A Summary of NCHRP Project 18-13 and Some Other Stuff

Report Number NCHRP 749

Specifications and Protocols for Acceptance Tests of Fly Ash Used in Highway Concrete

Larry Sutter

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Acknowledgements

NCHRP 18-13 Specifications and Protocols for Acceptance Tests of Fly Ash Used in Highway Concrete

Larry Sutter[1], Doug Hooton[2], Scott Schlorholtz[3]
&
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Dave Hand[1], Andre de Groot[2]

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[2] University of Toronto
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First…So What's Up With Fly Ash?

So What's Up With Fly Ash?

- Good question! Hard to predict but likely…

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- 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?

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- But when? **Another Good question!**

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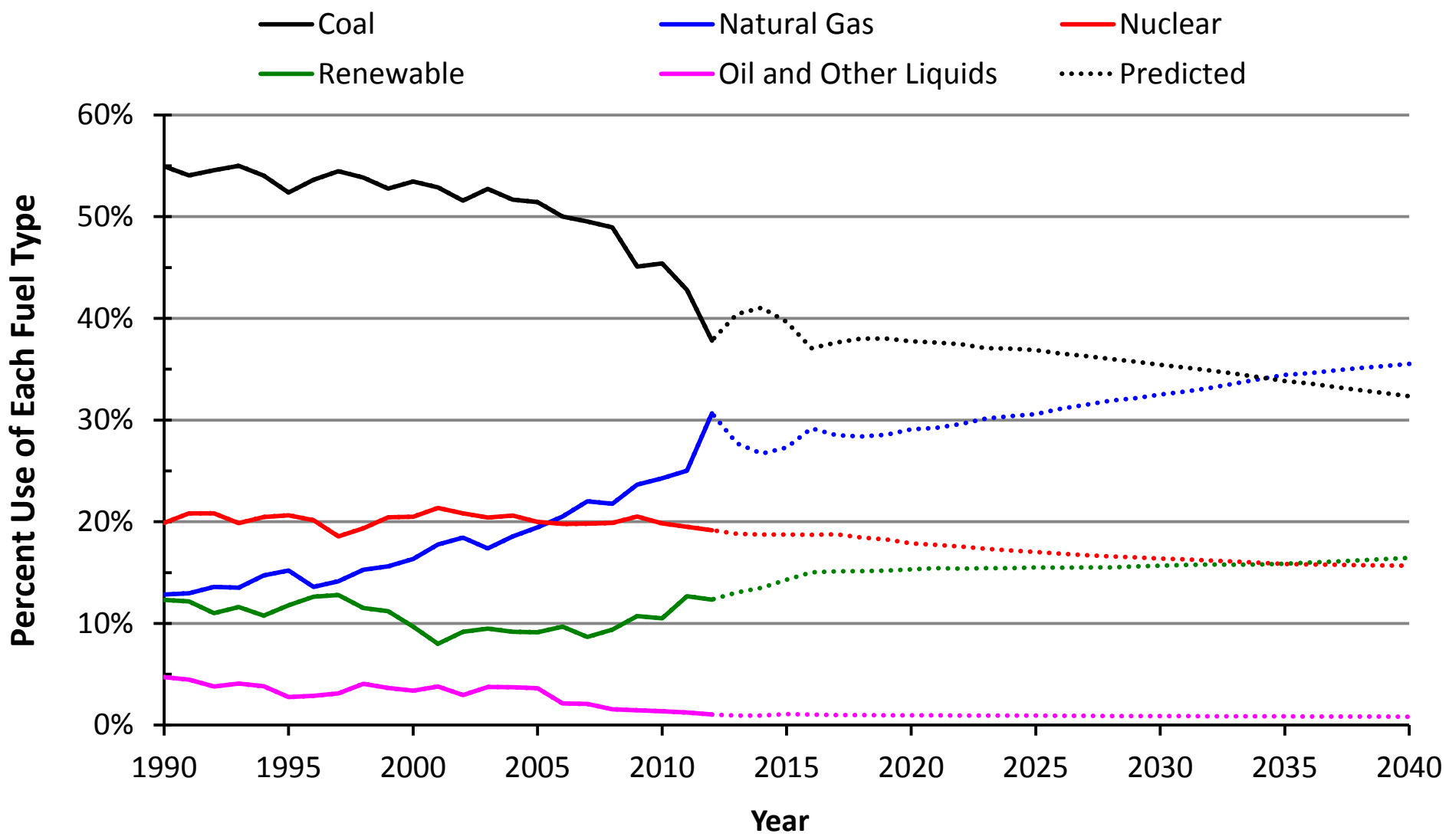
Source: U.S. Energy Information Administration



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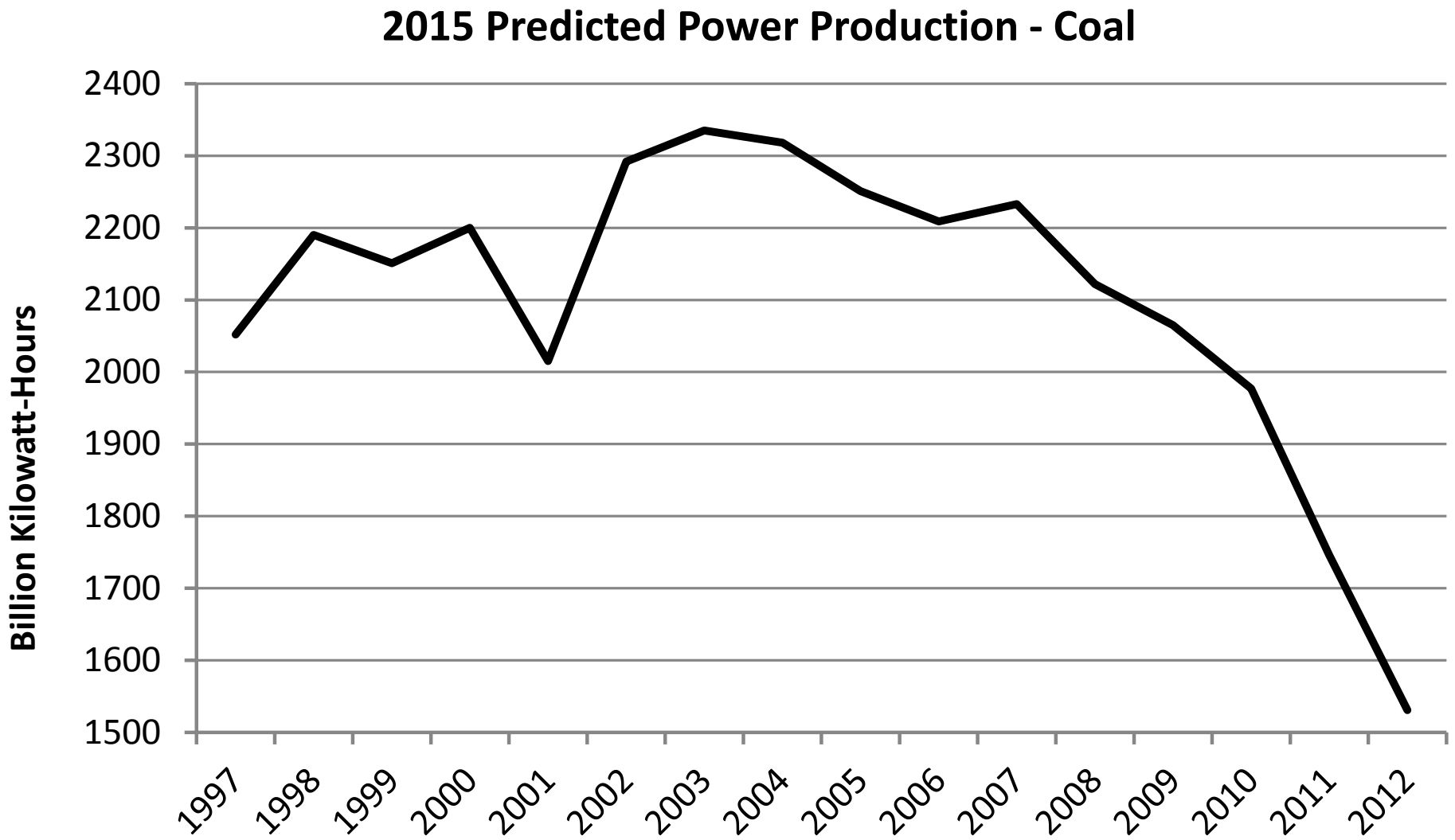

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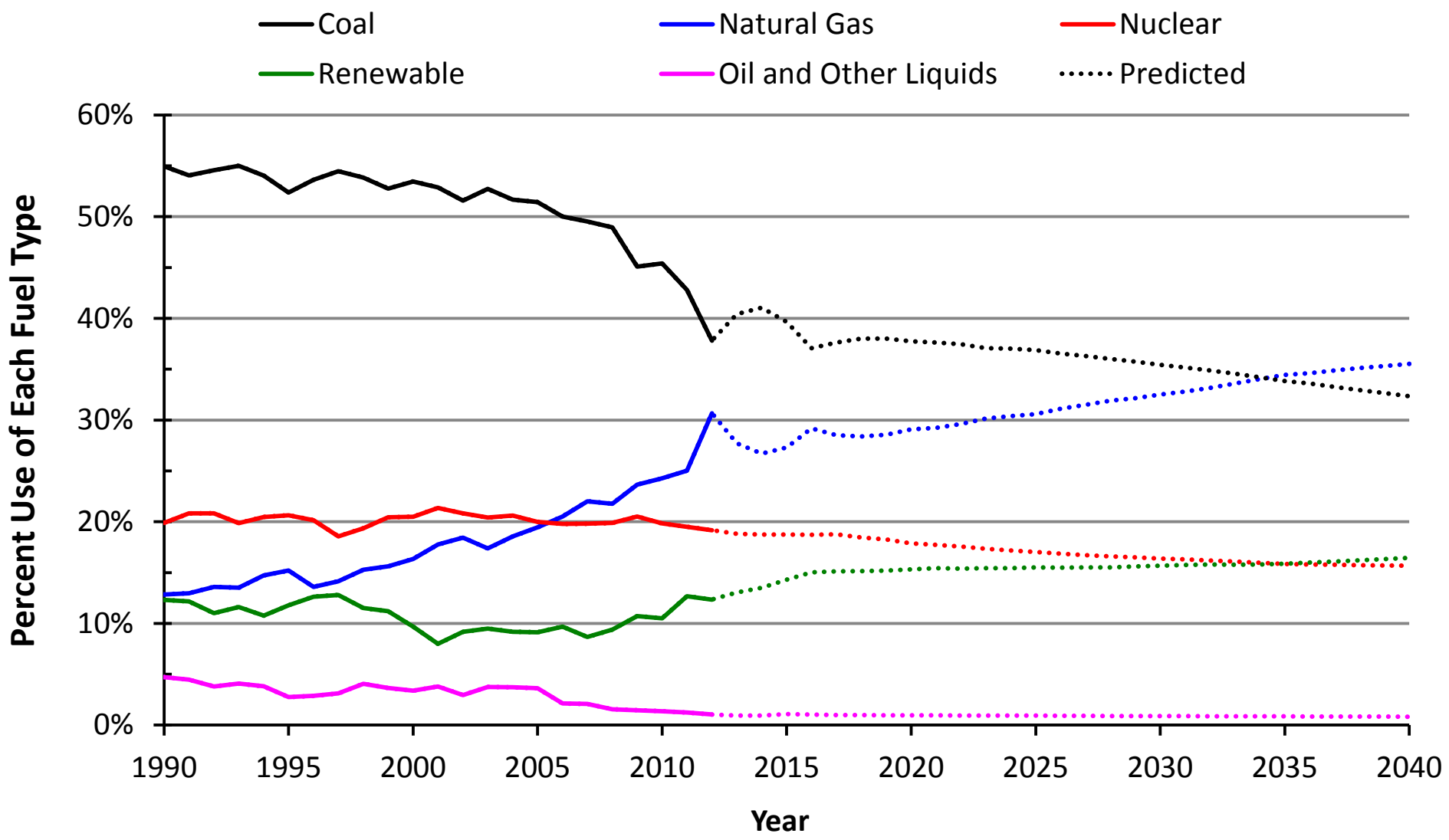

So What's Up With Fly Ash?

- Domestic fly ash reserves will be decreasing over the next 20 years and beyond
  - 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 Up With Fly Ash?

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

So What's Up With Fly Ash?

- 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 Up With Fly Ash?

- Natural Pozzolan
  - With decreased fly ash supplies, natural pozzolan reserves once overlooked are being considered – and they should be
  - Similar to Class F ash (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 decreases

So What's Up With Fly Ash?

