Use of Chemical Admixtures to Enable Successful Manufacture of Concrete with Low Portland Cement Content

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ACI Spring 2015 Convention Kansas City

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Outline

- General Mix Design Strategy with HVFA
- The setting time and early strength challenge
- Chemical admixture options and approach
  - Flexing Polycarboxylate Technology
  - Mapping Set and Strength Accelerators
- Harnessing chemical admixture synergies to maximize early strength development

Acknowledgment

W.R. Grace R&D

General Mix Design Strategy for HVFA Concrete Mixtures

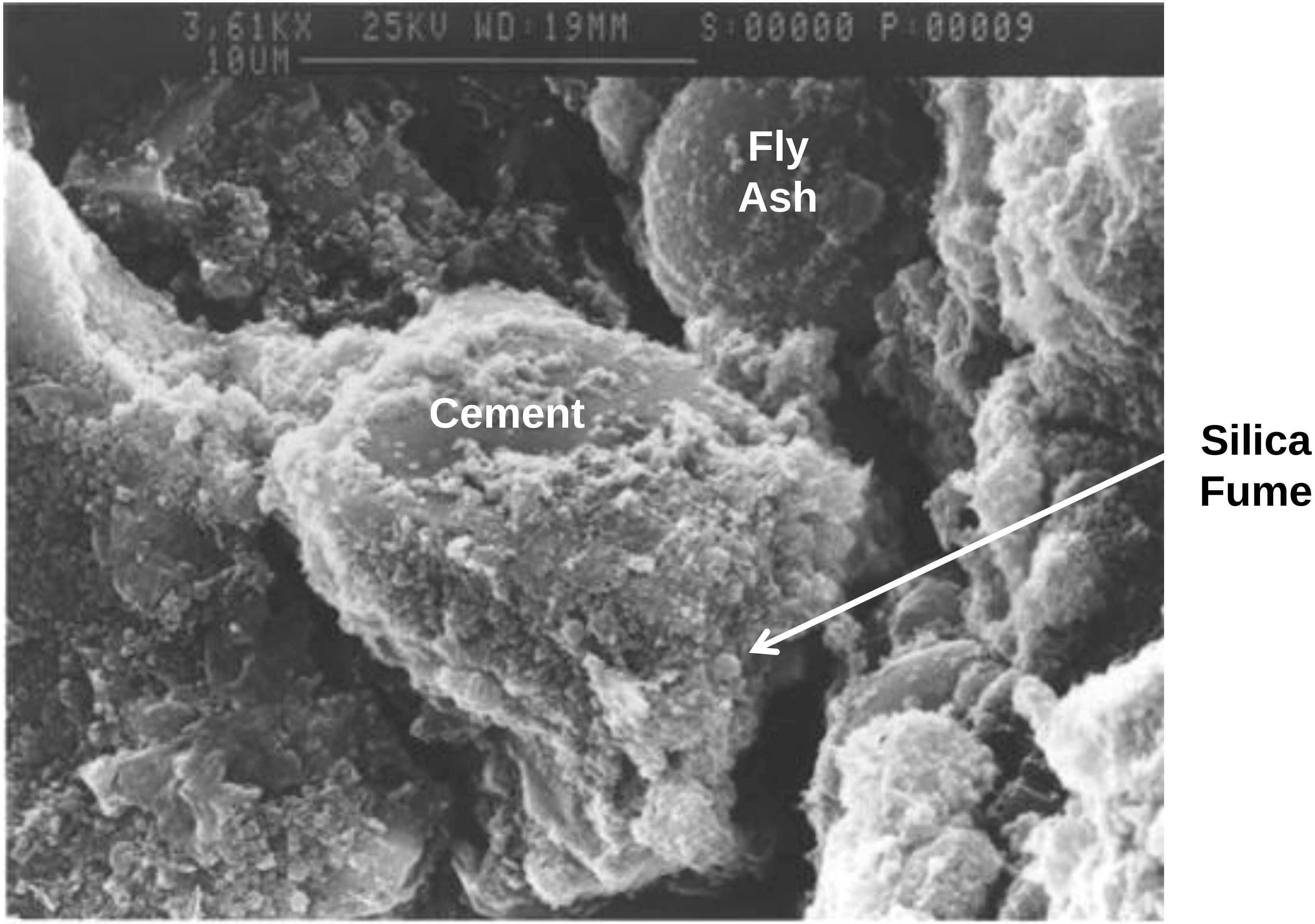
• Cementitious Content	375-800 pcy (220-470) kg/m^3)
• Cement/SCM	40-60%
• w/c	<0.40
• WR/MRWR/HRWR	Essential
• Set Accelerator	Req’d for set/early strength
• Air Entrainment	Freeze-thaw applications

Factors inhibiting increased cement replacement by SCMs

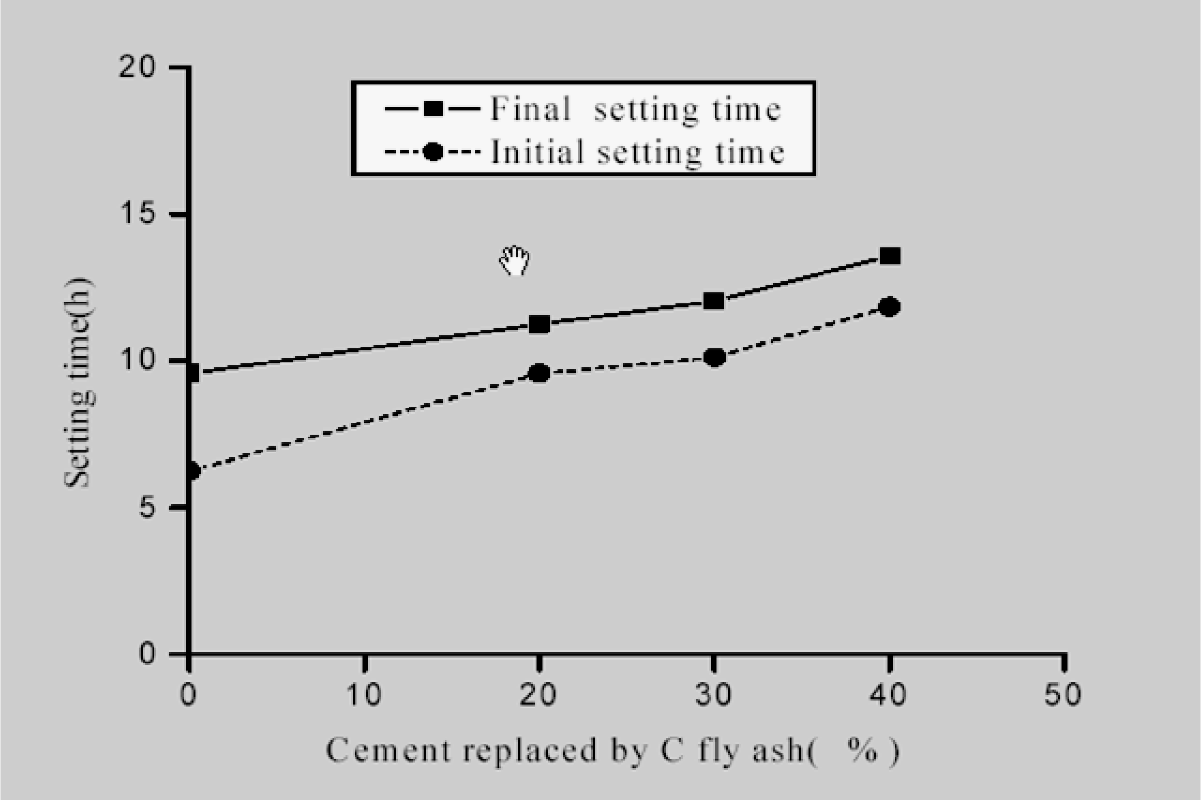
- **Retarded set and strength development** *
- **Excessive retardation at cold temperatures** *
- **Inconsistent air entrainment** *
- **“Stickiness”** *
- **Prescription specified mix designs**
- **Spot shortages of quality materials**

***Opportunity for Chemical Admixtures**

SEM of 1-day Concrete with Cement and Fly Ash



Impact of Fly Ash Replacement on Setting Time



BSA = 819 m^2/kg, main particle size ~ 6 micron

Sample ash	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Cl^-
C	48.2	30.31	5.57	3.85	1.05	1.34	0.60	0.30	0.009

Increasing SCM Content, increases initial and final set times

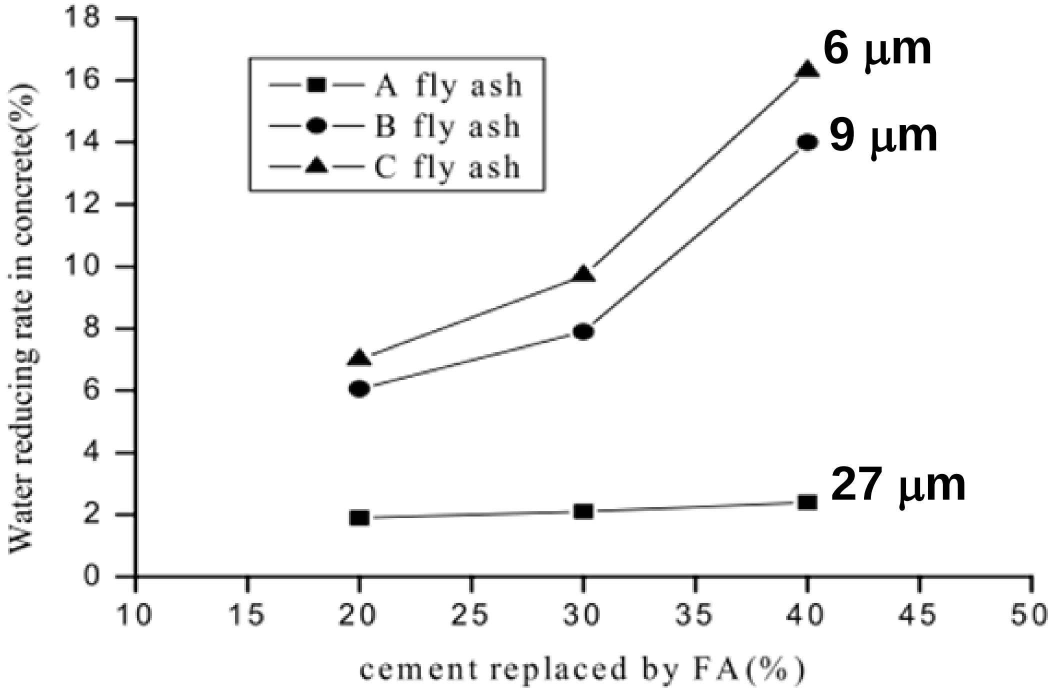
Yijin, L., Zhou, S., Jian, Y. and Yingli, G. "Effect of Fly Ash on the Fluidity of Cement Paste, Mortar, and Concrete," International Workshop on Sustainable Development and Concrete Technology, Beijing, May 2004.

Municipal Specifications Adjust Fly Ash Content as a Function of Temperature (Austin, TX)

	Hot Weather	Moderate Weather	Cold Weather
Cement, lbs/cy	300	325	400
Fly Ash, lbs/cy	150	125	100
% Replacement	33%	28%	20%

http://www.ci.austin.tx.us/greenbuilder/fs_flyashconcrete.htm

Water Reduction by SCMs - Replacement Level & Particle Size



Ash collected from precipitator and air classified into 3 fractions.

