Modified ASTM C359 Early Stiffening of Mortar to Anticipate Complex Cement-Admixture Interactions

Ara A. Jeknavorian, Ph.D.
Jeknavorian Consulting Services
Chelmsford, MA 01824

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Jeknavorian Consulting Services

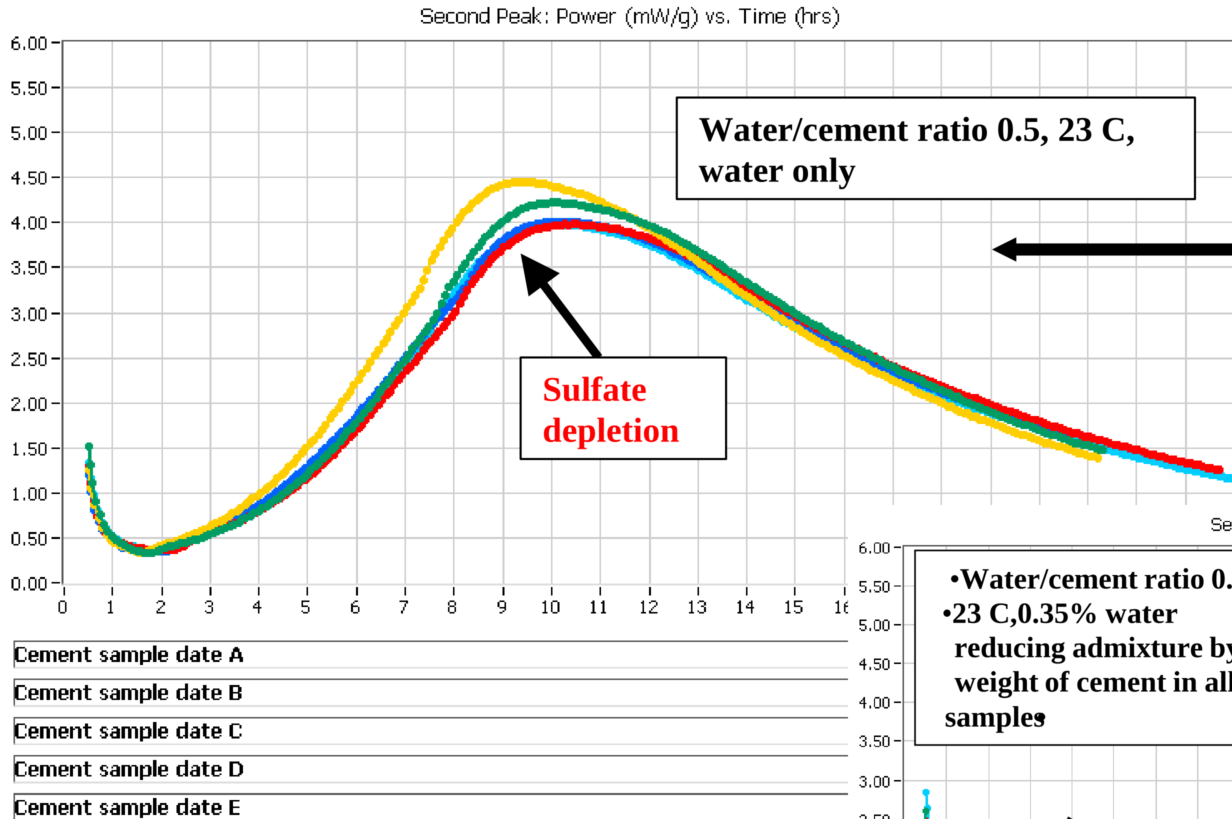
Outline

- Advantages/limitations of Predictave/Diagnostic Mortar Tests
- Applicability of the Modified ASTM C359 Test
- Modified ASM C359 Mortar Tests for Evaluating Cement-Admixture Interactions
- Case Studies
- Origins of Cement-Admixture Incompatibility
- A Few Fixes to Cement-Admixture Incompatibility
- Conclusions

Acknowledgement

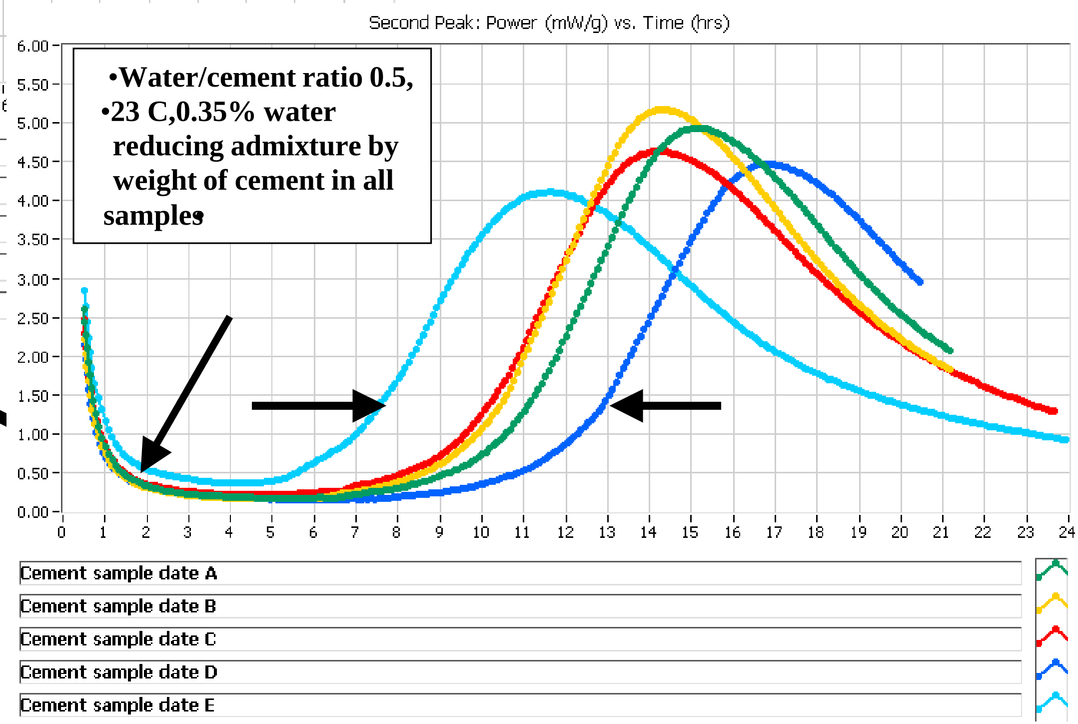
The mortar test protocols and test data were produced by the Lab Technical Services and R&D groups of the W.R. Grace Co.

Inconsistent Cement-Admixture Performance



5 Cement Samples From Same Plant - with reported setting time problems - Tested *Without Admixtures*

With Admixtures

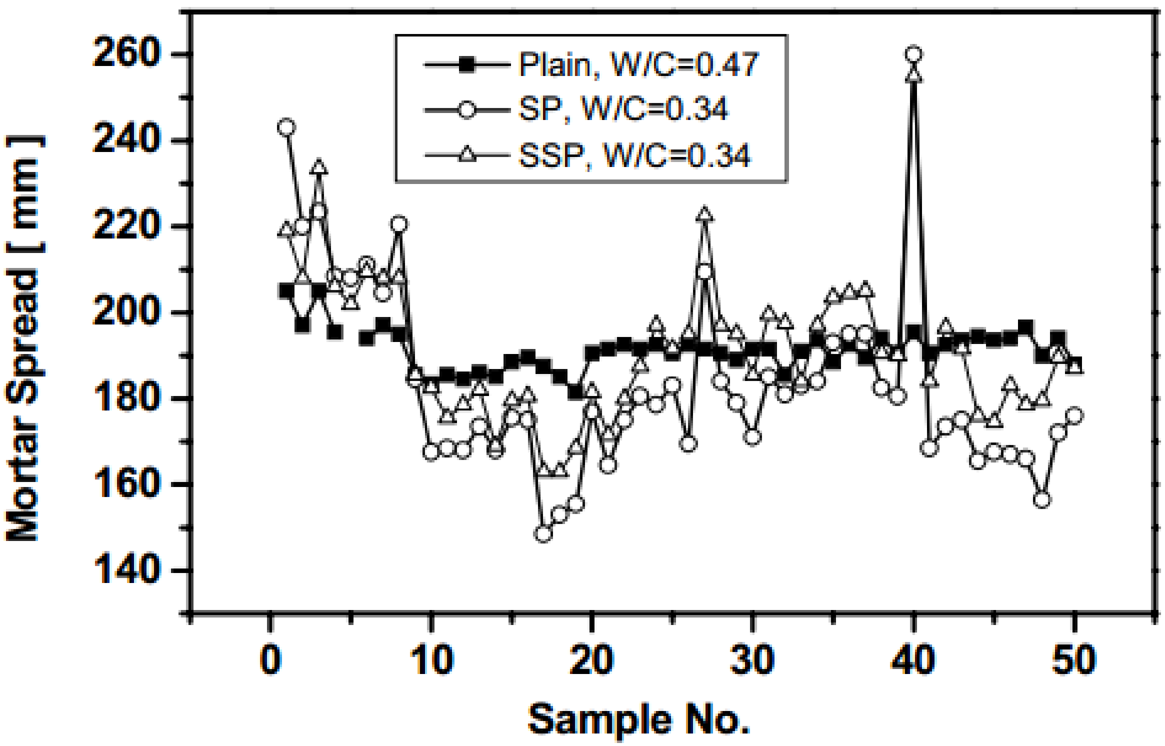


0.15% WRA [0.10% CS +0.05% TEA]

