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Advancing concrete knowledge

Innovations in Chemical Admixture Technology as Related to Sustainability

ACI Spring 2012 Convention
March 18 – 21, Dallas, TX

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Ara A. Jeknavorian is a Research Fellow with the Construction Products Division of W.R. Grace in Cambridge, Massachusetts. Starting in 1979 with the Technical Service group, Dr. Jeknavorian conducted has numerous investigations on the performance of concrete materials and chemical admixtures, and has developed numerous chemical and instrumental methods for troubleshooting cementitious systems. In 1995, he began product development for chemical admixtures, spearheading the introduction of polycarboxylate-based superplasticizers to N. America. He is an inventor on twelve (15) patents for concrete and masonry admixtures, and has authored over 30 publications in the field of analytical chemistry of cementitious systems and the application of chemical admixtures for concrete. Dr. Jeknavorian is a member of the American Chemical Society, American Concrete Institute, and the ASTM C09 Committee on Concrete, where he has chaired the Chemical Admixtures Sub-Committee and has been recognized for outstanding service for his contribution to standards development for chemical admixtures. At the Sixth CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures (Nice 2000), Dr. Jeknavorian received recognition for outstanding contributions and achievements in the field of concrete admixture technology. Ara holds a Ph.D. degree in Analytical Chemistry from the University of Massachusetts.

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Chemical Admixtures of the Future: Opportunities and Challenges for Sustainable Concrete Production, Placement, and Service Life

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"Innovations in Chemical Admixture Technology as Related to Sustainability"
ACI Spring 2012 Convention - Dallas
ACI Committee 212 on Chemical Admixtures

Outline

- Recent Innovations in Admixture Technology
- Chemical Admixture Wish List
- Wonderful World of Polycarboxylates
- Dial-in Slump Retention with Time-Release PCE
- Admixtures For Aggregates
- "Nano" – Admixtures for Accelerated Strength Performance
- Admixture for Pervious Concrete

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Consulting the Admix Genie

Ah…yes…

The Future of Chemical Admixtures………

Are you ready??

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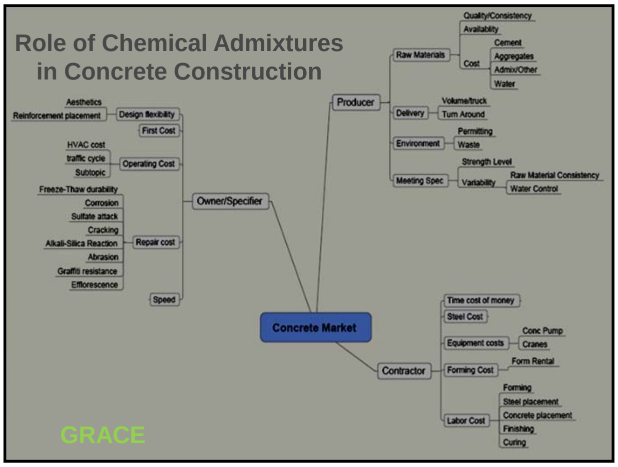
Role of Chemical Admixtures in Concrete Construction



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Latest Innovations in Admixture Technology

(over the past 10 years)

- Polycarboxylate-based Superplasticizers
- PCs for Self-Compacting Concrete
- Shrinkage Reducing Admixtures
- ASR Control Agents
- Admixtures for CLSM (Controlled Low Strength Material)
- Hydration Stabilizing Agents for Returned Concrete
- Antifreeze Admixtures (non-corrosive, alkali-free)
- Viscosity Modifying Admixtures
- Anti-washout Admixtures
- Slump Extending Admixtures
- Nano-Admixtures for High Early Strength
- Admixtures for Pervious Concrete
- Surface Enhancing Admixtures

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Addressing Concrete Durability Issues

Challenges

- Brittleness - cracking
- Dimensional stability
  - Thermal and hydration
- Permeability – water transport
  - ASR & DEF
  - Sulfate attack
  - Corrosion
  - Freeze/thaw