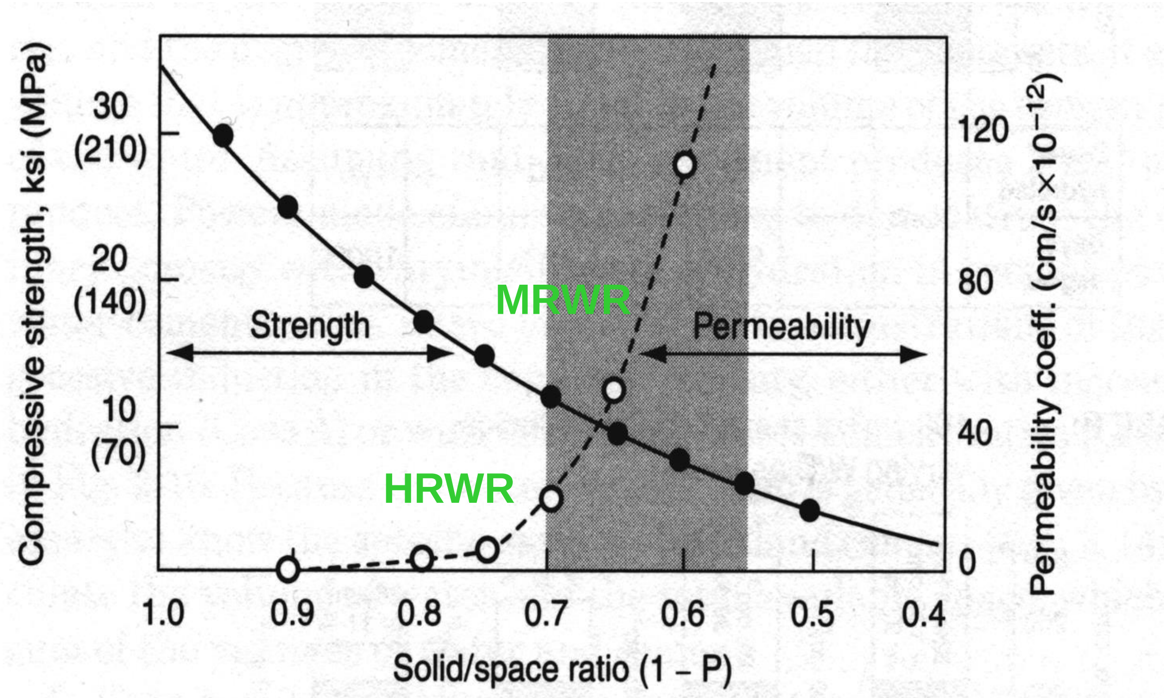
Increased Fineness favors more spherical morphology
Increased lubricating effect and packing density

Yijin, L., Zhou, S., Jian, Y. and Yingli, G. "Effect of Fly Ash on the Fluidity of Cement Paste, Mortar, and Concrete," International Workshop on Sustainable Development and Concrete Technology, Beijing, May 2004.

Chemical Admixture Strategy for Early Strength

- **Water Reduction with Polycarboxylate Technology**
- **Mapping/Selection Set and Strength Accelerators**
- **Harness Synergistic Interactions**

Influence of W/C on strength and permeability



Power's Equation:

Porosity or solid/space ratio, *x*, exponentially related to strength, *S*, and permeability.

$S=kx^3$, where k=34,000 psi (235 mpa)

P.K. Mehta, "Concrete Structure, Properties and Materials," p 33 (1986).

Superplasticizer Selection

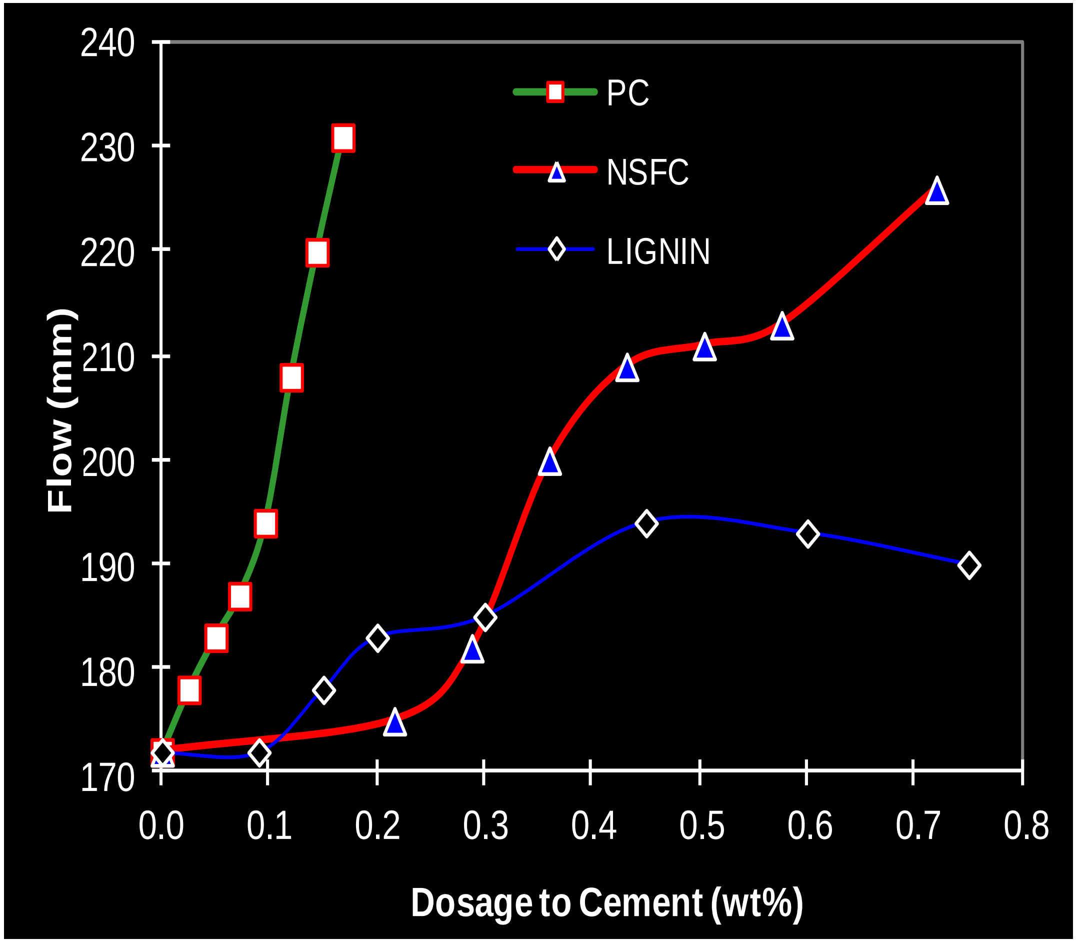
- Chose superplasticizer chemistry with maximum dose/slump efficiency.
- In general, the lower the dosage of water reducing admixtures to achieve a particular degree of concrete workability (slump), the less the impact on the rate of cement hydration.
- Maximize:

$$\frac{\text{Workability Increase or Water Reduction}}{\Delta\ \text{Set}}$$

$$\frac{\text{Early Strength Increase}}{\Delta\ \text{Workability or Water Reduction}}$$

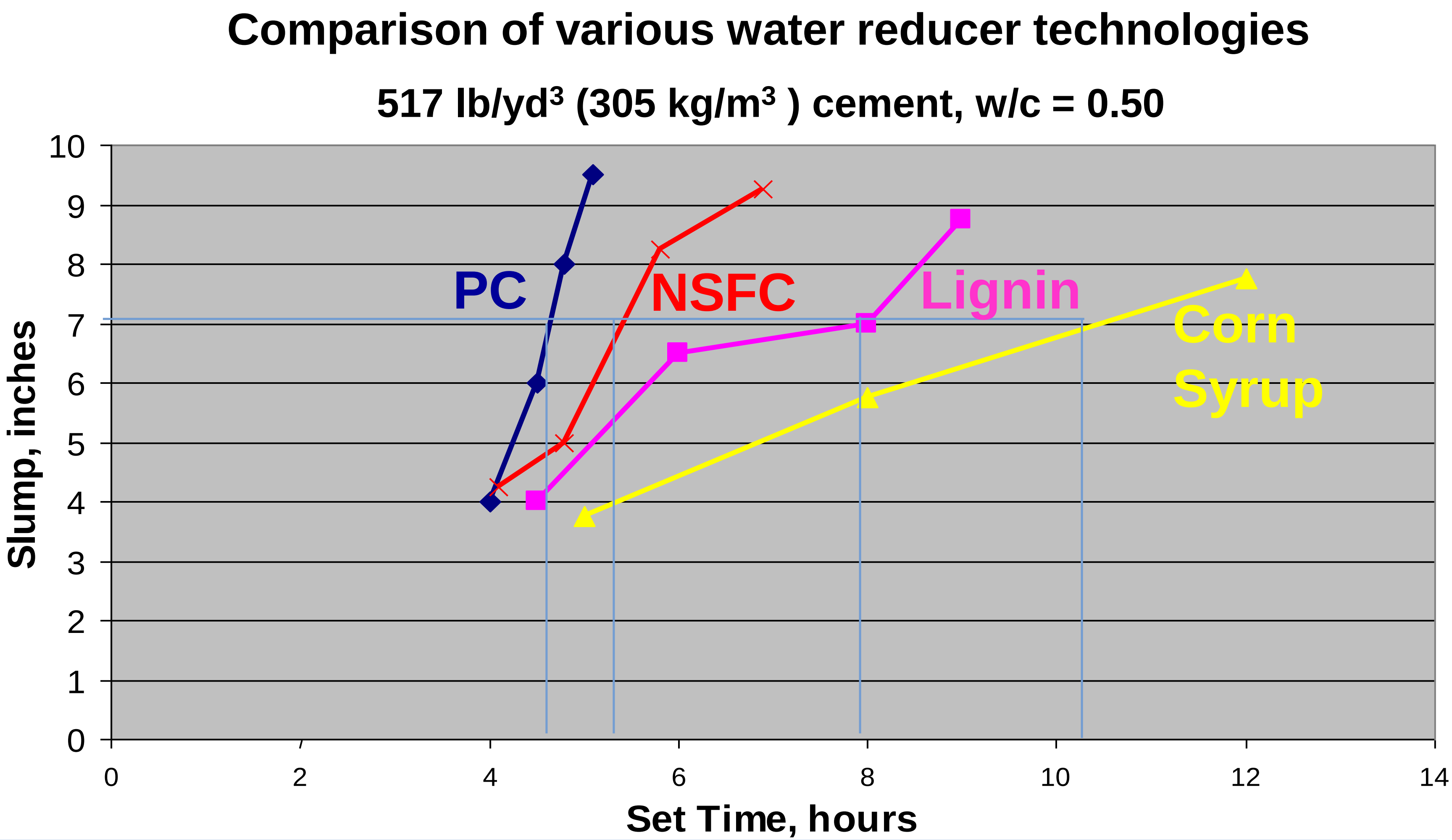
- Correlate dispersant selection with “stickiness”

Mortar Mixtures Dosed with Various Water Reducers
Comparison of dose/slump efficiency