0.20% MRWR [0.10% PC + 0.05% SG + 0.05% $Ca(NO_3)_2$]

Cement-Admixture Interaction: Impact on Variation in Mortar Spread

Investigating Variable Slump in Precast Production



Spread Variation

Control	**20 mm**
SP (MSFC)	**112 mm**
SSP (PC)	**70 mm**

Mortar mixes made with 50 grab samples cement

Admixtures: Control, MSFC, and PC

Measure mortar spread

The Effects of Cement Variations on Concrete Workability, *www.vannforeningen.no/ikbViewer/Content/543501/doc-26-3.pdf*. *b*y Juvas, kappi, Salo, and Nordenswan

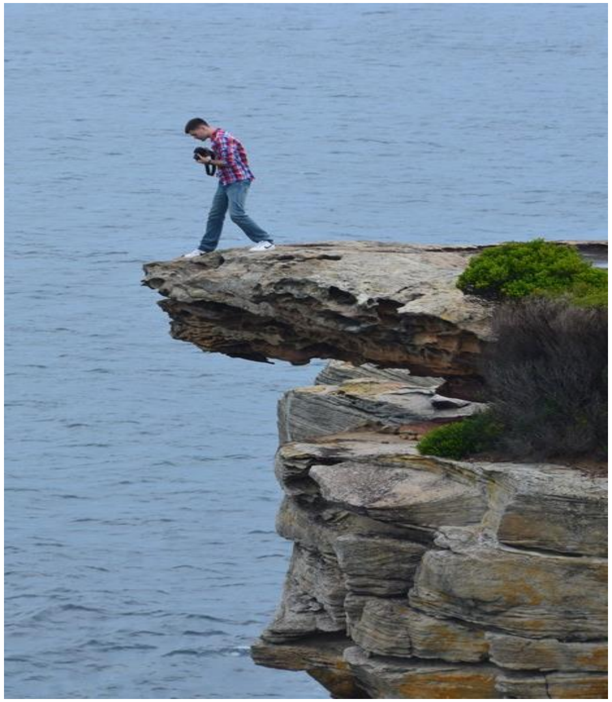
Indications of Cement-Admixture Incompatibility

- Unexpected change in dose-slump response
- Excessive slump loss
- Excessive retardation
- Low strengths
- Unusually high or low AEA doses

- "Odd" loads - one truck slumps or sets ok, the next doesn't, even though you check the plant and it all looks consistent.

Applicability of a Modified ASTM C359 Early Stiffening of Mortar Test

- The C359 Mortar Test is a well established industry standard.
- Low cost and quick. Improved manpower efficiency.
- Ongoing quality control tool to verify lot-to-lot performance uniformity for various concrete material.
- Proactively screen <u>possible relative</u> performance differences between:
  - Successive lots of same material
  - Alternate sources of materials
- Troubleshoot unexpected performance issues.
- Proactively finding the edge of disaster.



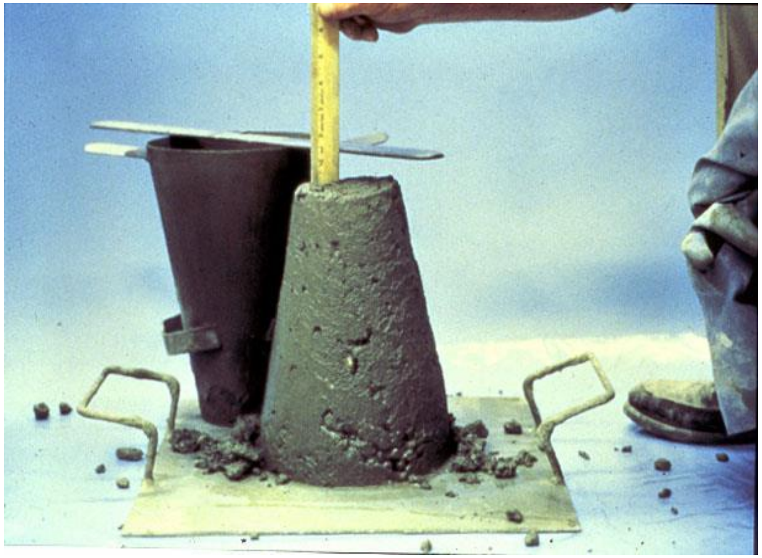
What can the Modified ASTM C359 Test Indicate?

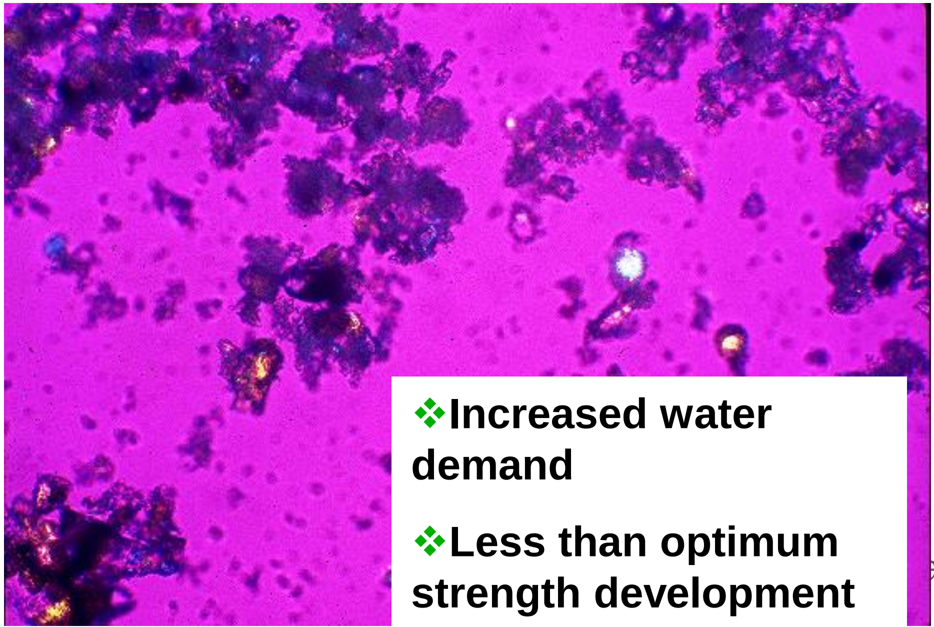
- Lack of Water Reduction by Water Reducing Admixture (WRA)
- Insufficient slump increase by WRA
- Rapid Slump Loss with WRA
- Increased water demand
- False and Flash setting tendency

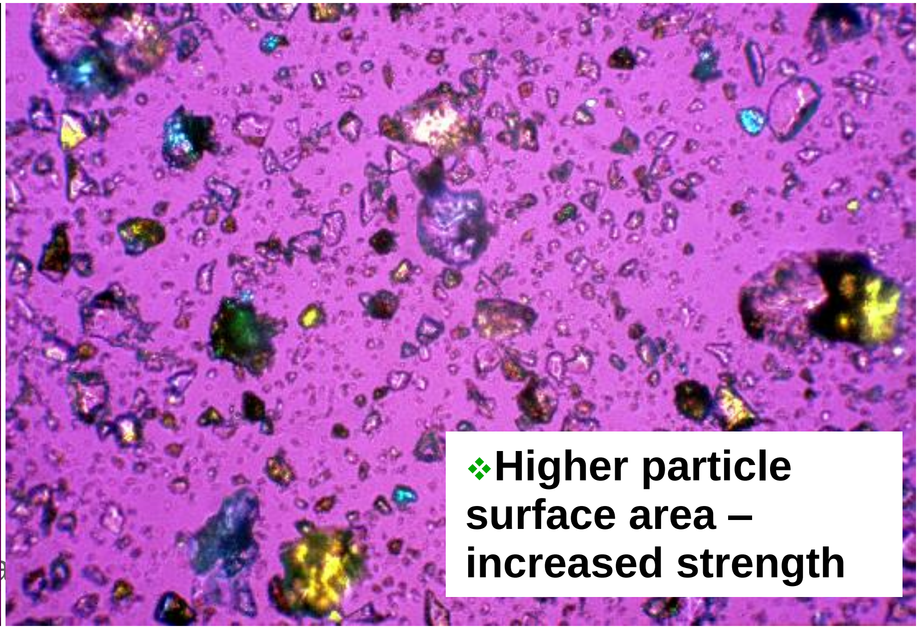
Note: Absolute mortar performance may not proportionately correspond to concrete performance.