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

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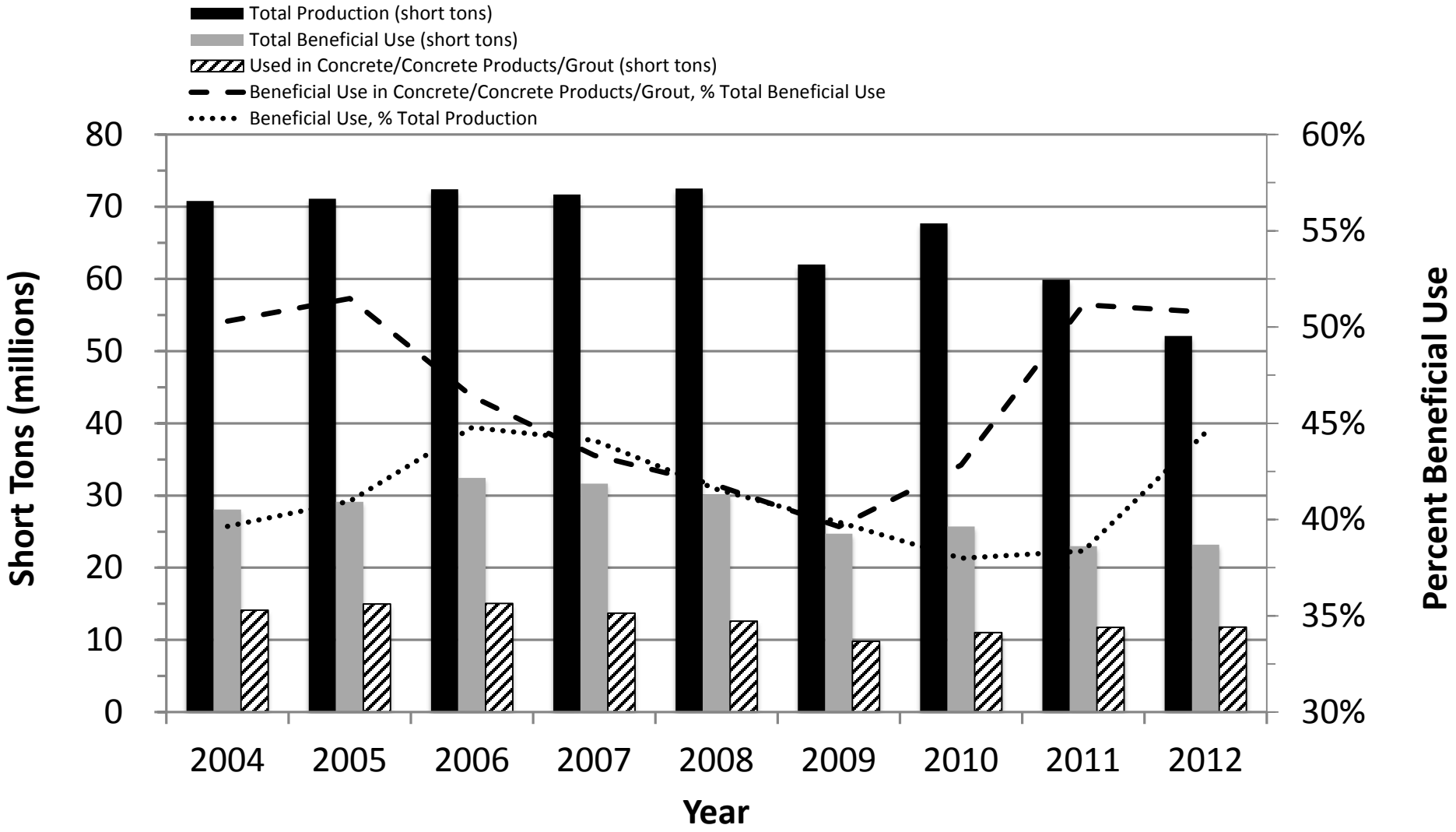

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NCHRP 18-13

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

NCHRP 18-13

- Characterization Study – evaluate existing specifications and classification methods for CFA
- Strength Test Study – investigate test methods for characterizing the strength activity of CFA
- 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 CFA to mitigate alkali-silica reaction in concrete

Characterization Study

- Gathered data on 100+ CFA sources
- Surveyed the SHAs to determine common sources used
- Selected 30 for comprehensive analysis
  - 17 Class F, 13 Class C
  - Selected sources from the 30 best suited for the other testing performed

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Summary of 30 Sources

- Sum of SiO_2, Al_2O_3, and Fe_2O_3: 51.8 to 92.7%
- Calcium oxide (CaO): 0.9 to 30.6%
- Na_2O_e: 0.3 to 7.9%.
- LOI: 0.1 to 5.6%
- Fineness: 10 to 24.0%
- Strength Index (7-day test value): 75 to 112%
- Strength Index (28-day test value): 80 to 120%
- Water requirement: 93 to 100%
- Density: 2.1 to 2.8g per cubic-centimeter

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Also made blends to achieve higher LOI

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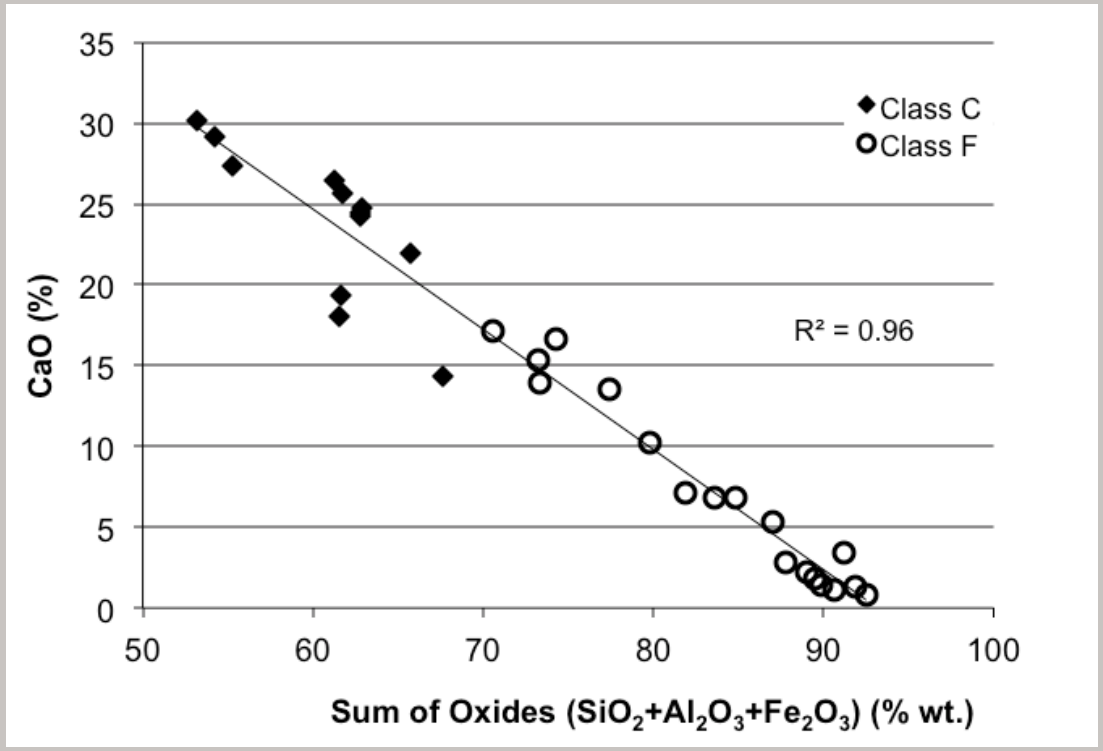
- Strength Index (7-day test value): 75 to 112%
- Strength Index (28-day test value): 80 to 120%
- Water requirement: 93 to 100%
- Density: 2.1 to 2.8g per cubic-centimeter

Characterization Study

- Characterized 30 sources using ASTM C311 methods
  - All AASHTO M 295 Required and Optional Chemical and Physical Properties
  - Pozzolanic Activity Index (PAI) using ASTM C311 methods
  - Qualitative XRD
- Quantitative XRD and TGA/DTA on 8 selected sources

Chemical Classification



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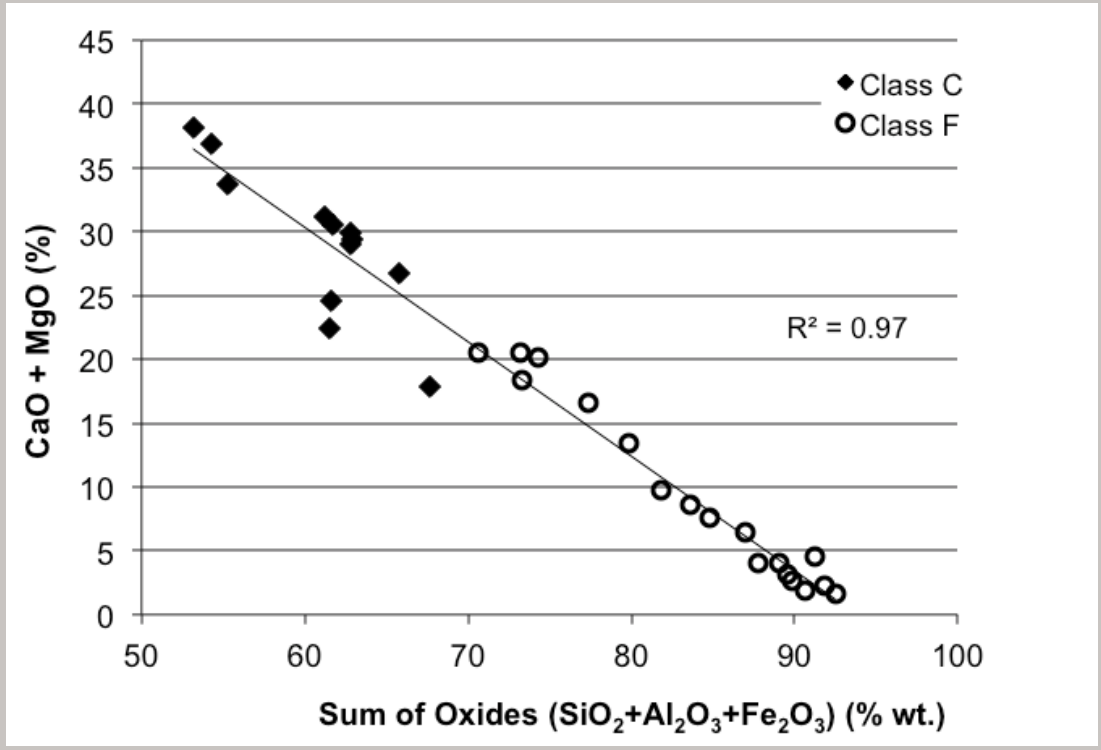

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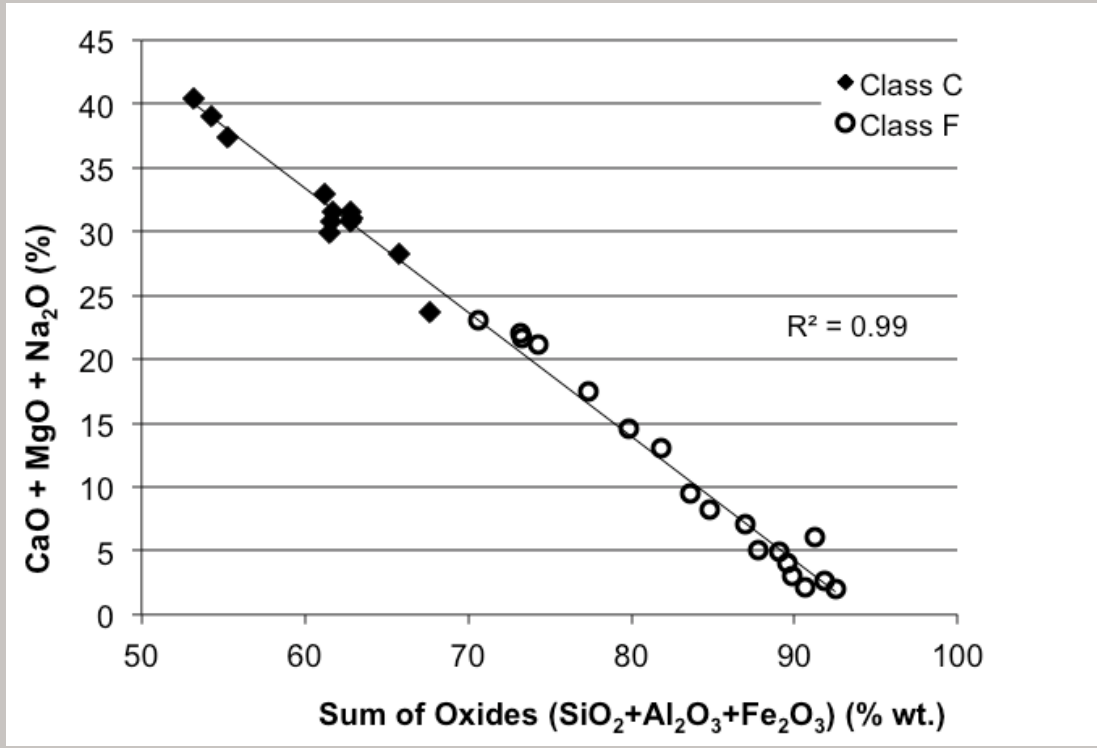

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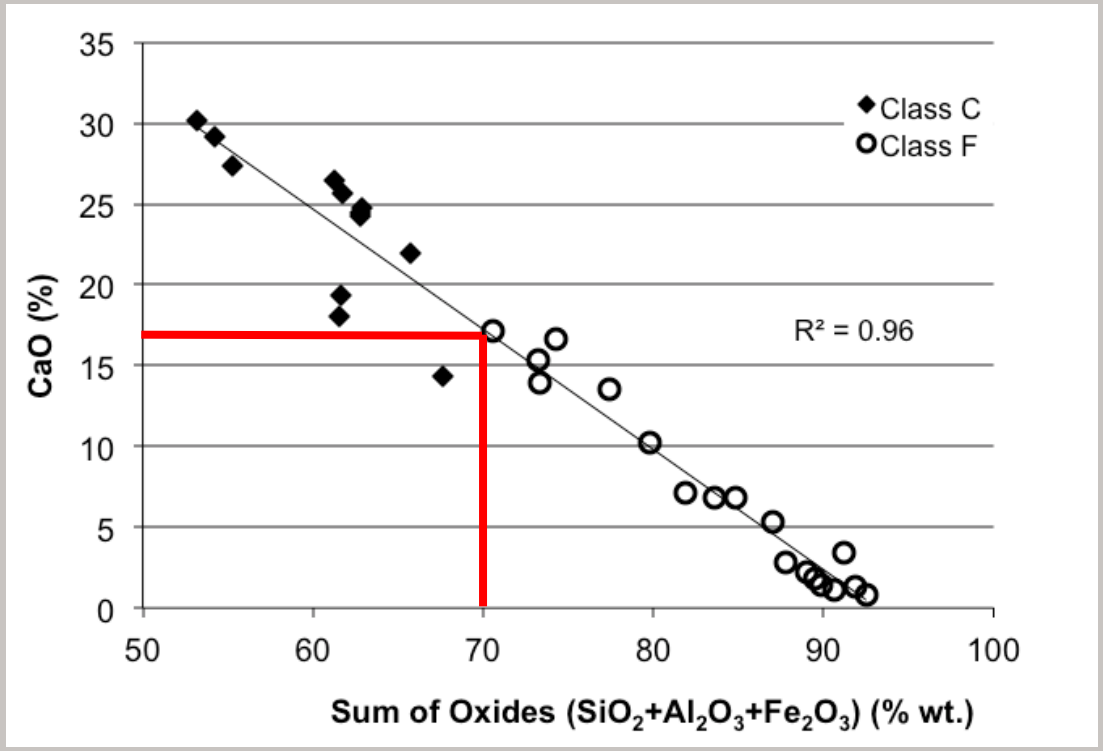
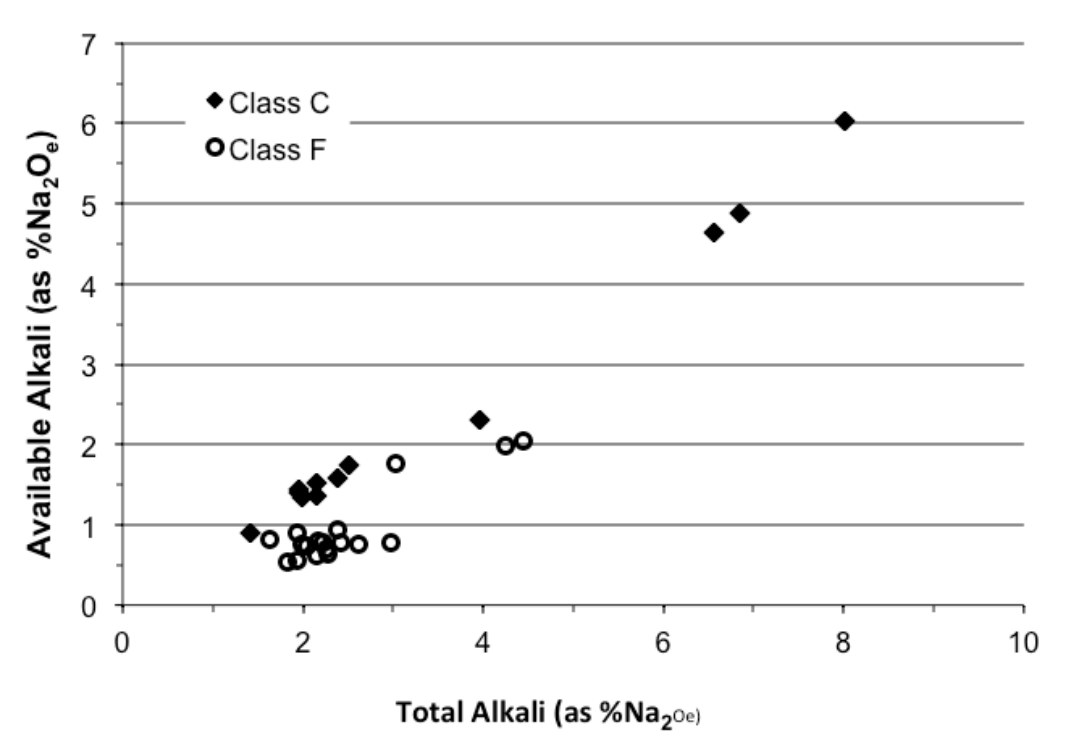