PCE most dose/slump efficient

Slump Increase as a Function of Set Time

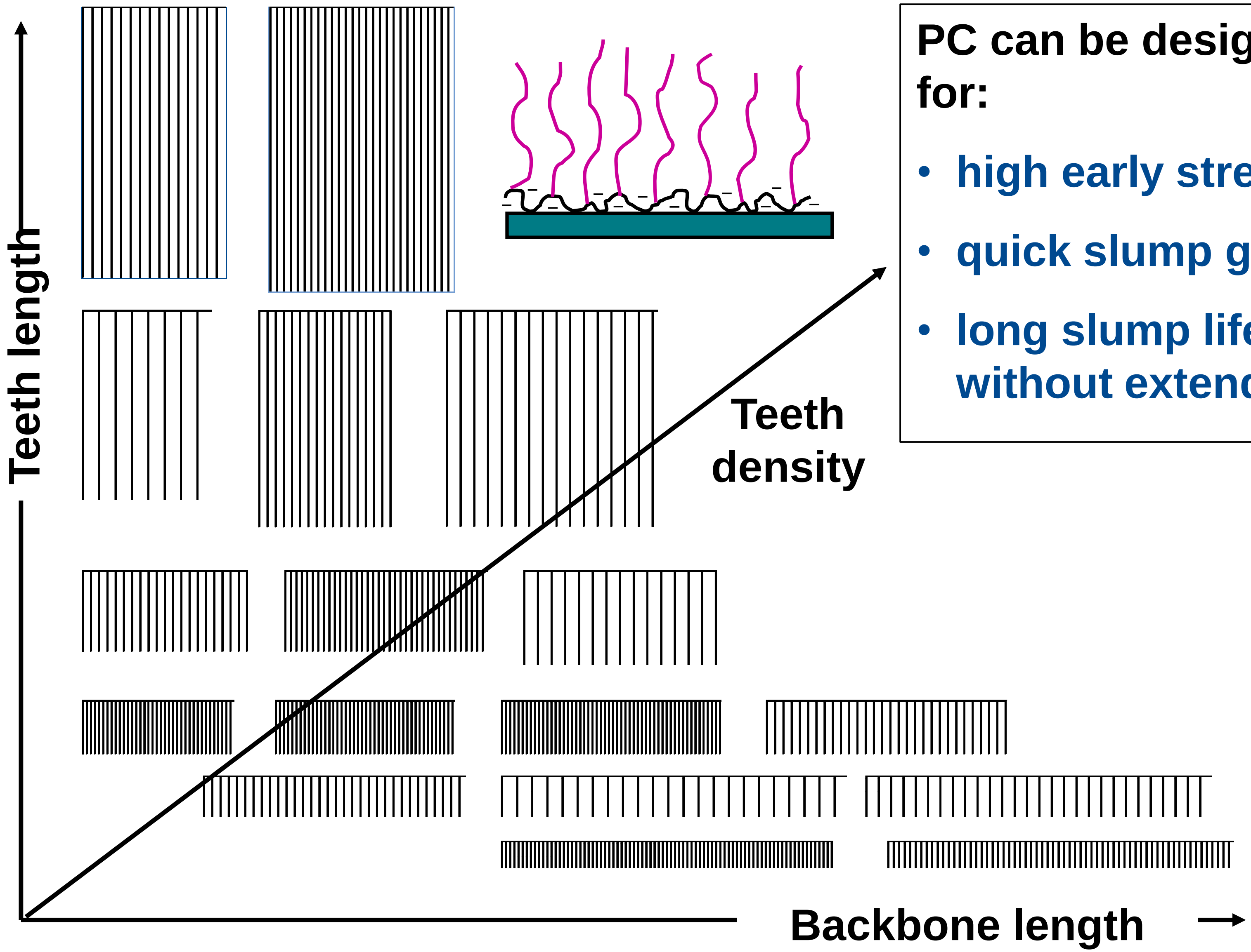


PC provides most favorable slump/Δ set

Set Times when dispersant dosed for 3➡7” (180 mm) slump:

PC – 4.5 hrs NSFC - 5.5 hrs Lignin - 8 hrs Corn Syrup – 10.25 hrs

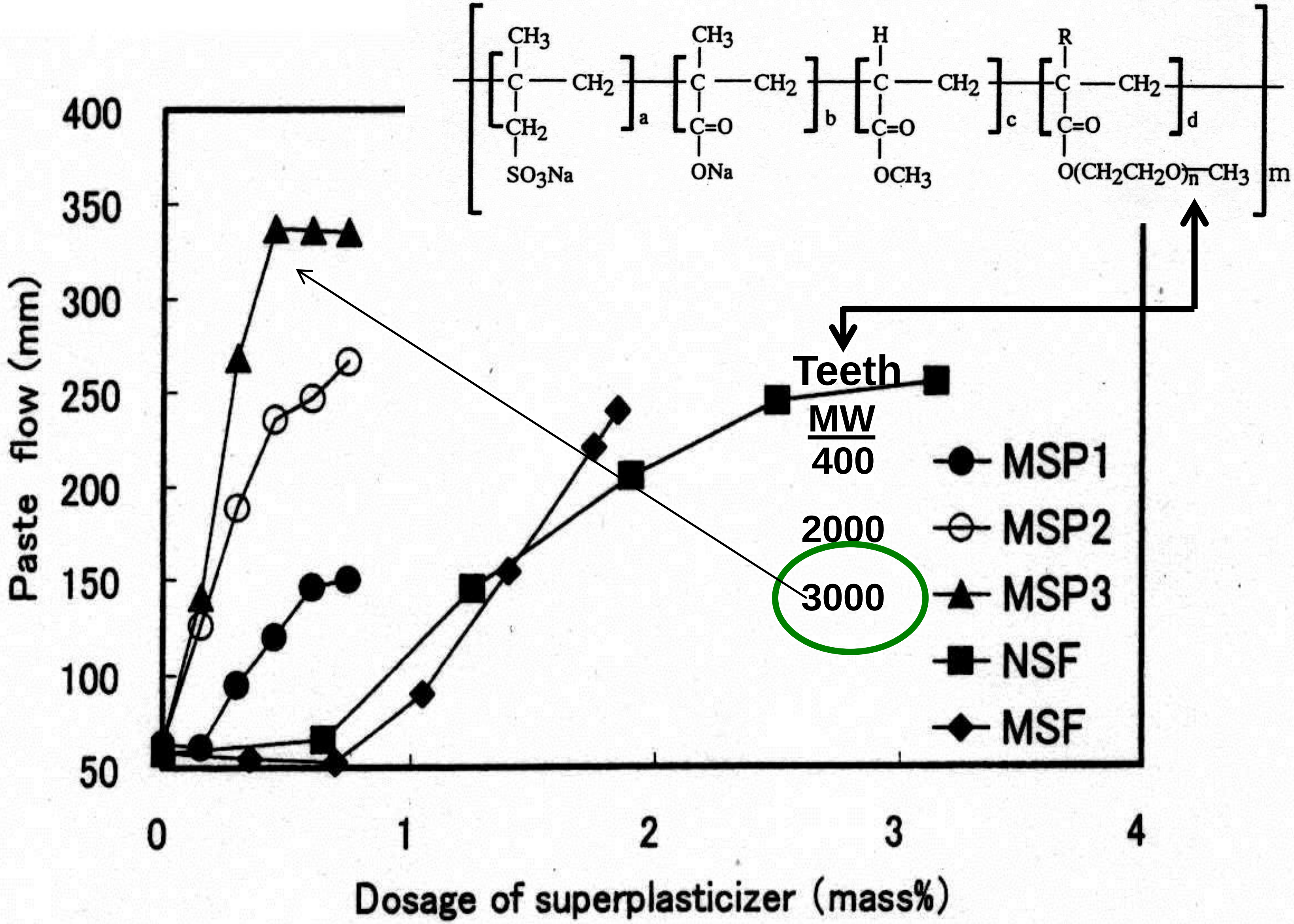
PCs can be designed for a Wide Range of Performance



PC can be designed for:

- high early strength
- quick slump gain
- long slump life without extended set

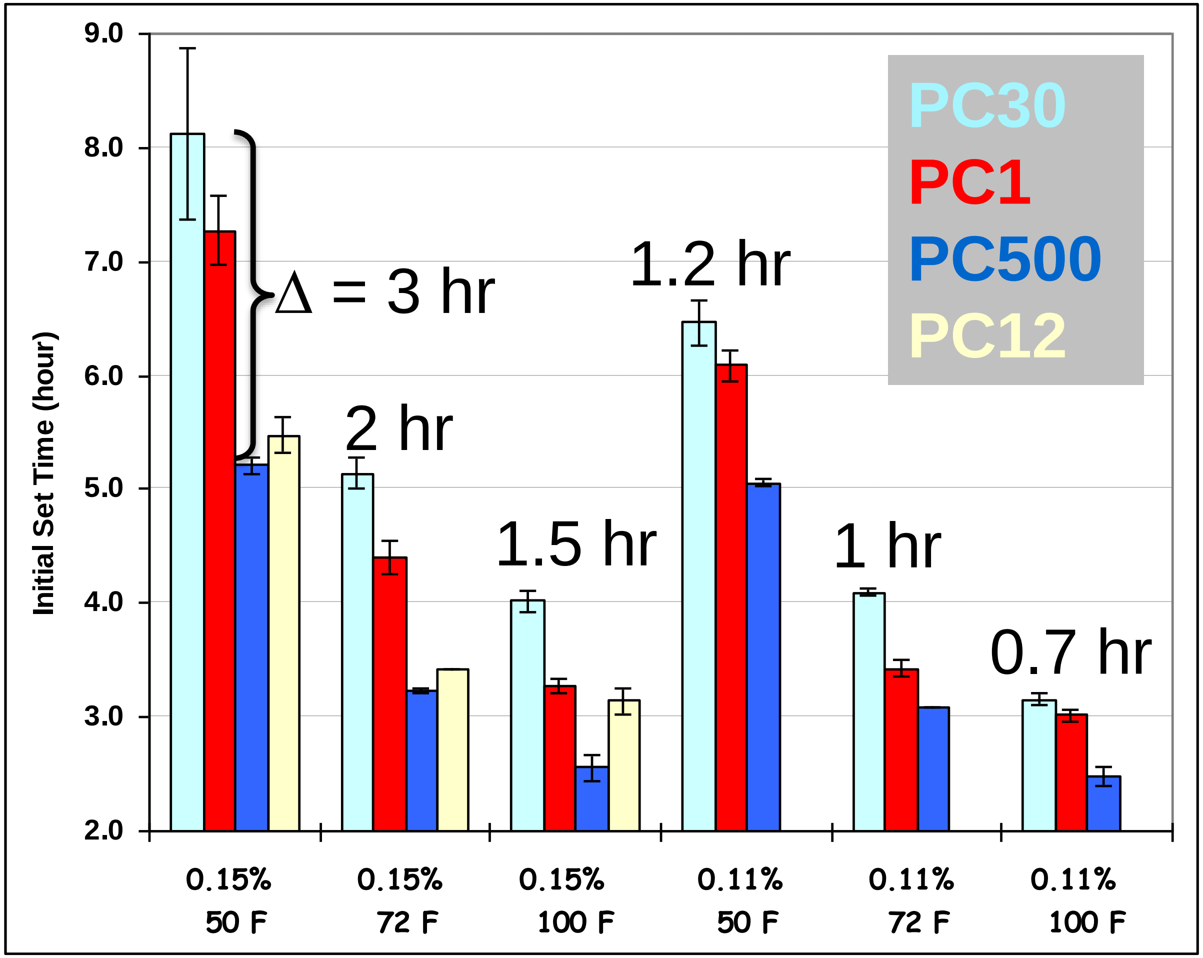
Paste Flow as a Function of Superplasticizer Structure and Dosage, 20°C