Expected Cement Dispersing Action of Superplasticizers

This is what should happen when you add a WR/HRWR to any Concrete







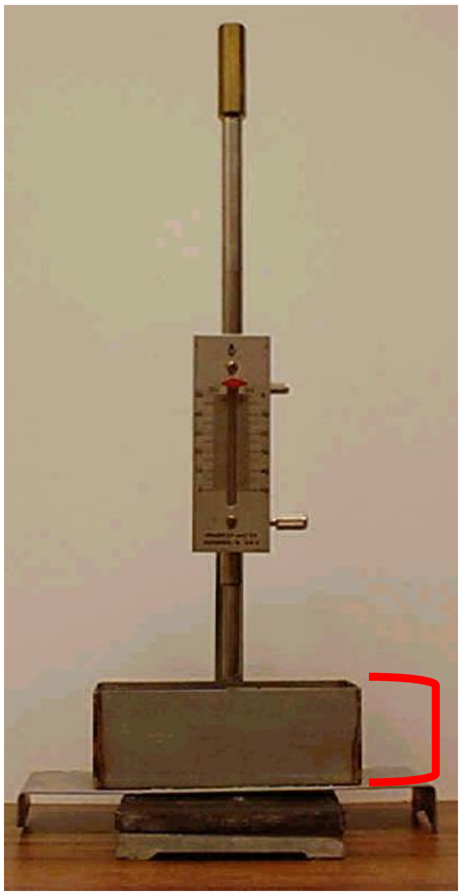
ASTM C359 Method Summary

1. **Prepare mortar with specified amounts of cement, sand, and water.**
2. **Cast a bed of mortar**
3. **Make penetration measurements with modified Vicat apparatus at set intervals. Measure temperature with every penetration reading.**
4. **Remix mortar, re-cast bed, and continue penetration measurements.**

Lab Set up for ASTM C359 Test

ASTM C359 Early Stiffening of Mortar Test

Detecting Cement – Admixture Incompatibilities



50 mm

600g cement

600 g sand

w/c = 0.30*

* Revised procedure calls for variable w/c

Modified C 359 Procedure for Admixture Addition

1	Add sand and cement, mix 10 sec slow speed	0-10 sec
2	Add water	10-15 sec
3	Mix medium speed	15 sec - 1:15
4	Stop and scrape, measure temp	1:15 - 2:00
5	Mix medium speed	2:00 - 2:15
	Stop, fill ISC vial, place in ISC	2:15 - 3:00
6	Stop, fill container (trough)	2:15 - 3:00
7	Initial penetration	3:00
8	Penetration readings	5, 8, and 11 minutes
9	Remix	11:15
10	Sop, fill container	12:00
10	Penetration reading	13:00
11	Penetration reading	16:00
12	Penetration reading	19:00

Admixture Addition Modes

Mix Wat Add'n	1 min del.	2 min Del.
10 sec		
	1:15	
		2:15

ASTM C 359 Early Stiffening Results w/ Fixed Water Content

(W/C = 0.30, Original C359 Method)

Penetration in mm / ºC

Cement →	006	017	051	133	143	170
Initial	3 / 24.1	31 / 24.8	50+ / 23.7	50+ / 24.7	50 / 23.4	50+ / 24.5
5 Minutes	1 / 25.6	1 / 25.2	45 / 23.7	50+ / 24.5	45 / 23.2	50 / 24.5
8 Minutes	1 / 25.6	1 / 25.1	29 / 23.5	50+ / 24.5	41 / 22.9	48 / 24.5
11 Minutes	1 / 25.2	0 / 24.6	6 / 23.2	47 / 24.2	10 / 22.8	48 / 24.0
Remix						
13 Minutes	2 / 23.6	46 / 23.5	50+ / 21.5	50+ / 23.0	48 / 22.2	50+ / 22.6
16 Minutes	2 / 23.6	38 / 23.5	50 / 21.4	50+ / 23.0	34 / 22.0	50+ / 22.6
Issue →	Water Demand	False Set	False Set		False Set	

As can be expected, a wide range in mortar flow and stiffening can be expected as a function of cement source.

ASTM C 359 Early Stiffening Results, Cement 006

Impact of W/C

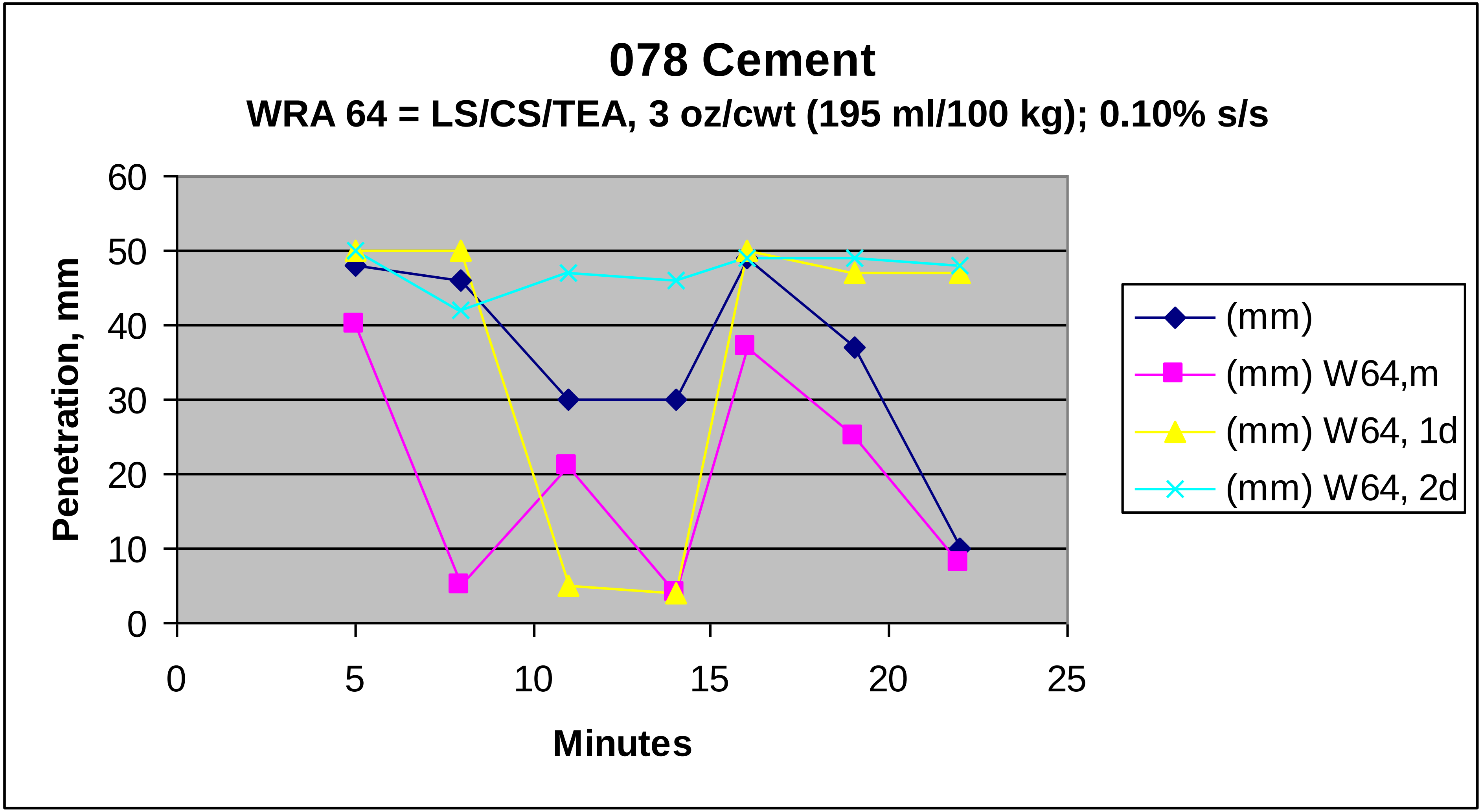
Penetration in mm / ºC

Current Approach

W/C Ratio →	0.300	0.304	0.308	0.312	0.316
Initial	3 / 24.1	4 / 24.0	22 / 23.8	40 / 24.0	49 / 23.8
5 Minutes	1 / 25.6	4 / 24.5	6 / 24.1	16 / 24.4	36 / 24.2
8 Minutes	1 / 25.6	2 / 24.2	4 / 24.2	5 / 24.5	8 / 23.7
11 Minutes	1 / 25.2	1 / 24.1	2 / 24.1	3 / 24.3	3 / 23.4
Remix					
13 Minutes	2 / 23.6	3 / 22.8	19 / 22.8	39 / 22.9	46 / 22.0
16 Minutes	2 / 23.6	2 / 22.9	5 / 22.8	14 / 23.0	27 / 22.1

