American Concrete Institute
Always advancing

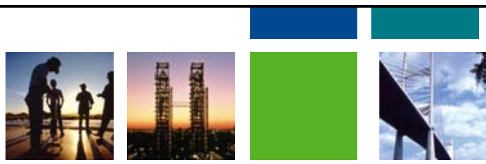
Hydration of Low Portland Cement Binders: Recent Advances in Experiments and Modeling, Part 1 of 2

ACI Spring 2014 Convention
March 23 - 25, Reno, NV

Current Practice on the Use of Admixtures to Enable Successful Manufacture of Concrete with Low Portland Cement Content

By

Josephine H Cheung, Principal Engineer, W. R. Grace & Co, Cambridge, MA



Current Practice on the Use of Admixture to Enable Successful Manufacture of Concrete with Low Portland Cement Content

Josephine Cheung, Ph.D.
Ara A. Jeknavorian*, Ph.D.

GRACE Construction Products

*Jeknavorian Consulting Services

Outline

- Commercial Mix Designs with HVFA
- The setting time and early strength challenge
- Chemical admixture options and approach
- Making HVFA concrete with minimal set and strength delay
- Keeping an eye on the potential for unexpected cement-SCM-admixture performance

General Mix Design Strategy for HVFA Concrete Mixtures

Minimum Powder Content	375-700 pcy (220-420 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

Benefits of SCMs

- Lower cost
- Use of by-products
- Decreased permeability
- Reduced sulfate attack
- Reduced efflorescence
- Reduced shrinkage
- Reduced heat of hydration
- Reduced alkali silica reactivity
- Increased workability and slump retention
- Improved finishing
- Reduced bleeding
- Reduced segregation

Then, why aren't SCMs used consistently at 40-50% cement replacement??

Factors inhibiting increased cement replacement by SCMs

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

***Opportunity for Chemical Admixtures**

GRACE

7

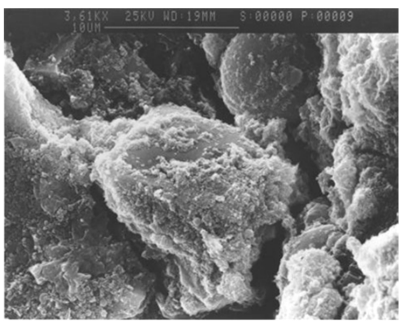
Outline

- Commercial Mix Designs with HVFA
- The setting time and early strength challenge
- Chemical admixture options and approach
- Making HVFA concrete with minimal set and strength delay
- Keeping an eye on the potential for unexpected cement-SCM-admixture performance

GRACE

8

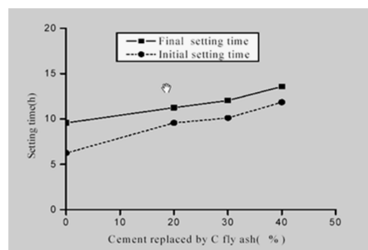
SEM of FA and Cement Hydration



GRACE

9

Fly Ash Replacement Level and 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

More SCM, longer set

GRACE

10 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.

Seasonal Adjustment of Fly Ash Content

	Hot Weather	Moderate Weather	Cold Weather
Cement	300 lbs.	325 lbs.	400 lbs.
Fly ash	150 lbs.	125 lbs.	100 lbs.
% Replacement	33%	28%	20%

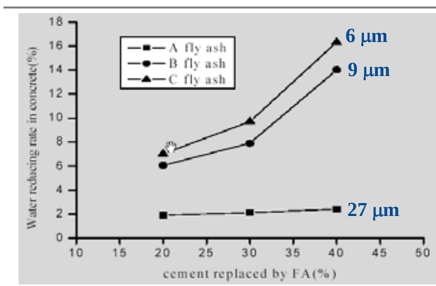
Lower SCMs at lower temp

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

GRACE

11

Water Reduction by SCMs - Replacement Level & Size



Ash collected from precipitator and air classified into 3 fractions.

Increased Fineness = more spherical morphology
More lubricating effect and packing density

GRACE

12 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.

Effect of 40% FA on Concrete Performance

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/cm	%solids/cm	mm	%	(hr:min)	(hr:min)	MPa	MPa	MPa
Baseline	0	0.50		140	1.5	4:22	6:33	7.0 (1000 psi)	19.6 (2800 psi)	27.5 (4000 psi)
+ fly ash	40	0.50		215	0.9	9:20	13:01	3.1	11.7	16.9

slump much higher than baseline
5 hr reduction in set
1D strength = 44% of baseline
7D strength = 60% of baseline

GRACE

Effect of HVFA on Concrete Performance – water cut

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/cm	%solids/cm	mm	%	(hr:min)	(hr:min)	MPa	MPa	MPa
Baseline	0	0.50		140	1.5	4:22	6:33	7.0 (1000 psi)	19.6 (2800 psi)	27.5 (4000 psi)
+ fly ash	40	0.50		215	0.9	9:20	13:01	3.1	11.7	16.9
+6% water cut	40	0.47		145	0.9	8:27	11:59	3.4	13.8	19.4