Solution Strategies

- Improve ductility - Macro fibers
- Reduce shrinkage – SRA
- Improve curing (self-curing) - Polyacrylics
- Reduce permeability
  - Admixtures to lower w/c - Superplasticizers
  - Reactive Void Fillers - Microsilica, limestone
  - Integral waterproofing - Stearates
- QC of raw materials – Paste Calorimetry
- Freeze-Thaw - Air entrainment w/ Surfactants, Wood Rosins, Tall Oil
- Corrosion Inhibitor– Calcium Nitrite
- ASR – Lithium Salts

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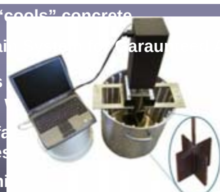
Chemical Admixture Wish List

- A water reducing admixture that demonstrates uniform performance with all cements or cement/SCM combinations.
- An admixture which can perform as a normal, mid- and high range water reducer - "linear dose/slump response with neutral set."
- A simple ... ble cement-admixtu...
- An admixture that "cools" concrete
- Universal Air Entrai... arau... ir Content
- Admixture systems ... ent levels (50% +) of Portland cement ...
- An admixture that fa... gnificantly increases robustnes... rn for failed loads.
- Integral curing admi...
- Dial-in slump retention without extended set and independent of cement chemistry and temperature.

Will the slump cone be replaced by a hand-held rheometer??



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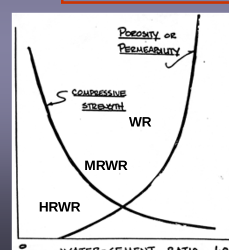
Effect of Water Reduction on Concrete

Cement dispersion is the most important and extensively used technical capability chemical admixtures provide in producing *sustainable* quality concrete mixtures.

Compressive Strength or Permeability = $k/(w/c)^3$



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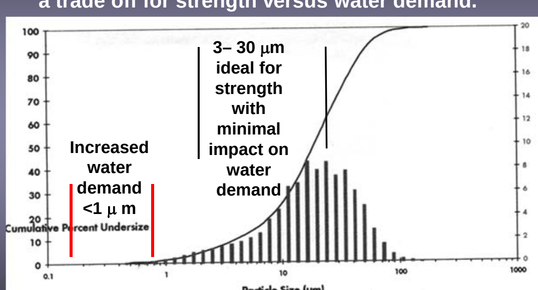
Particle Size Distribution, ASTM C 150 T-I Cement

The PSD for essentially all Portland Cements have a trade off for strength versus water demand.



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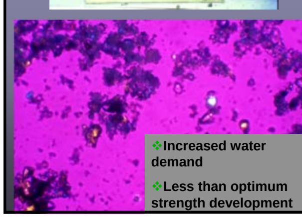
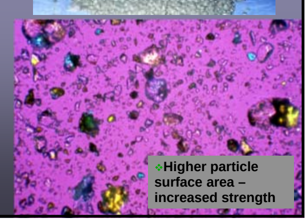
Photomicrograph – Cement Dispersing Action of Superplasticizers





Technical Performance: Superplasticizers

Benefits of Superplasticized Concrete
Mix Proportions, kg/m3

	Reference	High Strength	Flowing Concrete	Cement Reduced Mix
Cement	356	356	356	267
Sand	712	742	772	845
Stone	1127	1216	1068	1187
Water	178	133	178	133
Superplasticizer, l/m3	-	0.9	0.9	0.6
W/C	0.50	0.38	0.50	0.50
Slump, mm	115	125	240	125
Compressive Strength, MPA				
1-day	9.7	19.2	11.9	10.5
7-day	28.3	39.4	31.2	29.5
28-day	35.3	46.8	38.3	36.8

