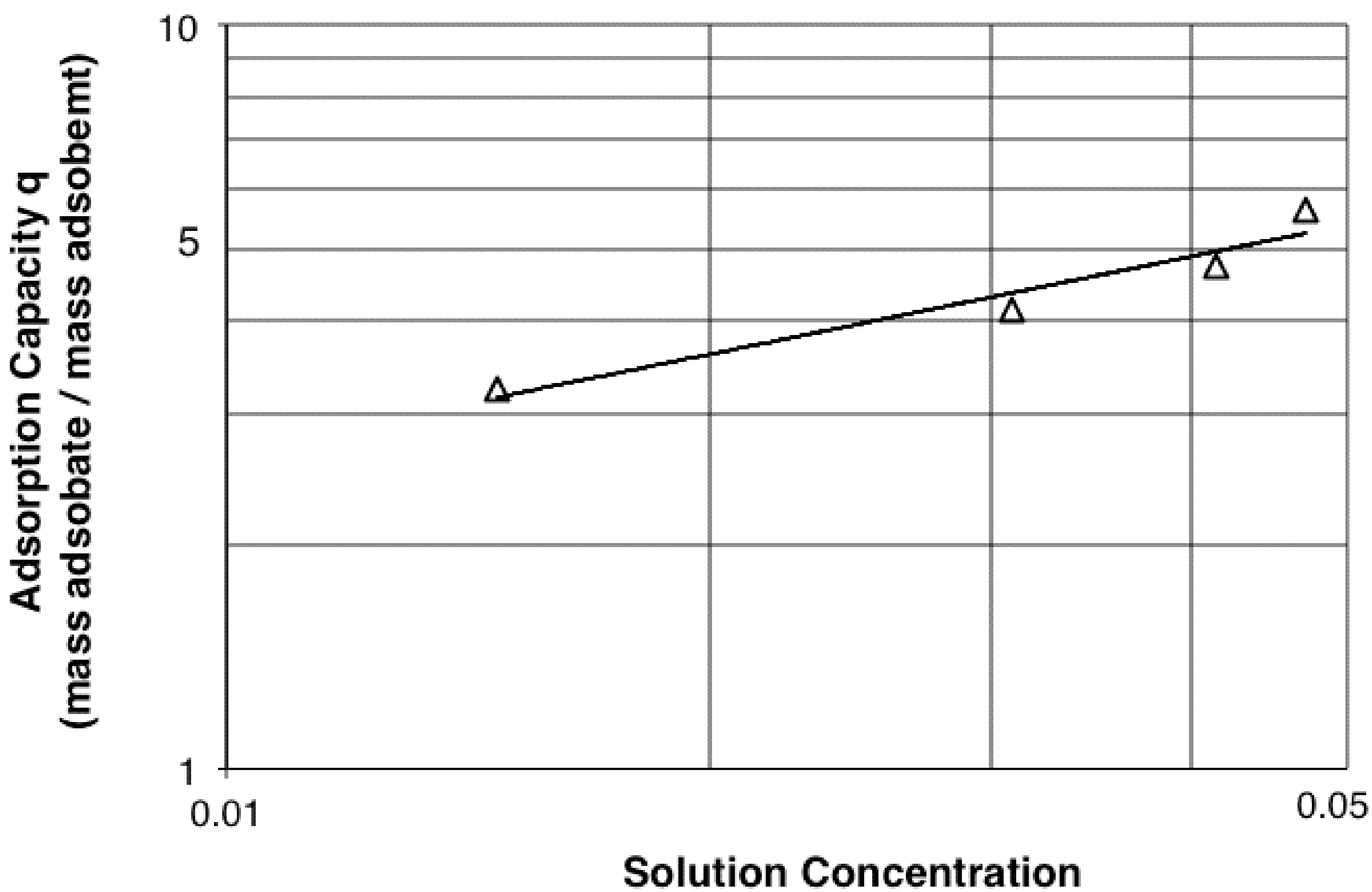
- Adsorption characterized by an adsorption isotherm
- Multiple adsorption models and isotherms
- Freundlich Isotherm

$$q = K \times C^{1/n}$$

  - q = mass of adsorbate adsorbed per unit mass of adsorbent, mg/g
  - K = Freundlich isotherm capacity parameter, (mg/g) $(L/mg)^{1/n}$
  - C = Solution concentration, mg/L
  - 1/n = Freundlich isotherm intensity parameter, dimensionless