Nawa et. Al. Nice Conf. HRWR, 2000

Effect of Four PC on Set Time of Concrete with 40% Slag

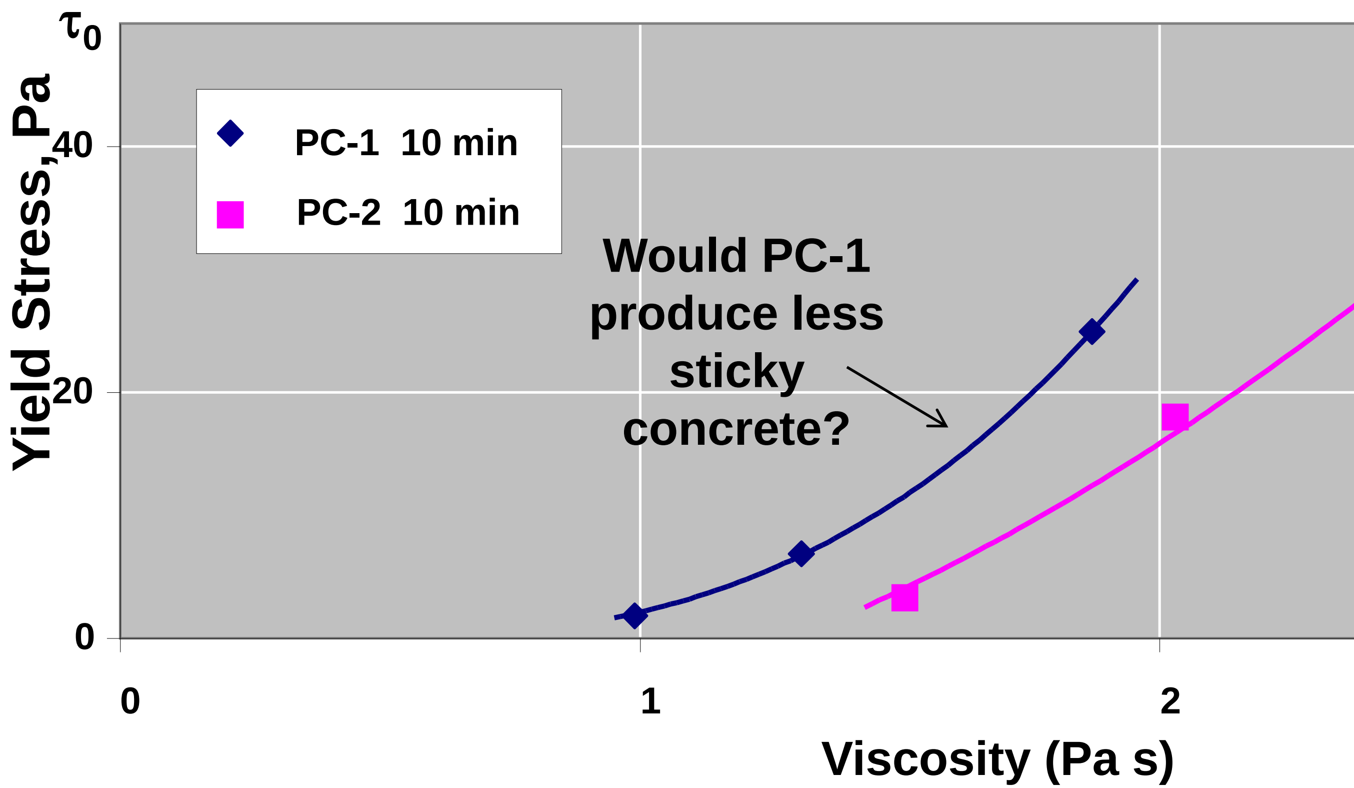
Mix design :
708 lb/yd^3,
40% Slag,
w/cm = 0.45

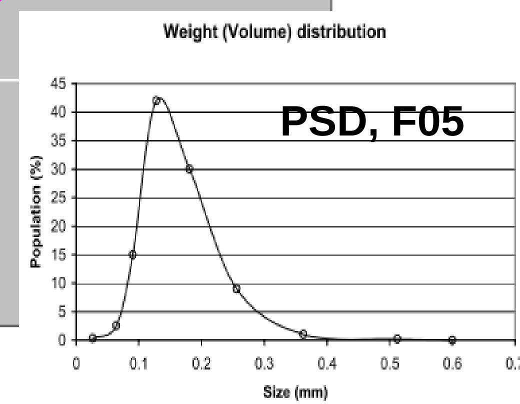


Set time differences among PCs increases with both dosage and lower temperatures.

PC Selection for Optimum SCC Rheology

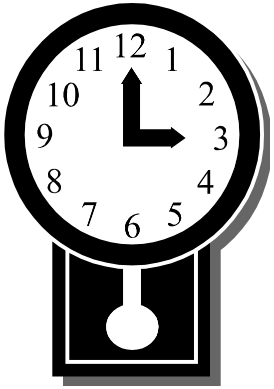
Rheological Measurements of PC-admixed Micromortar Mixtures. C=30g; Sand=54g; w/c = 0.5





- **At same t_0, the micro mortar containing PC- 1 has lower viscosity than the micromortar admixed with PC-2.**
- **Lower Viscosity is favored to help reduce “sticki-ness” factor with HVFA concrete.**

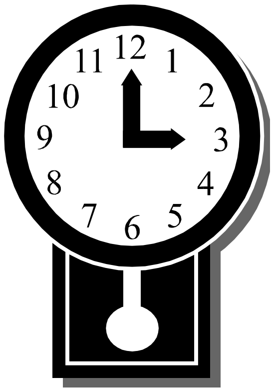
Mapping Set and Strength Accelerators



Versus

Accelerators: Setting Time vs. Strength Gain

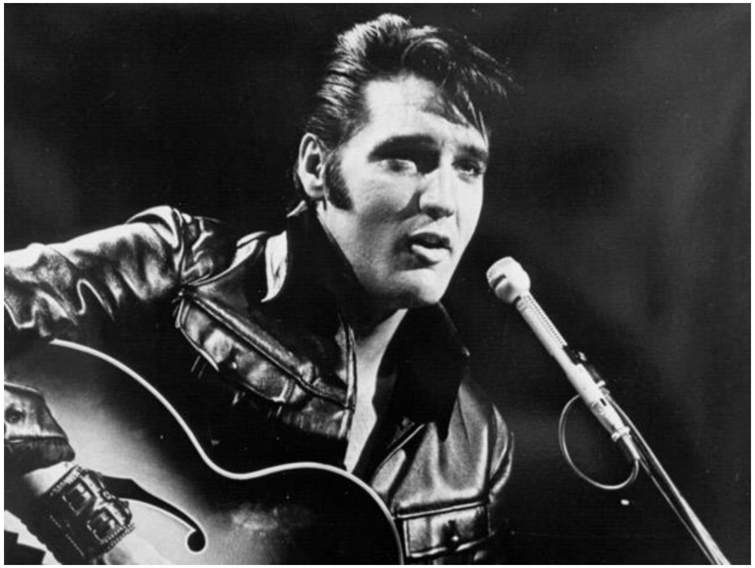
- **Some accelerators may generally be more suitable for a particular performance.**
- **<u>Setting time </u>is primarily influences flatwork finishing and the timing for heat curing**
- **<u>Strength gain </u>is primarily impacts early form removal**



Versus

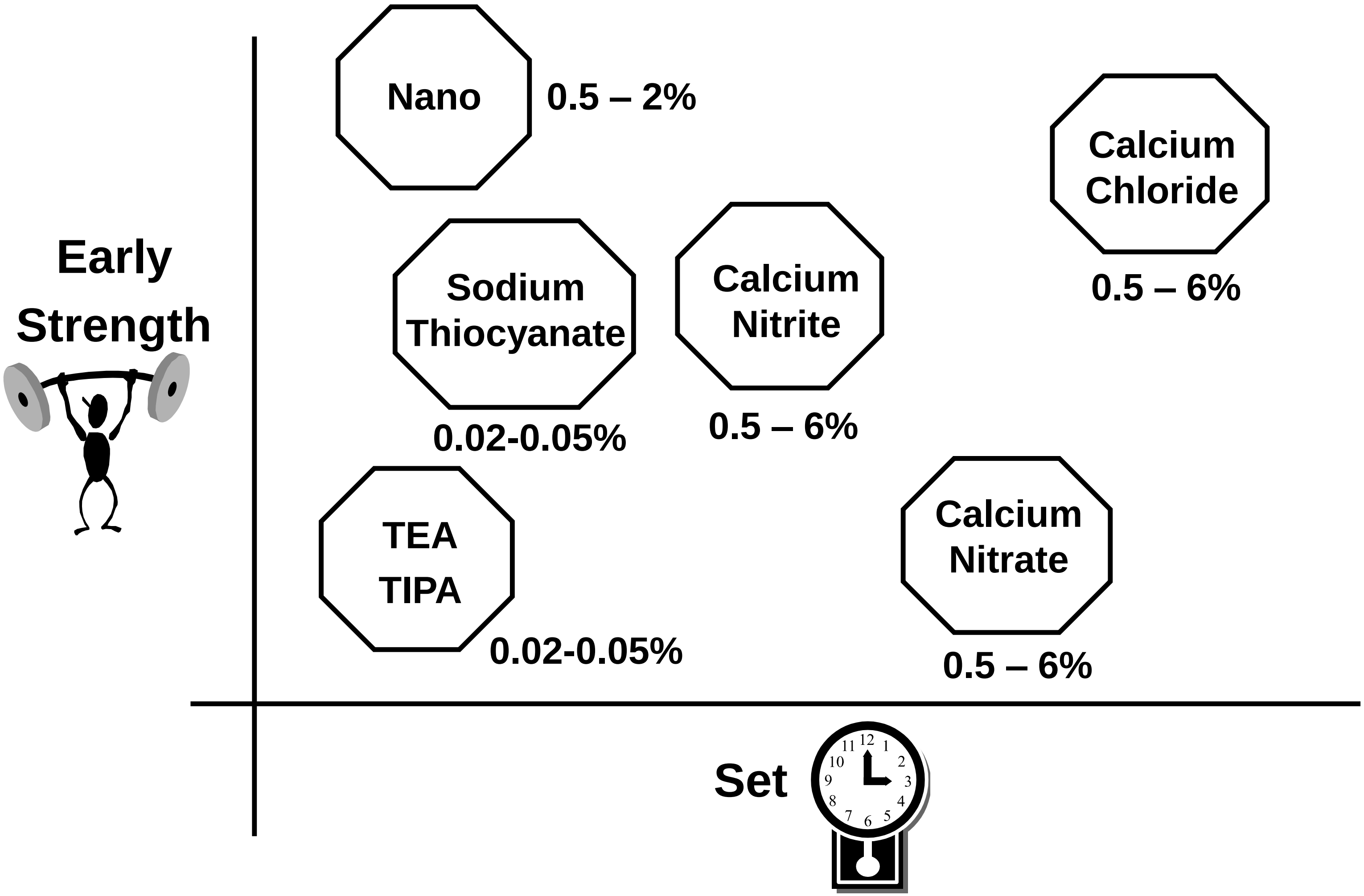
Accelerators: Chloride vs Non-Chloride

- **Calcium chloride is the most cost effective accelerator available but, adding chlorides to reinforced concrete can result in corrosion.**
- **In the presence of moisture and oxygen, chlorides initiate corrosion of reinforcing steel even in the high pH environment of concrete.**
- **Limits exist on the total permissible amounts of chloride in concrete.**



Calcium Chloride is the "King of Accelerators"