WR/MRWR/HRWR reduce cement, water, heat, porosity, & shrinkage

Unexpected Performance Changes in Cementitious Systems

- Cement Chemistry
  - Kiln fuels, interground additions, variable forms of gypsum
- Supplementary Cementitious Materials
  - Fly ash, slag, silica fume, metakaolin
- Chemical Admixture
  - More complex formulations
  - Multiple Admixtures (i.e. WRA, HRWR, AEA, Accel)

ASTM Sub-committee *C01.90.02/C09.90 Joint Task Group on PASTE SYSTEM PERFORMANCE*

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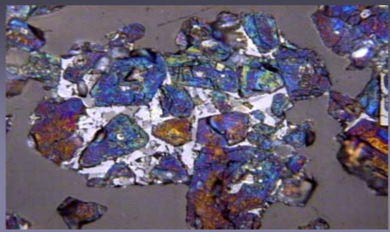
Portland Cement Clinker



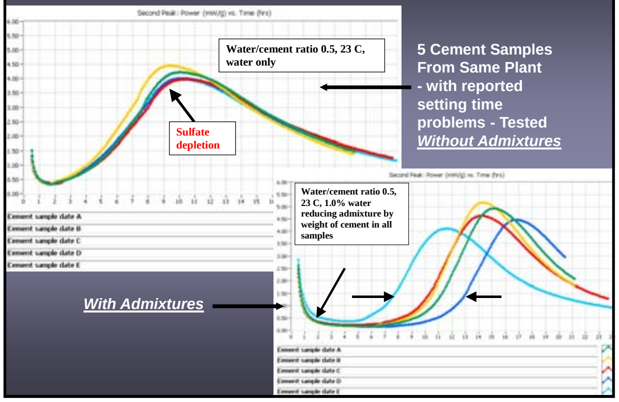
MAJOR COMPOUNDS IN PORTLAND CEMENT

Compound	Mineral Phase	Chemical Formula	Cement Notation	Mass Range, %
Tricalcium silicate	alite	3 CaOSiO2	C3S	25 - 65
Dicalcium silicate	belite	2 CaOSiO2	C2S	10 - 50
Tricalcium aluminate	aluminate	3 CaOAl2O3	C3A	3 - 12
Tetracalcium aluminoferrite	ferrite	4 CaOAl2O3Fe2O3	C4AF	8 - 14
Sodium/potassium sulfate	Alkalis			

+

Inter-ground Calcium Sulfate – Gypsum, Plaster, and/or Annhydrite

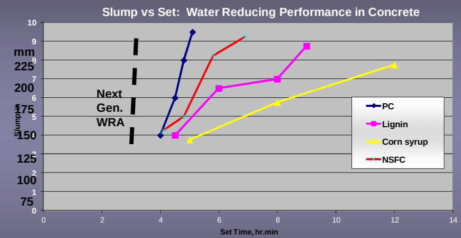
Probing Cement-Admixture Issues with Calorimetry



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

With Admixtures

Typical Slump vs Set Response for various WRAs



Slope [slump/set] = F[WRA dose,chemistry]

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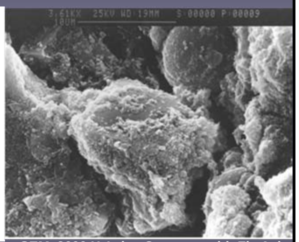
SCMs Can Provide a Multitude of Benefits for Concrete Properties