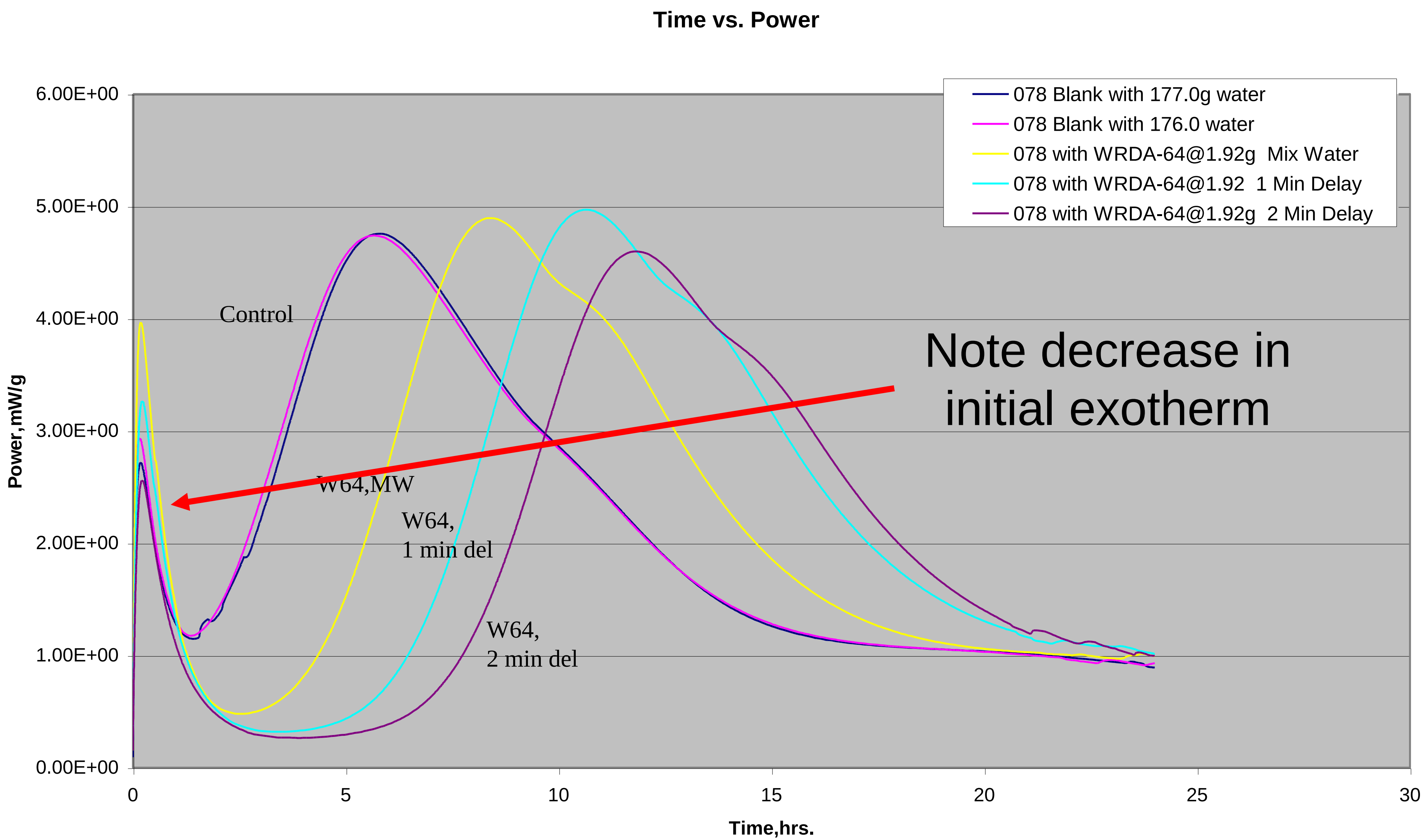
C359 test most effective when initial penetration starts 46-49 mm.

Impact of Chemical Admixture Addition Time on Stiffening of ASTM C359 Mortars



Admixture induced stiffening can be overcome by delaying time of addition after mixing of cement and water.

Isothermal Calorimetry on Mortars with Mix Water and Delayed Admixture Dosages



Delayed Addition leaves increased amount of admixture to both disperse and retard silicate phases.

C359 Test with Water Cut

Impact of Delayed Addition of Admixture on Early Stiffening

Case #0388 0023

Mix	**1** **Depth/Temp**	**2** **10% water cut** **Depth/Temp**	**3** **Mix Water Add'n** **NSFC/LS** **10 oz/cwt** **10% water cut** **Depth/Temp**	**6** **1 min delayed add'n** **NSFC/LS** **10 oz/cwt** **10% water cut** **Depth/Temp**
Initial	50/79.1	43/79.9	50/79.5	50/79.9
3	50/79.0	9/79.8	50/81.5	50/80.0
5	50/78.4	7/79.5	12/81.6	50/80.0
8	50/78.1	5/79.2	3/81.6	31/79.7
11	49/----	5/78.8	3/81.4	20/----
Remix				
13	50/76.0	10/77.7	30/78.4	15/77.7
16	50/76.1	4/77.7	10/78.7	5/77.7
19	50/76	4/77.5	5/78.6	5/77.7

Note improvement in early stiffening; however, hydrating cement seems to be <u>"sulfate starved"</u> with time.

Concrete with "C" cement exhibits satisfactory performance. Concrete with Cement "N" experiencing rapid slump loss. Case #380-0220

C 359 Early Stiffening
C Cement

	Control	**LS/CS/Amine**	**CS/LS**
		4 oz/cwt	3 oz/cwt
wc	0.30	0.30	0.3
Initial	50/74.5	50/72.8	50/70.6
5	50/74.8	50/73.4	50/71.3
8	48/74.4	50/73.8	50/71.7
11	47/73.8	48/73.6	48/72.0
Remix			
13	50/74.3	50/72.6	50/70.0
16	50/73.6	50/72.4	50/70.4

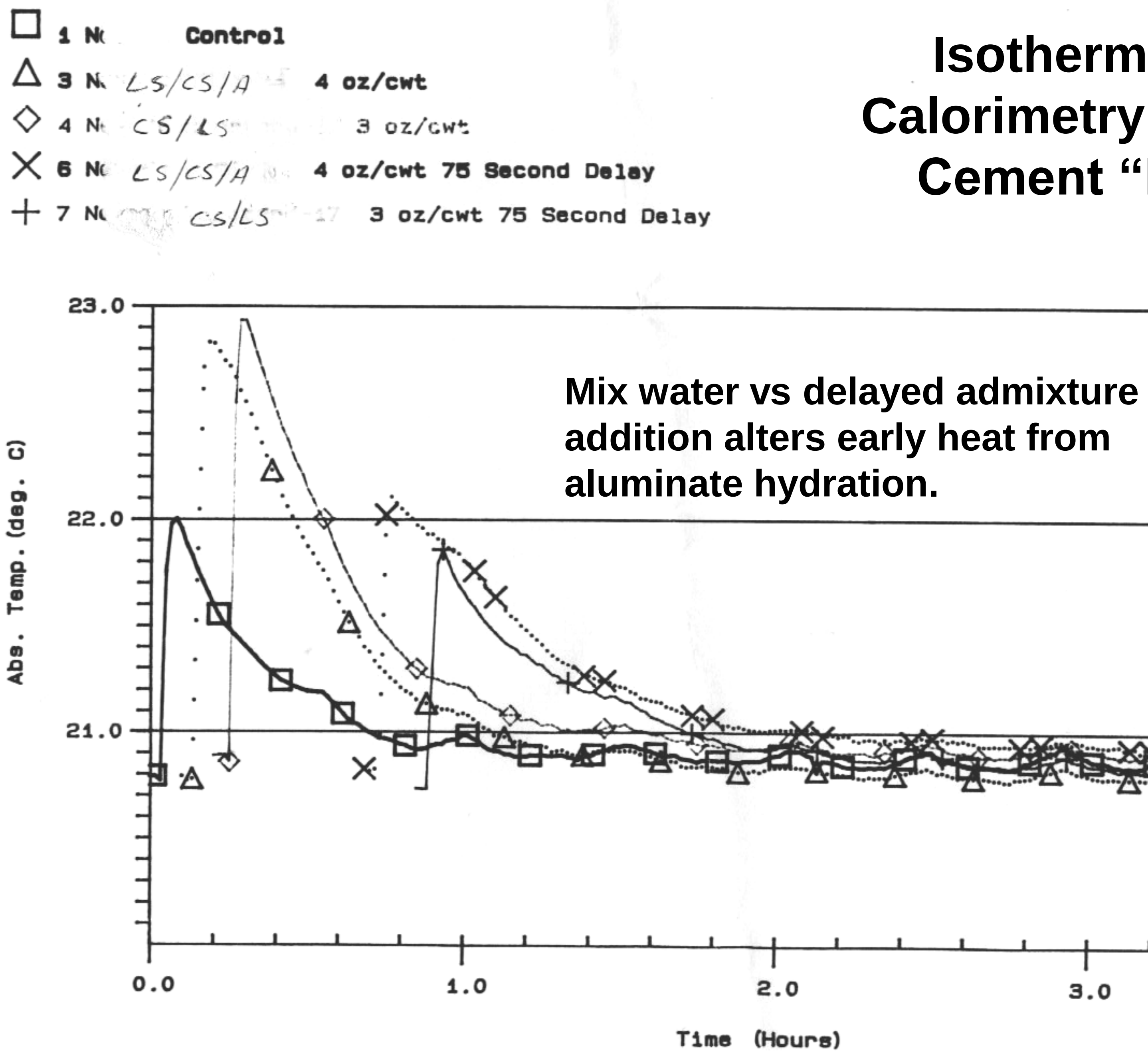
Cement C looks "normal", but all those "50s" don't say much