Available Alkali vs. Total Alkali



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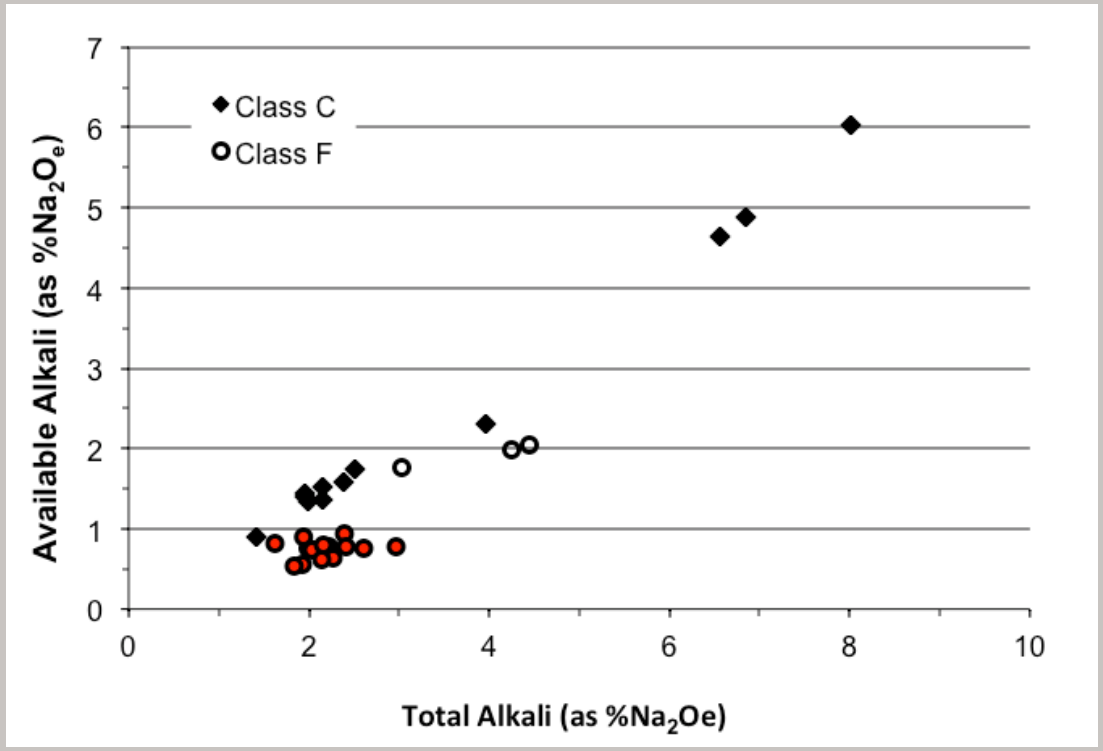
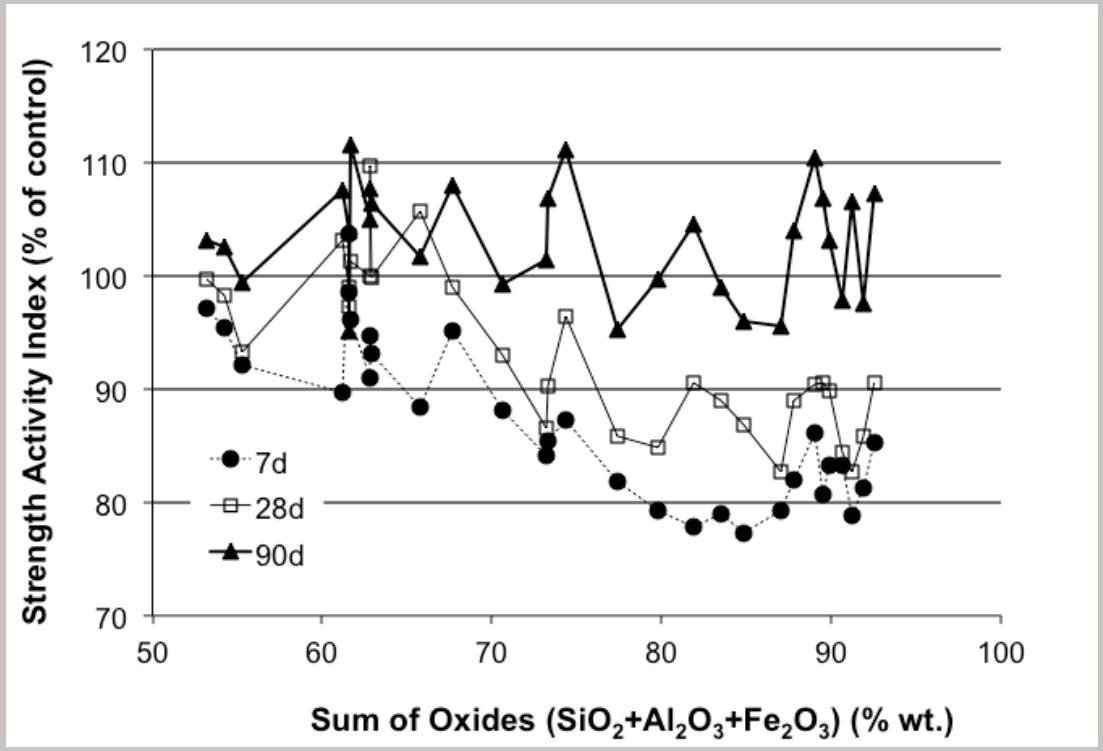


Strength Activity Index



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

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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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Keil Hydraulic Index

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

ID-% Replace.	KHI - 7 days (%)			KHI - 28 days (%)			KHI - 56 days (%)		
	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

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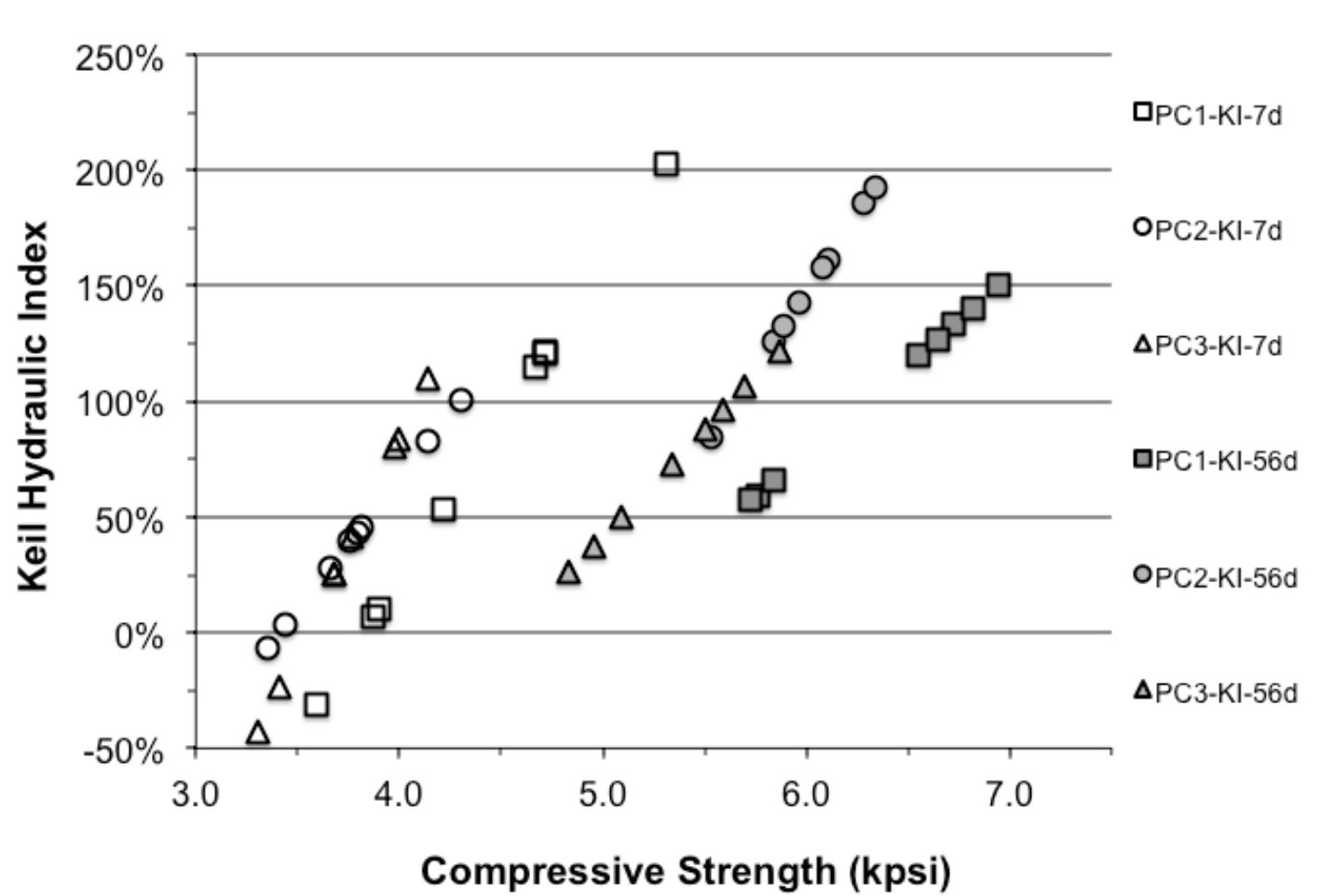
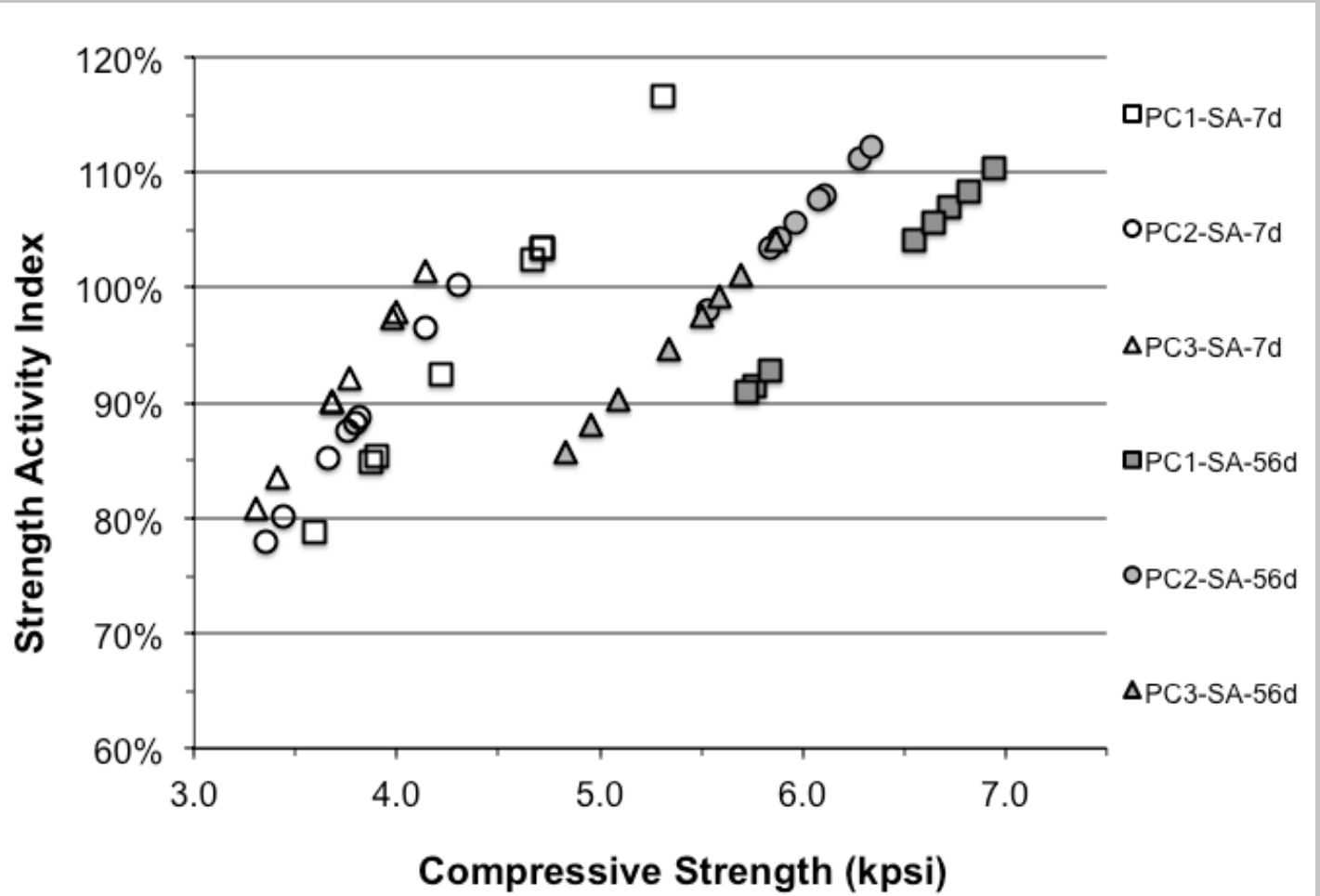