- 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



SEM, 3600 X:1-day Concrete with Fly Ash and Silica Fume

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

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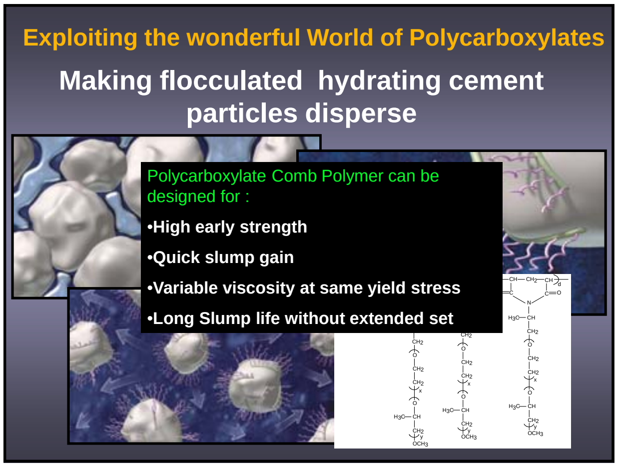
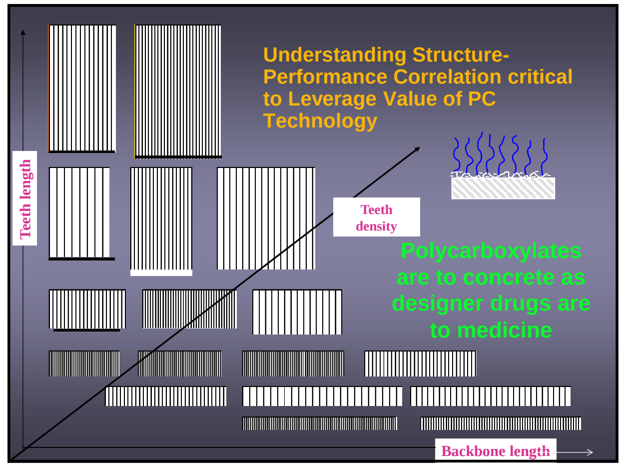
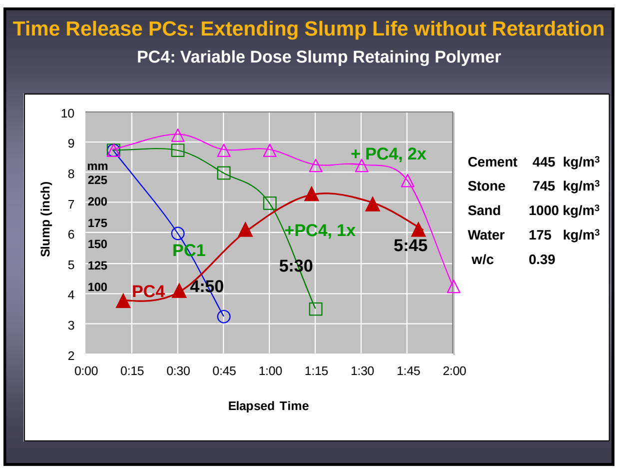
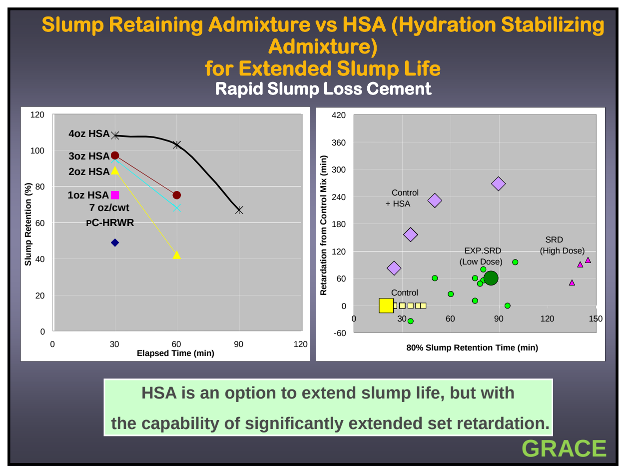

Exploiting the wonderful World of Polycarboxylates
Making flocculated hydrating cement particles disperse
Polycarboxylate Comb Polymer can be designed for :
•High early strength
•Quick slump gain
•Variable viscosity at same yield stress
•Long Slump life without extended set


Understanding Structure-Performance Correlation critical to Leverage Value of PC Technology
Teeth length
Teeth density
Polycarboxylates are to concrete as designer drugs are to medicine
Backbone length


