TTCC/NCC Conference
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Practical Semi-Adiabatic Calorimetry for Concrete Mixture Evaluation

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Definitions

- **calorimetry** cal·o·rim·e·try (kăl'ə-rĭm'ĭ-trē) *n.* –

  Measurement of the amount of heat evolved or absorbed in a chemical reaction, change of state, or formation of a solution.

- **adiabatic** adi·a·bat·ic (ā-dē-ə-ba-tik), *adj.* –

  Occurring without loss or gain of heat.

For our purposes:

- **semi-adiabatic calorimetry**, *n.* –

  Indication of the heat evolved from a cementitious mixture hydrating in an environment or container having some thermal insulation properties, according to a record of the mixture's changing temperatures over time.

Background

Compounds in portland cement clinker

Compounds responsible for most of the heat evolved during the first 24 hours of hydration

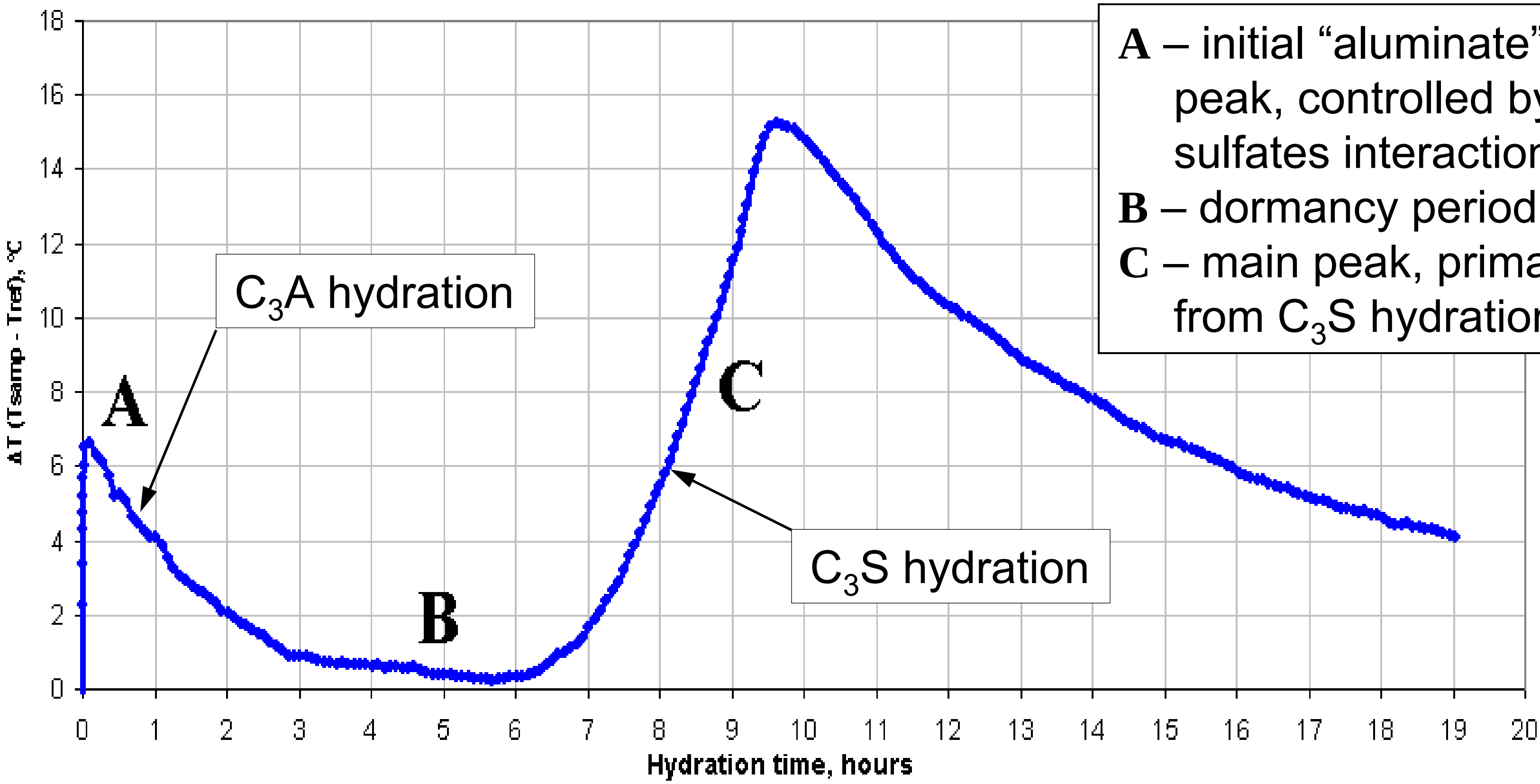
C_3S = $3CaO \cdot SiO_2$
(Tricalcium silicate)

C_2S = $2CaO \cdot SiO_2$
(Dicalcium silicate)

C_3A = $3CaO \cdot Al_2O_3$
(Tricalcium aluminate)

C_4AF = $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$
(Tetracalcium aluminoferrite)

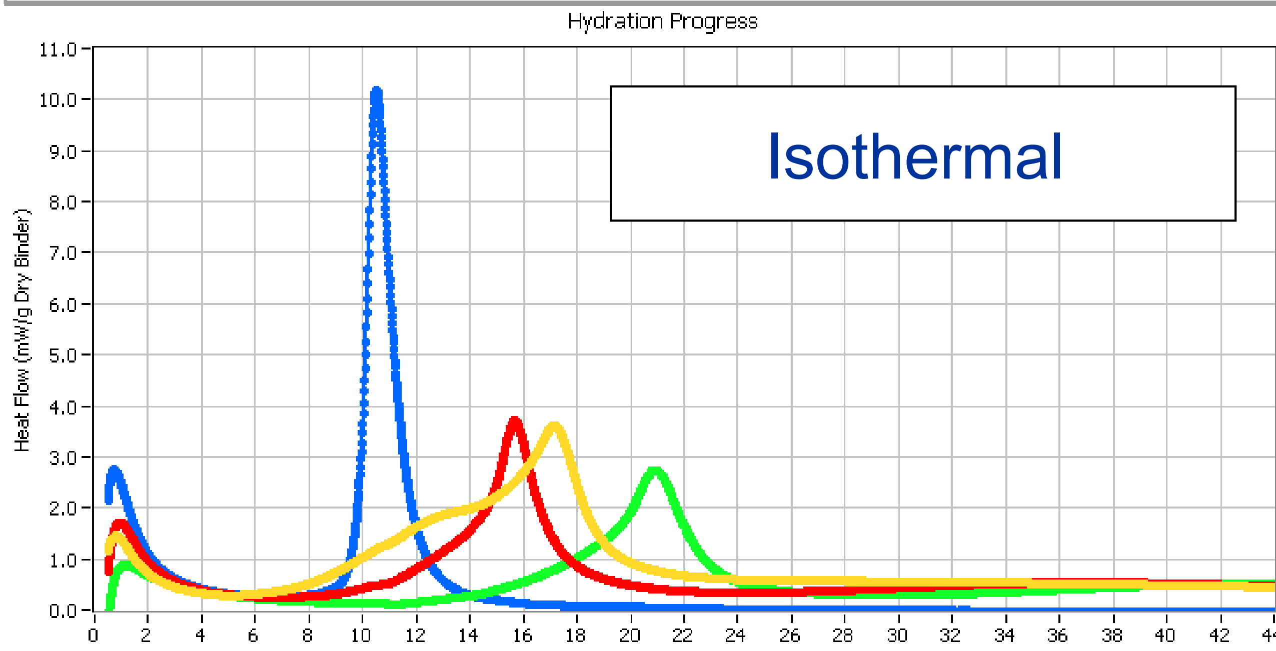
Background – C_3A and C_3S hydration

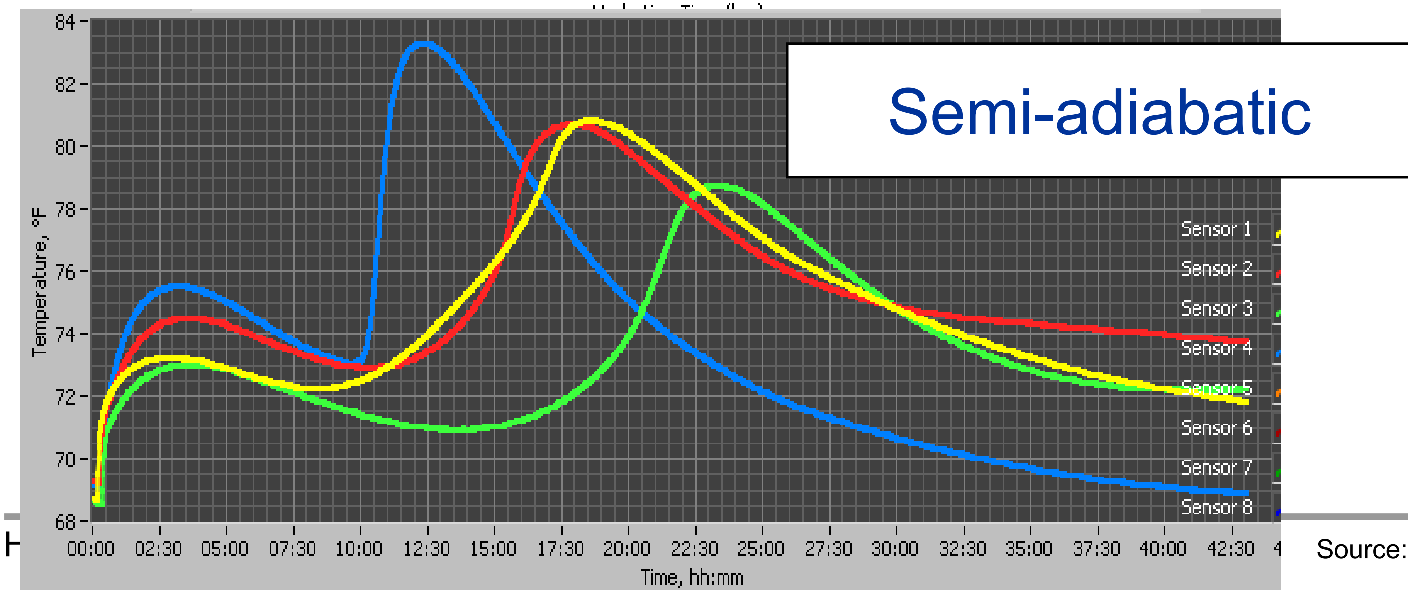


A – initial "aluminate" peak, controlled by sulfates interaction
B – dormancy period
C – main peak, primarily from C_3S hydration

The amount and timing of evolved heat during hydration are influenced by such factors as cement chemistry, mix temps, interaction of admixtures, sample mass effects, etc.

Isothermal versus semi-adiabatic calorimetry





Source: W. R. Grace

Isothermal versus semi-adiabatic calorimetry

- Isothermal calorimetry is usually preferred when quantitative results are needed

- Semi-adiabatic calorimetry:
  - Value is generally in comparative data
  - Simpler, less expensive equipment
  - Results are affected by certain variables
  - Useful in the field or the lab

Applications of semi-adiabatic calorimetry

- Comparing set time effects & hydration efficiency
  - Different admixtures, SCMs or cements
  - Sensitivity of admix dose, SCM replacement rate
  - Effects of mix temperature
- Troubleshooting concrete field problems
  - “Incompatibility” (sulfate balance) influences
  - Set time & other early hydration issues
- Cement production QC – optimizing sulfates content
- Coming soon – alternative time of set (C 403) method

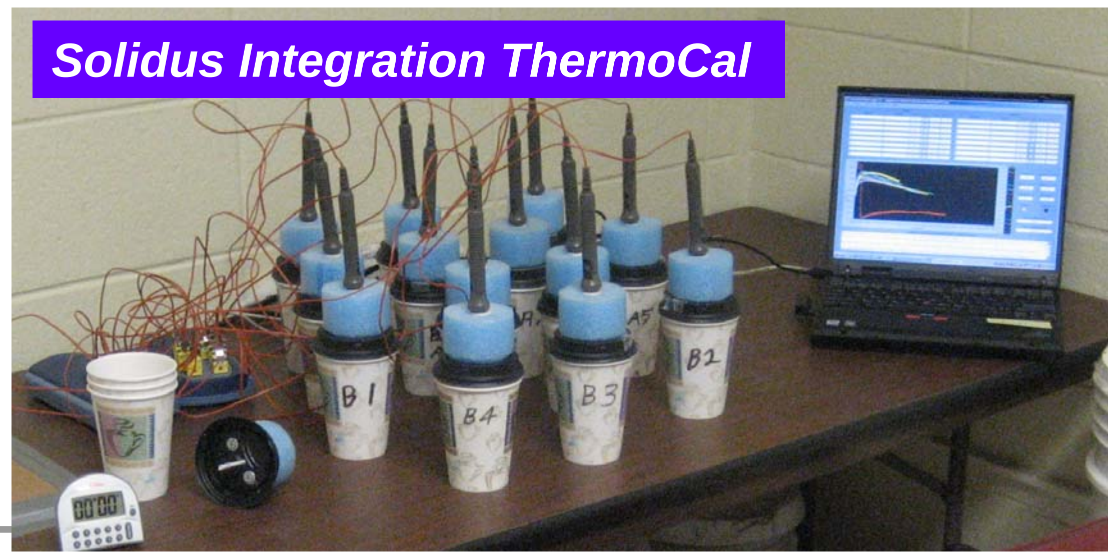
Measuring & recording temperature changes

Tipped Probe (Available in 1.5 meter and 3.0 meter cable length)
A tipped 150mm length 5mm OD 316 stainless probe with no handle. Probe and Cable are FDA food rated.
Each probe comes with a 1.5 Meter or 3.0 Meter length cable terminated with an MCX plug for input into the LogTag TREX Recorder.