Strength Activity Index



Strength Test Study

- *Take Aways*
  - The Keil Hydraulic Index provided a test that identified strength contribution separate from “filler” effects
  - The test was sensitive to the cement used
  - Other evaluations of the existing strength activity index showed increasing the specification limit to 85% eliminated inert materials
  - Need to change the time required for testing to accomdate some Class F ash

Carbon Effects on Air Entrainment Study

- *Effect of Carbon on Air Entrainment*
  - The LOI test is adequate for estimating the total carbon but does not adequately identify if the carbon will effect air entrainment
  - There is a need for a test to directly determine adsorption capacity
  - The foam index test is useful at determining the interaction of the fly ash with air entrainment admixtures but has not been standardized and is not part of AASHTO M 295 or ASTM C311

Carbon Effects on Air Entrainment Study

- Four tests evaluated:
  - Foam Drainage
  - Foam Index
  - Direct Adsorption Isotherm
  - Coal Fly Ash Iodine Number

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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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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)

Foam Index Test

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- Add AEA solution drop-wise
  - 5 % vol. AEA / Water solution
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- Shaken, not stirred

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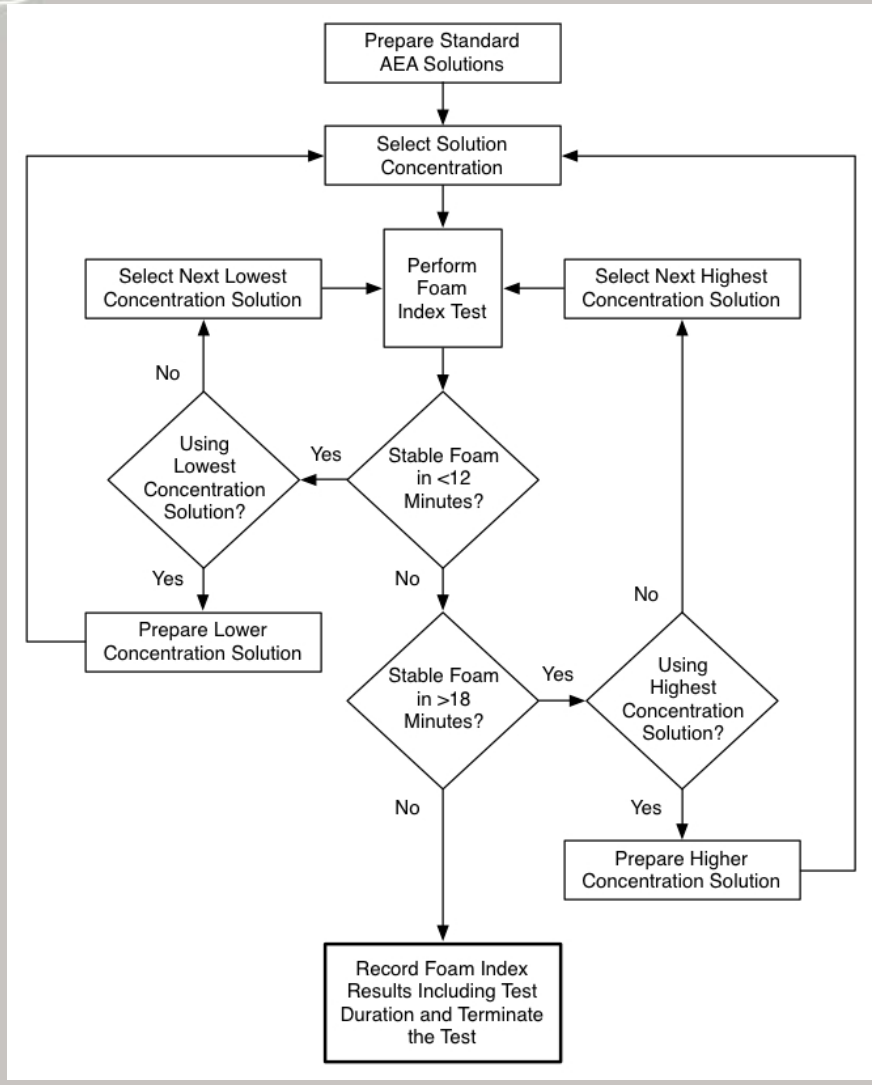
- 2 g ash, 8 g cement
- 25 mL water
- Add AEA solution drop-wise
  - 5 % vol. AEA / Water solution
  - (0.02 mL/drop)
- Shaken, not stirred
- Look for a stable foam
- Repeat…

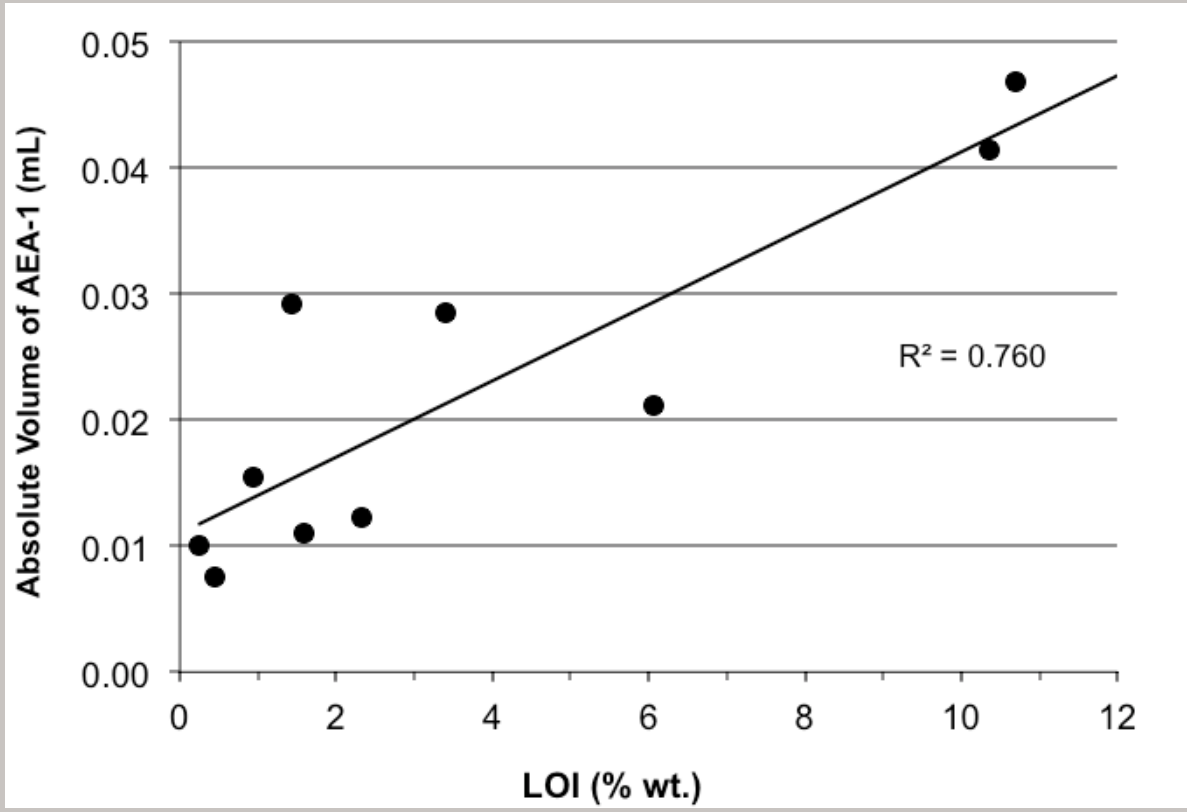
Foam Index Test

- Vary Solution Strength
  - 2, 6, 10, 15 %vol. AEA
- Achieve uniform contact time
  - 12 to 18 minutes
- Determine total AEA added
  - Foam Index



Foam Index Test

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



Adsorption Based Tests

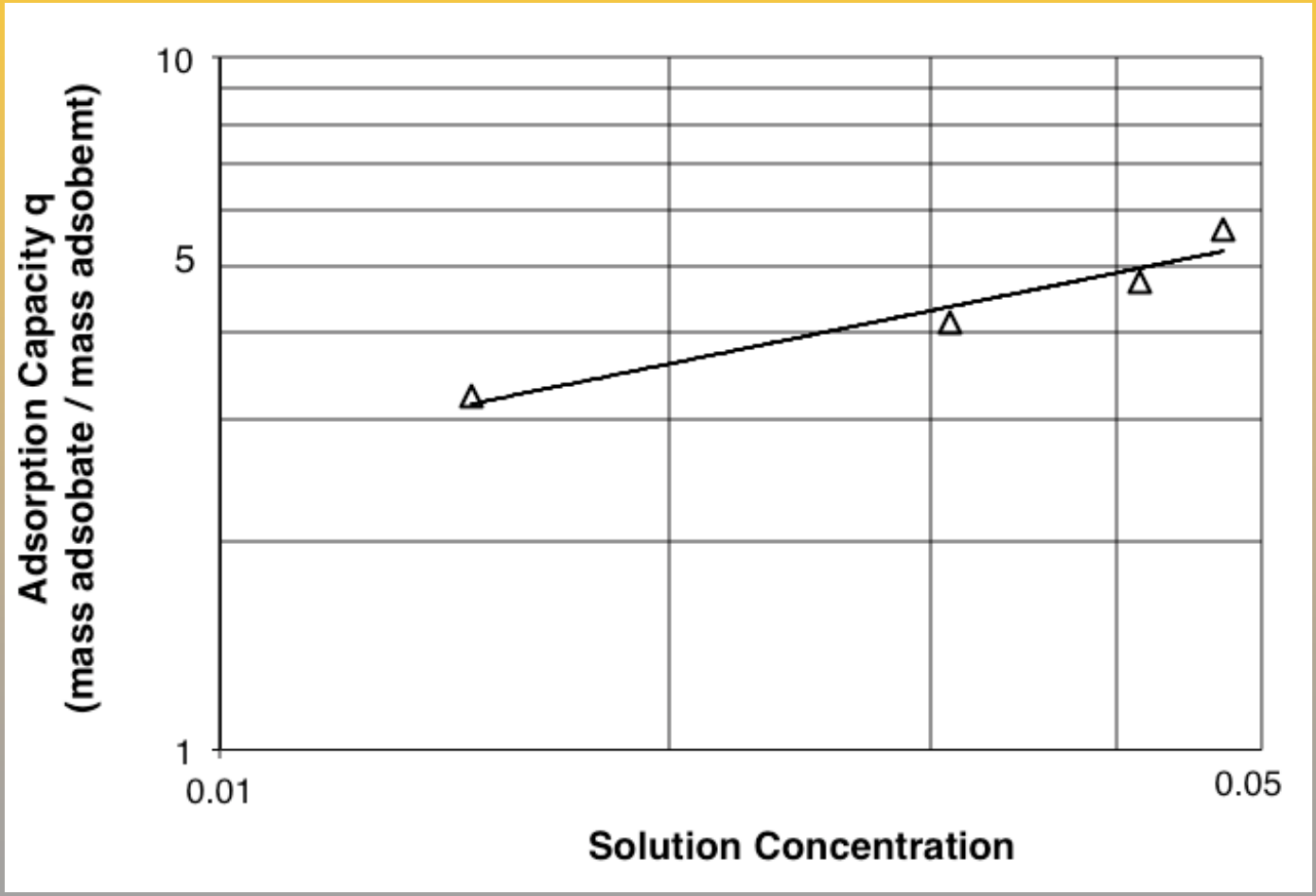
- Adsorption characterized by an adsorption isotherm
- Multiple adsorption models and isotherms
- Freundlich Isotherm