Time Release PCs: Extending Slump Life without Retardation
PC4: Variable Dose Slump Retaining Polymer
Slump (inch)
mm
225
200
175
150
125
100
+ PC4, 2x
+PC4, 1x
PC1
PC4
4:50
5:30
5:45
Elapsed Time
Cement 445 kg/m³
Stone 745 kg/m³
Sand 1000 kg/m³
Water 175 kg/m³
w/c 0.39


Slump Retaining Admixture vs HSA (Hydration Stabilizing Admixture)
for Extended Slump Life
Rapid Slump Loss Cement
Slump Retention (%)
4oz HSA
3oz HSA
2oz HSA
1oz HSA
7 oz/cwt
PC-HRWR
Elapsed Time (min)
Retardation from Control Mix (min)
Control
+ HSA
EXP SRD
(Low Dose)
SRD
(High Dose)
Control
80% Slump Retention Time (min)
HSA is an option to extend slump life, but with
the capability of significantly extended set retardation.
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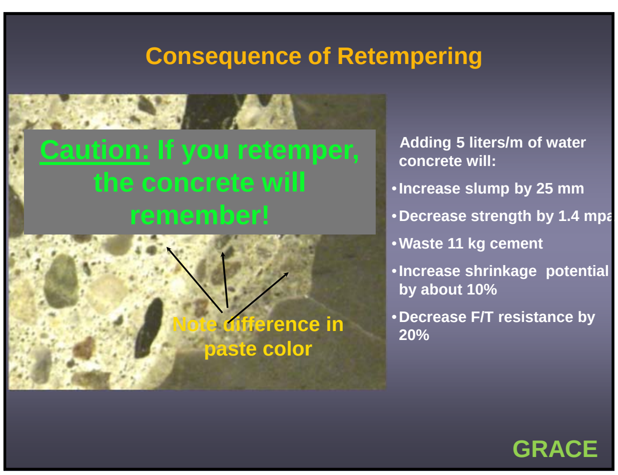
Consequence of Retempering
Caution: If you retemper, the concrete will remember!
Note difference in paste color
Adding 5 liters/m of water concrete will:
•Increase slump by 25 mm
•Decrease strength by 1.4 mpa
•Waste 11 kg cement
•Increase shrinkage potential by about 10%
•Decrease F/T resistance by 20%
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Chemical "Admixtures" for Sand
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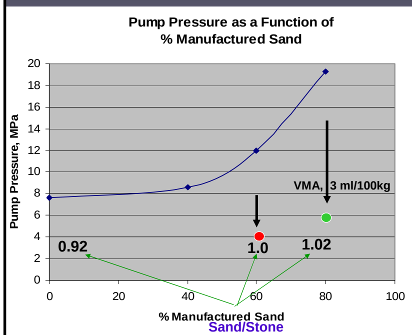
Effect of Manufactured Sands and Viscosity Modifying Admixture (VMA) on Pump Pressure



Mix Design, kg/m^3

Cement 248

Fly Ash 65

Water 178 – 186 kg/m^3

WRA 260 ml/100 kg

Slump 115-127 mm

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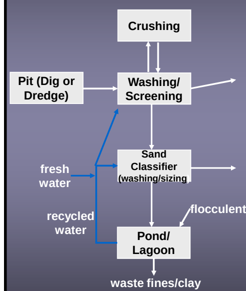
Clay Mitigating Admixture
Aggregate Production: Sand and Gravel



Wet Screening

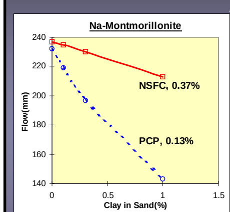
Cyclone (sand classifier)

Settling Pond

Screw (sand classifier)

Note: Individual plant operation/layout may vary widely.