Semi-adiabatic calorimetry equipment

Grace AdiaCal®

Solidus Integration ThermoCal

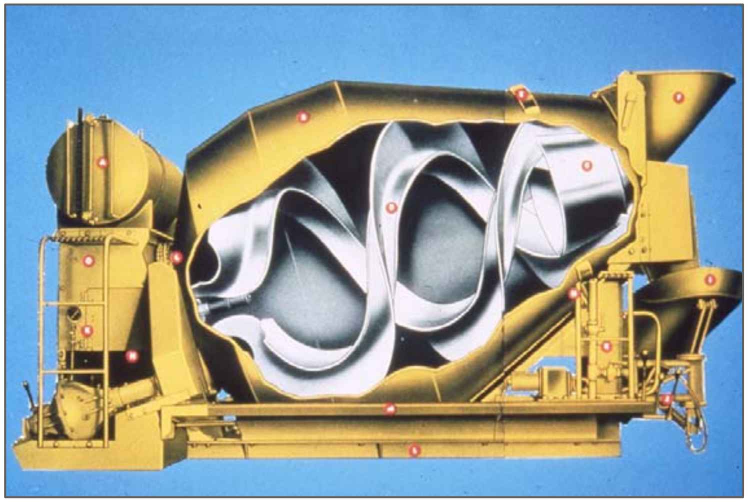


Semi-adiabatic calorimetry equipment

Test method variables

- Mortar or paste?
- Mixing method / equipment
- Volume / mass of test sample?
- How much insulation?
- Initial mixture temperature
- Environment temperature
- Control of environment temperature

Test method variables and considerations



Mixing equipment & procedures

- Mortar:
  - Wet-sieved concrete
  - C 305 (4 min.)
- Paste:
  - C 305 (2¼ min.)
  - Hand-held kitchen mixer
  - Kitchen-type blender
  - 1 minute or less may be adequate mixing time
- Differences in mixing shear may influence results

Test method variables and considerations

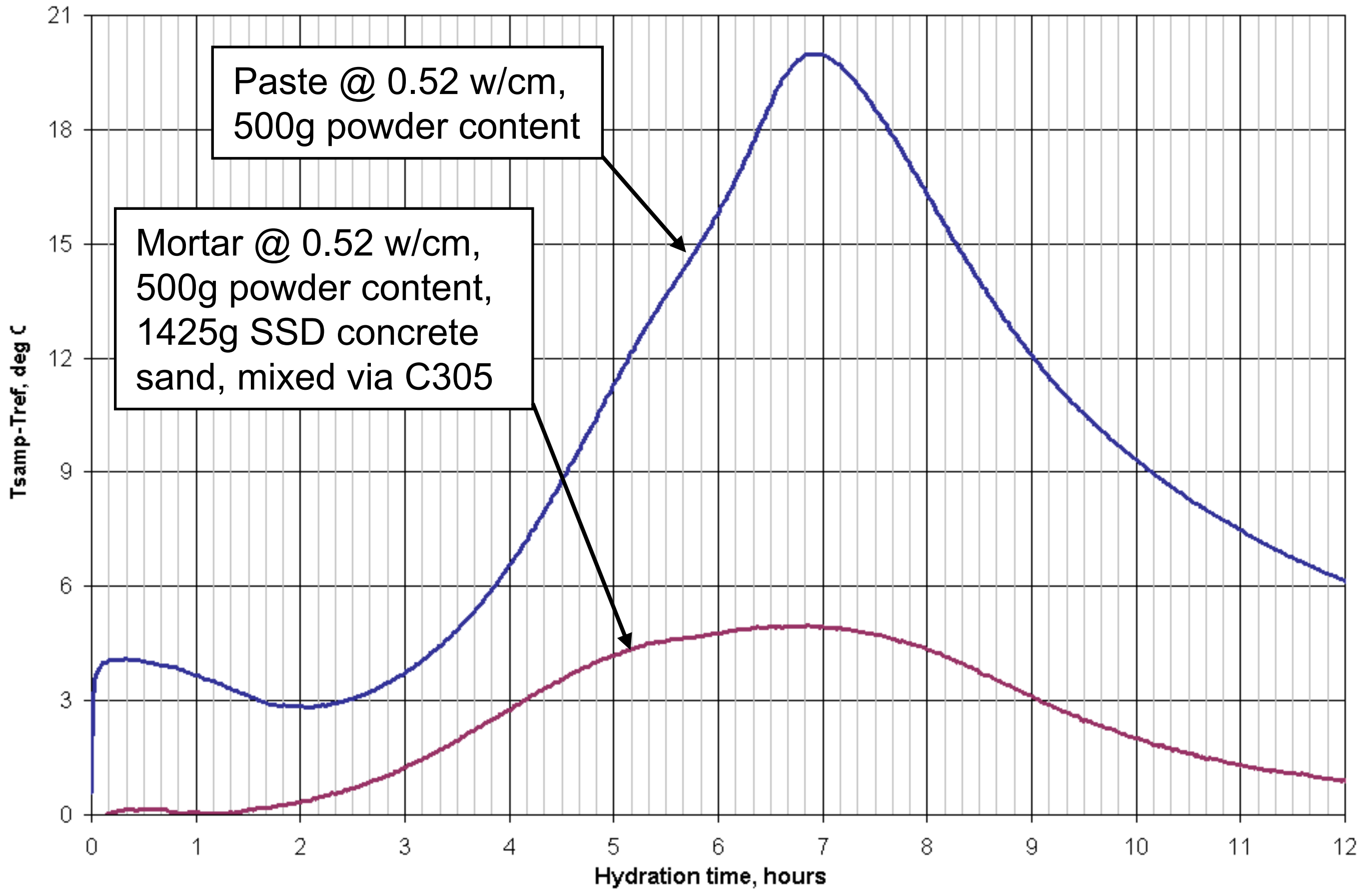
Mortar or concrete versus paste

- Lab vs. field
- Concrete & mortar better represent field set times
- Paste is preferred for comparing some hydration effects
- Paste mixing is faster
- Choice should also consider sample mass effects

Test method variables and considerations

Mortar vs. paste

90 degrees F mixtures with 25% Class F ash and water reducer

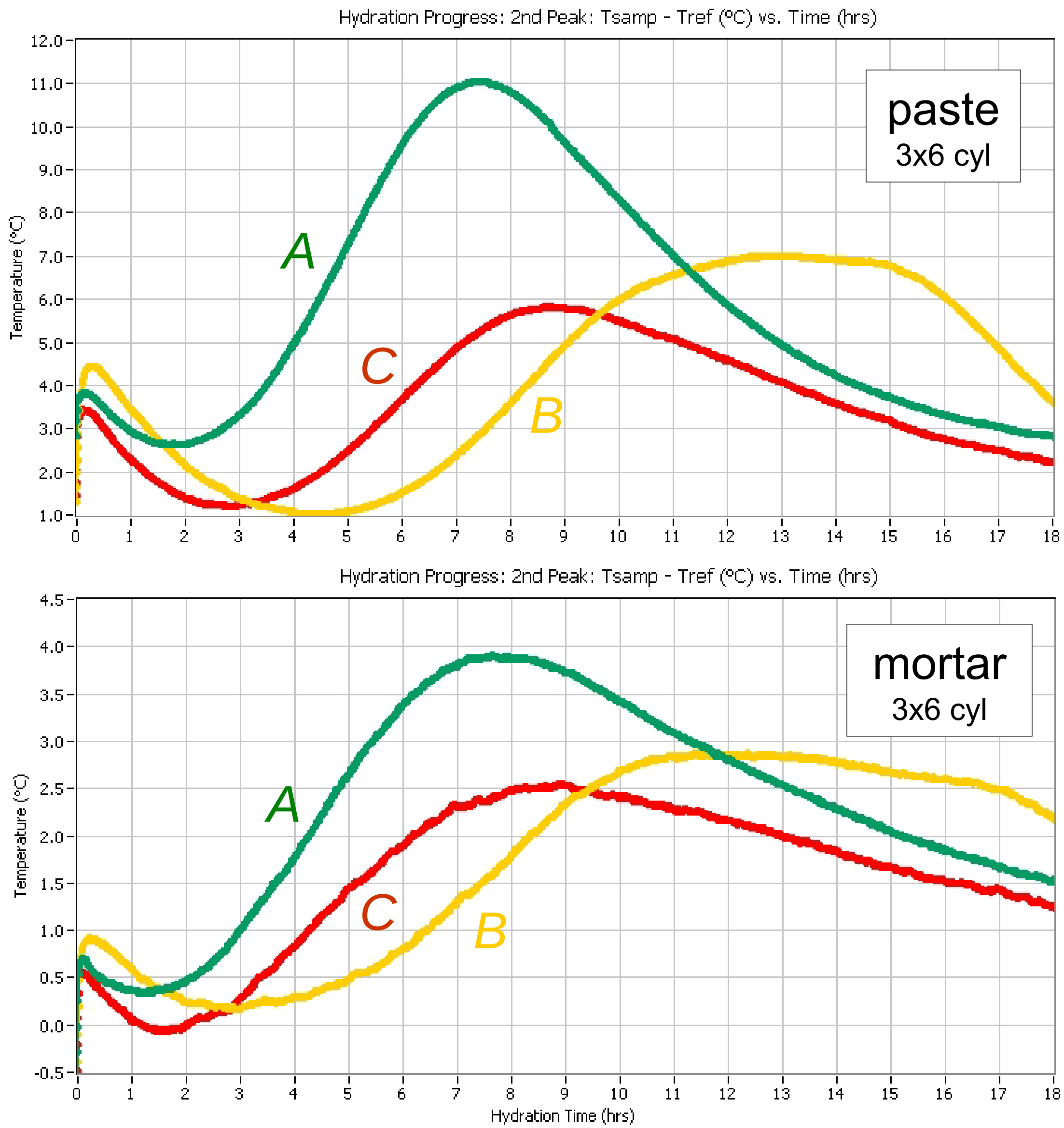


Test method variables and considerations

Mortar vs. paste

73 deg F mixtures:

- *A) no ash or admix, w/c = 0.54*
- *B) 25% C ash + 3 oz/cwt type A WR, w/cm = 0.51*
- *C) 25% F ash + 4 oz/cwt MR WR, w/cm = 0.51*



Test method variables and considerations

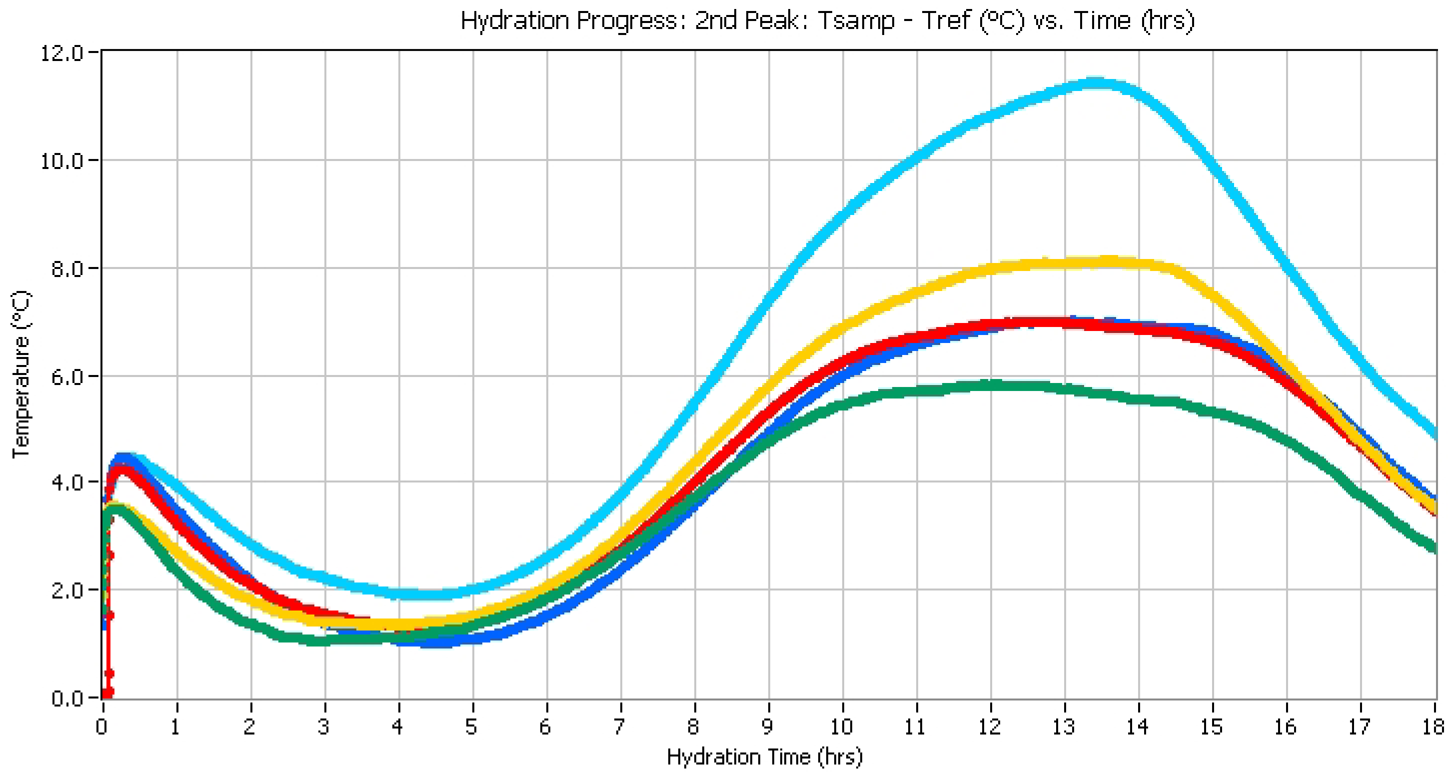
Sample mass & insulation

- Affect magnitude of peaks and possibly timing
- Affect rate of heat decay after exotherm peaks
- Insulation choices should depend on
  - Importance of ambient temp effects
  - Magnitude of peaks expected
  - Test objectives
- Main peak shapes can be influenced by sample mass and/or insulation value of container