N Cement

	Control	LS/CS/Amine	LS/CS/Amine	CS/LS	CS/LS
			1 min 45 sec delay		1 min 45 sec delay
		4 oz/cwt	4 oz/cwt	3 oz/cwt	3 oz/cwt
	0.30 w/c	0.30 w/c	0.30 w/c	0.30 w/c	0.30 w/c
Initial	50/77.1	50/77.6	50/72.4	50/73.3	50/72.2
5	50/77.4	48/77.5	50/72.3	50/74.3	50/72.5
8	45/77.5	20/77.8	50/72.3	25/74.9	50/72.5
11	45/77.2	10/77.6	50/72.4	5/74.9	50/72.6
Remix					
13	50/74.7	50/74.8	50/72.0	50/72.9	50/71.9
16	50/75.0	45/74.7	50/72.0	50/73.0	50/72.0

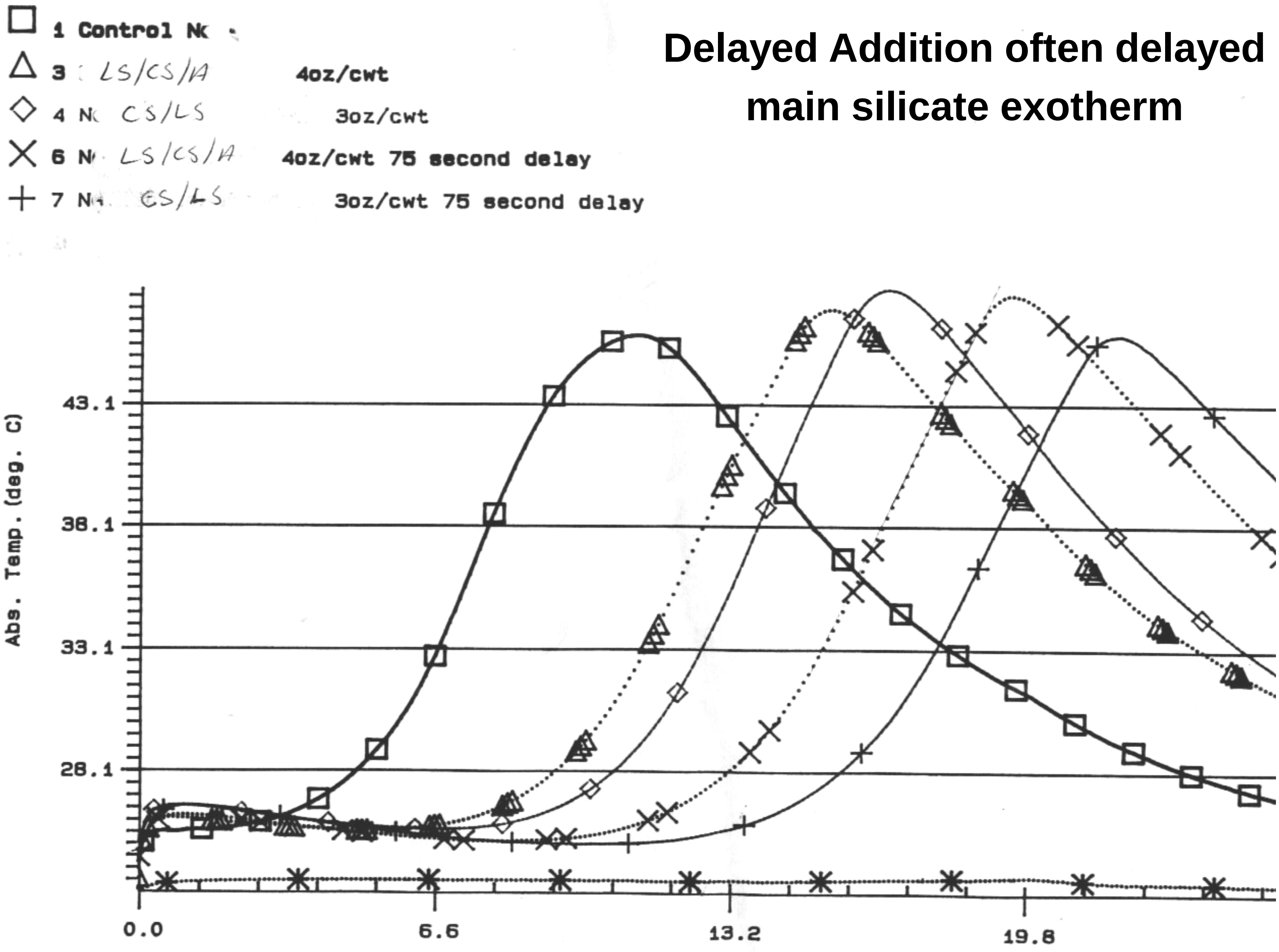
- **Early stiffening with admixture eliminated with delayed addition “TEA effect” of C4AF not apparent.**
- **Admix seems to be “inducing” false set or delaying an inherent false set in the cement.**

Isothermal Calorimetry with Cement "N"



Mix water vs delayed admixture addition alters early heat from aluminate hydration.

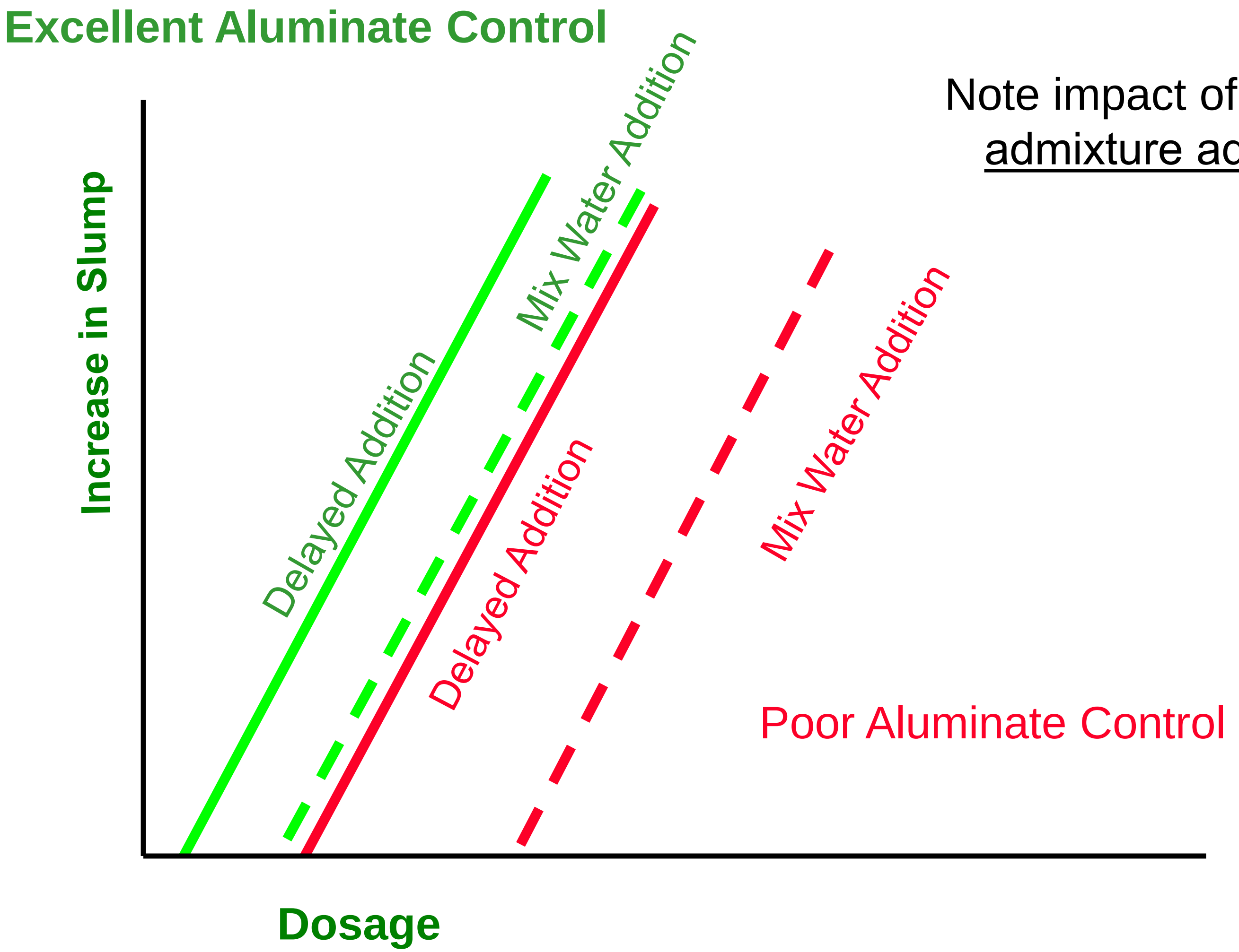
Delayed Addition often delayed main silicate exotherm