Freundlich Isotherm

Slope = 1/n   Intercept = log K



Direct Adsorption Isotherm

INTERNATIONAL

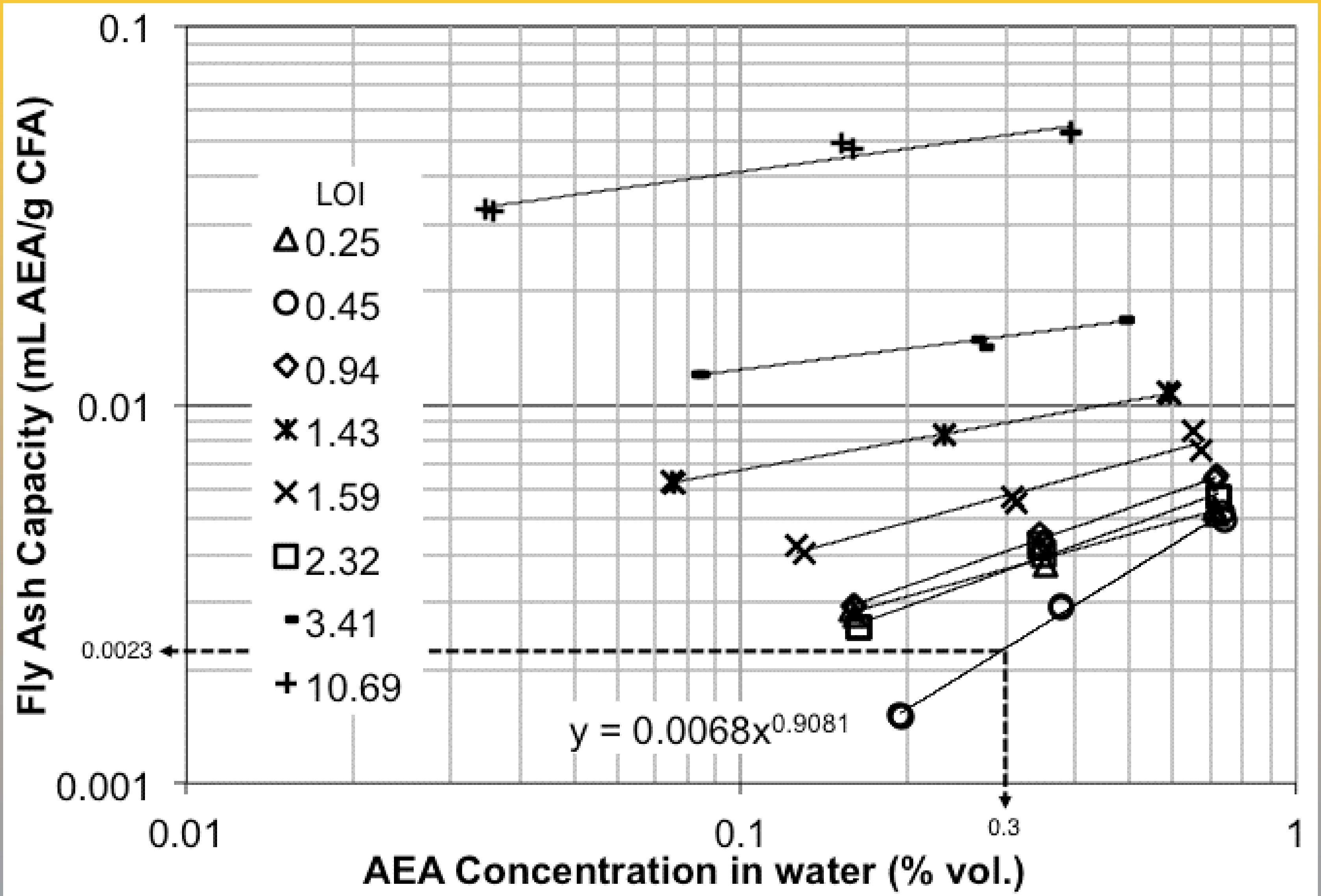
Designation: D3860 – 98 (Reapproved 2008)