Test method variables and considerations

Sample mass comparison, paste (minimal insulation)

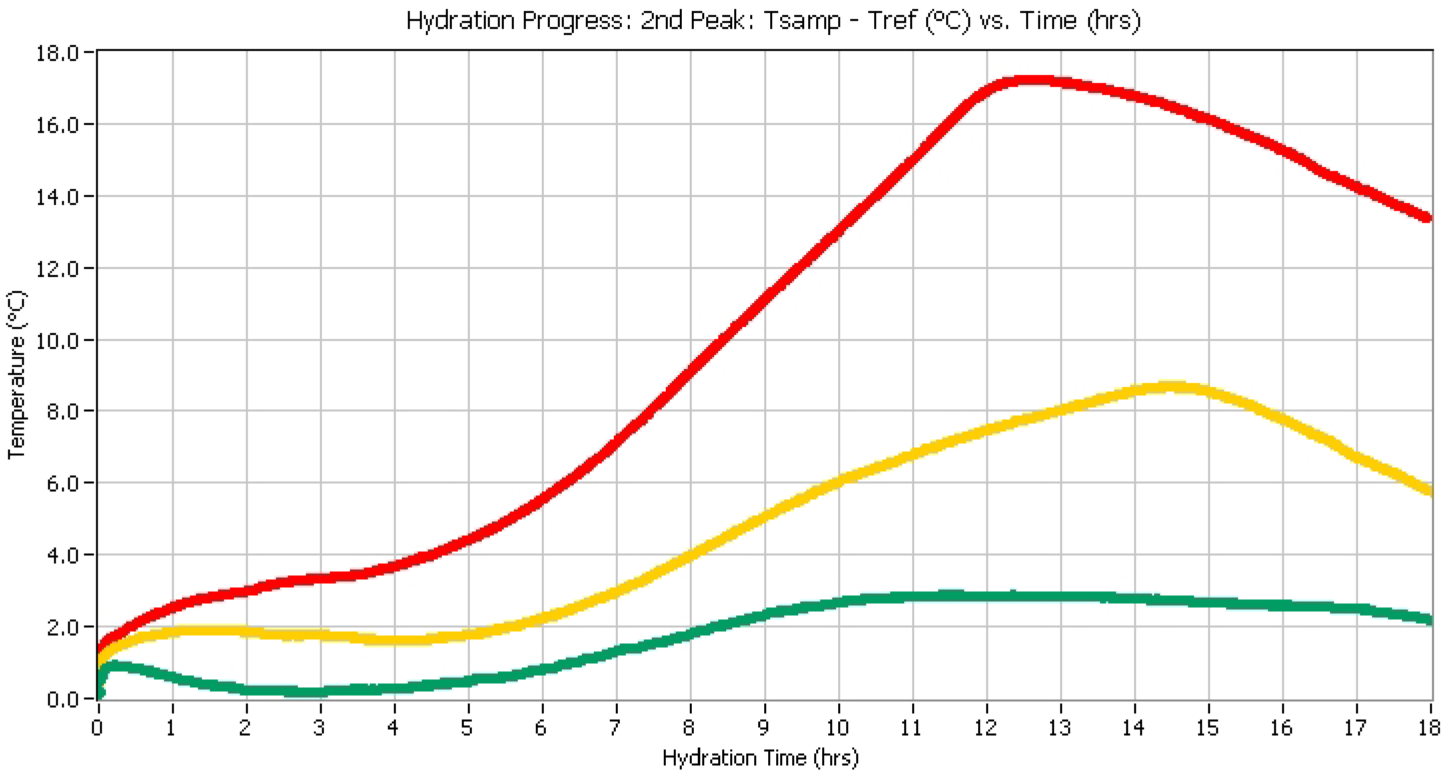
Mixtures with 25% Class C ash and water reducer at 73 degrees F
Cylindrical samples ranging from 135cc (2” x 2.6”) to 1070cc (4” x 5.2”)



Test method variables and considerations

Insulation effects, paste

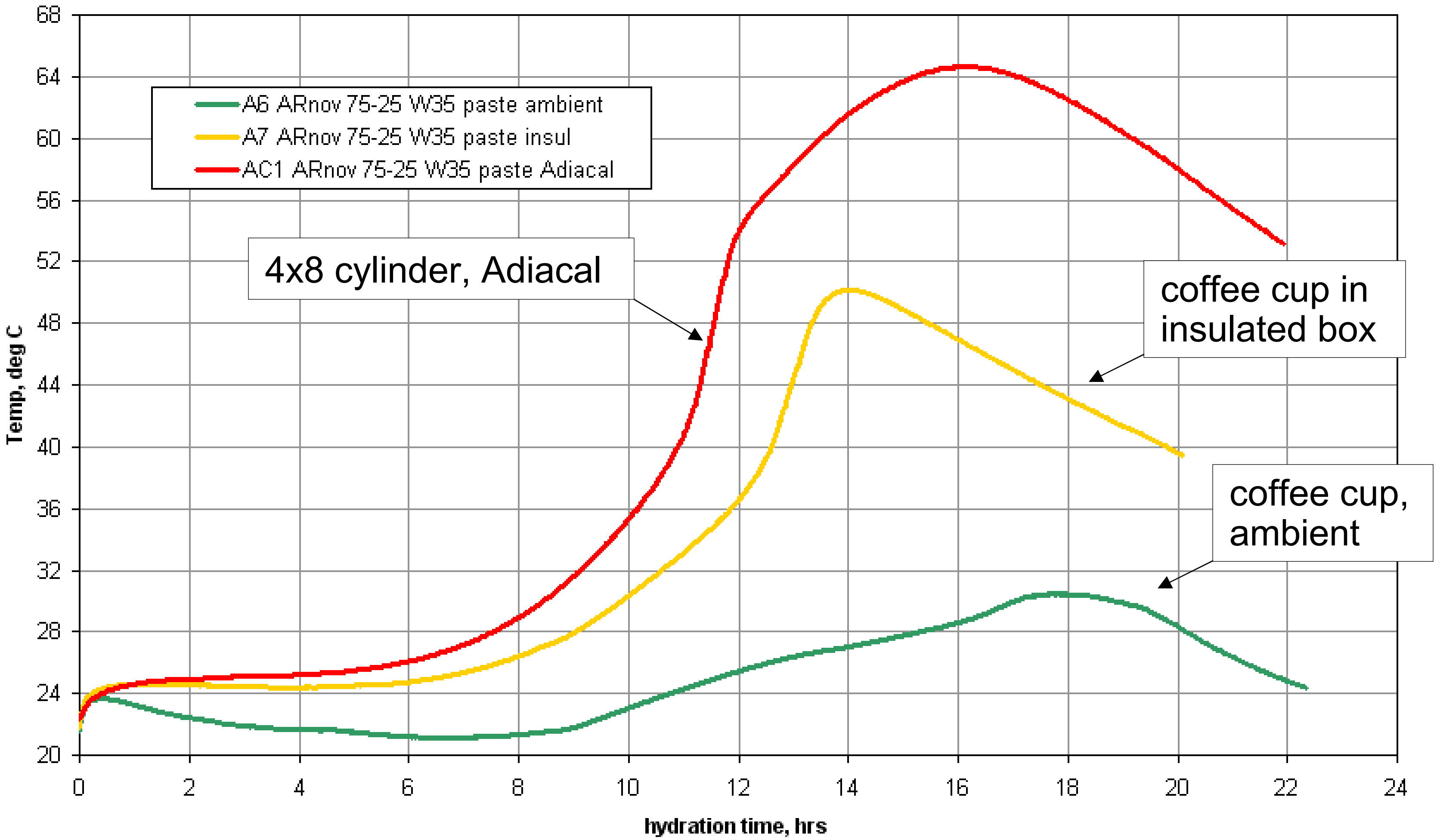
Paste mixtures with 25% Class C ash and water reducer at 73 degrees F in 3x6 cylinders with varying levels of insulation



Test method variables and considerations

Effects of sample mass & insulation, paste

73 degrees F paste mixtures with 25% Class C ash and water reducer

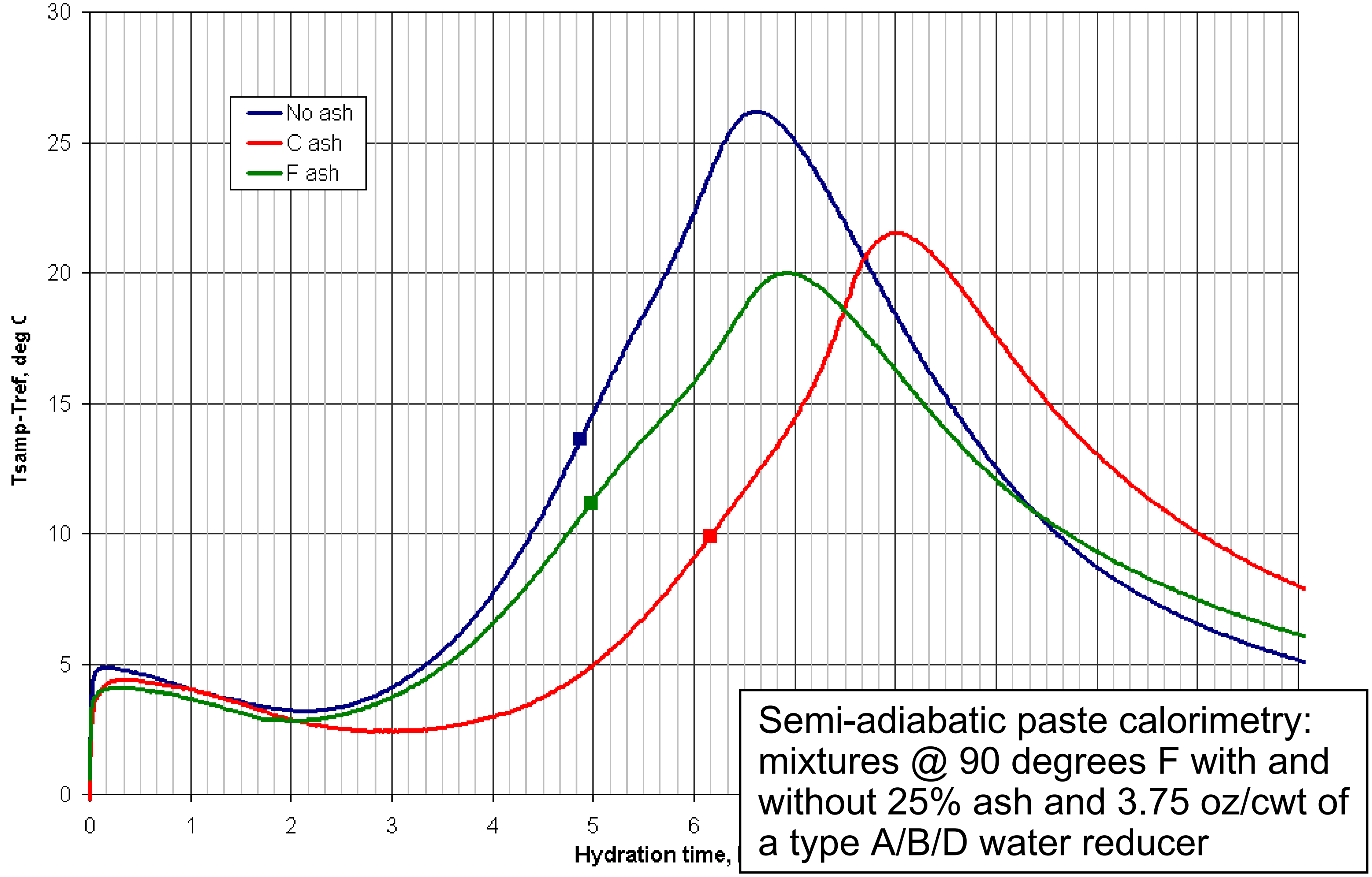


Set time evaluation with SAC

- Methods under development for a C 403 alternative:
  - Highly insulated samples of concrete or mortar
  - Mathematical procedures for determining set time from data
    - "Derivatives"
    - "Fractions"
    - "4th order fit"
- Relative time-of-set comparisons can be made using a simple visual indication of the point half-way up the C_3S heat rise (50% of peak).