Impact of Delayed Addition

Relative impact of “aluminate control” with sulfate on dose-slump response.

Note impact of <u>“delayed admixture addition.”</u>



Possible Causes of Admixture-Related Rapid Stiffening of Mortar

- Imbalance created with rate of aluminate reactivity and sulfate availability.
  - Admixtures decreases sulfate solubility
  - Admixture increases reactivity of aluminate through cement dispersion.
  - Admixture shifts false set to the time of penetration measurements.
  - Admixture accelerates ettringite formation
- Interestingly, early stiffening problems - whether false set or flash set – w/ and w/o admixtures – can occur with all concrete materials conforming to their respective specs.
- Concrete materials rarely, if ever, qualified with admixtures.

Basic Cement Hydration – Many Complex Chemical Reactions

Tricalcium silicate (Alite, C_3S) $\xrightarrow{\text{water}}$ Calcium silicate hydrate (CSH) + $Ca(OH)_2$

Dicalcium silicate (Belite, C_2S) $\xrightarrow{\text{water}}$ Calcium silicate hydrate (CSH) + Ca(OH)2

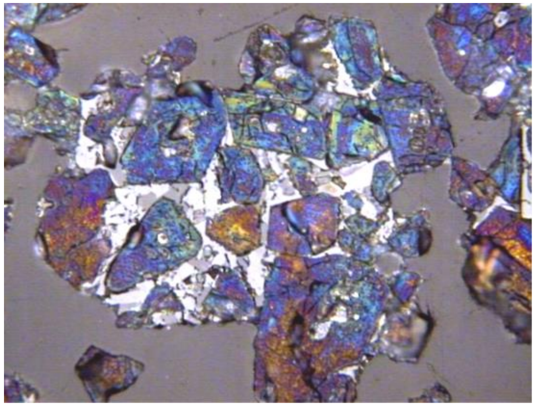
Tricalcium aluminate (C_3A) $\xrightarrow{\text{water}/Ca(OH)_2}$ Tetracalcium aluminate hydrate (BAD!!)

(Arch enemy of water reducing agents)

$\xrightarrow{\text{water/gypsum}}$ $C_3AS_3H_{30\text{-}32}$ ettringite, AFt

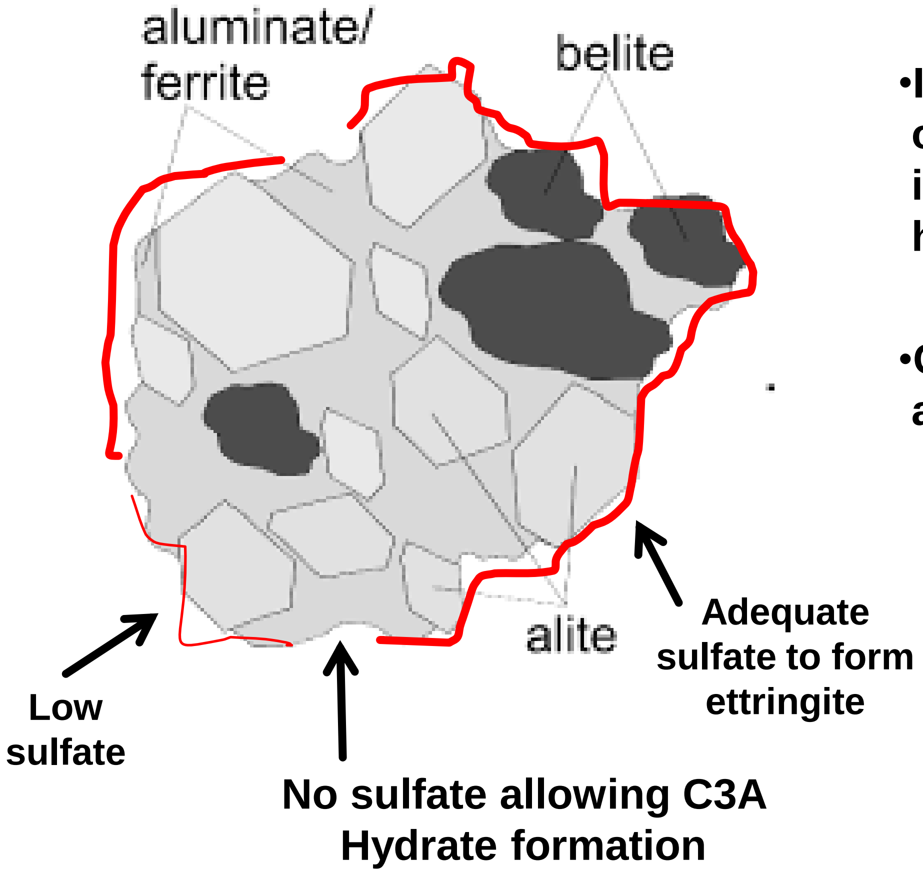
Tetracalcium aluminoferrite (C_4AF) $\xrightarrow{\text{water}/Ca(OH)_2}$ Calcium aluminoferrite hydrate

C_3A: Continuous phase in cement. Reactivity must be balanced with sulfate availability, otherwise, severe setting problems can occur.



Abnormal Cement-Admixture Interactions: Possible Explanation

Aluminate hydrates



- Let's assume the red line represents inter-ground sulfate on surface of cement.

- It is believed that there are localized areas of C3A where insufficient available sulfate is available to eliminate direct C3A hydration.

- Consequences of direct C3A hydration in absence of sulfate:
  - -Large exotherm
  - -Rapid stiffening/hardening
  - -Rapid/extensive chemi-adsorption of organic molecules/polymers