6% water reduction with fly ash
similar slump as baseline
4 hr retardation in set
1D strength = 48% of baseline
7D strength = 70% of baseline

GRACE

Outline

- Commercial Mix Designs with HVFA
- The setting time and early strength challenge
- Chemical admixture options and approach
- Making HVFA concrete with minimal set and strength delay
- Keeping an eye on the potential for unexpected cement-SCM-admixture performance

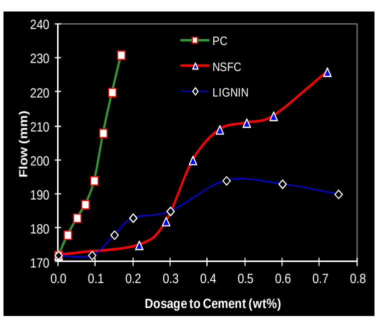
GRACE

Strategies to choosing Chemical Admixture

- **Choose appropriate dispersing chemistries**
  - **maximum dose/slump efficiency because 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 water reduction/increment of set time increase**
  - **maximize early strength development**
- **Choose appropriate accelerating additives**
  - **desires ones that give synergies with dispersing chemistries**

GRACE

Comparison of dose/slump efficiency by reducer types

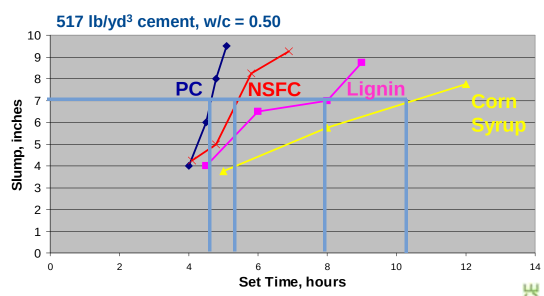


PCE most dose/slump efficient

GRACE

Comparison of water reduction/set time efficiency by reducer types

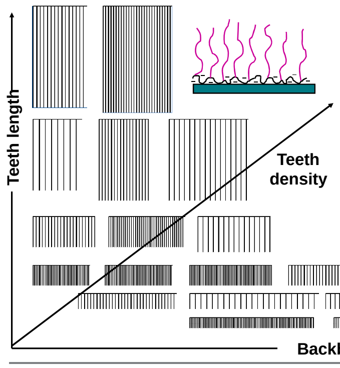
517 lb/yd^3 cement, w/c = 0.50



PCE gives best slump/Δ set

GRACE

Maximize early strength development by PC design

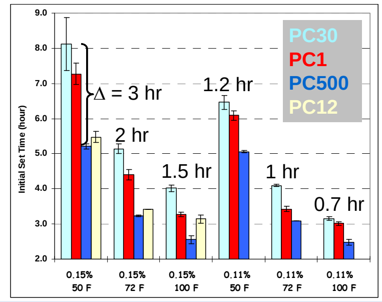


PC can be designed for:
- high early strength
- quick slump gain
- long slump life without extended set

19

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

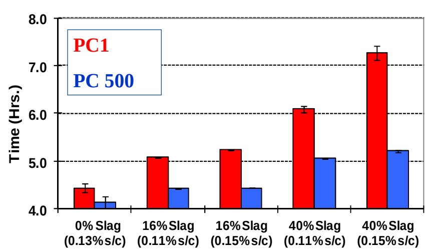
Mix design :
708 lb/yd³,
40% Slag,
w/cm = 0.45



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

20

Effect of Slag Content and PC Type On Setting Time



Set time longer and set time differences higher in mixes with higher slag content

21

Effect of Cement-Fly Ash-Admixture Combinations on Concrete Performance

Additional 18% water reduction with polycarboxylate-based HRWR

Mix	Fly Ash (Class F)	Water	Admixture	Slump	Air	Initial Set	Final Set	Comp. Strength 1-Day	7-Day	28-Day
	% replace	w/cm	%solids/cm	mm	%	(hr:min)	(hr:min)	MPa	MPa	MPa
Baseline	0	0.50		140	1.5	4:22	6:33	7.0 (1000 psi)	19.6 (2800 psi)	27.5 (4000 psi)
+ fly ash	40	0.50		215	0.9	9:20	13:01	3.1	11.7	16.9
+6% water cut	40	0.47		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

24% water reduction with fly ash from baseline
similar slump as baseline,
3.5 hr retardation in set,
1D strength = 79% of baseline
7D strength > baseline

22

Outline

- Commercial Mix Designs with HVFA
- The setting time and early strength challenge
- Chemical admixture options and approach
- Making HVFA concrete with minimal set and strength delay
- Keeping an eye on the potential for unexpected cement-SCM-admixture performance

23

NSFC/Calcium Nitrite vs. PC/Calcium Nitrite

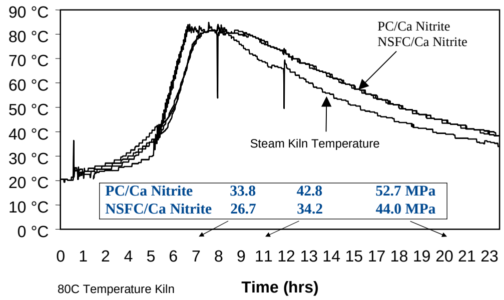
Steam-Cured Concrete: 390 kg/m³ (658 lb/ft³) Type II Cement, w/cm = 0.32

		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.