Relative set times - "50% of peak" comparisons

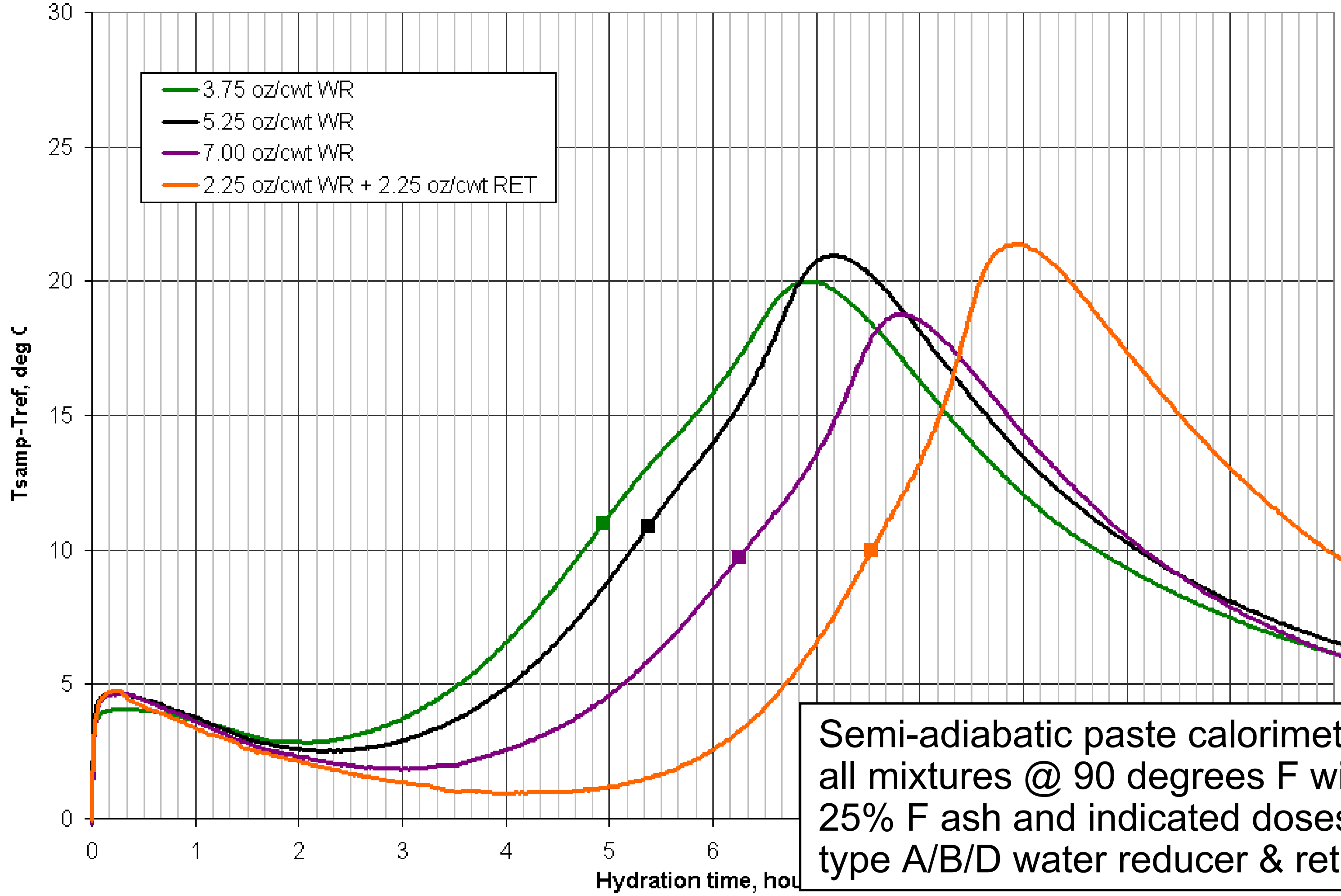
Influence of Class C and Class F fly ash



Semi-adiabatic paste calorimetry: mixtures @ 90 degrees F with and without 25% ash and 3.75 oz/cwt of a type A/B/D water reducer

Relative set times - “50% of peak” comparisons

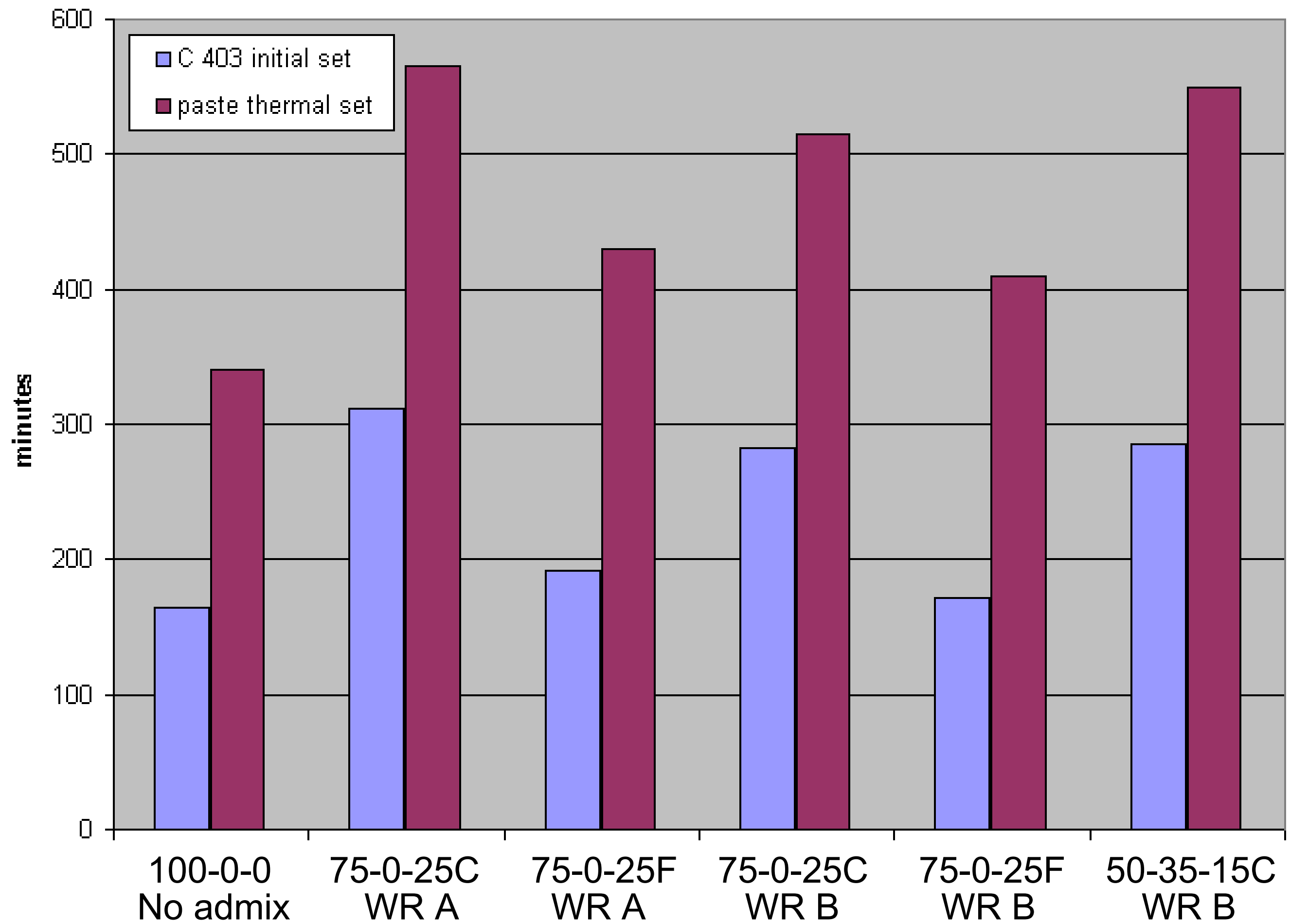
Influence of admix dose & retarder



Semi-adiabatic paste calorimetry: all mixtures @ 90 degrees F with 25% F ash and indicated doses of type A/B/D water reducer & retarder

Comparison of C 403 concrete initial set (lab mixes) and paste “thermal set” (50% of peak) indications, SAC

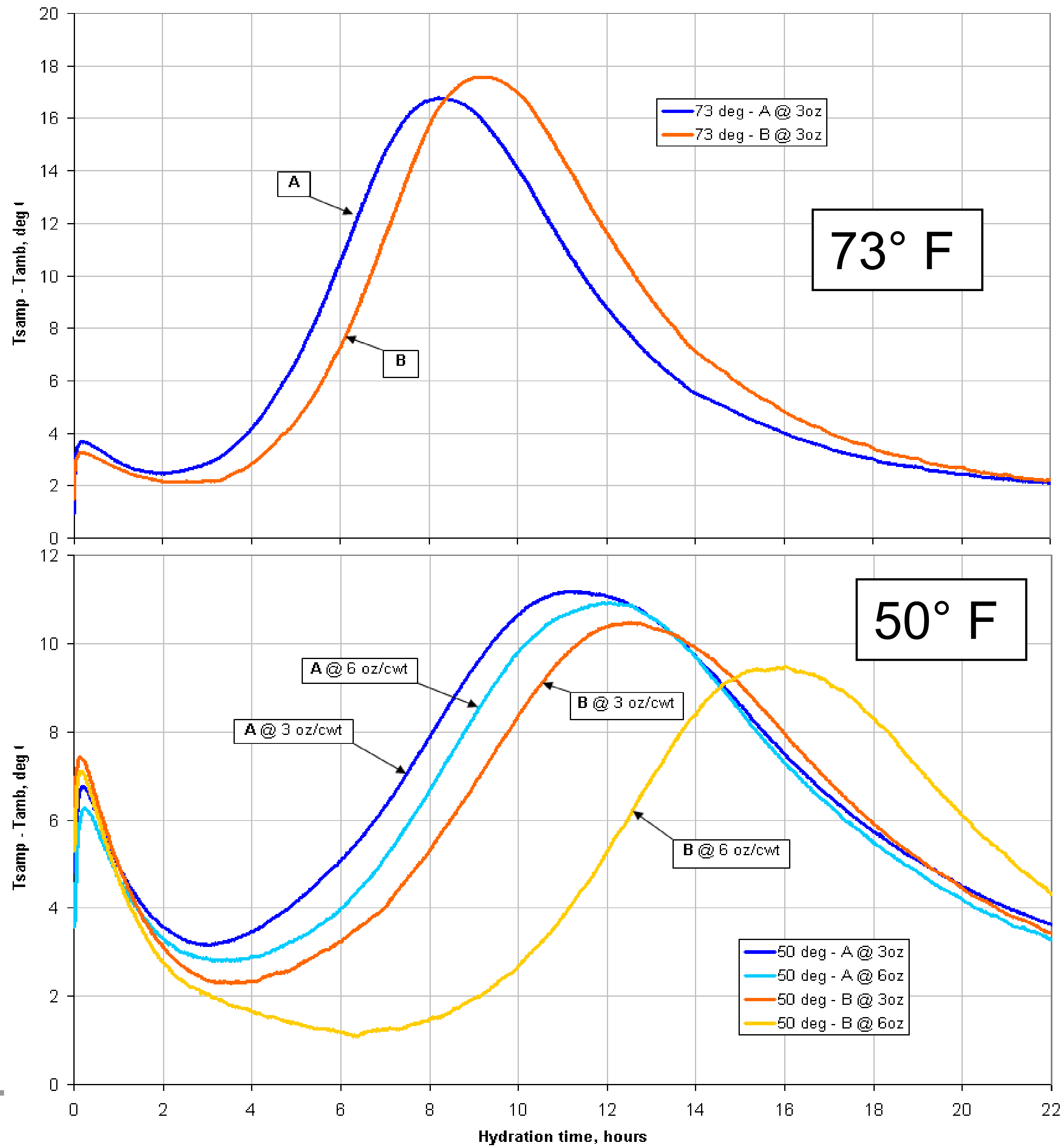
Lab concrete vs. semi-adiabatic paste calorimetry: all mixtures @ 73 degrees F, with and without normal doses of water reducing admix and indicated cementitious blends of cement-slag-ash(C/F)



Relative set times

Two admixtures compared for temperature & dosage effects

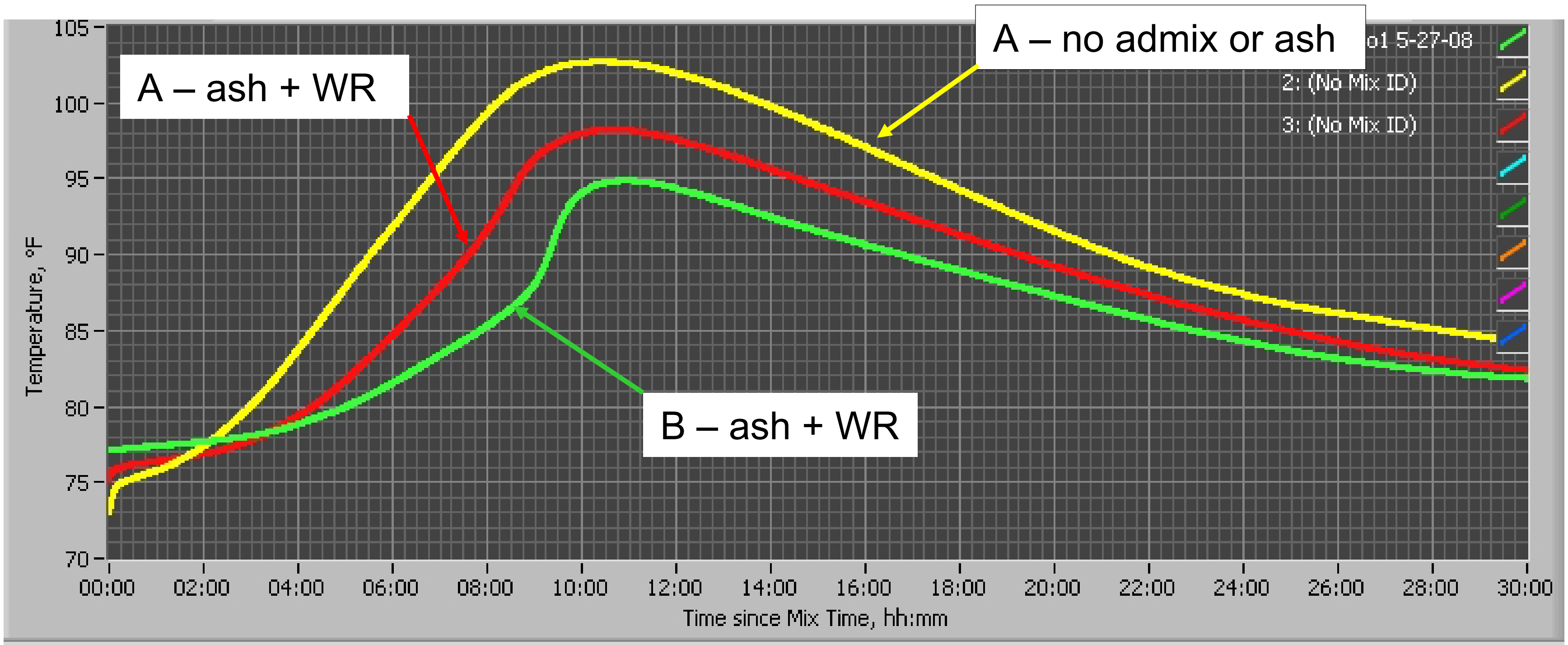
Semi-adiabatic paste calorimetry: 0.40 w/c cement-only mixtures @ 73 or 50 deg F, with 3 or 6 oz/cwt of 2 different candidate mid-range admixtures



Holcim (US) Inc.