Intercalation of Sulfonated Polymer in C_3A Hydrate

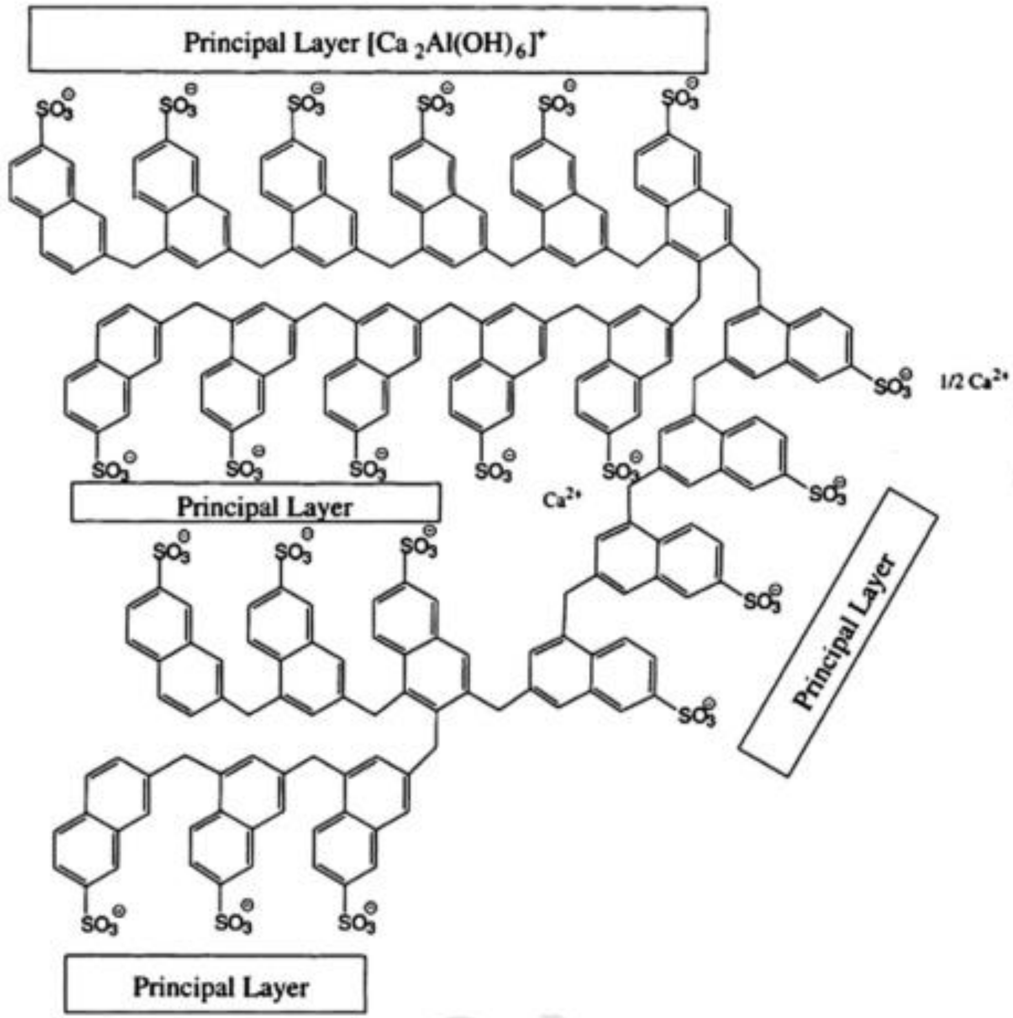
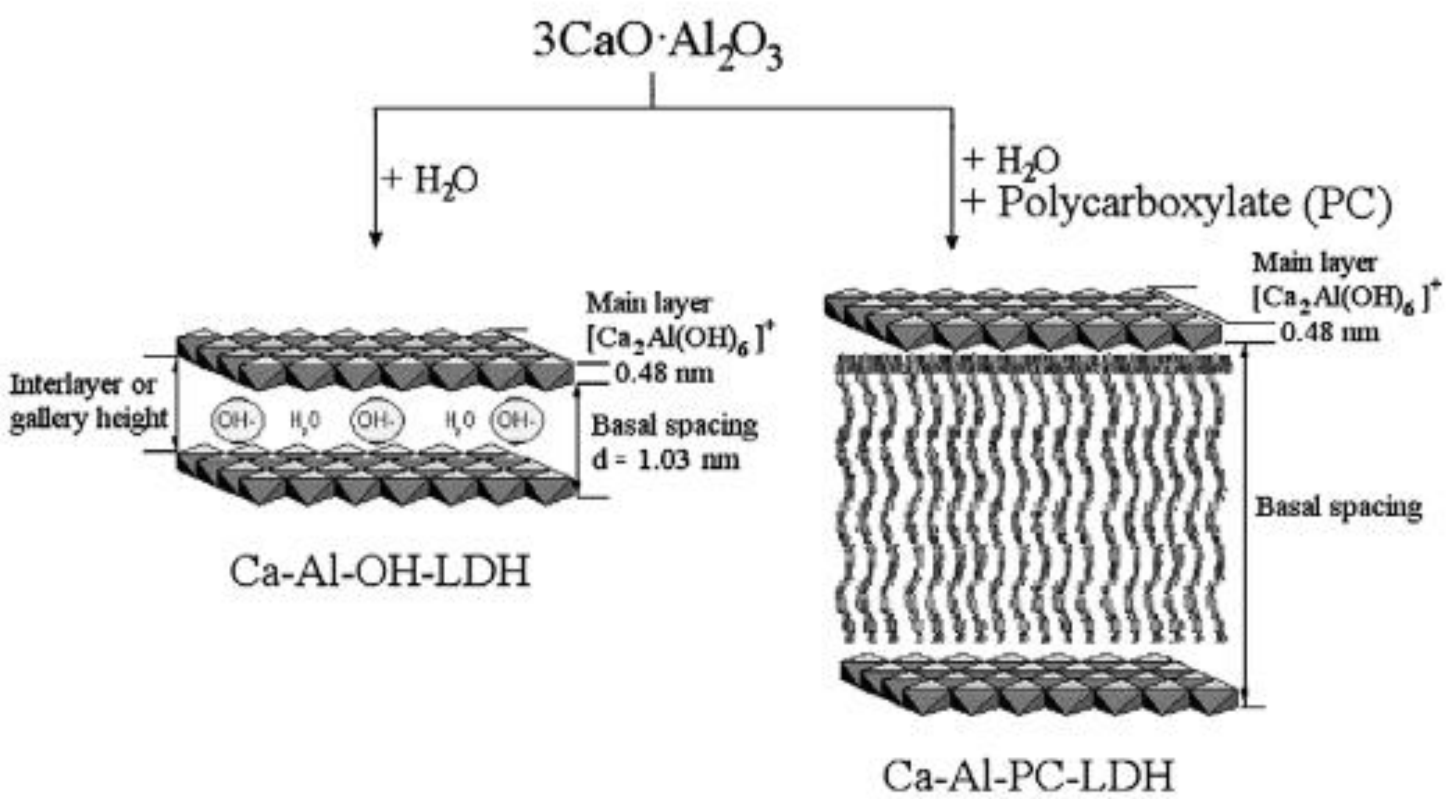


Fig. 15. Structural model proposed by Fernon et al. [101] for C_4AH_x with polynaphthalene sulfonate.

[101] V. Fernon, A. Vichot, N. Le Goanvic, P. Colomber, F. Corazza, U. Costa, Interaction between Portland cement hydrates and polynaphthalene sulfonates, Fifth CANMET/ACI conference on superplasticizers in concrete, ACI, 1997, pp. 225–248, SP-173.

Synthetically Prepared C3A-PCE

J. Plank et al. / Inorganica Chimica Acta 359 (2006) 4901–4908



Forms of Inter-ground Calcium Sulfate that can found in Portland Cement

Gypsum $CaSO_4 \cdot 2H_2O$

normal additive to cement production

dehydrates to plaster if mills are hot (most are)

Controls aluminate well if aluminate has normal activity

Plaster $CaSO_4 \cdot 1/2\ H_2O$ "hemihydrate"

only comes from dehydration of gypsum in mill – not added

causes false set if too high

best for control of very active aluminate

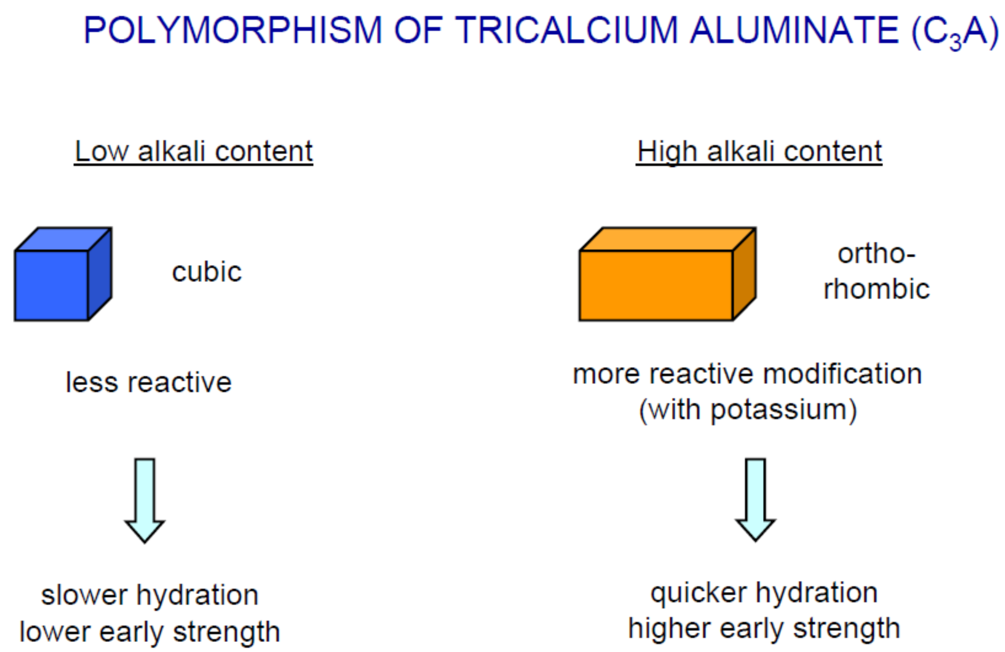
Anhydrite $CaSO_4$

added to limit false set or lower cost

poorest control of aluminate – implicated in flash set

admixtures can depress rate of solubility

C3A in Portland Cement



- **Orthorhombic C3A (sometimes called alkali-aluminate) is formed when alkalis are incorporated into the C3A crystal lattice.**
- **The orthorhombic form of C3A is more reactive versus the cubic structure.**
- **Changes in Ortho C3A/cubic C3A contribute to inconsistent admixture performance.**