24

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



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

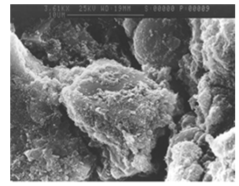
GRACE

25

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

Why?

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



GRACE

26

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

Materials	Concrete	Mortar	Cement paste
Cement	420 kg/m³	420 kg/m³	200 g
Natural Sand, FM 6.61	830 kg/m³	861 kg/m³	-
Stone, ASTM C33, No.67	1040 kg/m³	-	-
Water	180 kg/m³	180 kg/m³	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%

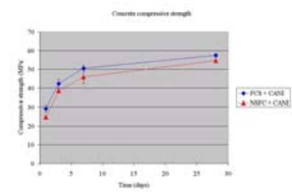
C. Porteneuve, A. Jeknavorian, F. Serafin, K.L Scrivener, E. Gallucci, G. Gal
American Ceramic Society Meeting, Baltimore, April 2005

GRACE

27

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

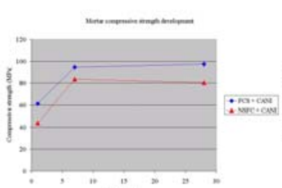


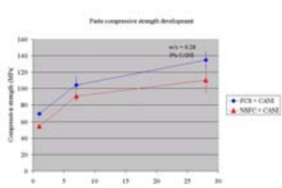
PC/CANI gave shorter set and higher strength than NSFC/CANI

GRACE

28 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 – Mortar & Paste Performance



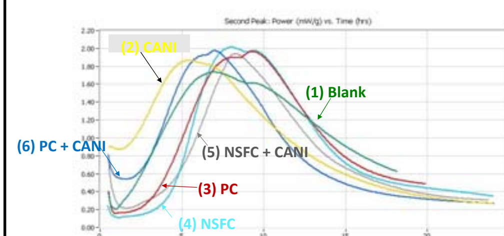


PC/CANI gave shorter set and higher strength than NSFC/CANI

GRACE

29 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 – Calorimetry



PC/CANI accelerates

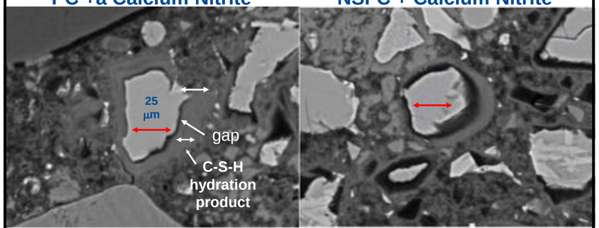
NSFC/CANI retards

GRACE

30 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 +a 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

PC/CANI vs NSFC/CANI – CH by SEM

Image	PCS+CANI	NSFC+CANI
1	9.6	10.8
2	15.4	8.6
3	13.5	8.7
4	11.4	6.4
5	10.8	8.4
6	15.2	-
Average CH amount (%)	**12.7**	**8.6**
Standard deviation (%)	2.4	1.6

More CH for PC/CANI than NSFC/CANI

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

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

420 kg/m³ 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
slight increase in slump from baseline
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 \ "F" Fly Ash CaO Content	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

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

Outline

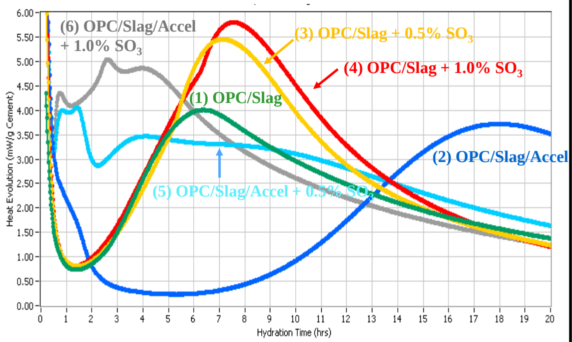
- Commercial Mix Designs with HVFA
- The setting time and early strength challenge
- Chemical admixture options and approach
- Making HVFA concrete with minimal set and strength delay
- Keeping an eye on the potential for unexpected cement-SCM-admixture performance

Tools for Probing Paste Performance (New Standards)

ASTM Subcommittee C01.48/C09.48
Performance of Cementitious Materials-Admixture Combinations

ASTM C 1679-07
Standard Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry

Effect of Sulfate in Cement/Slag/Accelerator Pastes (Isothermal Calorimetry)



Key Learnings

- Proper selection of admixture systems (HRWRs and accelerators) can enable use of high volume cement replacement by SCMs.
- HRWRs, through the use of polycarboxylate technology, can be optimized for use with HVFA concrete mixes.
- One cannot assume admixture systems will automatically work as usual when using high levels of SCMs.
  - Most SCMs have some impact on the sulfate balance.
  - Portland cement is usually optimized for mixes without SCM.
  - Isothermal or semi-adiabatic calorimetry can detect potential interactions.

GRACE