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

  - 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

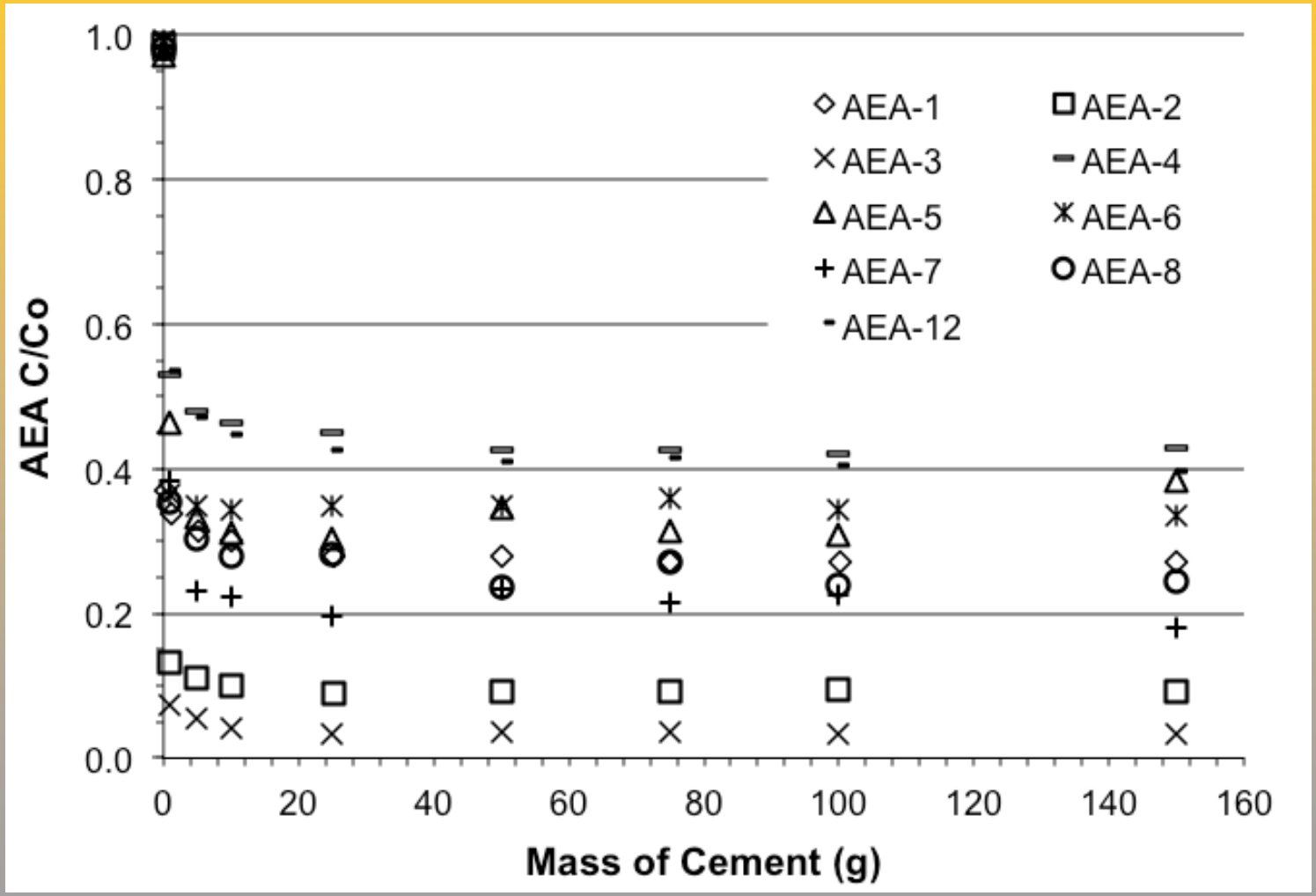
Designation: D3860 – 98 (Reapproved 2008)

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

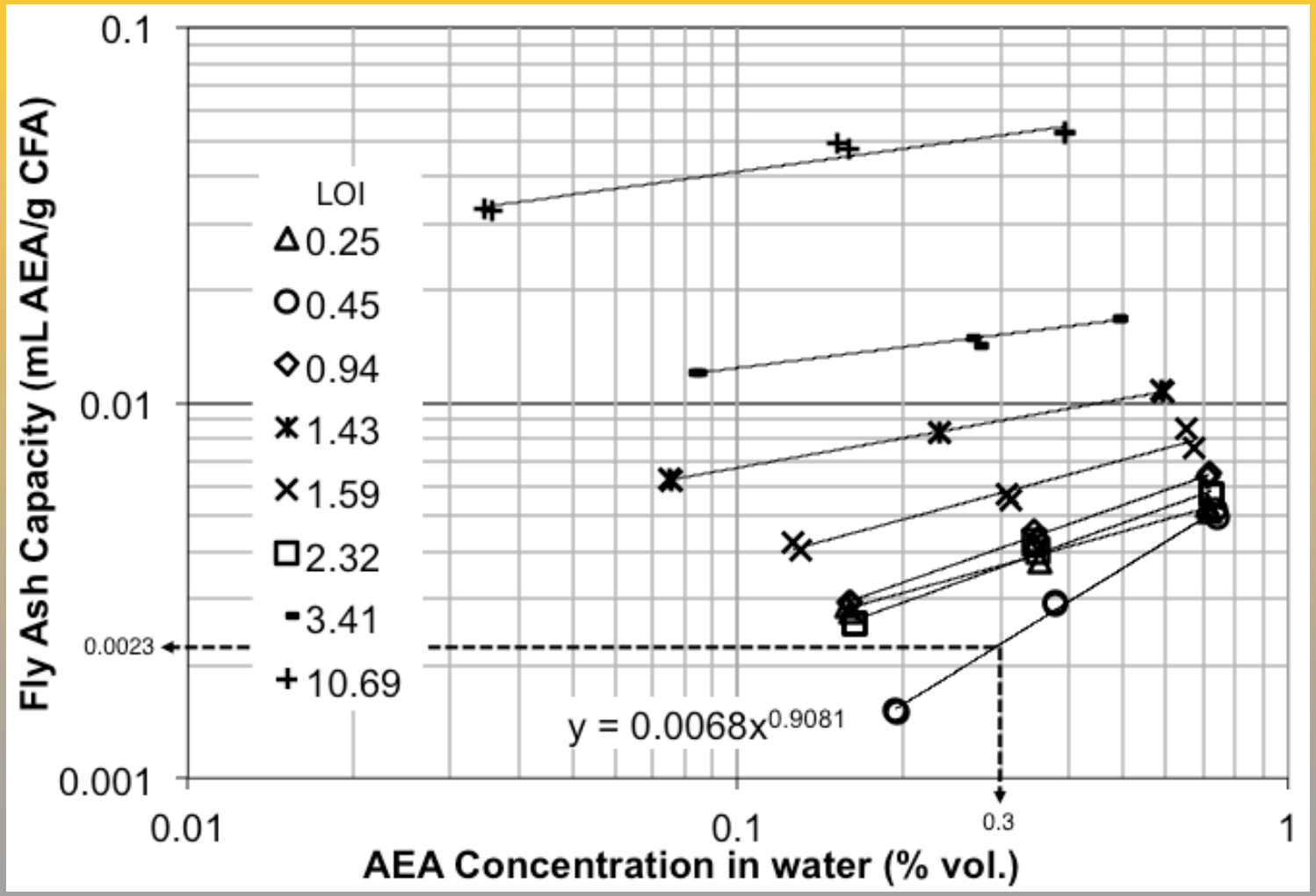
Direct Adsorption Isotherm

Cement Effect



Direct Adsorption Isotherm

determines AEA adsorption "capacity"