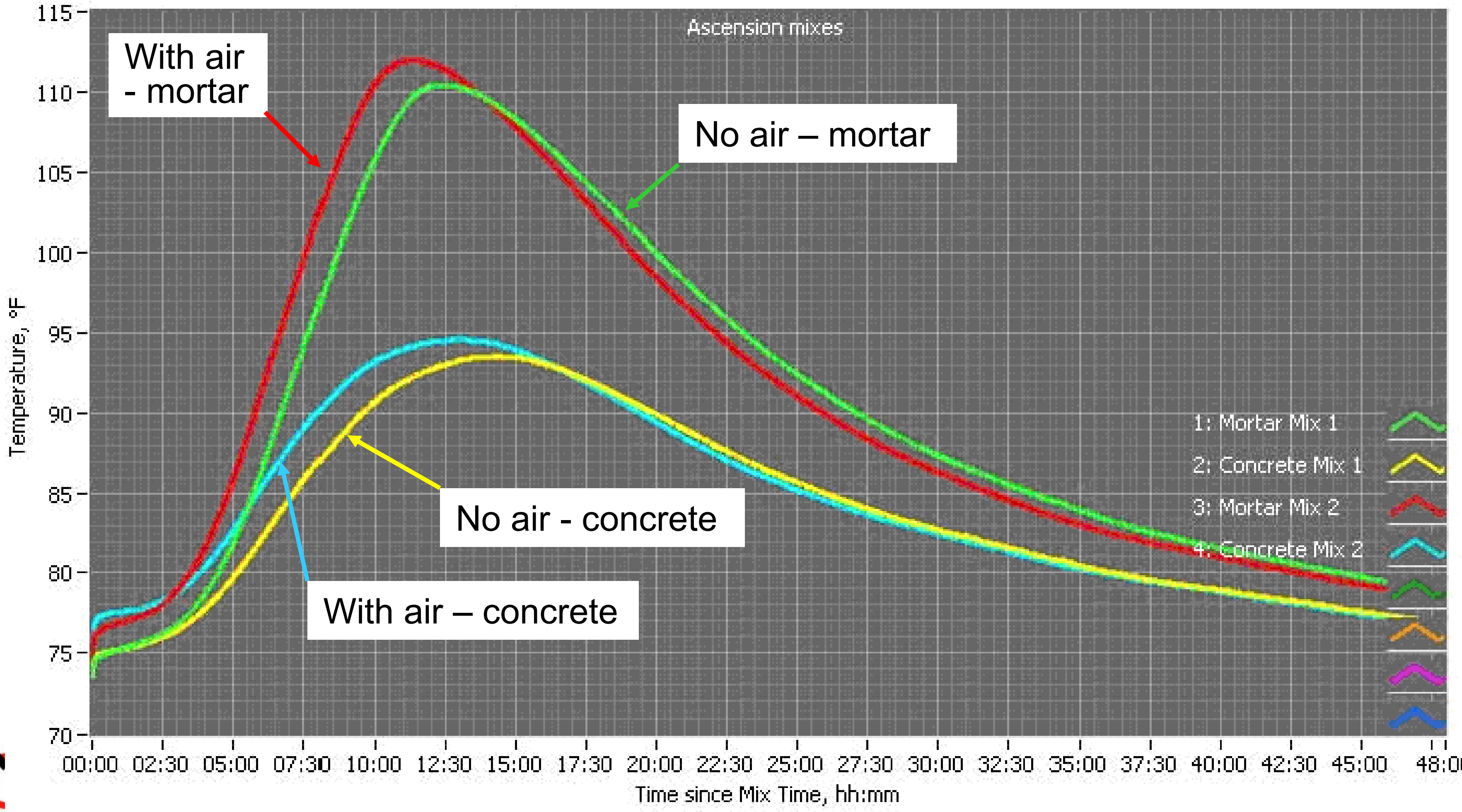
4x8 concrete cylinders - Adiacal

517 pcy concrete mixtures at constant slump, with or without 25% C ash, 3 oz/cwt type A/B/D WR, 2 different type I cement samples (same source)



4x8 concrete cylinders - Adiacal

Mortar vs. concrete – 470 pcy concrete at constant slump, with 10% C ash and 3.2 oz/cwt type A/B/D WR, with or without AE.



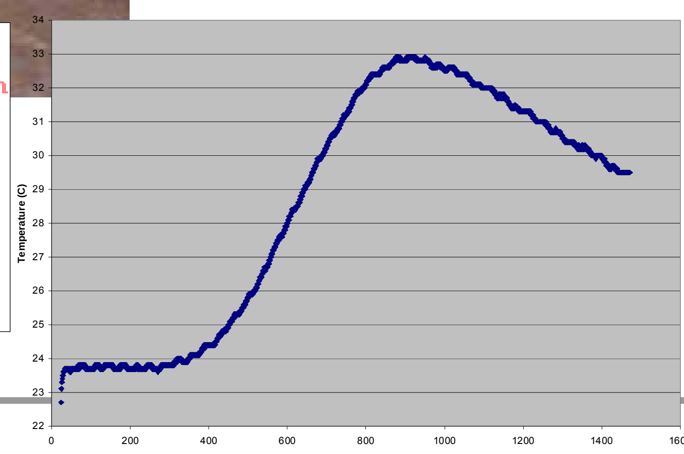
Developing ASTM set time method

Current draft of C09.23 "thermal" set time document specifies highly insulated 6" to 7"-diameter samples of concrete

Designation: X XXXX-XX   Ballot Item

Standard Test Method for
Determination of Setting Time of Concrete by the Temperature Method[1]

This standard is issued under the fixed designation X XXXX; 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 (ε) indicates an editorial change since the last revision or reapproval.



Sulfate balance influences and issues

"Incompatibility" of concrete materials

- Responsible for certain concrete performance issues
- Cement SO_3 content is spec limited and typically optimized using procedures that do not account for other influences.
- Other materials and conditions affect demand for sulfates:
  - Admixtures
  - Some SCM's, especially Class C fly ash
  - Hot weather
- If early C_3A hydration becomes uncontrolled due to the depletion of soluble sulfates, erratic behavior results:
  - Unpredictable (sometimes extreme) set effects and / or slump loss
  - Interrupted silicate hydration & strength gain

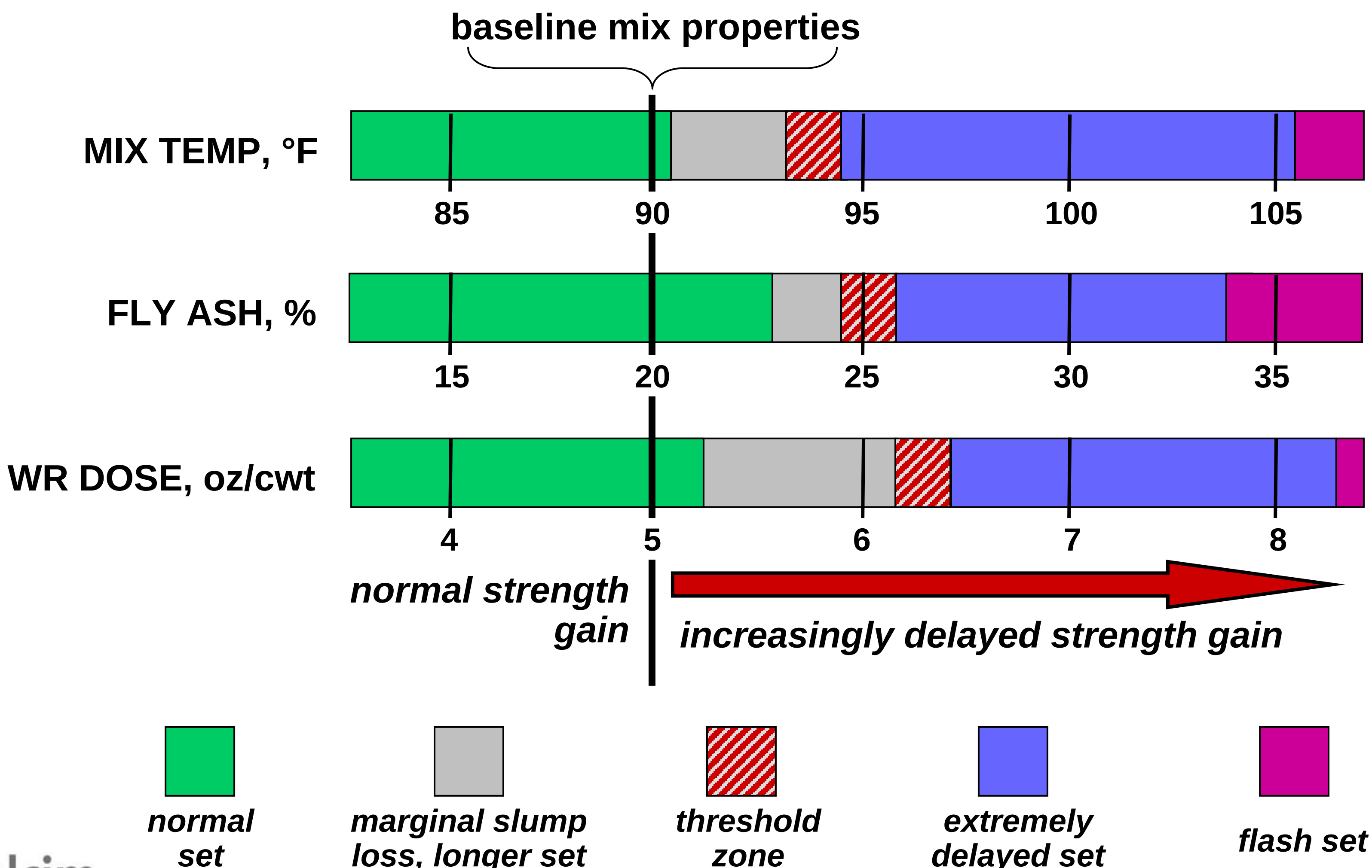
Sulfate balance influences and issues

Related concrete behavior

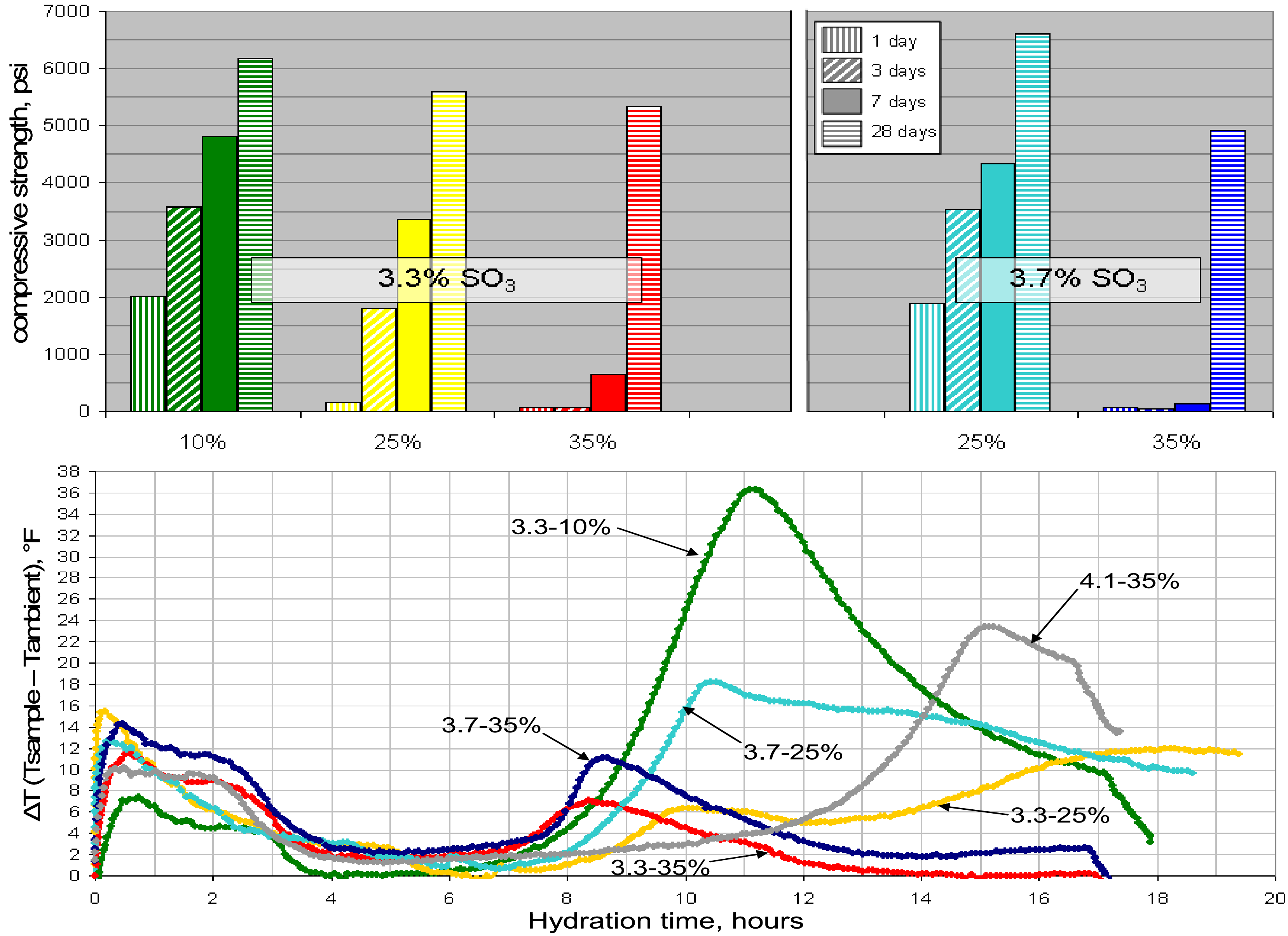
- Mild influences - typically with higher temps:
  - Some increase in slump loss
  - Slight extending of set time
  - Unexpected responses to admixtures
- Nearer the incompatibility threshold:
  - Sluggish strength gain
  - More severe slump loss, extended set
- True incompatibility behavior:
  - No normal set, 24 to 48 hours or longer, or…
  - Flash set (extreme cases)
  - Interrupted strength gain for several days