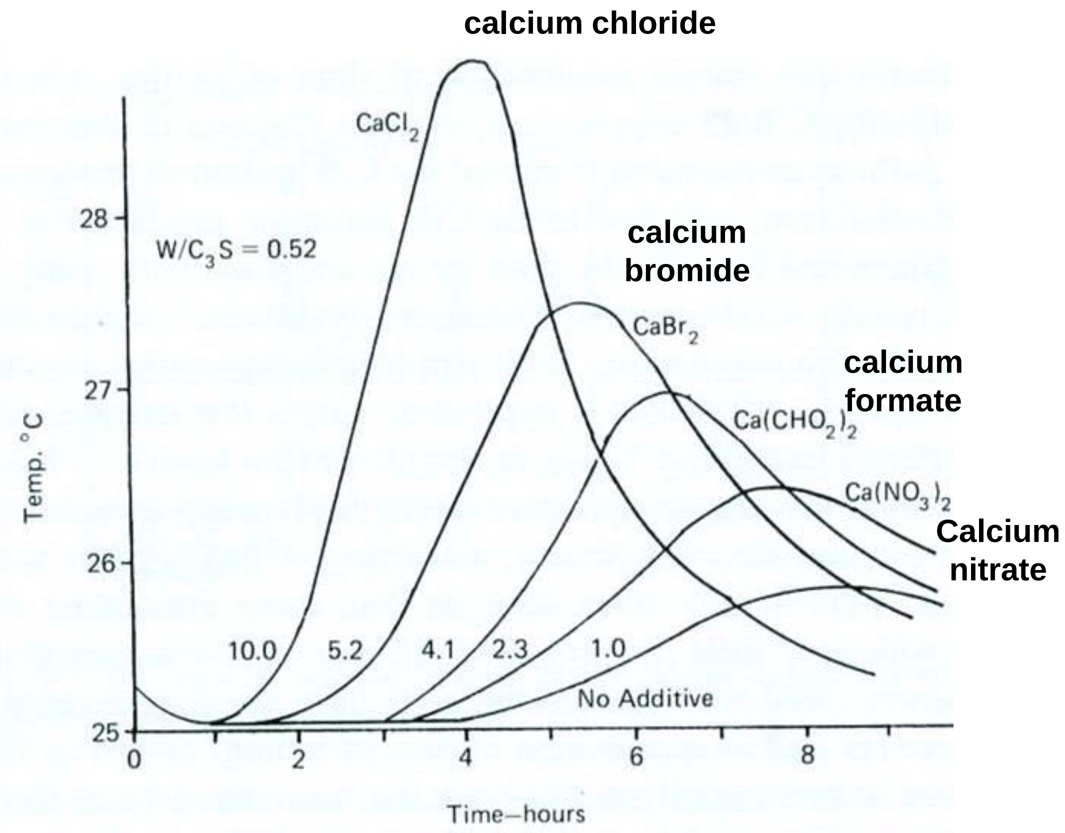
Mapping Accelerator Technologies for Set and Strength



Isothermal calorimetry of C_3S dosed with 2% of various calcium salts

- **Calcium Chloride most cost effective, most uniform response across wide range of cement chemistries**

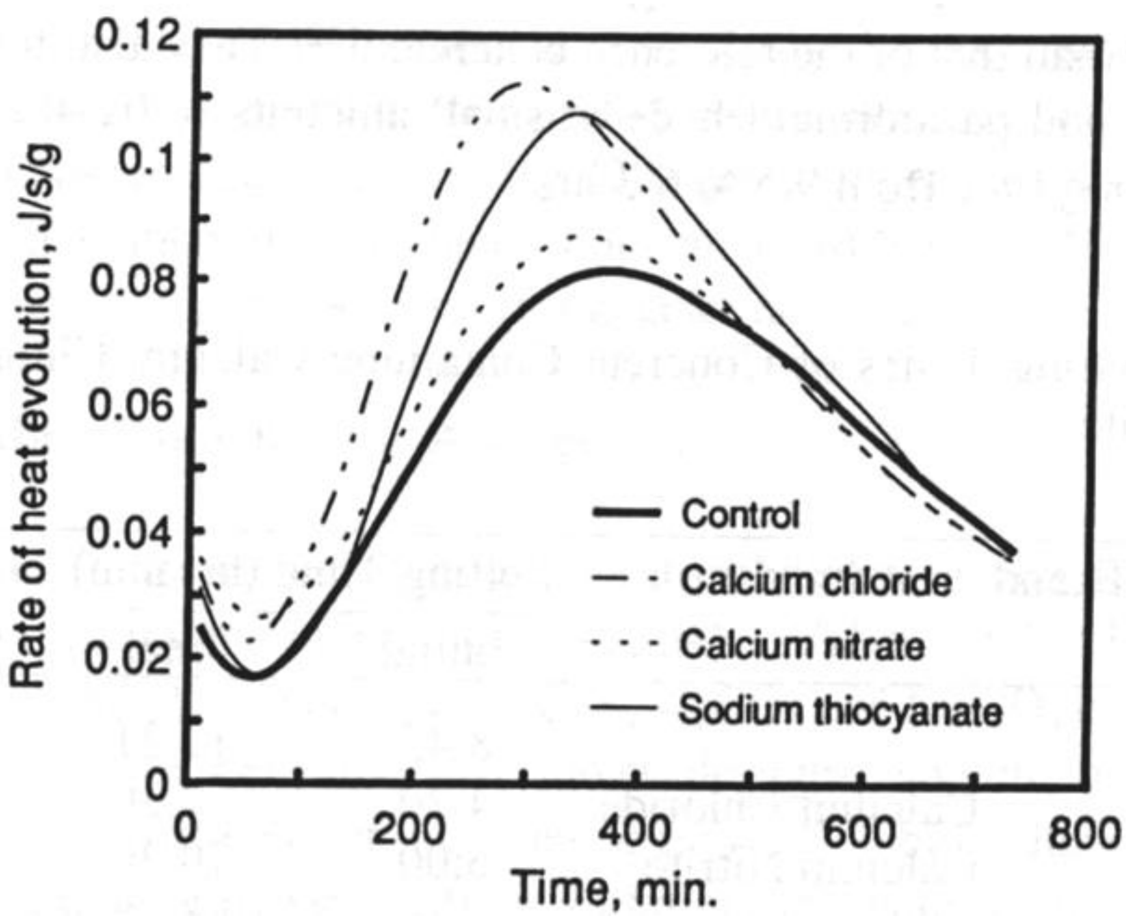
- **Calcium nitrate is most common set accelerator platform. Normally, supplemented with other additives.**



Dodson

Relative Set/Strength Performance of Chloride, Nitrate, and Thiocyanate

- $CaCl_2$ effects both set and strength
- NaSCN primarily effects strength
- $Ca(NO_3)_2$ primarily effects set.



Chemical Admixture Synergies with Polycarboxylates

1 + 1 > 2 !

Air and Strength



Concrete admixed with PC-HRWR and Calcium Nitrite

Prestressed Piles

Chowan River Bridge,

Edenton, NC

NSFC/Calcium Nitrite vs. Polycarboxylate/Calcium Nitrite

Plant Steam-Cured Concrete

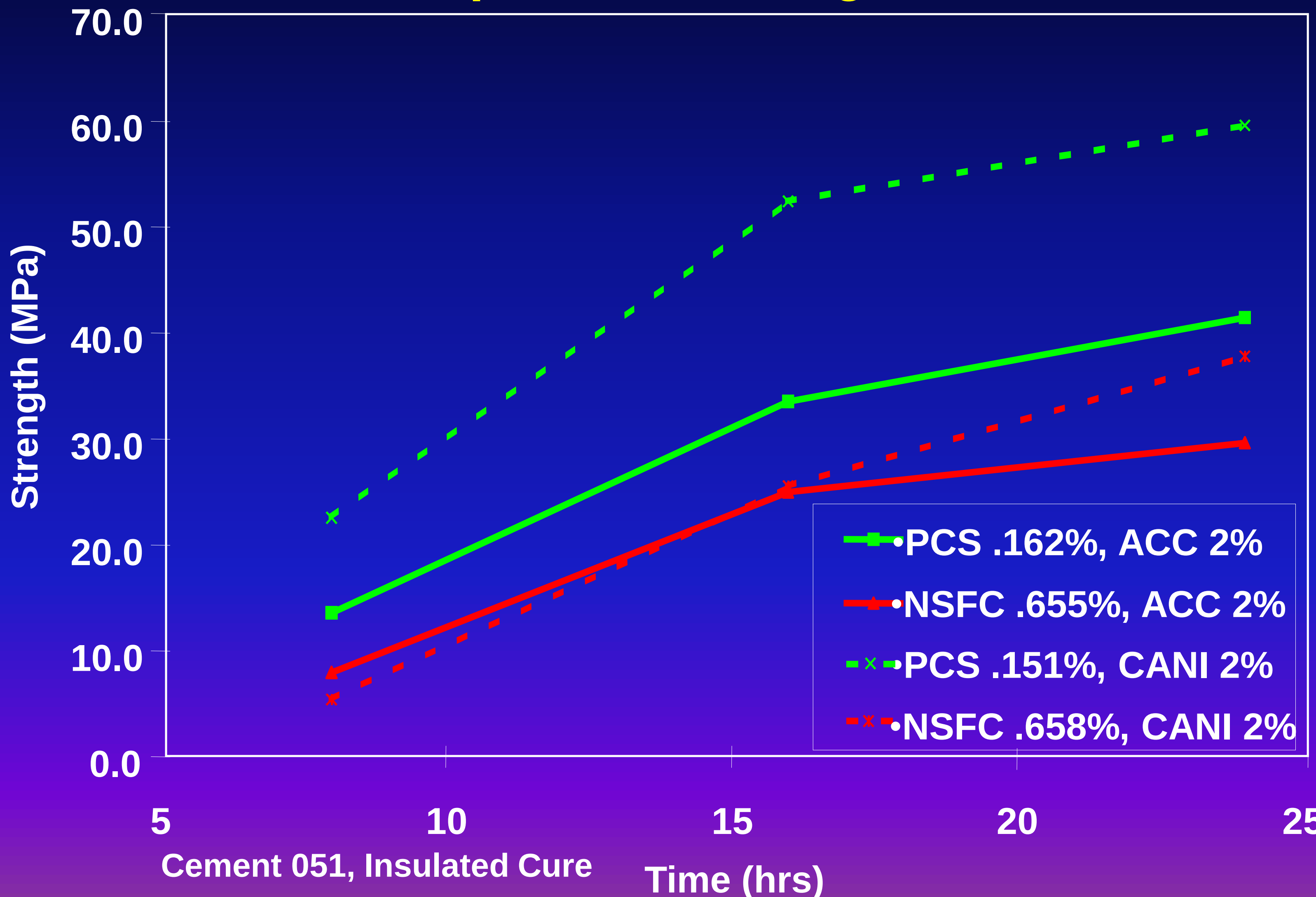
390 kg/m³ (658 lb/yd³) Type II Cement, w/cm = 0.32

		NSFC+WR	PC
Polycarboxylate	ml/100kg	--	455
NSFC	ml/100kg	1300	--
WR	ml/100kg	130	--
Calcium Nitrite	l/m³	26.6	26.6
AEA	ml/100kg	78	39
Slump	mm	75	115
Air	%	5.4	5.5
Initial Set	Hr:Min	3:50	2:30
1-D Comp. Strength	MPa	32.4 (4700 psi)	43.1 (6250 psi)