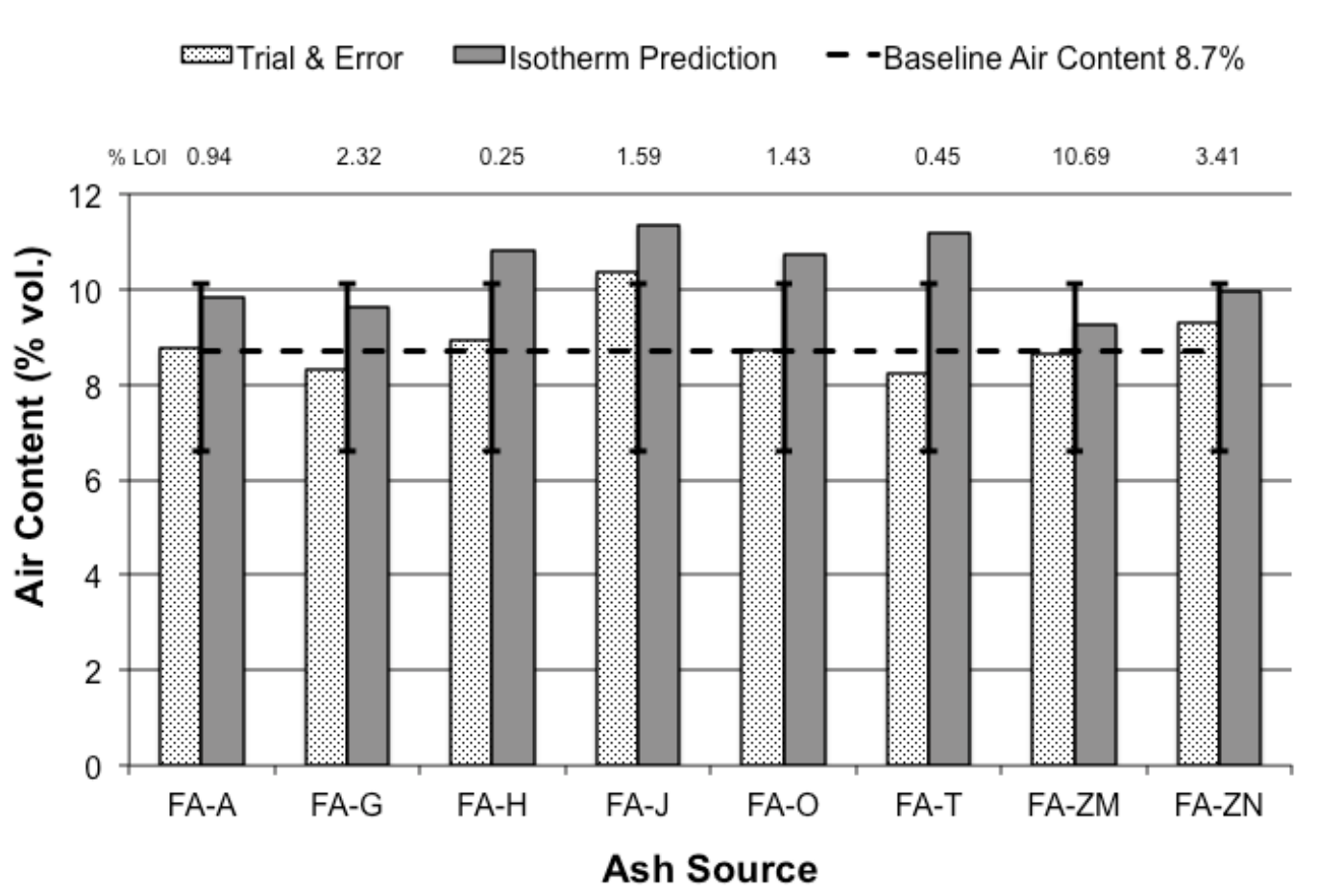


Direct Adsorption Isotherm

- 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

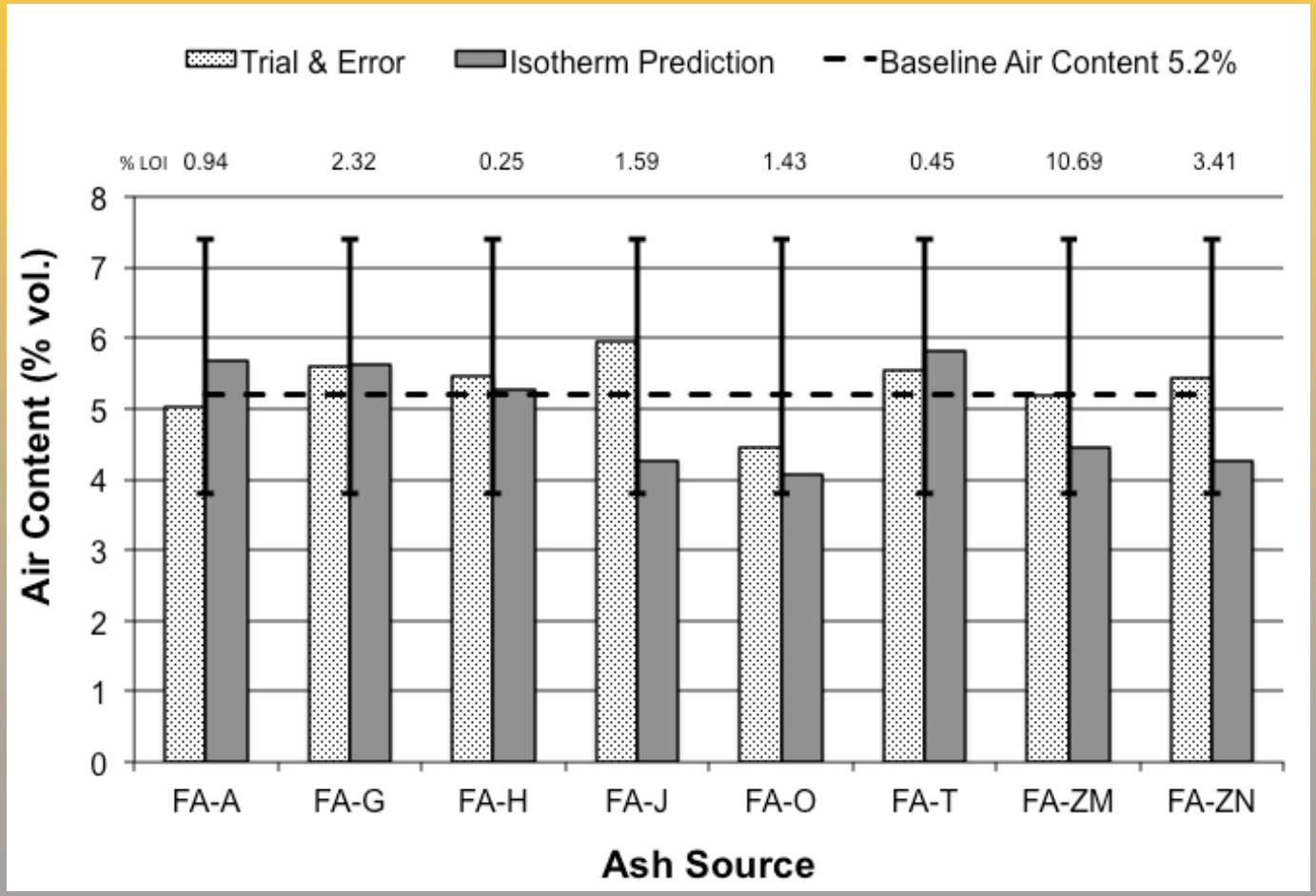
Direct Adsorption Isotherm

Vinsol resin



Direct Adsorption Isotherm

Alpha olephin sulfonate



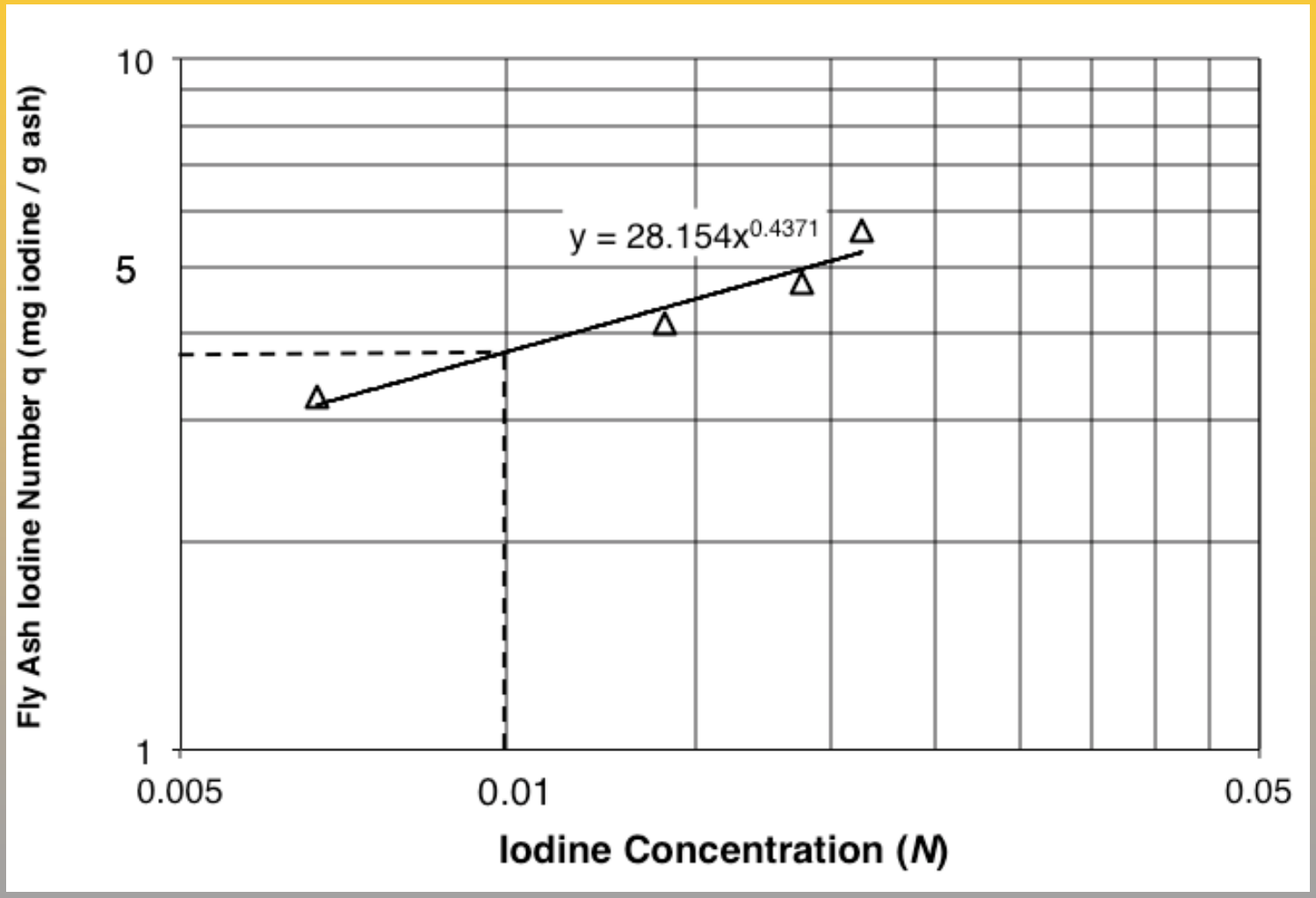
Coal Fly Ash Iodine Number

Designation: D4607 – 94 (Reapproved 2006)

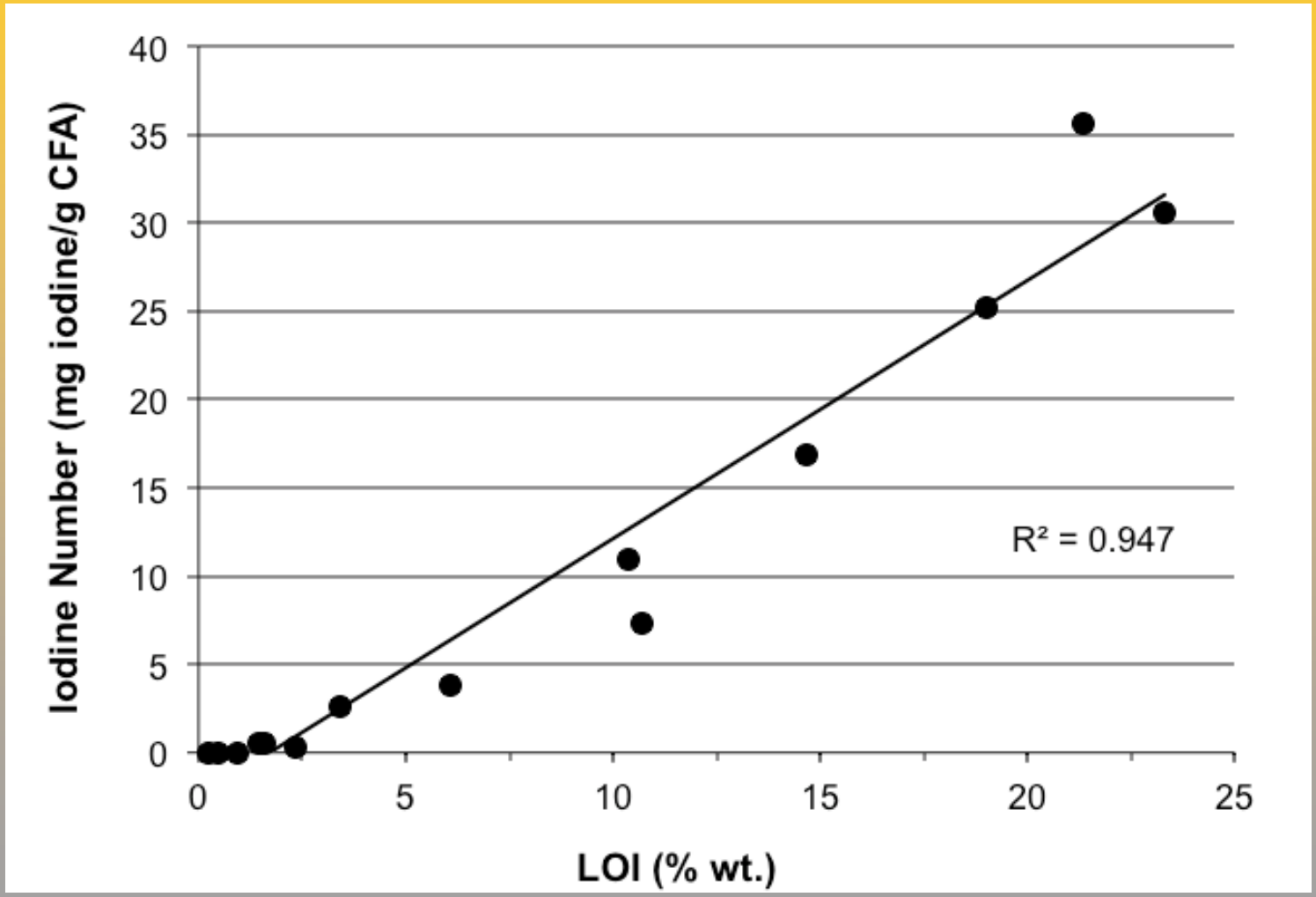
Standard Test Method for
Determination of Iodine Number of Activated Carbon[1]

- 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)

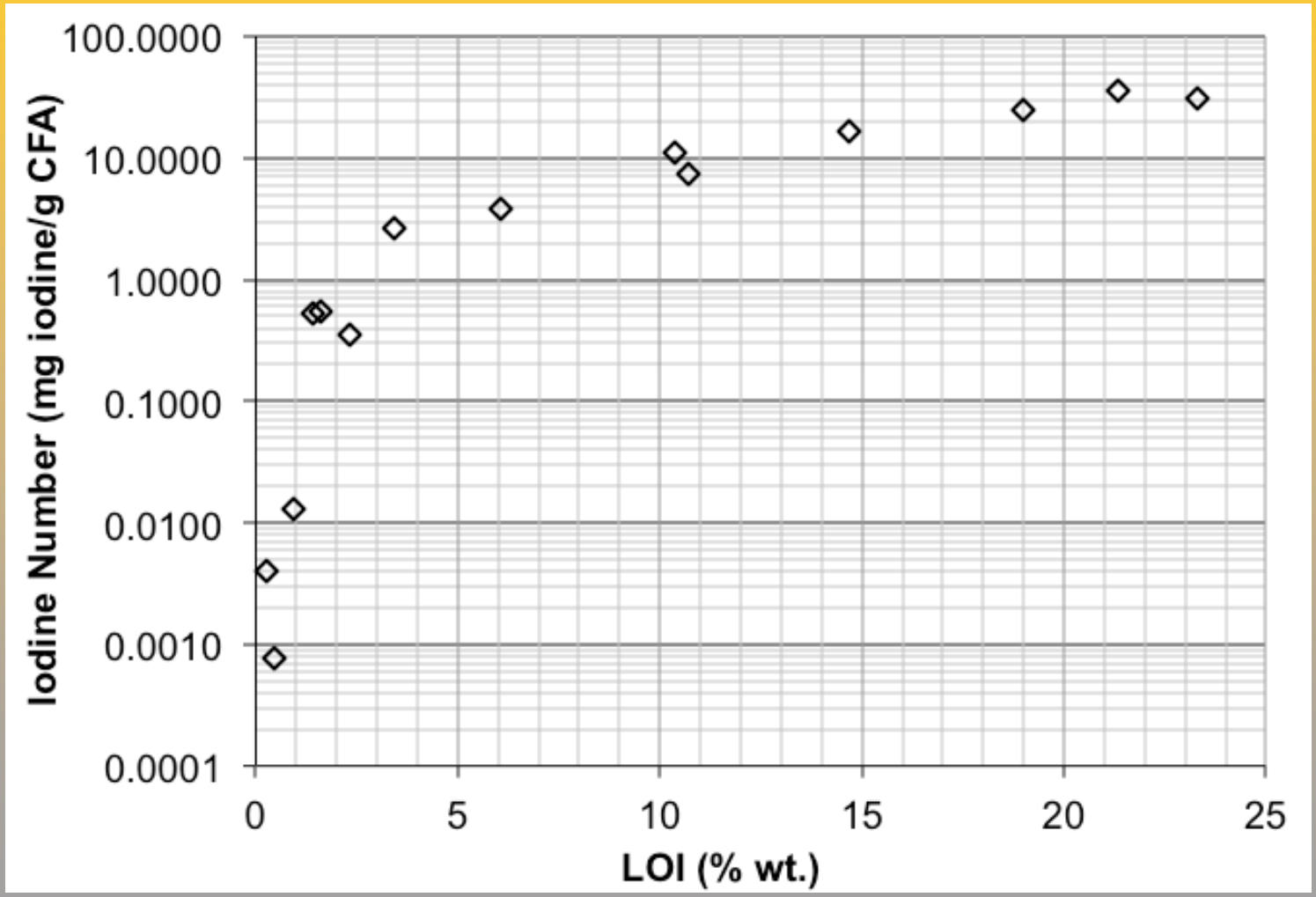
Coal Fly Ash Iodine Number



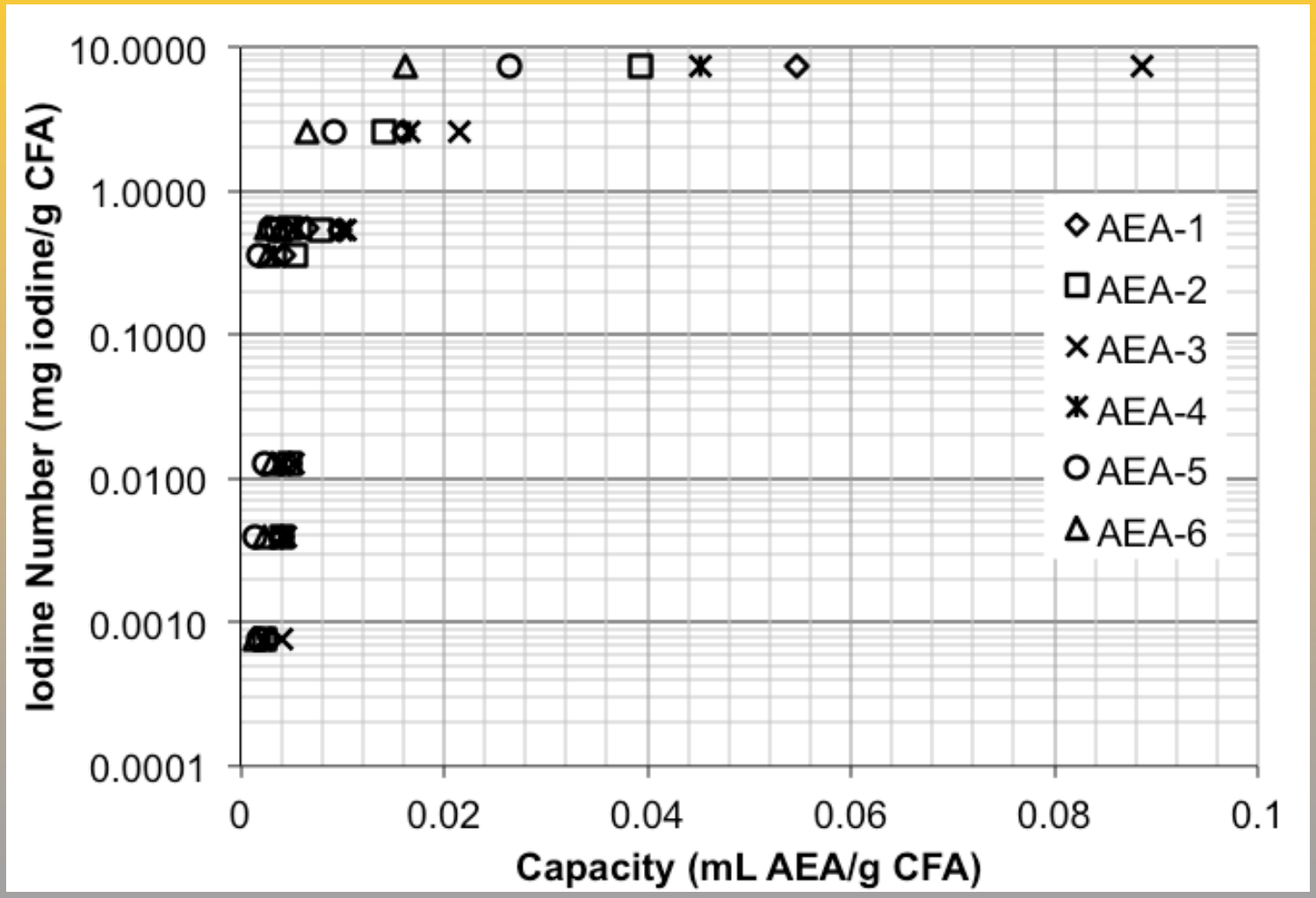
Coal Fly Ash Iodine Number



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

CHANGES SINCE REPORT

- Issues with filtration after acidification
  - Switched to nitric acid rather than hydrochloric
- Seeking faster version
  - Adopted single point isotherm based on ASTM D1510