•(See http://www.springerlink.com/content/d63w6761l7l23559/fulltext.pdf)

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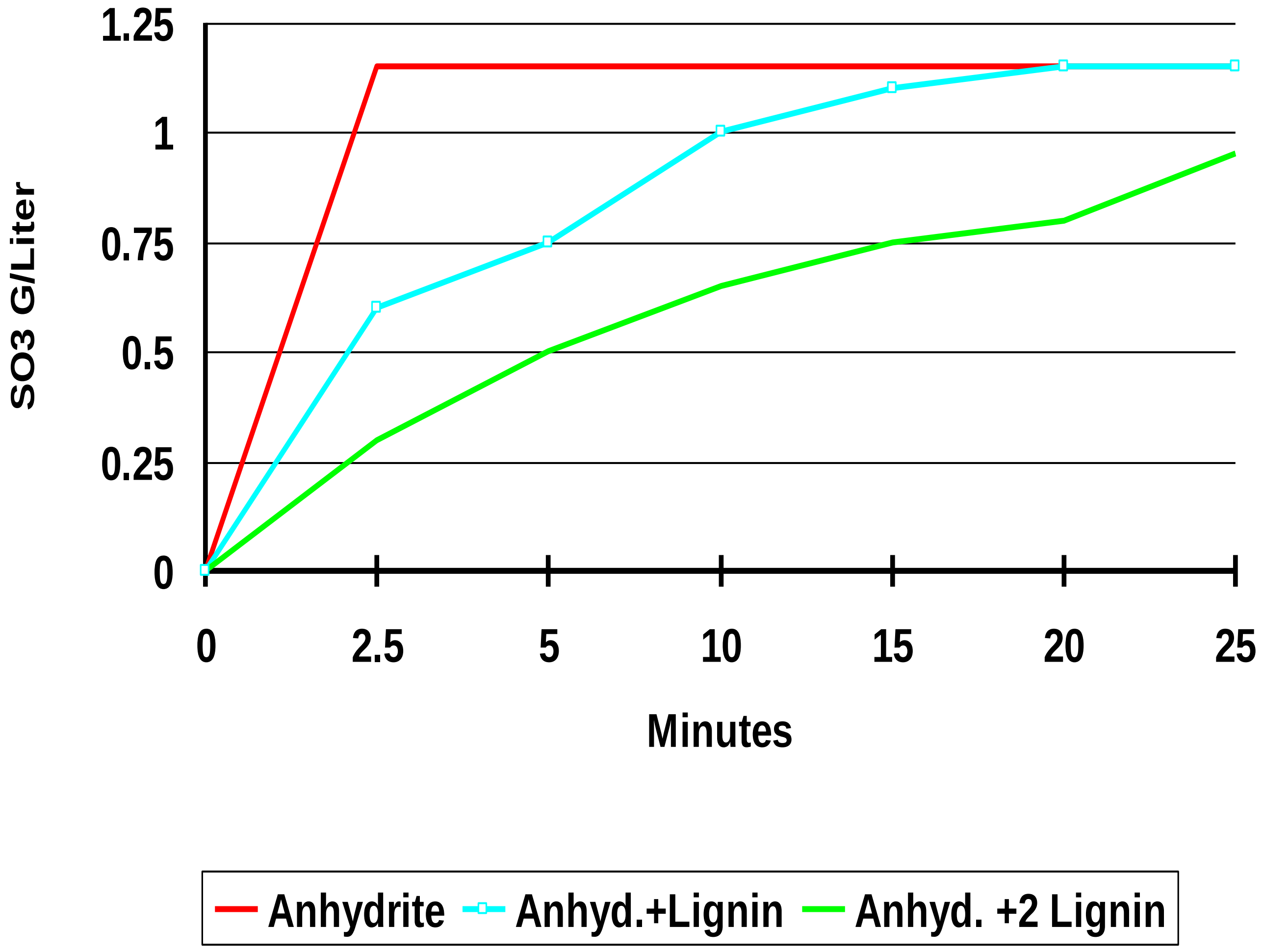
Impact of Admixture on Anhydrite Solubility Rates

Certain dispersants can alter sulfate solubility!!



V. H. Dodson, T.D. Hayden, Another look at the Portland Cement / Chemical admixture incompatibility problem, Cem Concr Res 19 (1989) 52 – 56.

Impact of delayed addition on sulfate solubility for C3A-anhydrite System

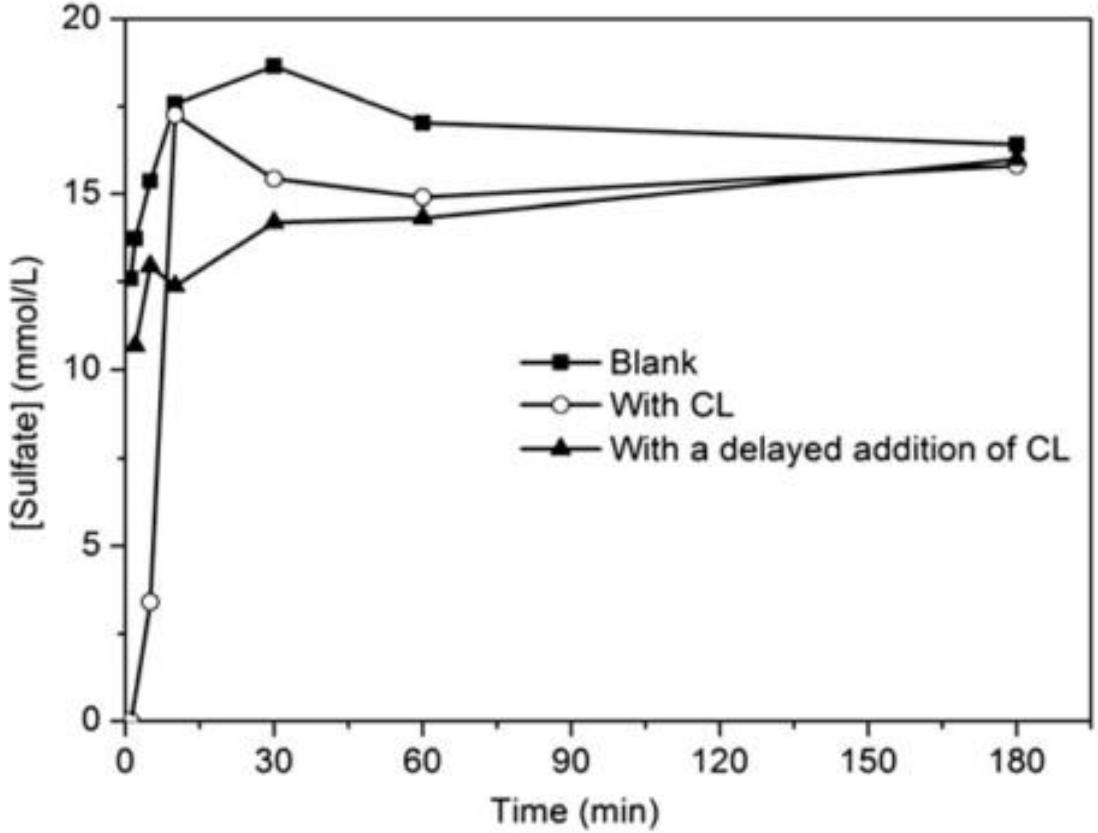


Fig. 2. SO_4^{2-} concentration vs. time during the C_3A–anhydrite hydration in the saturated $Ca(OH)_2$ solution (L/S = 10).

Effect of calcium lignosulfonate on the hydration of the tricalcium aluminate–anhydrite system

Xiaoping Wang, Yuxia Pang, Hongming Lou, Yonghong Deng, Xueqing Qiu *

School of Chemistry and Chemical Engineering, State Key Laboratory of Pulp & Paper Engineering, South China University of Technology, Guangzhou, Guangdong, China

Possible Approaches to Address Cement-Admixture Issues

- **Delayed Addition - A Universal Fix?**
  - **Allows SO_3 to be available closer to aluminate reactivity**
- **Change Order of Addition with Multiple Admixtures**
- **Alternate Admixtures**
- **Work with cement producer to understand problem possibility modifying cement, especially adjusting SO_3.**

Summary

- The ASTM C359 test can be modified to accommodate admixtures, and potentially indicate cement-admixture incompatibilities.
- Low cost, efficient, and easy to perform.
- Useful for verifying cement lot-to-lot uniformity, with and without chemical admixture.
- Use of the C359 test in conjunction with isothermal calorimetry and cement mineral analysis have provide mechanistic understanding of good vs bad cement-admixture interactions.
- Modifications to the C359 test can include both admixture and SCM variations.

Thank you for your attention.
All questions most welcome.

Jeknavorian Consulting Services