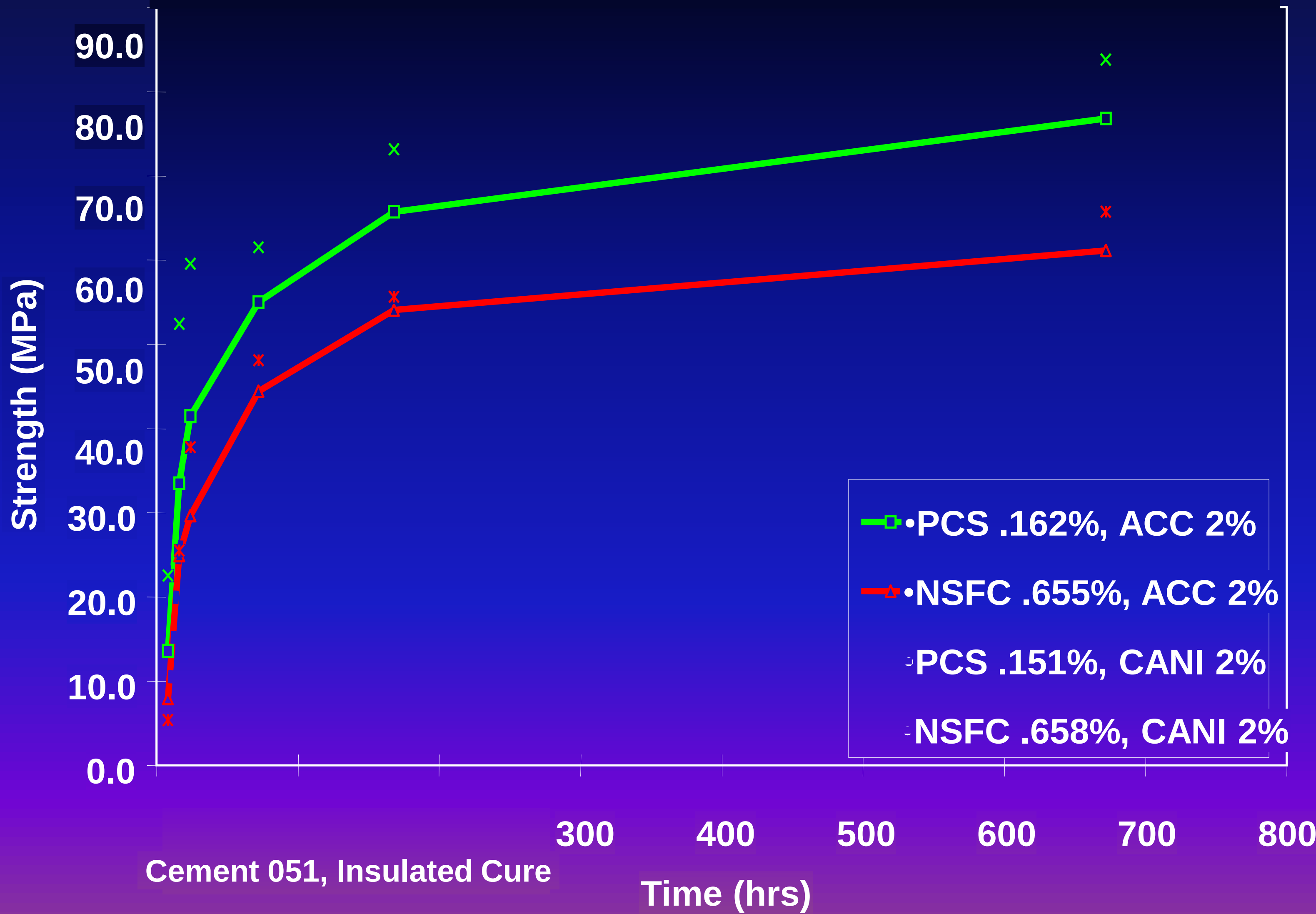
Jeknavorian, A. et. al. Synergistic Interaction of Condensed Polyacrylic Acid-Aminated Polyether Superplasticizer with Calcium Salts, SP-195: The Sixth Canmet/ACI Conference on Superplasticizers and Other Chemical Admixtures in Concrete, SP 195, 2000, 585-600.

Test Series I, Insulated Cure, Cement 051

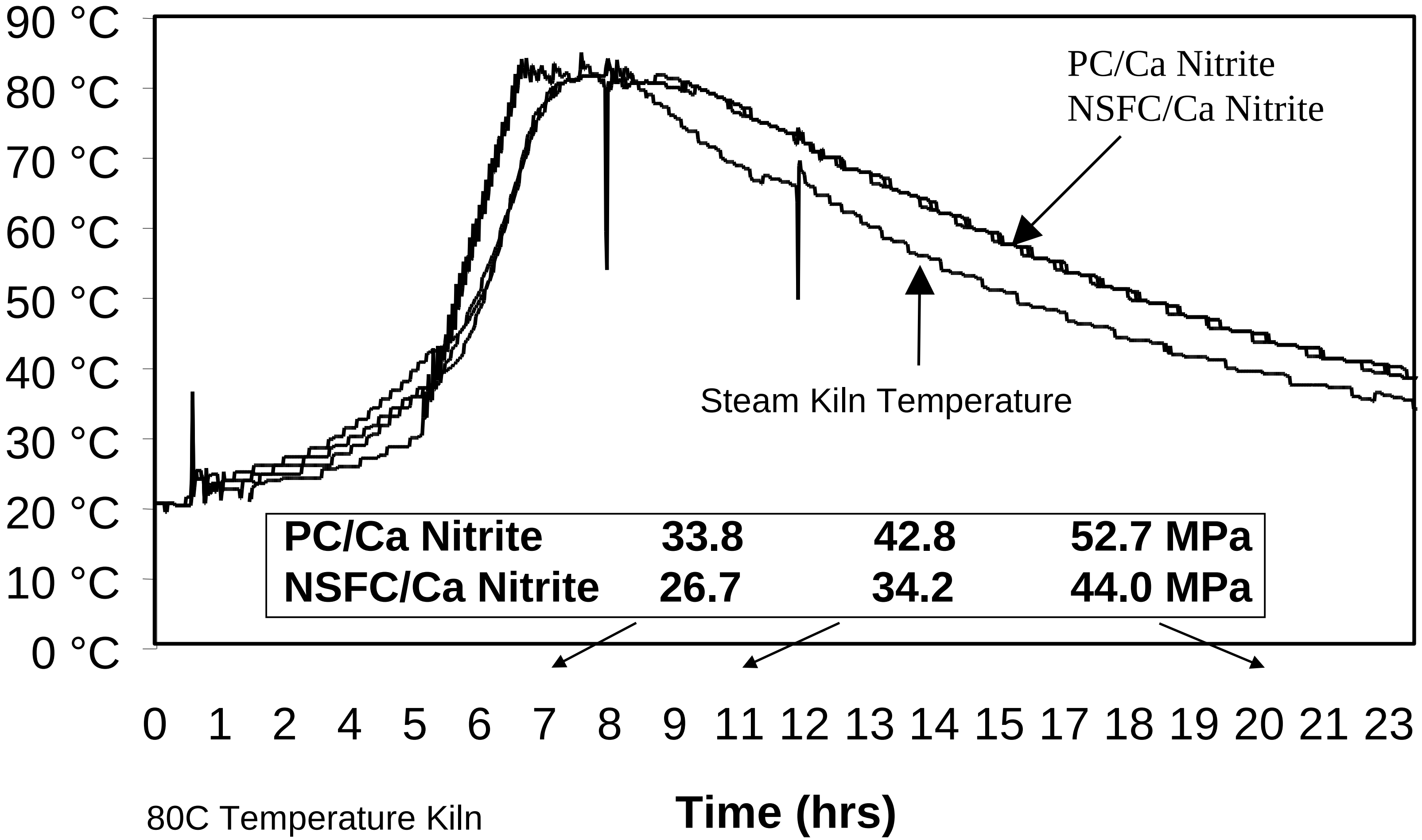
Compressive Strength → 24hr



Test Series I, Insulated Cure, Cement 051
Compressive Strength → 28-day (672 hr)



PC/Calcium Nitrite vs. NSFC/Calcium Nitrite @ 80C



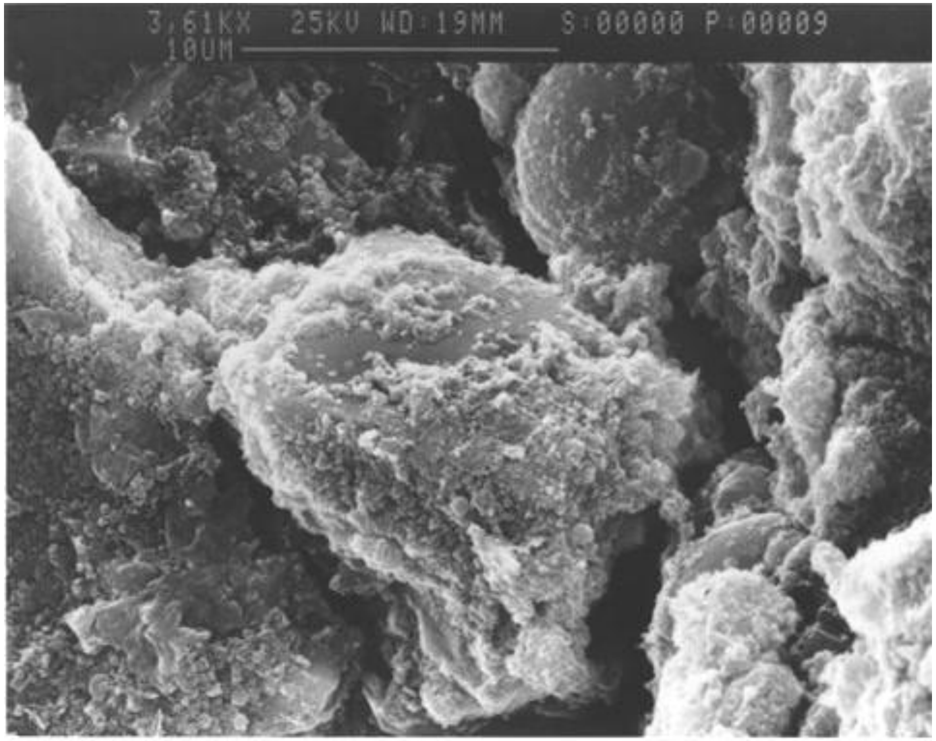
20-26% strength increase for PC/calcium nitrite vs. NSFC/calcium nitrite with comparable temp traces

Jeknavorian, A. et. al. Synergistic Interaction of Condensed Polyacrylic Acid-Aminated Polyether Superplasticizer with Calcium Salts, SP-195: The Sixth Canmet/ACI Conference on Superplasticizers and Other Chemical Admixtures in Concrete, SP 195, 2000, 585-600.

Synergistic Strength Increase: PC/Calcium Nitrite vs NSFC/Calcium Nitrite

Why?

- **Hydration kinetics?**
- **Microstructure development?**
- **ITZ?**
- **Pore size distribution?**
- **Other?**



Effect of Chemical Admixtures on the Microstructural Development of Portland Cement Mortars and Concretes

Materials	Concrete	Mortar	Cement paste
Cement	420 kg/m^3	420 kg/m^3	200 g
Natural Sand, FM 6.61	830 kg/m^3	861 kg/m^3	-
Stone, ASTM C33, No.67	1040 kg/m^3	-	-
Water	180 kg/m^3	180 kg/m^3	56 g
15 μm quartz	-	-	10 g
w/c	0.43	0.43	0.28
PCS dosage (% s/c)	0.13%	0.13%	0.13%
NSFC dosage (% s/c)	0.6%	1.2%	1.2%
CANI dosage (% s/c)	1.0%	1.0%	1.0%

C. Porteneuve, A. Jeknavorian, F. Serafin, K.L Scrivener, E. Gallucci, G. Gal·
American Ceramic Society Meeting, Baltimore, April 2005