Example: sulfate balance effects of changes in temperature, fly ash %, or water reducer dosage

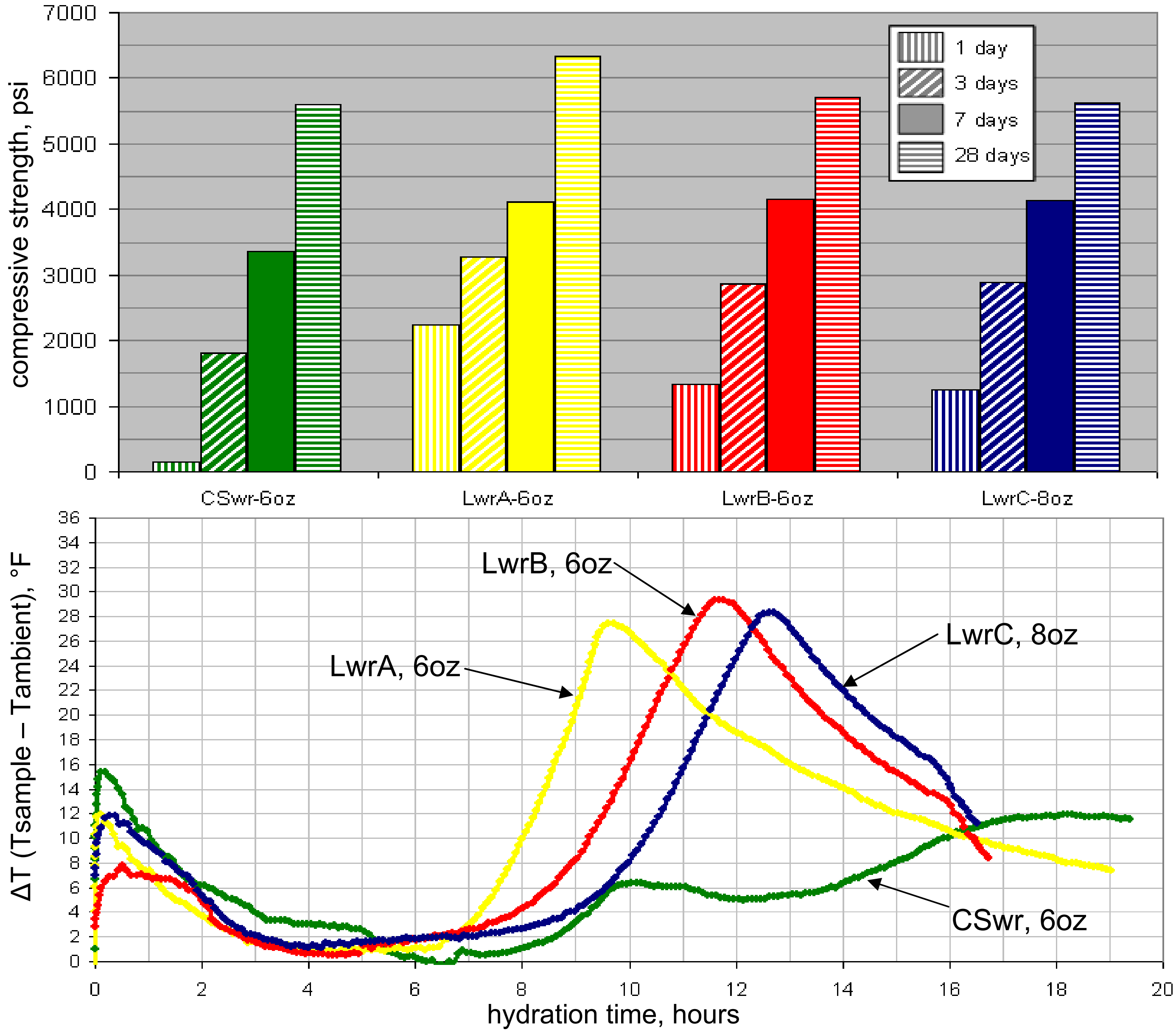
baseline mix has 20% ash with 5 oz/cwt water reducer at 90°F



Semi-adiabatic paste calorimetry & mortar cubes: effects of fly ash content, mixtures with 6 oz/cwt type A/B/D water reducer, 90º F initial temp, cement SO_3 = 3.3 or 3.7%



Semi-adiabatic paste calorimetry & mortar cubes: effects of different admixtures compared in mixtures with 25% fly ash, 90º F initial temp, cement SO_3 = 3.3%



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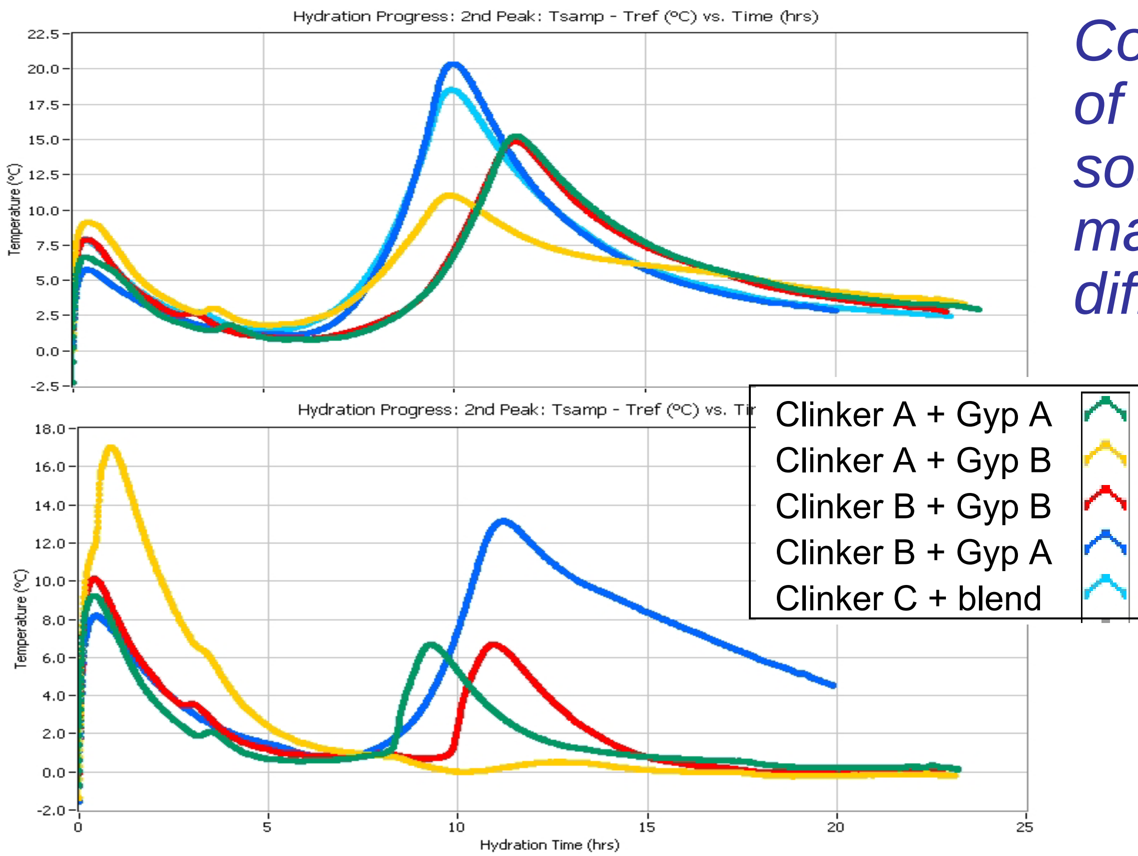
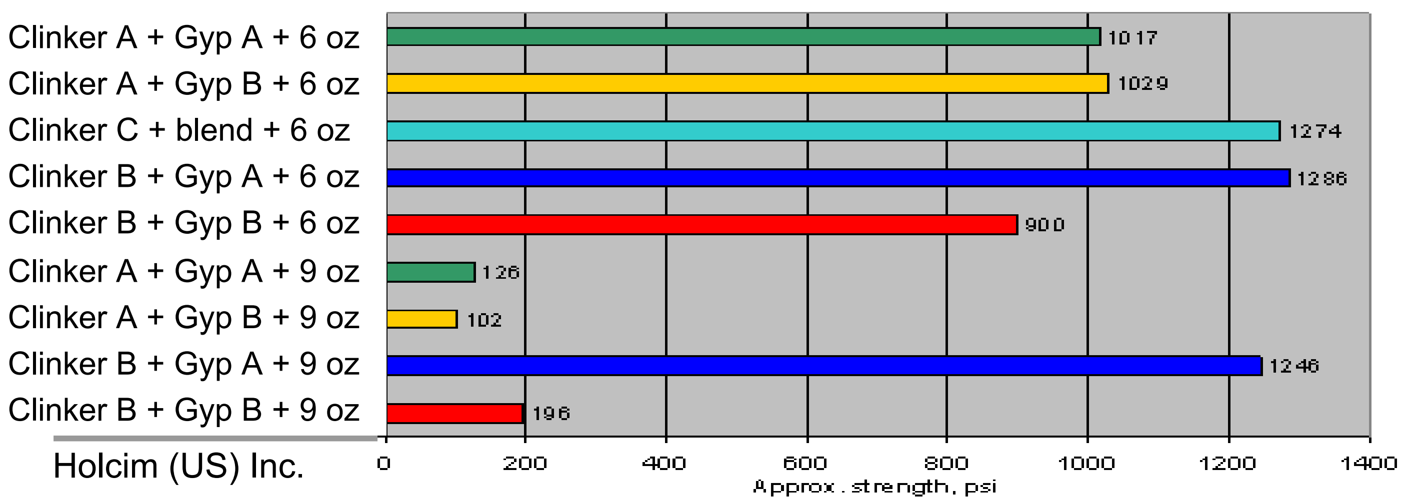
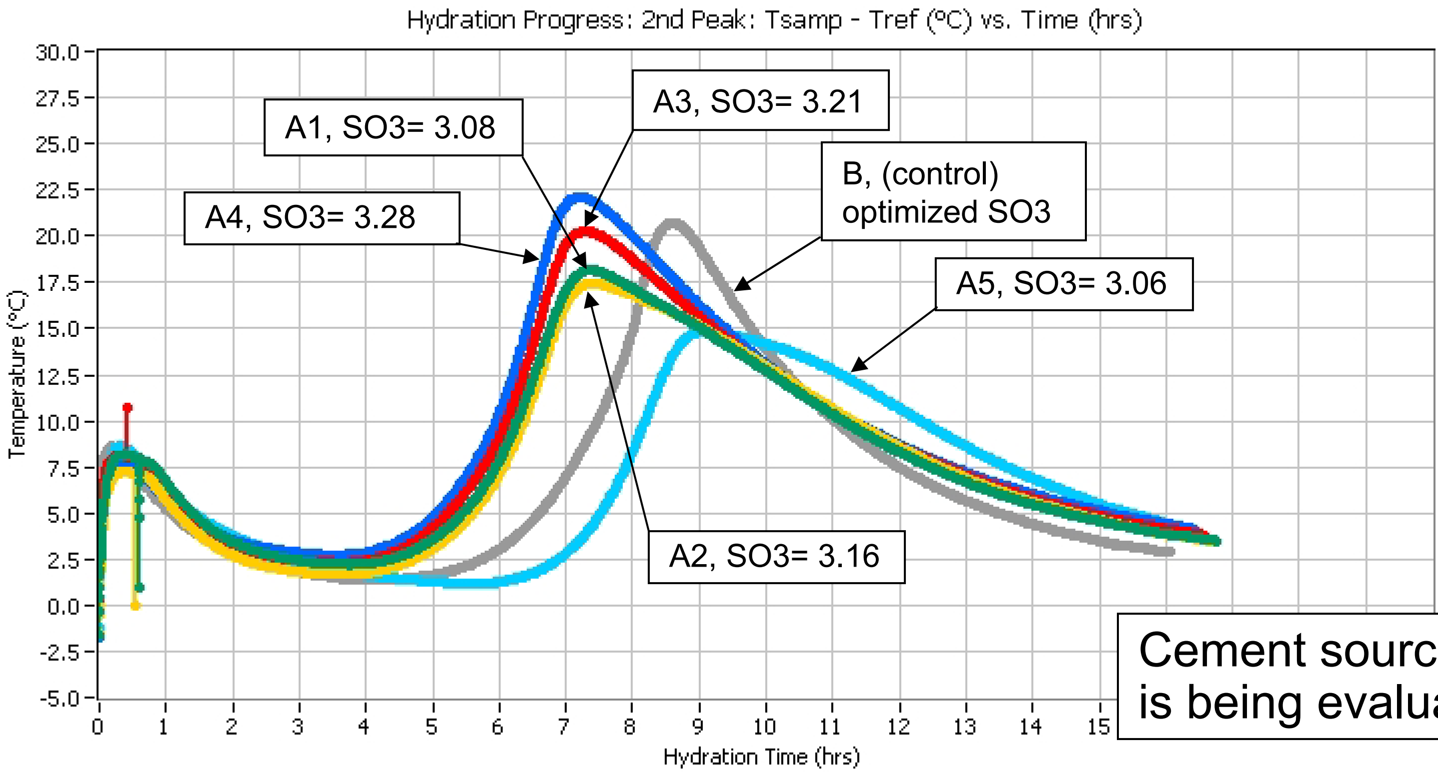
Comparison of effects of different gypsum sources on cements made from two different clinkers