Limits on Clay in Concrete Aggregate (United States)

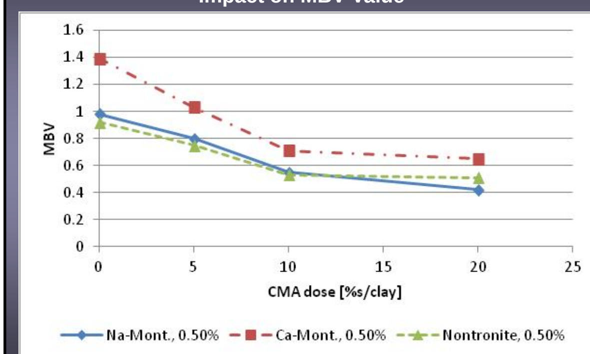


The Methylene Blue test provides direct measure of clay content.

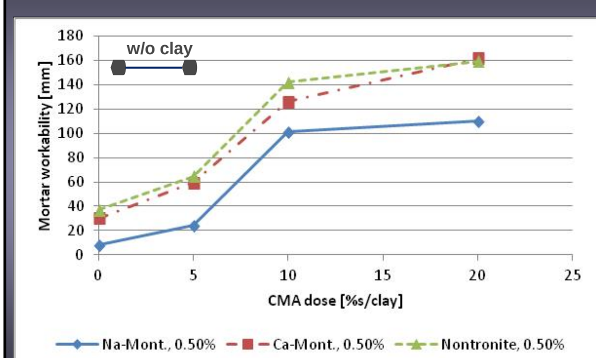
- ASTM C 33 Standard Specification for Concrete Aggregates
  - Material finer than 75 µm
    - <3-5% for sand and gravel
    - <5-7% for manufactured sand
  - Clay lumps and friable particles
    - 3% max
- Sand Equivalent (ASTM D 2419) or Durability Index Test (ASTM D 3744 or California 227 and 229)
  - Typically requires lower clay than ASTM C33 limits
  - Does not distinguish effectively between clay and non-clay fines
- Methylene Blue Value (not commonly specified)

Clays can be present in natural or manufactured sands.

CMA – Clay Mitigating Admixture
Impact on MBV Value



Impact of CMA on Mortar Flow
Mortar Mix = 450 g cmt/1400 g sand/0.2% Clay/ 0.50w/c; 0.12% PC



New UV-Methylene Blue Test

- Methylene blue is a function of clay content and clay activity
- A novel test method was developed to expedite and improve MBV results
  - Existing titration method (e.g. AASHTO TP 57): titration test to determine amount of methylene blue solution absorbed by clay
  - New Grace UV-MBV method: UV-vis measurement of methylene blue solution to determine methylene blue dye depletion for solution in presence of clay bearing aggregates
    - One mixing of methylene blue solution rather than gradual titration enables faster results
    - Test is performed on entire sand sample, ensuring representative results

Titration Method

Gradual titration end point determined upon appearance of blue halo.

New UV Method

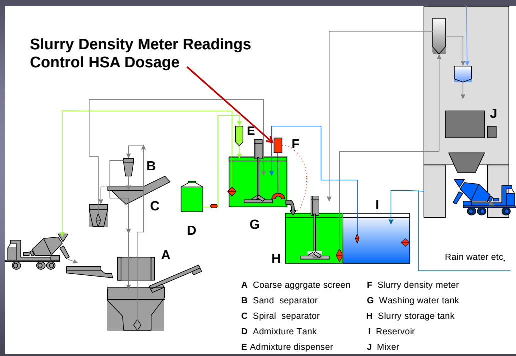
Methylene blue solution after mixing with clay-bearing sand, ready for UV measurement.

Methylene blue is a function of clay content and clay activity.

Clay mineral	MB value g(dye)/kg(clay)
Kaolinite (K)	13
Illite (I)	65
Smectite (S)	260

Source: Yool, A.I.G., Lees, T.P., and Fried, A. (1998). "Improvements to the Methylene Blue Dye Test for Harmful Clay in Aggregates for Concrete and Mortar" *Cement and Concrete Research*, 28(10), 1417-1428.