PC/CANI vs NSFC/CANI – Concrete Performance

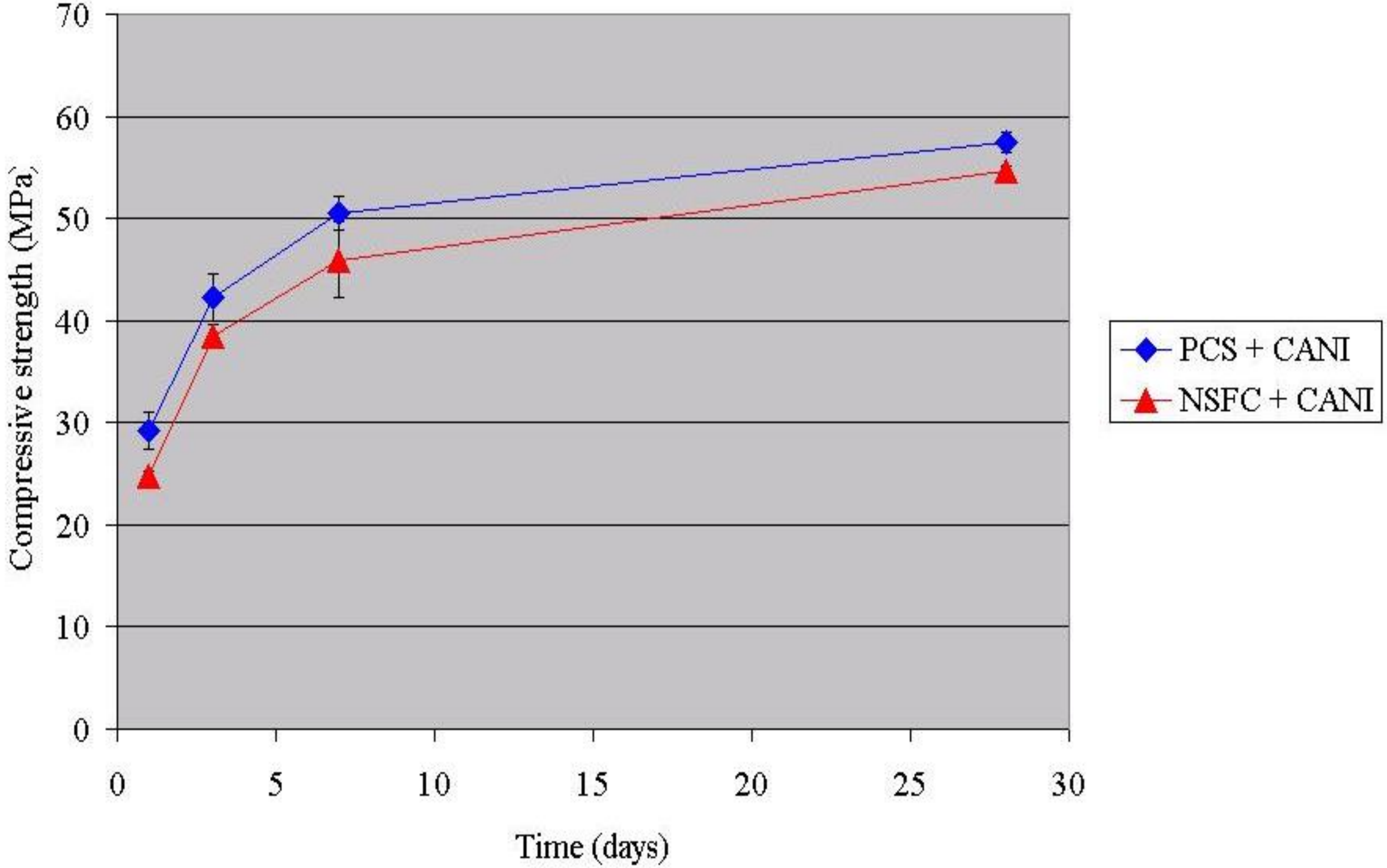
	PCS + CANI	NSFC + CANI
9-minute Slump (mm)	229	216
Air (%)	2.50%	2.20%
Initial setting time (hh:mm)	3:47	4:15

PC/CANI gave shorter set and higher strength than NSFC/CANI

C. Porteneuve, A. Jeknavorian, F. Serafin, K.L Scrivener, E. Gallucci, G. Gal·
American Ceramic Society Meeting, Baltimore, April 2005

Concrete Compressive Strength

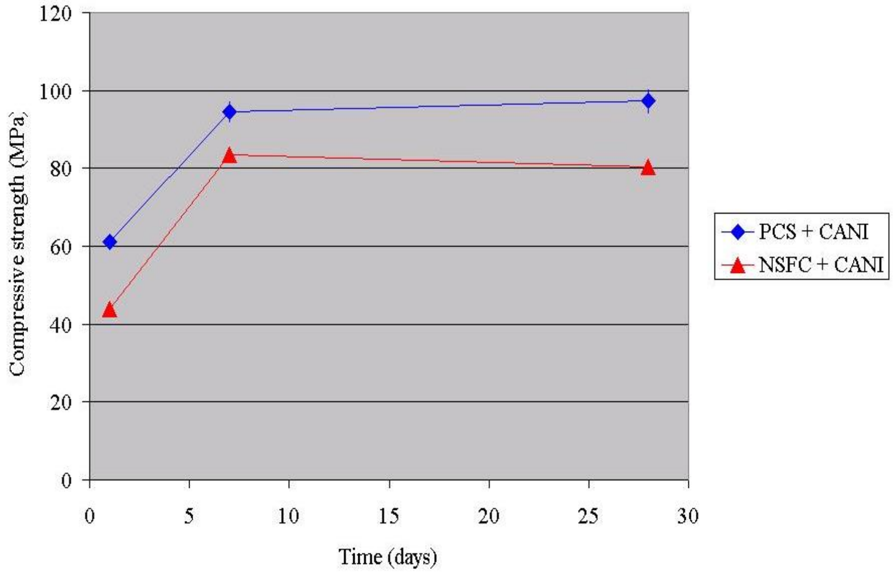
PCS/CANI vs NSFC/CANI



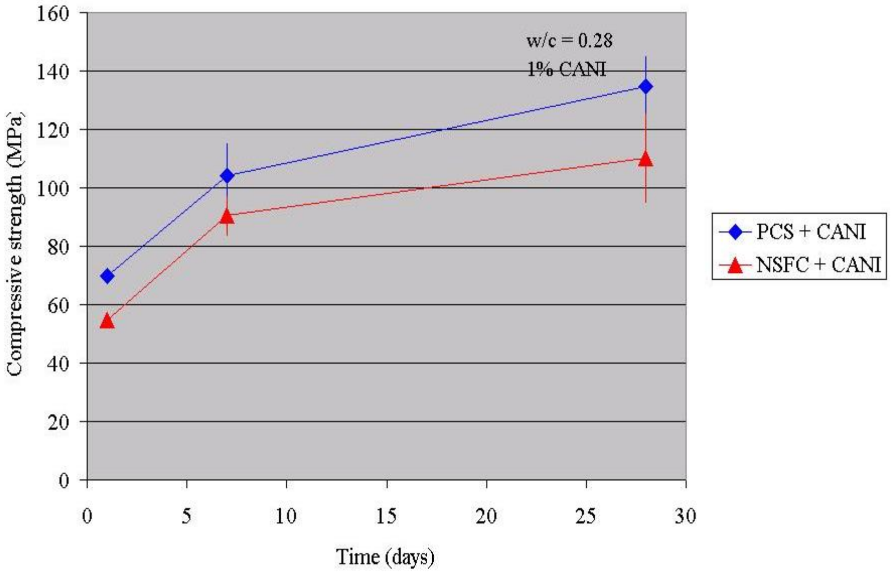
Synergistic strength effect of PCS/CANI confirmed.

PC/CANI vs NSFC/CANI – Mortar & Paste Performance

Mortar



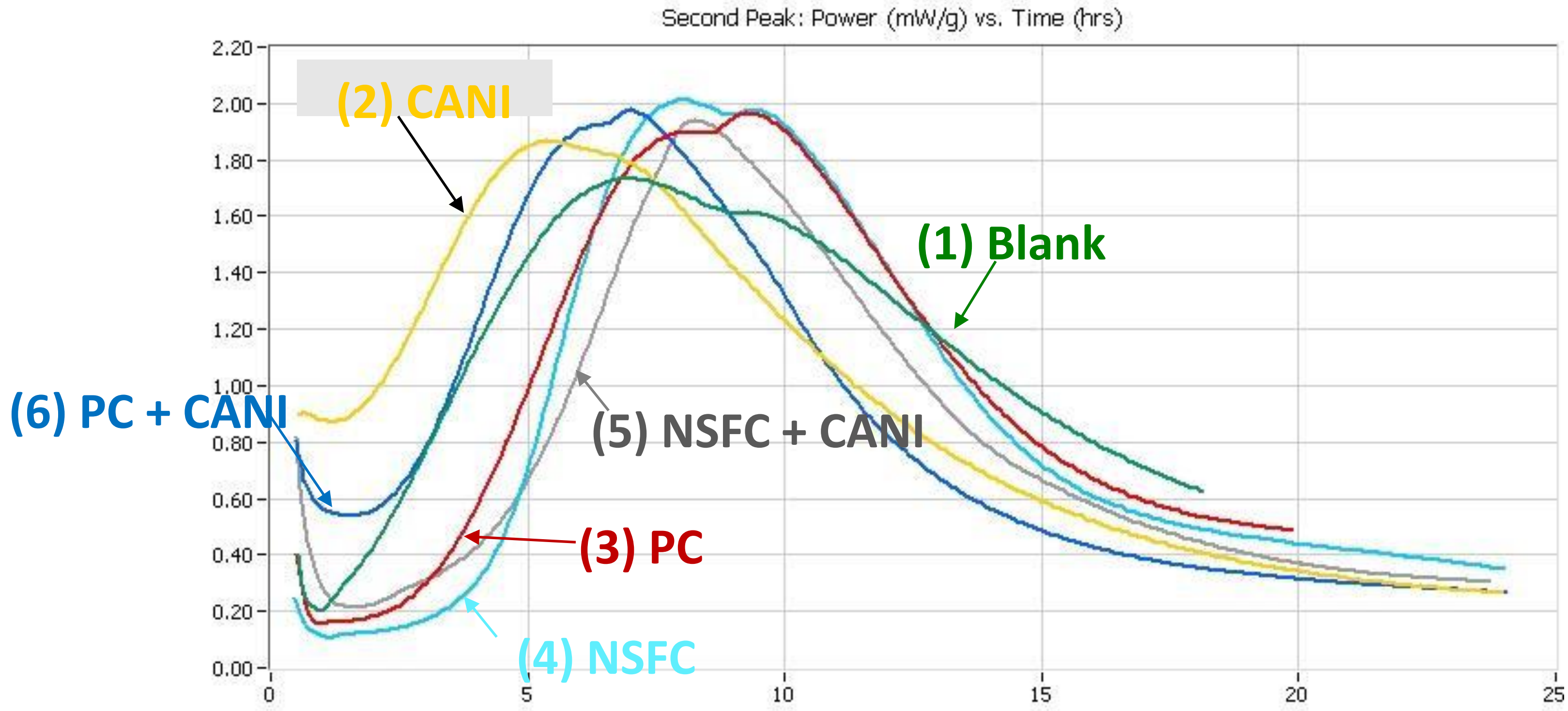
Paste



PC/CANI consistently produced higher compressive strengths in both mortar and paste mixtures.