Standard Practice for Determination of Adsorptive Capacity of Activated Carbon by Aqueous Phase Isotherm Technique[1]

- Based on existing ASTM test method with modifications:
  - Modified procedure for determining solution concentration
    - COD test versus spectroscopic methods
  - Needed to account for the contribution of cement

Direct Adsorption Isotherm

determines AEA adsorption "capacity"



Direct Adsorption Isotherm

- Measures the adsorption capacity of the ash *AND* the adsorption capacity of the AEA
- Can be used to estimate AEA dosage
- Simple execution
  - Scales
  - Beakers & Stir Plate & Filtration
  - COD Kits & Colorimeter

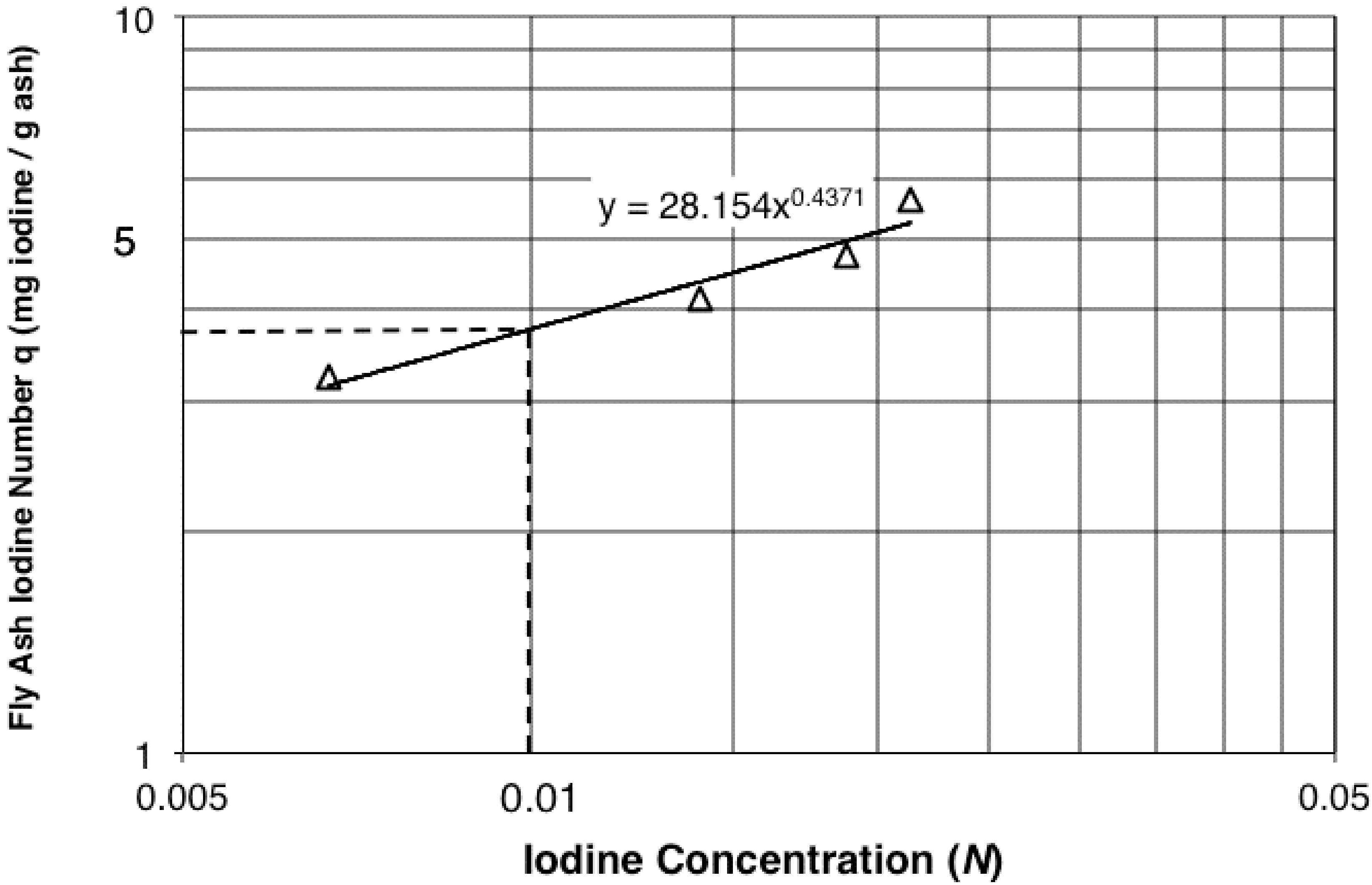
Coal Fly Ash Iodine Number

Designation: D4607 – 94 (Reapproved 2006)

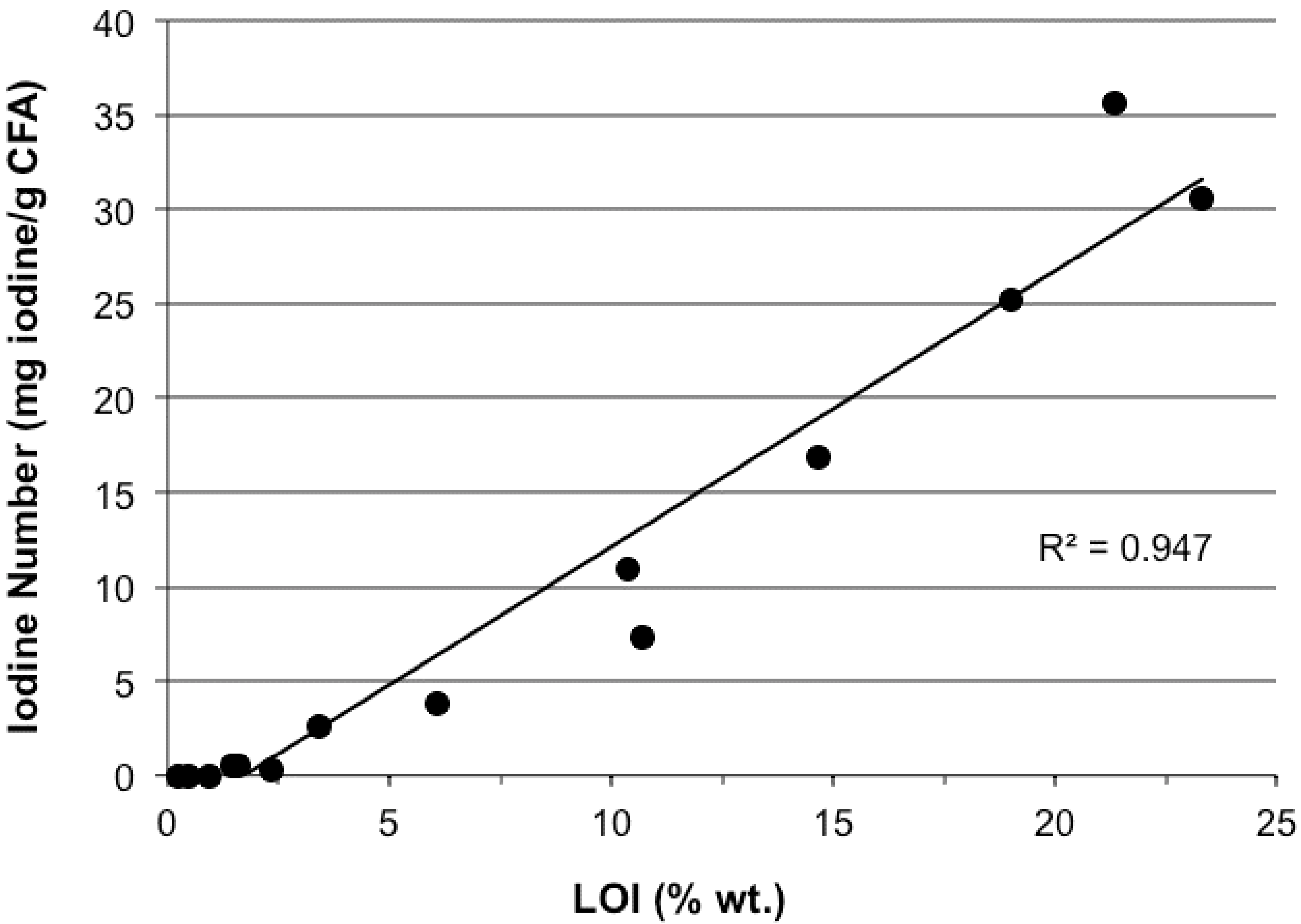
Standard Test Method for Determination of Iodine Number of Activated Carbon[1]