Designation: D1510 – 13

Standard Test Method for Carbon Black—Iodine Adsorption Number[1]

CHANGES SINCE REPORT

- Issues with filtration after acidification
  - Switched to nitric acid rather than hydrochloric
- Seeking faster version
  - Adopted single point isotherm based on ASTM D1510
- New method published in Wisconsin Highway Research Program Report WHRP 0092-12-04

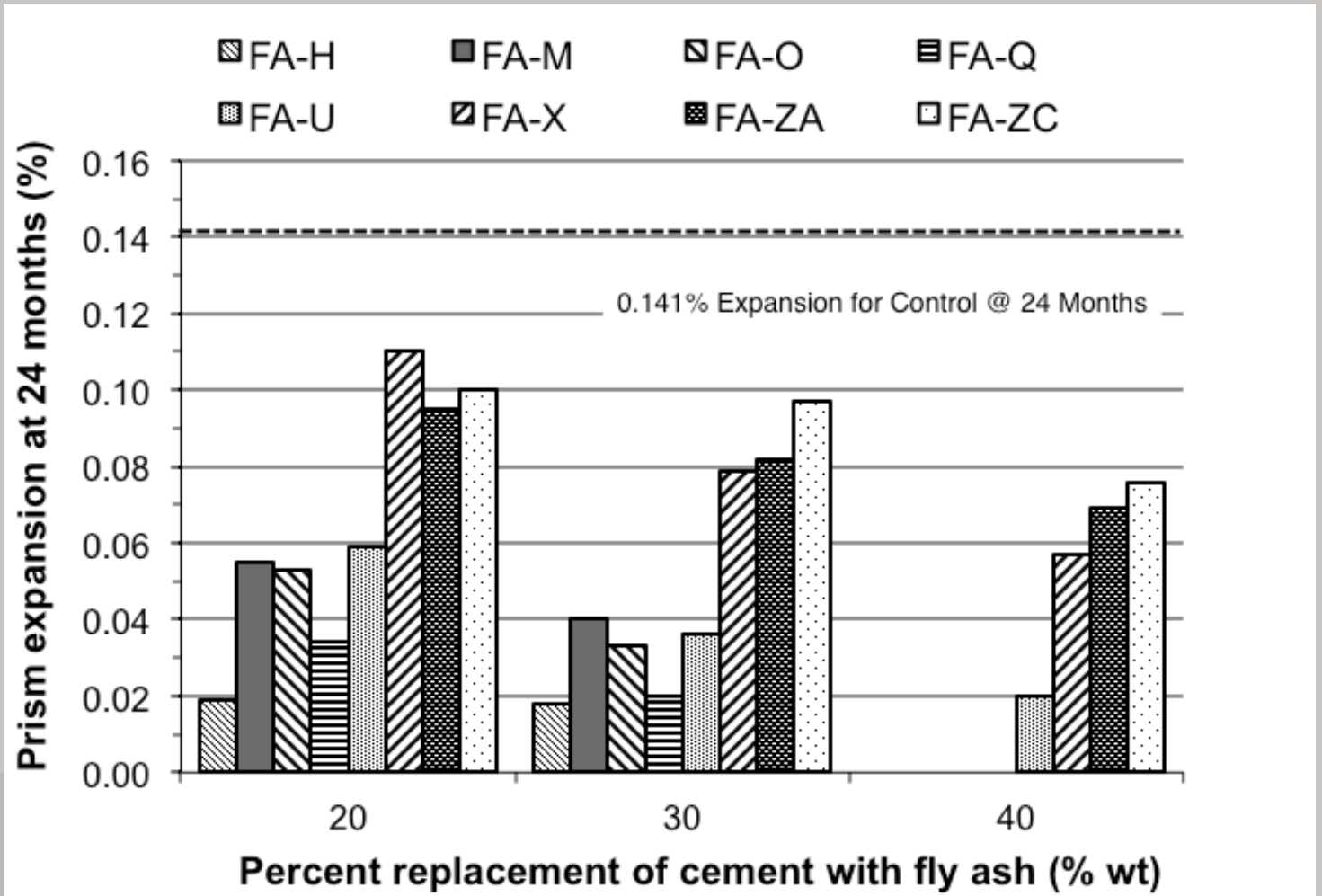
Carbon Effects on Air Entrainment Study

- *Take Aways*
  - Publish a standardized version of the foam index test that provides a uniform test time and mechanical agitation
  - Specify use of the the coal fly ash iodine number to evaluate ash adsorption potential
  - Specify use of the direct adsorption isotherm test to evaluate fly ash – air entrainer combinations

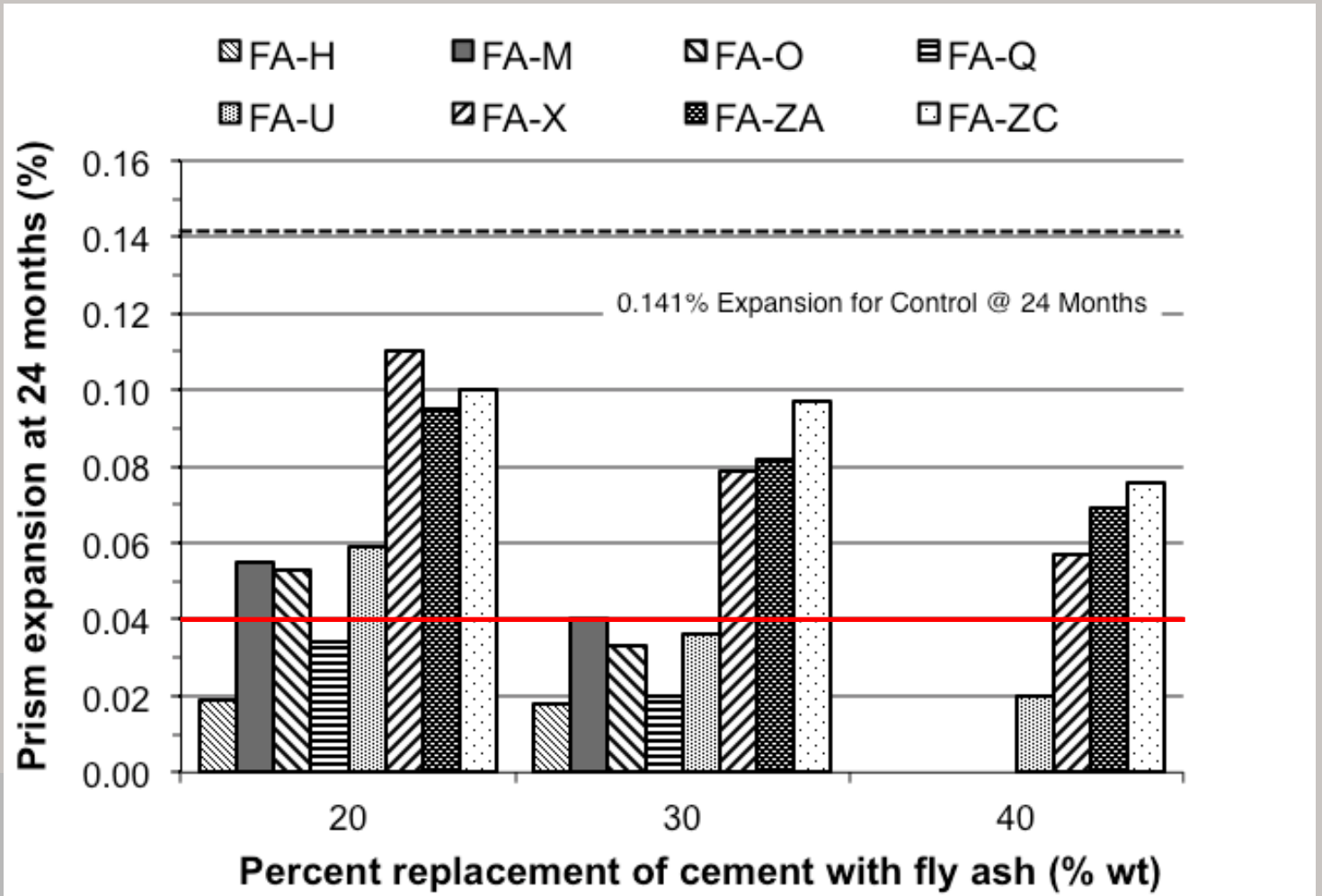
ASR Mitigation Study

- Evaluate protocols for applying existing test methods (ASTM C1567 and ASTM C1293)
- Evaluate the Alkali Leaching Test (Shehata and Thomas, 2006) and correlate with the results of ASTM C1293 and ASTM C1567
  - The alkali leaching test is used to determine the free alkalis available to be leached from a particular combination of cement and fly ash

ASTM C1293


FA-H
FA-M
FA-O
FA-Q
FA-U
FA-X
FA-ZA
FA-ZC
0.141% Expansion for Control @ 24 Months
Prism expansion at 24 months (%)
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
20
30
40
Percent replacement of cement with fly ash (% wt)