Concrete Recycling w/ Hydration Stabilizing Admixture



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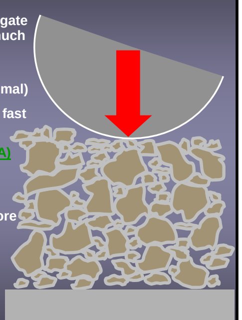
Chemical Admixtures for Pervious Concrete

Concrete Admixtures for Pervious Concrete

- Maximize Compaction & Flowability (HRWR/VMA/Retarder)
  - Strength related mainly to voids content (aggregate compacted voids content and paste volume), much less to paste strength (w/cm, silica fume)
  - High compactability needed for consistent performance (field compaction sometimes minimal)
  - High compactability expected to correspond to fast truck unloading
- Reduce Paste Drain & Water Sensitivity (HRWR/VMA)
  - Proper paste rheology needed to prevent paste collecting at bottom of section
  - Enable paste composition with less cement, more water
- Lengthen Curing Window (Retarder -VMA)
  - Increase water content
  - Retard cement hydration
  - Bind water



b/b_0=(agg compaction in concrete)/(maximum agg compaction)

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Importance of Paste Drain

Example of pervious concrete mixture with water content too high, resulting in sealed surface.

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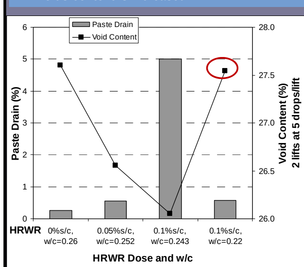
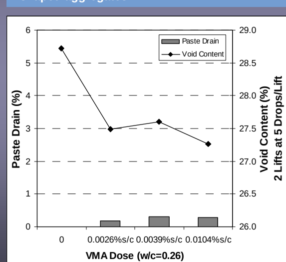
Impact of HRWR and VMA on Fluidity and Voids Content

- Increasing HRWR reduced void content but increased paste drain.
  - Acceptable at a dose of 0.05%s/c but excessive at a dose of 0.10%s/c.
  - Paste drain was reduced by reducing w/c, but voids content is increased.

- In contrast, viscosity modifying admixture reduced void content without an associated large increase in paste drain.
- VMA used in study is known to impart shear thinning rheology and enable use of poorly shaped aggregates.





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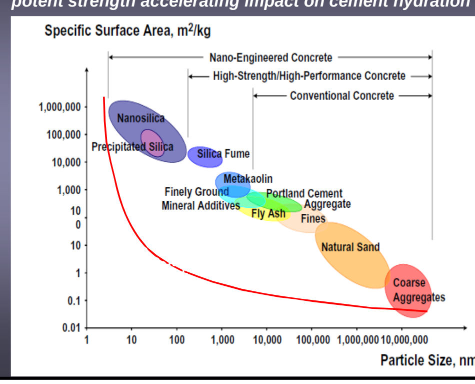
Chemical Admixtures based on Nano-particles

The reactivity associated with the increased surface area has a potent strength accelerating impact on cement hydration



Nano Seed/ Particles for Concrete

Calcium silicates

Magnesium silicates

Lime, CaO
Hydrated Lime, Ca(OH)2

Calcium Carbonate, CaCO3

Titanium oxide, TiO2

Silica, SiO2

Iron Oxides

Carbon nanotube

All of these particles, when present in the nano-size range, have the ability to promote nucleation of cement hydration products, thus accelerating cement hydration process and strength gain.