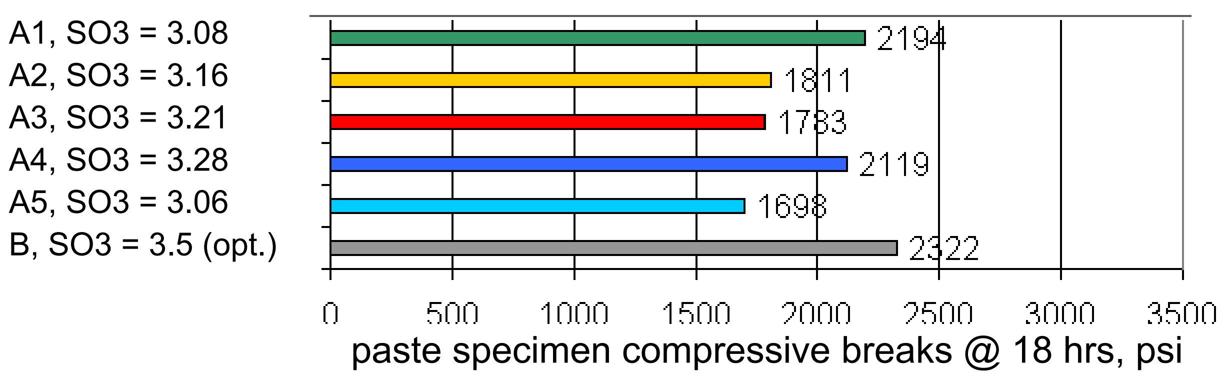
Cement plant QC testing – effects of different gypsum sources, 90 degree F mixtures with 25% Class C ash + 6 oz/cwt admix (upper) or 9 oz/cwt (lower)



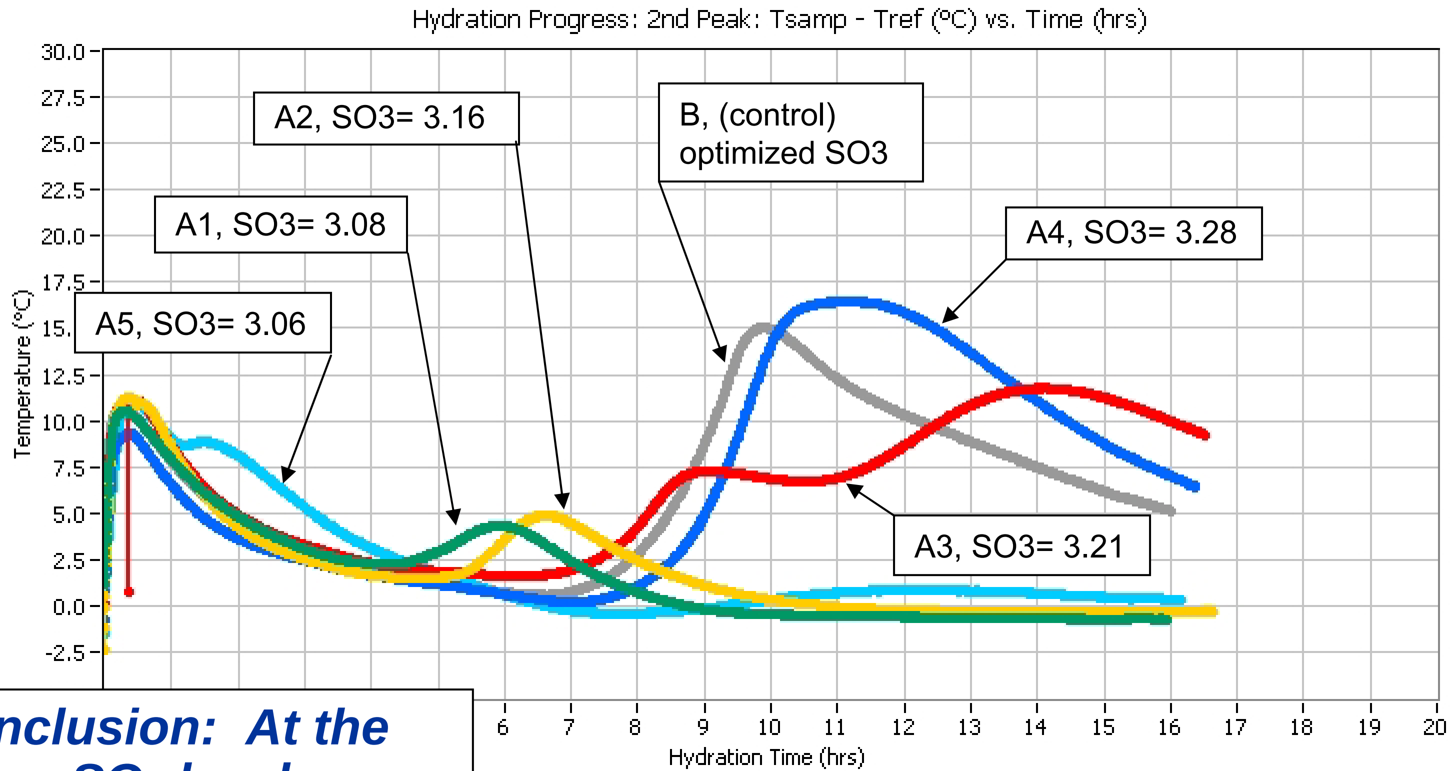
Cement sulfates evaluation: semi-adiabatic paste calorimetry, 0.40 w/cm mixtures @ 95 deg F, 25% Class C ash, 4 oz/cwt WR, cement samples @ various SO_3 %



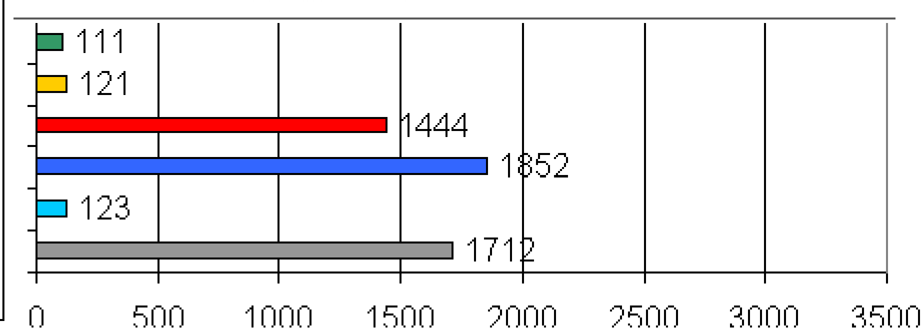
Cement source “A” is being evaluated.



Cement sulfates evaluation: admixture sensitivity comparison, same mixtures with admix dosage doubled, to 8 oz/cwt WR



Conclusion: At the lower SO_3 levels, cement source "A" may be under-sulfated for use in aggressive mixes at higher temperatures.



ASTM methods - hydration kinetics using calorimetry

Designation: X XXXX-XX

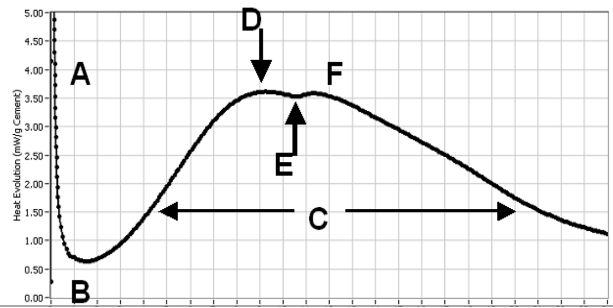
Standard practice for

Measuring hydration kinetics of hydraulic cementitious mixtures using isothermal calorimetry

1. Scope

1.1 This practice describes the apparatus and proce
hydration kinetics of hydraulic cementitious mixtures,
including those containing admixtures, various suppler
and other fine materials, by measuring the thermal pow

NOTE 1- Paste specimens are often preferred for m
individual reaction peaks are important or for particula



X XXXX DRAFT 6-23-08

Standard practice for

Measuring hydration kinetics of hydraulic cementitious mixtures using semi-adiabatic calorimetry

us and procedure for measuring relative differences in
us mixtures in paste, mortar, or concrete (Note 1),
rious supplementary cementitious materials (SCM),
perature change over time using a semi-adiabatic
; equipment.

eferred for mechanistic research when details of
for particular calorimetry configurations. Mortar or
ave better correlation with concrete setting and early
ed to evaluate different mixture proportions for

Designation: X XXXX-XX **Ballot Item #1**

Standard Test Method for
Determination of Setting Time of Concrete by the Temperature Method[1]

This standard is issued under the fixed designation X XXXX; 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 (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of time of setting of concrete by means of monitoring the temperature change of a concrete specimen from a representative concrete mixture

Cost

“Hotel room” calorimetry

	Monday, 9-22-08	73 deg. F calorimetry - paste											
Channel	Mix ID	w/cm	cement			SCM			water, g	Admixture			mix time
			source/sample	SO3	wt. (g)	material	%	wt (g)		product	oz/cwt	ml	
1	A - 25% C ash + 4oz	0.40	Cement A, type I/II	3.41	525	C ash	25%	175	280	type A	4	1.82	7:18pm
2	A - 25% C ash + 6oz	0.40	Cement A, type I/II	3.41	525	C ash	25%	175	280	type A	6	2.73	7:28pm
3	A - 25% C ash + 8oz	0.40	Cement A, type I/II	3.41	525	C ash	25%	175	280	type A	8	3.64	7:36pm
4	A - 25% F ash + 6oz	0.40	Cement A, type I/II	3.41	525	F ash	25%	175	280	type A	6	2.73	7:46pm
5	B - 25% C ash + 4oz	0.40	Cement B, type I/II	3.71	525	C ash	25%	175	280	type A	4	1.82	7:56pm
6	B - 25% C ash + 6oz	0.40	Cement B, type I/II	3.71	525	C ash	25%	175	280	type A	6	2.73	8:05pm
7	B - 25% C ash + 8oz	0.40	Cement B, type I/II	3.71	525	C ash	25%	175	280	type A	8	3.64	8:15pm
8	B - 25% F ash + 6oz	0.40	Cement B, type I/II	3.71	525	F ash	25%	175	280	type A	6	2.73	8:25pm

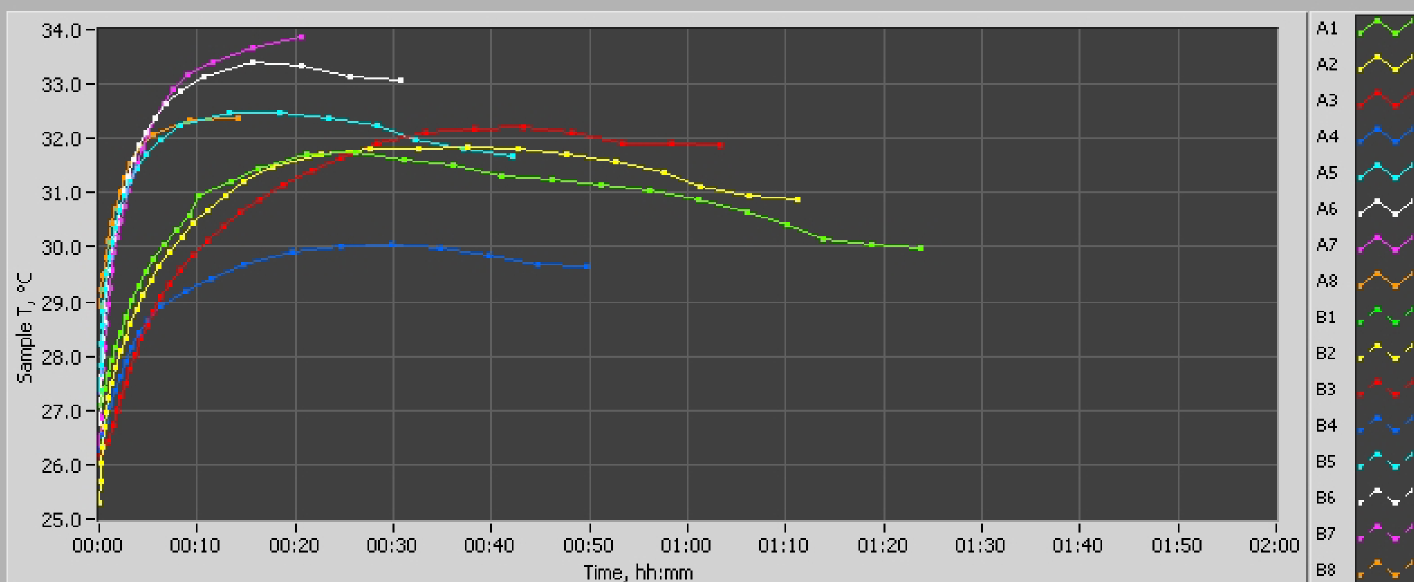
Initial temp rise, all mixes (1:25 into testing)

Block A

	Sample ID	Comment	T, hh:mm	Log	t, hh:mm	Temp, °C
1	1 - Samp A 25% C ash + 4oz		30:00	✓	01:24	29.98
2	2 - Samp A 25% C ash + 6oz		30:00	✓	01:13	30.82
3	3 - Samp A 25% C ash + 8oz		30:00	✓	01:04	31.86
4	4 - Samp A 25% F ash + 6oz		30:00	✓	00:53	29.61
5	5 - Samp B 25% C ash + 4oz		30:00	✓	00:43	31.65
6	6 - Samp B 25% C ash + 6oz		30:00	✓	00:34	32.96
7	7 - Samp B 25% C ash + 8oz		30:00	✓	00:24	33.93
8	8 - Samp B 25% F ash + 6oz		30:00	✓	00:14	32.36