C. Porteneuve, A. Jeknavorian, F. Serafin, K.L Scrivener, E. Gallucci, G. Gal·
American Ceramic Society Meeting, Baltimore, April 2005

PC/CANI vs NSFC/CANI – Paste Calorimetry

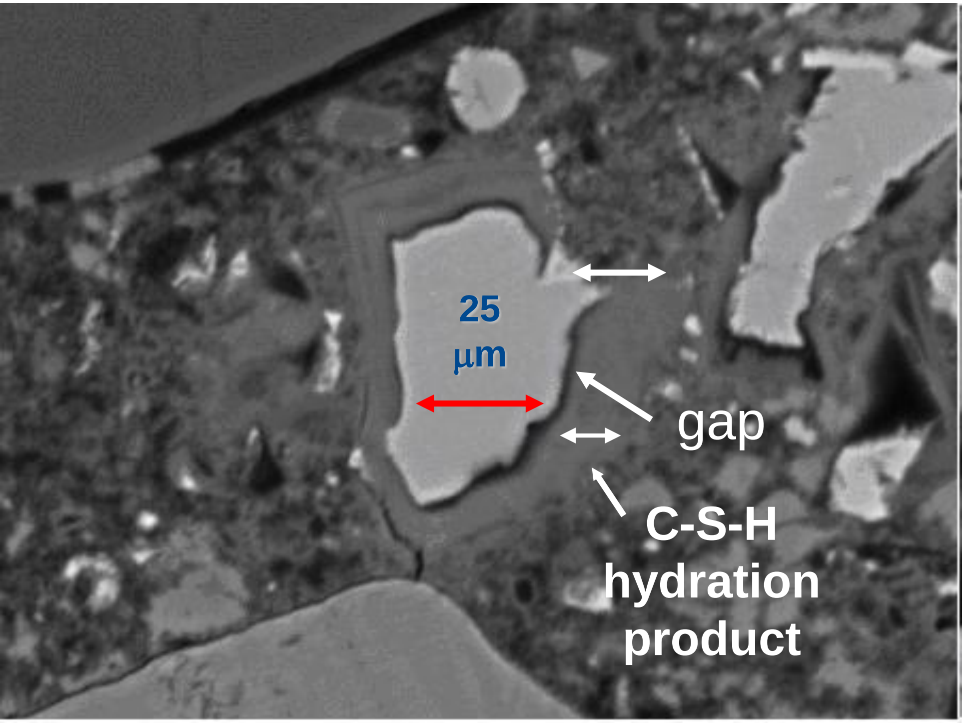


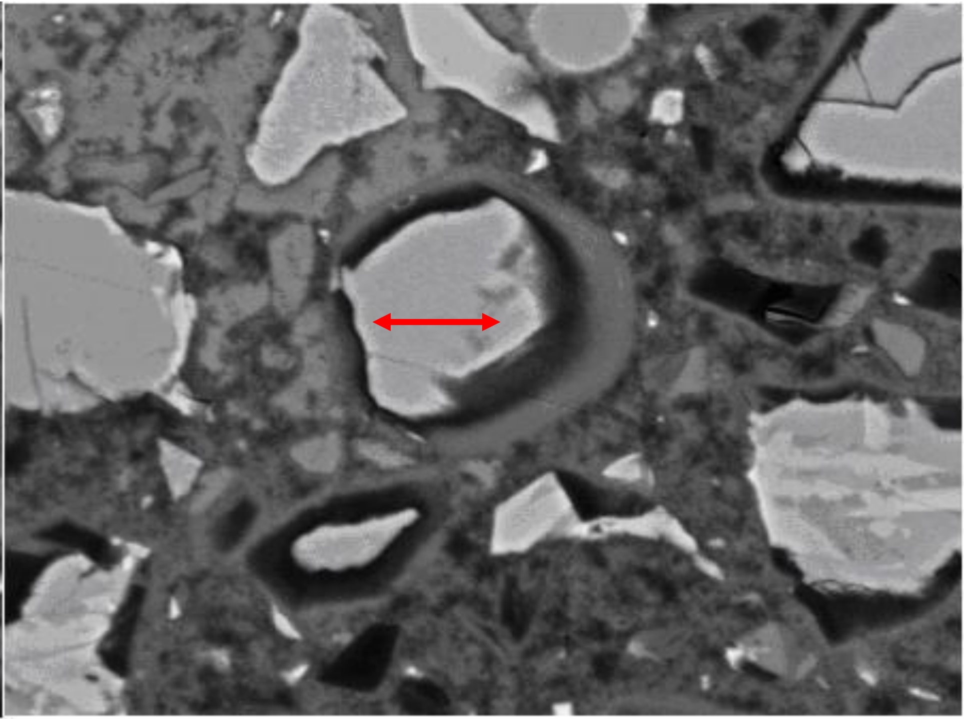
Main exotherm occurs earlier with PC/CANI, but total heat comparable to NSFC/CANI.

C. Porteneuve, A. Jeknavorian, F. Serafin, K.L Scrivener, E. Gallucci, G. Gal·
American Ceramic Society Meeting, Baltimore, April 2005

Probing Concrete Microstructure with Backscattered Scanning Electron Microscopy (BSEM)

PC + Calcium Nitrite | **NSFC + Calcium Nitrite**





	PC + $Ca(NO_2)_2$	NSFC+ $Ca(NO_2)_2$
Gap size, μm	0.1	0.7
C-S-H layer thickness	1.5	0.8

Statistical Analysis of BSEM of 1-day old concrete

PCS/ CANI	**Grain (μm)**	**C-S-H (μm)**	**Gap (μm)**	**Grain (μm)**	**C-S-H (μm)**	**Gap (μm)**
Average	**13.1**	**2.4**	**0.5**	**24.4**	**2.7**	**0.1**
Standard deviation	**2.0**	**0.7**	**0.8**	**4.2**	**0.5**	**0.3**

NSFC/ CANI	Grain (μm)	C-S-H (μm)	Gap (μm)	Grain (μm)	C-S-H (μm)	Gap (μm)
Average	12.4	1.2	0.8	27.8	1.5	0.7
Standard deviation	3.0	1.0	0.3	3.2	0.5	0.2

- **For both grain sizes, the C-S-H layer is thicker with PCS/CANI**
- **The NSFC/CANI sample exhibits a more significant gap between the anhydrous cement grain and the inner C-S-H**

Effect of PCE/Calcium Nitrite for 60/40 OPC/Ash Concrete

420 kg/m^3 total cementitious

Mix	Fly Ash (Class F)	Water	Admixture	Slump	Air	Initial Set	Final Set	Comp. Strength 1-Day	7-Day	28-Day
	% replace	w/c	%solids/cm	mm	%	(hr:min)	(hr:min)	mpa	mpa	mpa
Baseline	0	0.50		140	1.5	4:22	6:33	7.0	19.6	27.5
+ fly ash	40	0.50		215	0.9	9:20	13:01	3.1	11.7	16.9
+6% water cut	40	0.46		145	0.9	8:27	11:59	3.4	13.8	19.4
+18% water cut	40	0.38	0.13% PC-500	145	3.2	7:48	10:59	5.5	22.1	28.2
+CANI	40	0.38	0.13% PC-500 2.0% Ca Nitrite	165	3.6	5:20	8:15	6.0	24.3	30.1

- **24% water reduction with fly ash**
- **1 hr retardation from baseline**
- **1D strength = 86% of baseline**
- **7D strength > baseline**

Performance Map of HRWR/HES System

Reference = 20% fly ash w/ HRWR. Test Mix = 50% fly ash w/ HRWR + HES

Strength target = 80% 1-day Ref.; Set target = < 60 min Initial set

Cement Alkalinity	2.5% (Low)	3.7%	4.8%	8.9%	11.3%	12.6% (High)
High	63% 30 mins	62% 100 mins	52% 100 mins	65% 20 mins	68% 80 mins	69% 20 mins
	71% 10 mins	73% 110 mins	72% 70 mins	71% 45 mins	84% 80 mins	81% 35 mins
Low	77% 45 mins	78% 105 mins	63% 110 mins	93% 15 mins	84% 50 mins	83% 30 mins

"F" Fly Ash CaO Content

1D strength% vs. reference

Set retardation vs. reference

Strength: 10+% lower

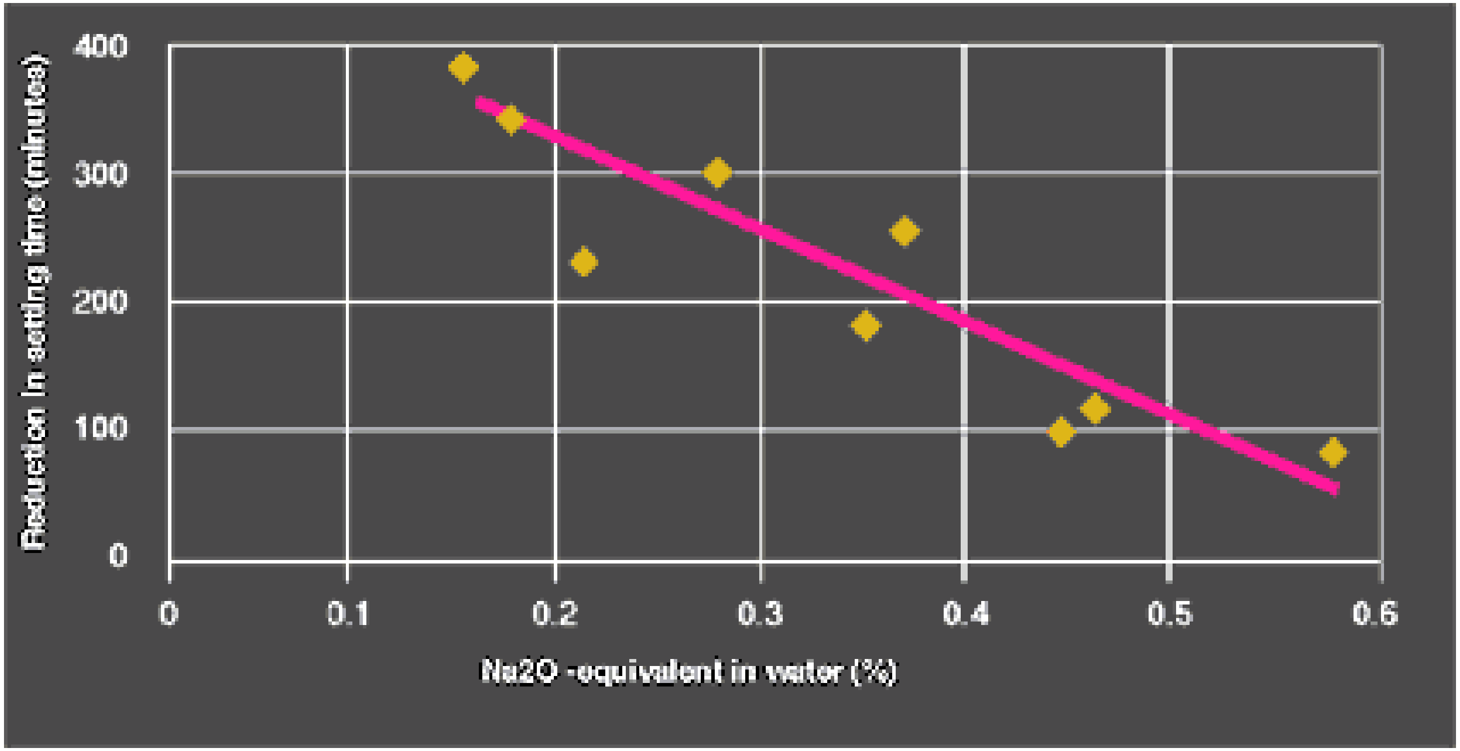
Strength: 3~8% lower

Strength target achieved

Strength target performance met w/ low alkali cement + high CaO ashes

Set performance difficult to predict, fly ash-dependent.

Effect of Cement Alkali Content on Set Acceleration by Calcium Nitrate



Increasing alkali content means increased soluble sulfate and hydroxide, both of which precipitate calcium ions

•www.baustoffchemie.de/en/db/set-accelerators

In Summary…….

- Proper selection of admixture systems (HRWRs and accelerators) can enable use of high volume cement replacement by SCMs.
- Polycarboxylate technology can be optimized for many diverse applications such as HVFA concrete mixes.
- Practical, cost-effective technologies for early activation of SCMs still needed.
- One cannot assume admixture systems will automatically work as usual when using high levels of SCMs.
- And just when you think, there is no hope to make that HVFA work for your application, remember…………

Thank you for your attention.
All questions most welcome.

Jeknavorian Consulting Services