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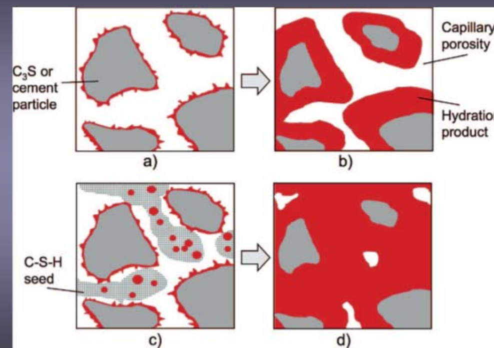
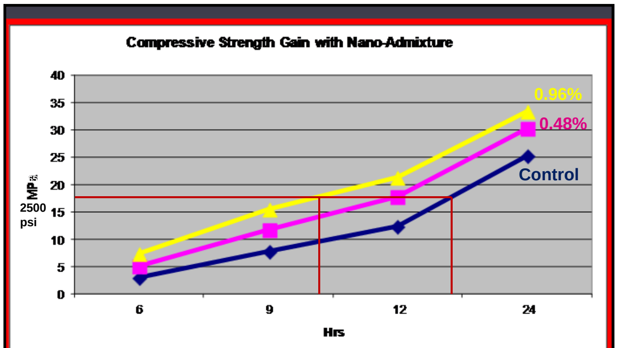
Nano Admixtures promote cement hydration in the pore volume to compliment topochemical reactions on cement surface



Seeding schematic (Thomas et al. 2009)



Nano-admixtures allow reaching strength targets at considerably earlier ages.

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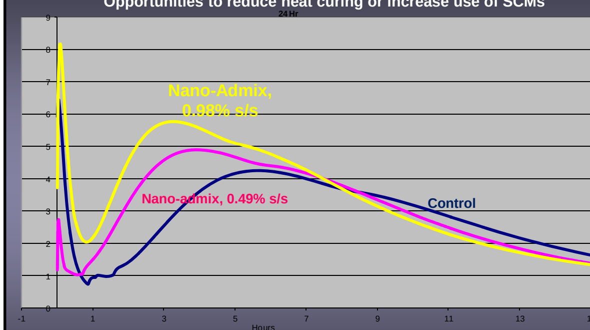
Isothermal Calorimetry of Mortar Mixes with Nano-Admixture

Opportunities to reduce heat curing or increase use of SCMs



Position and intensity of main exotherm hydration peak significantly modified

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Compressive Strength Data (mpa), Effect of Nano-Admix

Mpa	6 hr	% Ref	9 hr	% Ref	12 hr	%Ref	24 hr	%Ref	672 hr
Blank	2.9	100	7.8	100	12.3	100	25.2	100	
Nano-Admix	5.1	175.9	11.8	151.3	17.7	143.9	30.3	120.2	
Nano-Admix	7.3	251.7	15.4	197.4	21.3	173.2	33.5	132.9	

Nucleating effect from Nano-admixture capable of 2X impact on early age compressive strengths (22 C).

Nano-admixtures have the capability of allowing increased use of SCMs, reduced heat curing, and reducing cement contents.

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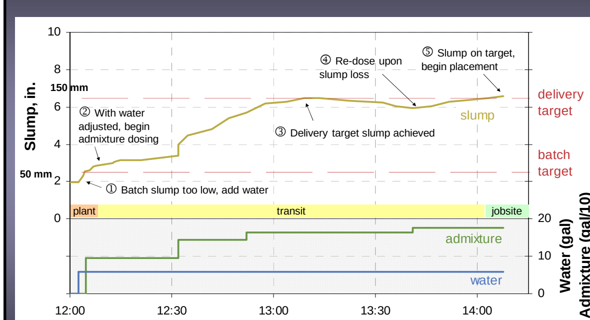
Automated Slump Control:
In -Transit Water and Superplasticizer Adjustments



Batch slump used to ensure proper water content (strength)
Admixture adjusted to delivery slump target (contractor)

Some final thoughts:

Regardless of what new and exciting admixture technologies are introduced into the concrete industry, successful routine production of cost-effective, high quality, and sustainable concrete will greatly be facilitated by:

- ✓Identify those parameters - materials, processes, structure design, and environment – that can transform in spec concrete construction into a case for litigation.
- ✓Learn how to predict and control those parameters – keeping away from the edge of disaster.

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Thank You!

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