- Based on existing ASTM test method with modifications:
  - HCl treatment to acidify the ash and remove SO_3
  - Initial solution strengths modified (0.025 N vs 0.1 N)
  - Target concentration for determining capacity differs from published test method (0.01 N vs 0.02)

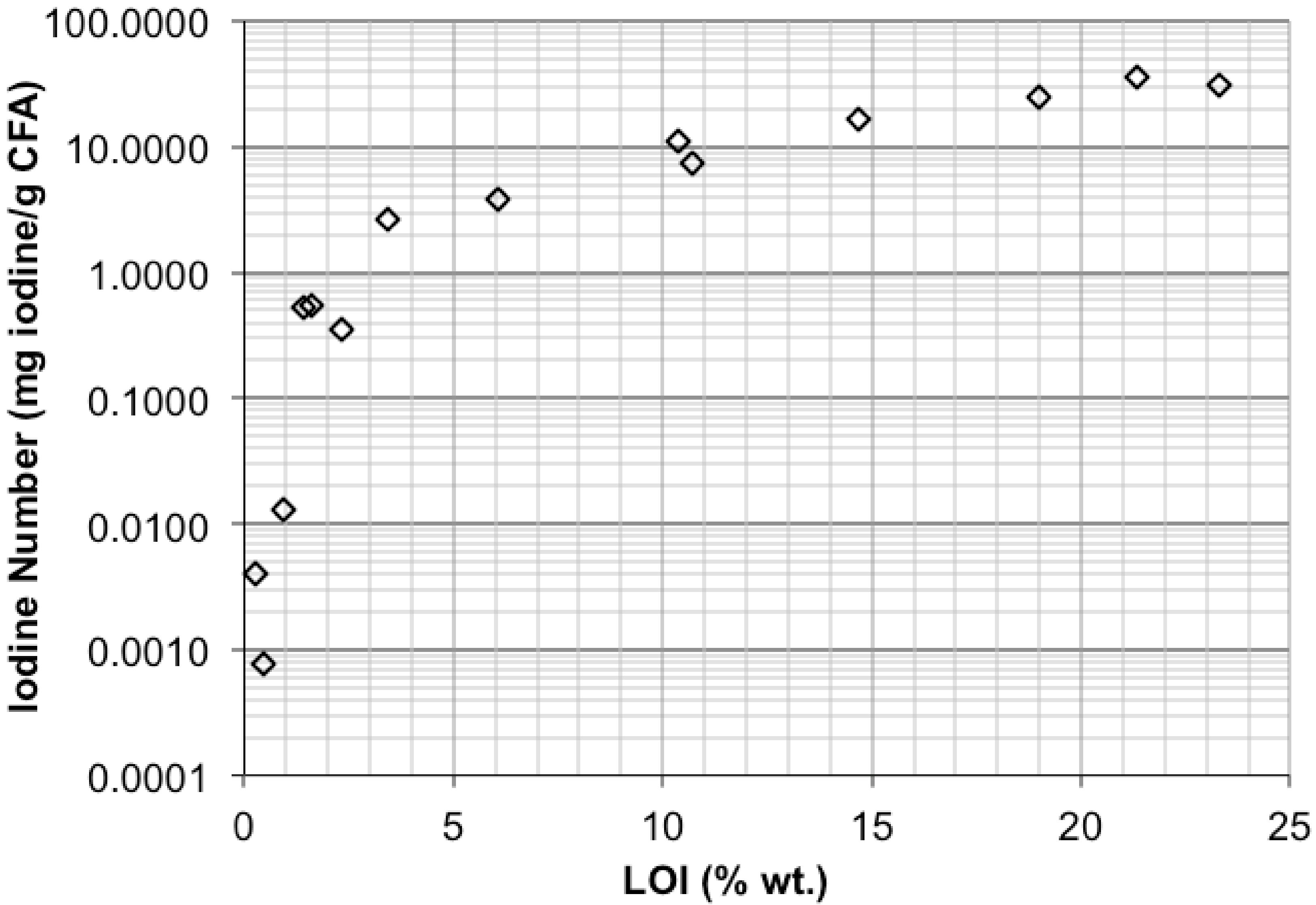
Coal Fly Ash Iodine Number



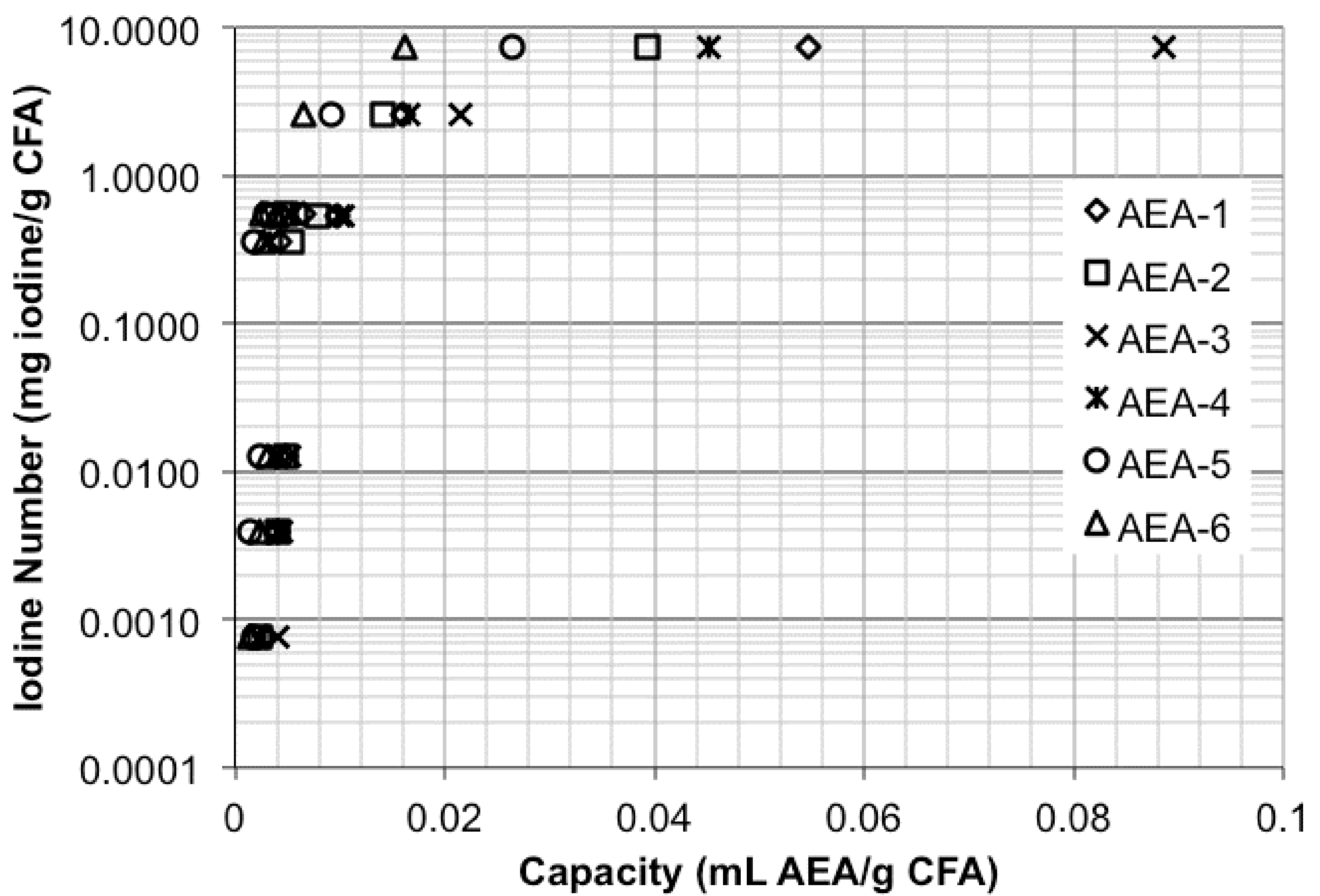
Coal Fly Ash Iodine Number



Coal Fly Ash Iodine Number



Iodine Number vs. Capacity



Coal Fly Ash Iodine Number

- Measures the adsorption capacity of the ash
- Does not account for the adsorption capacity of the AEA
- Simple execution
  - Scales
  - Beakers & Stir Plate & Filtration
  - Titration

Tests & Specifications

- The three new tests for carbon adsorption are being balloted at ASTM – hopefully adopted in the next year
- Specification limits need to be developed through experience
- Other tests have been proposed to evaluate "recovered" ash