Block B

	Sample ID	Comment	T, hh:mm	Log	t, hh:mm	Temp, °C
1			00:00		NaN	NaN
2			00:00		NaN	NaN
3			00:00		NaN	NaN
4			00:00		NaN	NaN
5			00:00		NaN	NaN
6			00:00		NaN	NaN
7			00:00		NaN	NaN
8			00:00		NaN	NaN



T Update, °C	t Update, hh:mm:ss
0.25	00:05:00

Block A CJT, °C	Block B CJT, °C
25.29	NaN

Reference Cell	Ref Cell T, °C
none	NaN

Measure

Calibrate

Block A Calibration File

(none)

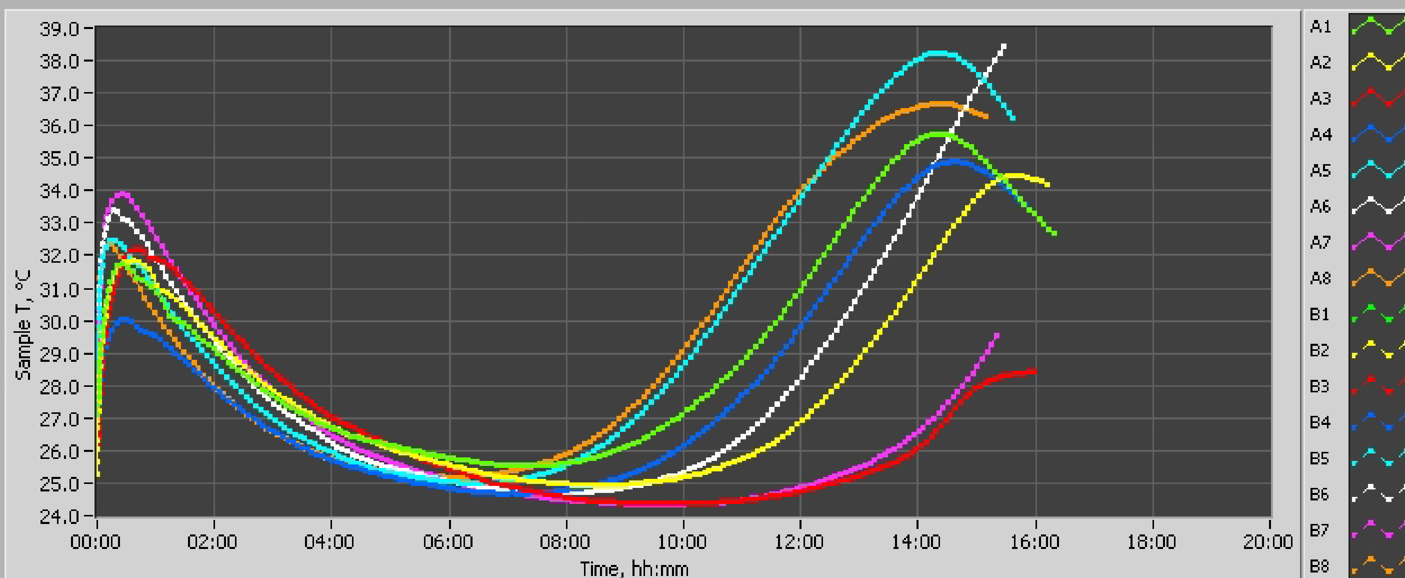
Block B Calibration File

(none)

Sample Info and Context Help (Move Mouse over Field of Interest)

+/- 16 hours into testing

	Block A							Block B					
	Sample ID	Comment	T, hh:mm	Log	t, hh:mm	Temp, °C		Sample ID	Comment	T, hh:mm	Log	t, hh:mm	Temp, °C
1	1 - Samp A 25% C ash + 4oz	3.41- C ash norm dose	30:00	✓	16:22	32.59	1			00:00		NaN	NaN
2	2 - Samp A 25% C ash + 6oz	3.41- C ash retard dose	30:00	✓	16:11	34.20	2			00:00		NaN	NaN
3	3 - Samp A 25% C ash + 8oz	3.41- C ash overdose	30:00	✓	16:01	28.45	3			00:00		NaN	NaN
4	4 - Samp A 25% F ash + 6oz	3.41- F ash retard dose	30:00	✓	15:51	33.53	4			00:00		NaN	NaN
5	5 - Samp B 25% C ash + 4oz	3.71- C ash norm dose	30:00	✓	15:40	36.11	5			00:00		NaN	NaN
6	6 - Samp B 25% C ash + 6oz	3.71- C ash retard dose	30:00	✓	15:32	38.66	6			00:00		NaN	NaN
7	7 - Samp B 25% C ash + 8oz	3.71- C ash overdose	30:00	✓	15:21	29.60	7			00:00		NaN	NaN
8	8 - Samp B 25% F ash + 6oz	3.71- F ash retard dose	30:00	✓	15:11	36.27	8			00:00		NaN	NaN



T Update, °C	t Update, hh:mm:ss
0.25	00:05:00
Block A CJT, °C	**Block B CJT, °C**
24.74	NaN
Reference Cell	**Ref Cell T, °C**
none	NaN

Measure

Calibrate

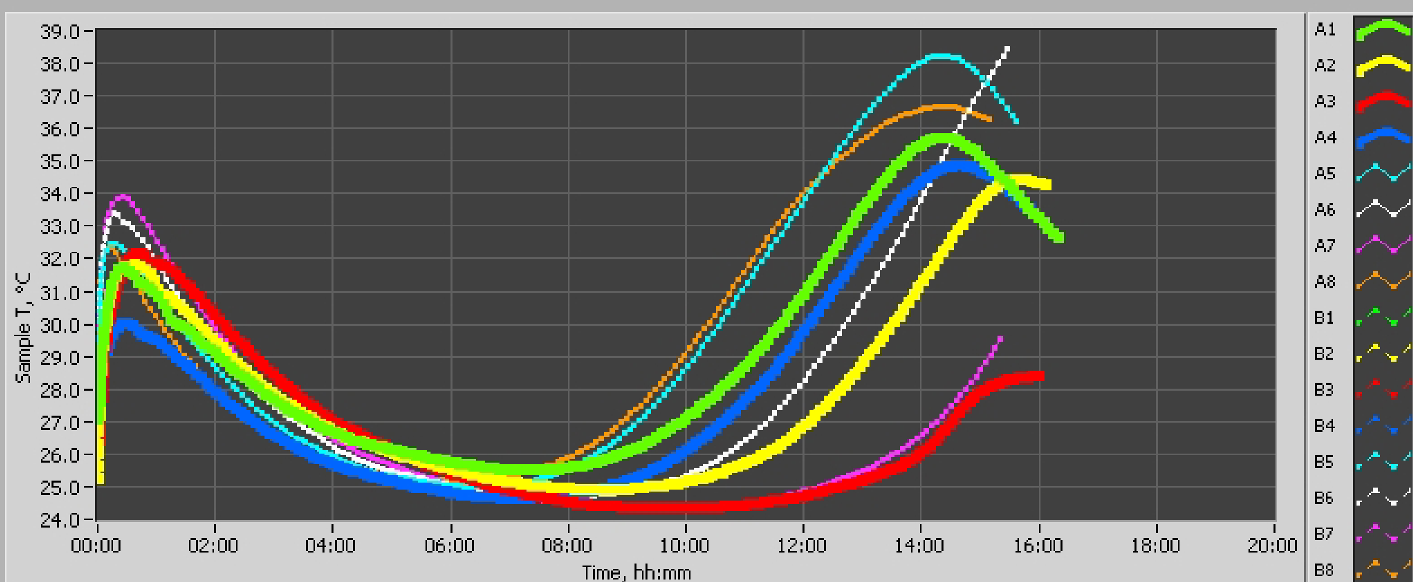
Block A Calibration File: (none)

Block B Calibration File: (none)

Sample Info and Context Help (Move Mouse over Field of Interest)

+/- 16 hours into testing

	Block A							Block B					
	Sample ID	Comment	T, hh:mm	Log	t, hh:mm	Temp, °C		Sample ID	Comment	T, hh:mm	Log	t, hh:mm	Temp, °C
1	1 - Samp A 25% C ash + 4oz	3.41- C ash norm dose	30:00	☑	16:21	32.60	1			00:00	☐	NaN	NaN
2	2 - Samp A 25% C ash + 6oz	3.41- C ash retard dose	30:00	☑	16:10	34.21	2			00:00	☐	NaN	NaN
3	3 - Samp A 25% C ash + 8oz	3.41- C ash overdose	30:00	☑	16:01	28.45	3			00:00	☐	NaN	NaN
4	4 - Samp A 25% F ash + 6oz	3.41- F ash retard dose	30:00	☑	15:50	33.56	4			00:00	☐	NaN	NaN
5	5 - Samp B 25% C ash + 4oz	3.71- C ash norm dose	30:00	☑	15:40	36.15	5			00:00	☐	NaN	NaN
6	6 - Samp B 25% C ash + 6oz	3.71- C ash retard dose	30:00	☑	15:31	38.62	6			00:00	☐	NaN	NaN
7	7 - Samp B 25% C ash + 8oz	3.71- C ash overdose	30:00	☑	15:21	29.56	7			00:00	☐	NaN	NaN
8	8 - Samp B 25% F ash + 6oz	3.71- F ash retard dose	30:00	☑	15:11	36.28	8			00:00	☐	NaN	NaN



T Update, °C: 0.25

t Update, hh:mm:ss: 00:05:00

Block A CJT, °C: 24.73

Block B CJT, °C: NaN

Reference Cell: none

Ref Cell T, °C: NaN

Measure

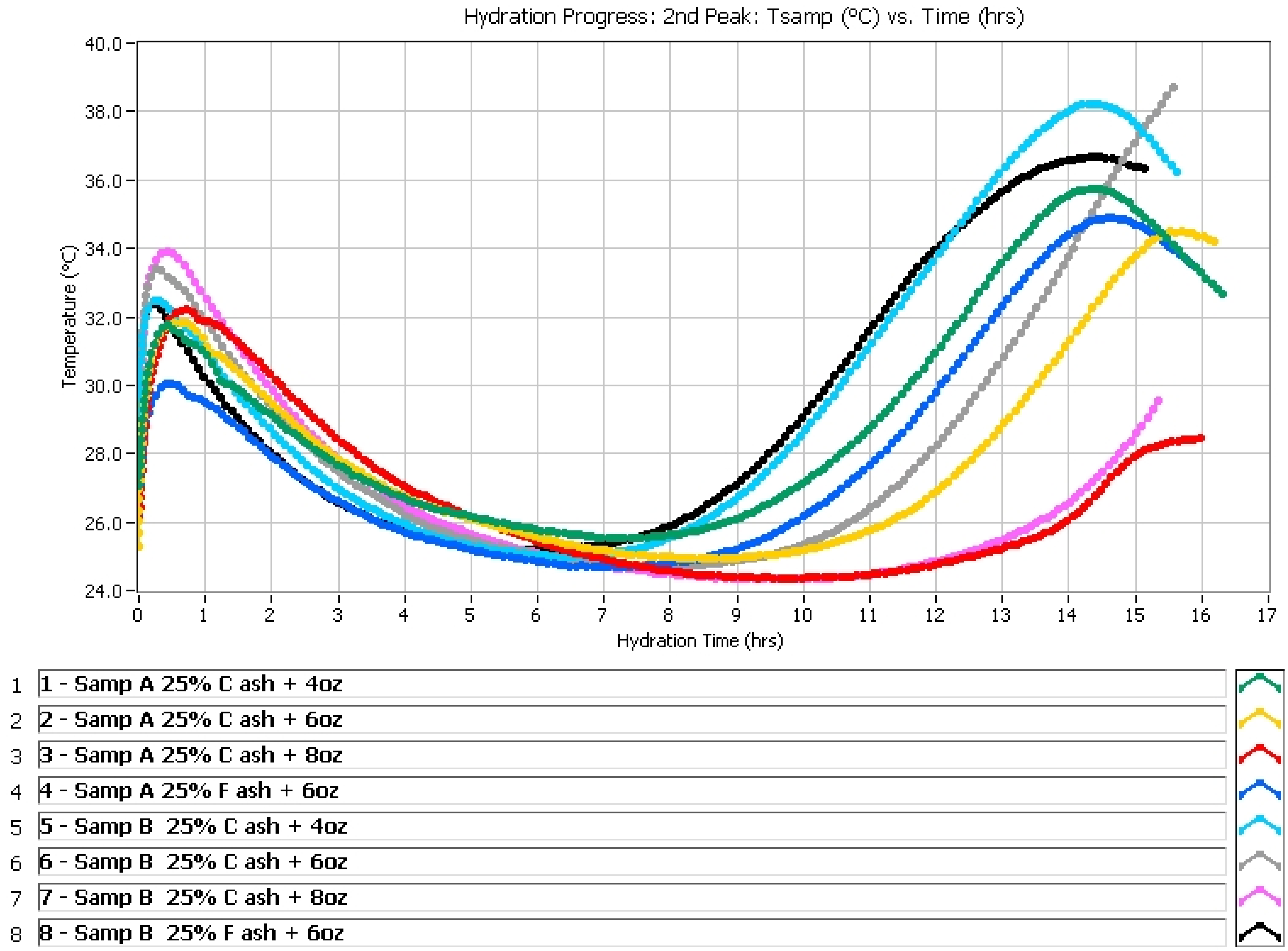
Calibrate

Block A Calibration File: (none)

Block B Calibration File: (none)

Sample Info and Context Help (Move Mouse over Field of Interest)

Graph of data using “Report Generator”



Holci

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Questions?

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