ASTM C1293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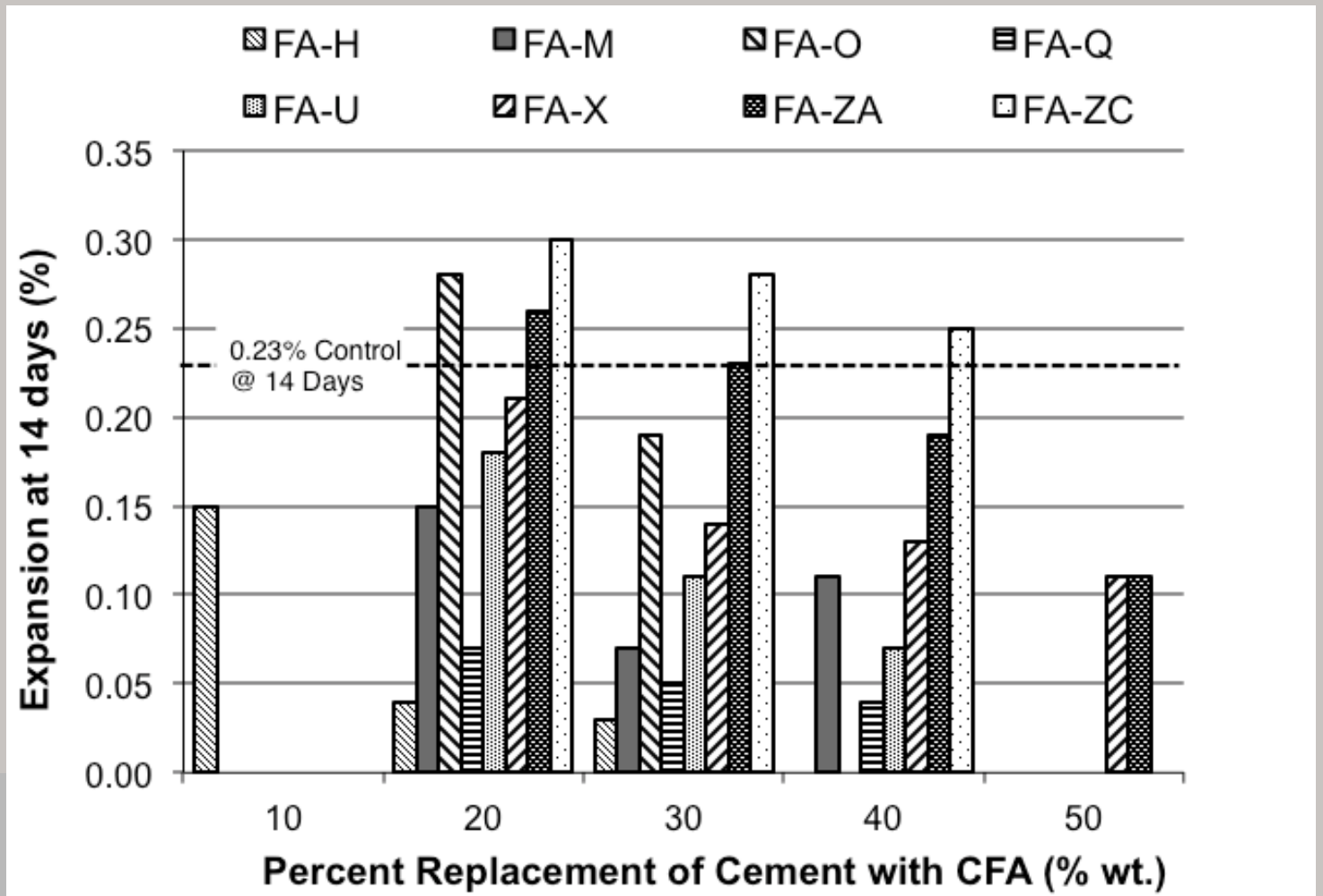
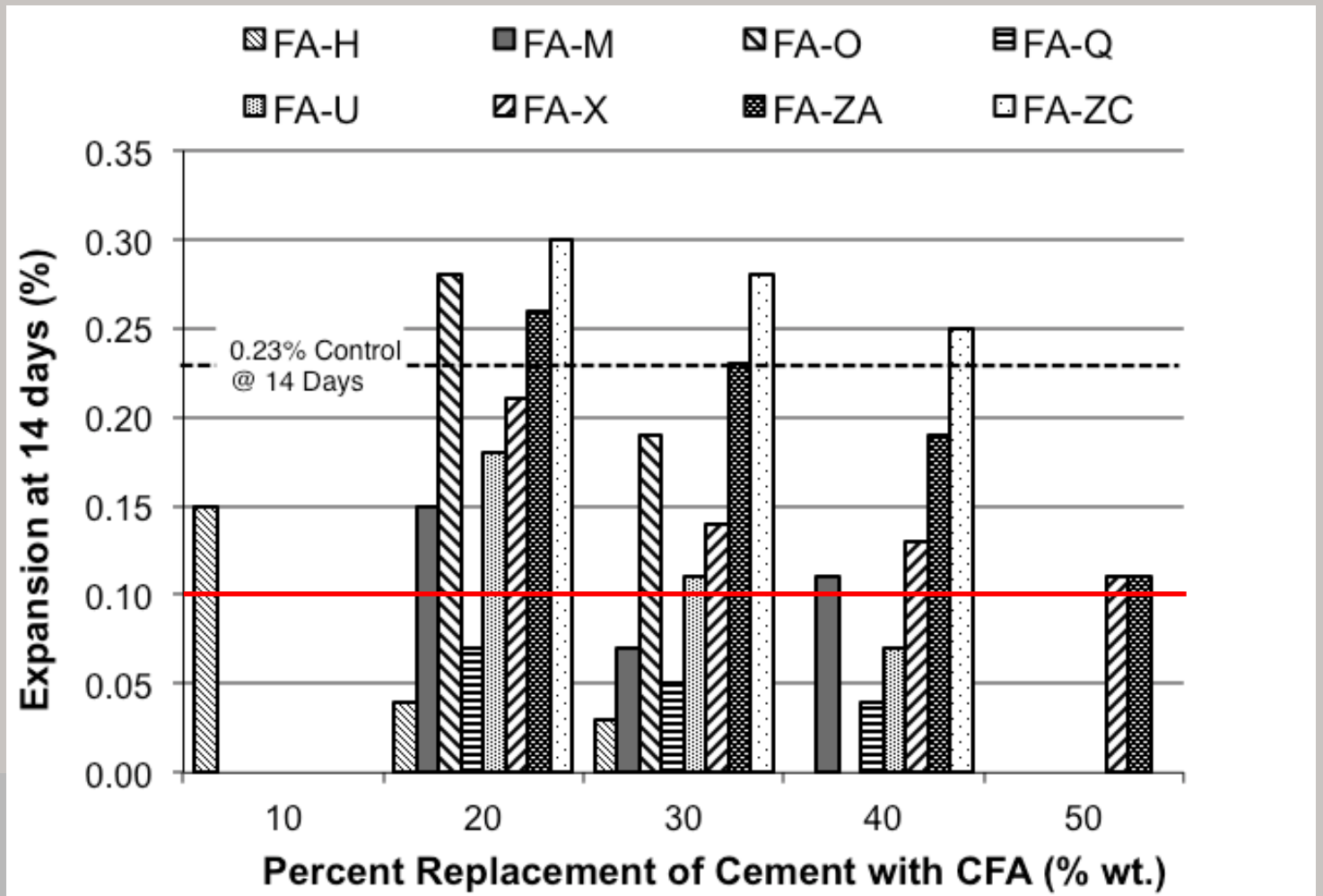
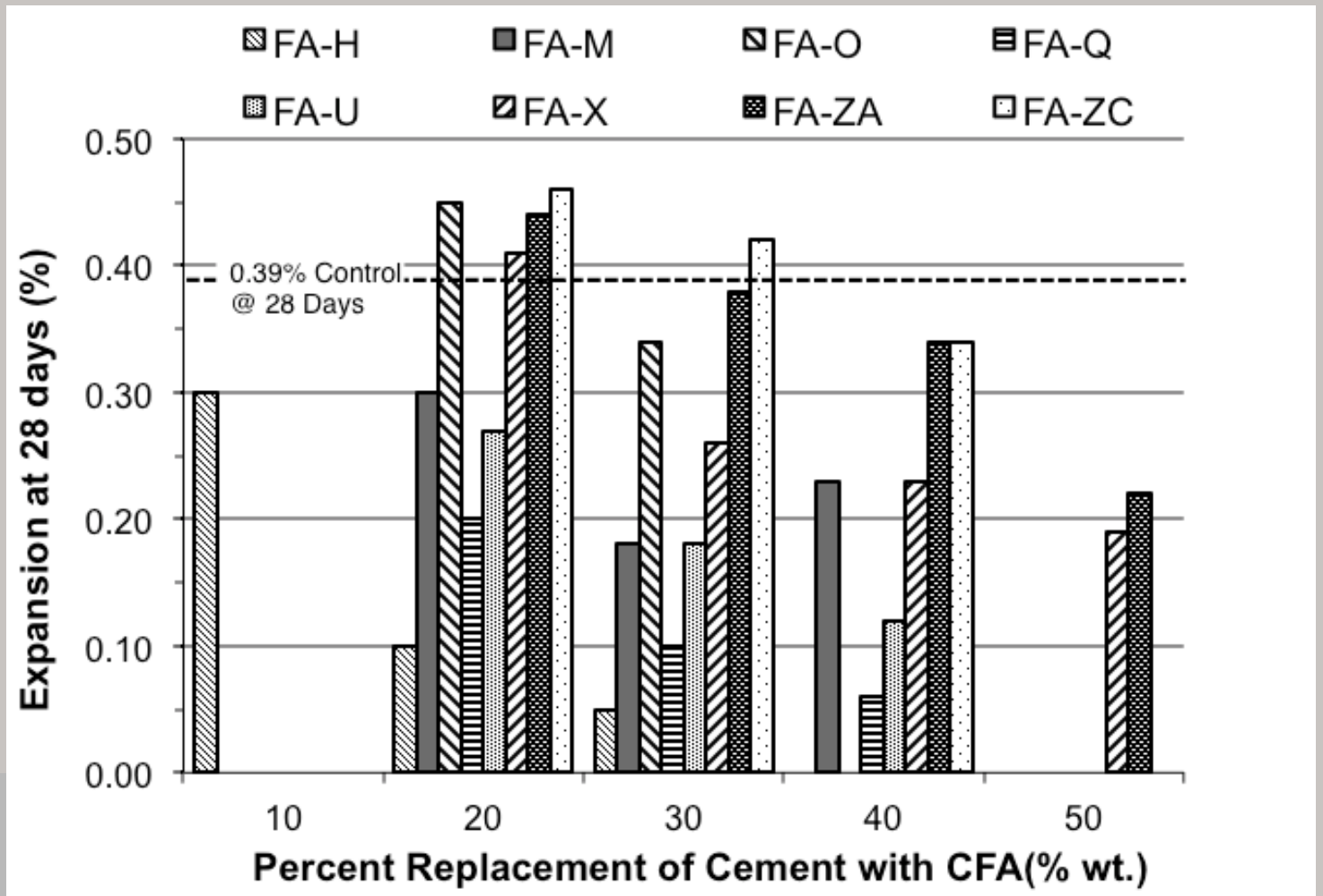
ASTM C1567 – 14 days



ASTM C1567 – 14 days



ASTM C1567 – 28 days



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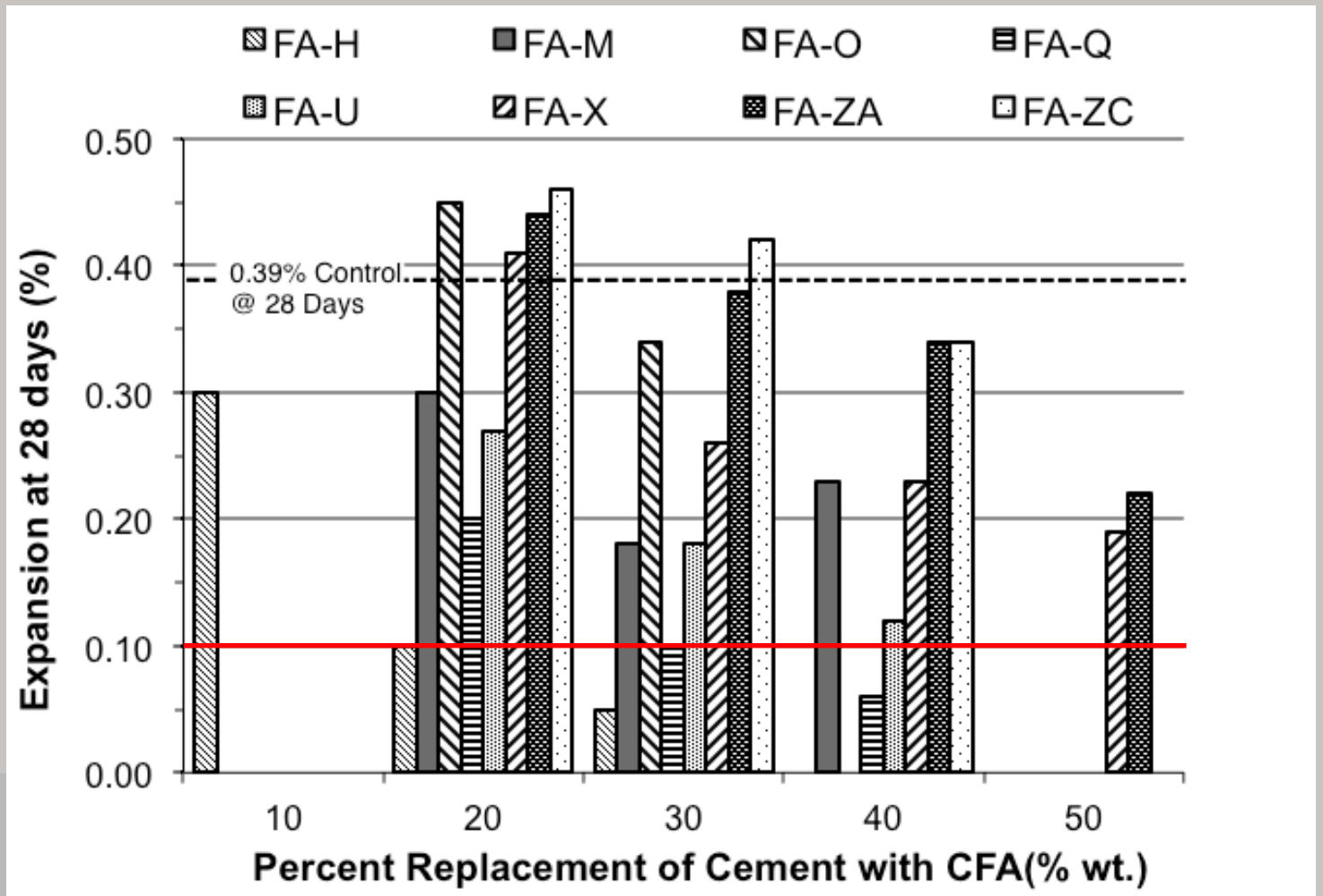
ASTM C1567 – 28 days



ASR Mitigation Study

- *Take Aways*
  - Confirmed the AASHTO PP-65 limits of 0.1% expansion @ 14 days for ASTM C1567
  - Provided data showing a 28-day limit on ASTM C1567 does not correlate with ASTM C1293
  - Alkali Leaching Test – no clear threshold of alkali release was identified that correlated with a 0.04% ASTM C1293 expansion

Recommended Changes to AASHTO M 295

- Add a maximum sum of the oxide limit (i.e., 70%) to the Class C classification
- Report CaO, MgO, Na_2O, and K_2O
- Adopt the use of the Iodine Number Test and the Direct Adsorption Isotherm Test under Optional Chemical Requirements

Recommended Changes to AASHTO M 295

- Raise the the Strength Activity Index to 85% of control BUT allow the material to be qualified at 7, 28, **OR** 56 days
- Delete the available alkali limit
- Delete use of ASTM C441 (Pyrex Glass Test) and adopt ASTM C1567 with a 14 day limit of 0.1%

Actions at ASTM

- Modifications to ASTM C311 LOI test and density test
- Adopt modified versions of the ASTM D3860, ASTM D1510, and the Foam Index Test
- Changes in fly ash definition
- Broad changes in fly ash characterization


I NEED YOU TO MAKE A POWERPOINT DECK FOR MY MEETING WITH INVESTORS.


DilbertCartoonist@gmail.com
Dilbert.com


I'LL BE TELLING THEM EVERYTHING I KNOW ABOUT TECHNOLOGY, COMPETITION, AND THE INDUSTRY.
SO . . . JUST THE ONE SLIDE?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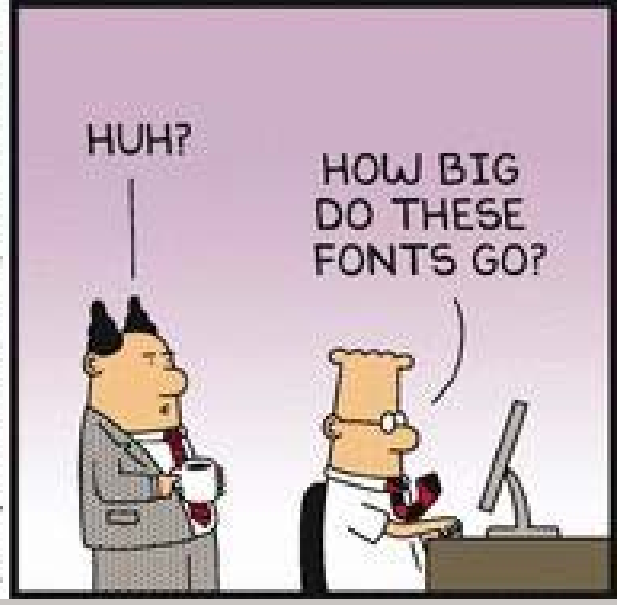
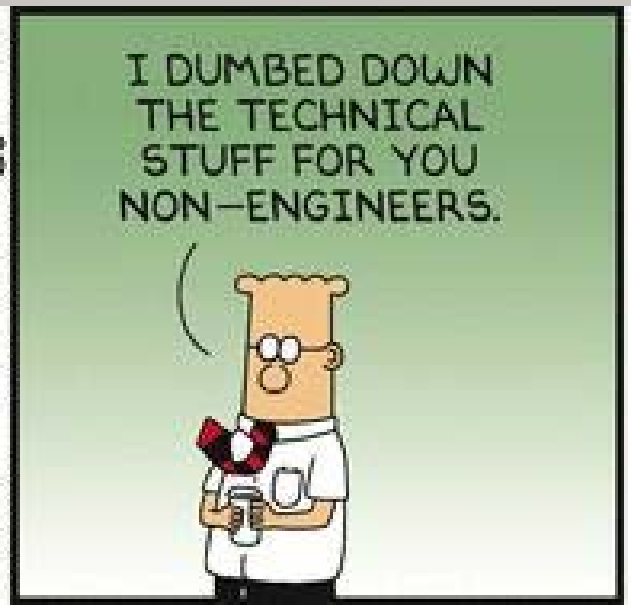

HUH?
HOW BIG DO THESE FONTS GO?

Questions?


I EMAILED YOU THE POWERPOINT SLIDE FOR YOUR INVESTOR MEETING.


DilbertCartoonist@gmail.com
Dilbert.com


I DUMBED DOWN THE TECHNICAL STUFF FOR YOU NON-ENGINEERS.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"TECH-NOLOGY: IT BE GOOD."
I WOULDN'T TAKE QUESTIONS.