  - Total organic content
  - Analysis of -325 fraction (bottom ash contamination)
  - More rigorous strength activity test

Tests & Specifications

- Changes to classification
  - Eliminate Class C and F, report the chemistry, let the user buy what they want – verify performance through testing
  - Eliminate sum of the oxides – replace with CaO
  - Adopt the CSA method that uses three classes
    - Class C – CaO content > 20%
    - Class CI – CaO content 15 – 20%
    - Class F – CaO content < 15%
- Changes to ash definition - recovered ash

Summary

- Fly ash will become increasingly more scarce
- The environment of a “single source” will be replaced with multiple sources
- Challenges of source variation
  - More inconsistency within a given source
  - Multiple sources
  - Quality

Summary

- Class C vs. Class F
- Class C ash (higher CaO) will be more common
- Considerations
  - Strength development
  - ASR mitigation
  - Mixture designs

Summary

- Class F ash is preferred for ASR mitigation
- Class C ash can mitigate but much higher replacement levels are required
- Alternatives include ternary blends of Class C ash and another SCM
  - Slag cement
  - Silica fume
  - Natural pozzolans

Summary

- More testing of ash and concrete mixtures will be required to ensure performance and consistency
- Recovered ash will become more common (typically recovered Class F) but quality must be verified by testing
- Don’t assume a “spec” ash (e.g., C618) will always perform – “trust but verify…”

Summary

- Major challenges facing the concrete producer:
  - Mixture designs using a Class F ash will need to be modified for use of a Class C ash or ternary blends
  - Getting consistent air (carbon)
  - Getting consistent reactivity from the ash and therefore consistent strength and heat evolution