Innovations in Chemical Admixture Technology as Related to Sustainability

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

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Chemical Admixtures and Concrete Sustainability – Mix Optimization for Constructability

It’s generally about clinker content
- Source of most of concrete’s CO2 footprint & embodied energy
- Higher SCM content (cement replacement) mix designs

Reduced clinker in OPC (higher LS%, process additions)
Other:
- Recycled / alternative aggregates
- Keeping concrete materials local

Celebrated projects & sustainability
- I-35 St. Anthony Falls Bridge, Minneapolis
  - Opened Sept. 2008
- 60 to 85% SCM mixes
  - 4000 to 5500 psi designs
  - ≤ 600 lb/yd^3 total cementitious content
- Slow hydrating mixes OK in forms but not flatwork!
- What are the limits for flatwork?

Dealing with high SCM content in finished placements
- Effects of higher levels of cement replacement
  - Setting time retardation
  - Slower strength gain
  - Temperature sensitivity
  - Incompatibility potential

Concerns:
- Finishing difficulties
- Cracking
- Surface durability
- Mix adjustments needed to restore performance
- High reliance on admixtures

Improving concrete sustainability
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Development of constructible, sustainable mixtures

- Increasing the SCM content without other adjustments for performance is not advised!
- Setting and early strength objectives must be similar to conventional mix designs
- Lower w/cm, more WR, accelerators
- Each combination of materials is unique
- Challenges posed:
  - Effects of changes are unpredictable
  - Materials selection is critical
  - Greater resulting temperature sensitivity
  - Increased possibility of incompatibility
  - Too many variables for mix development via laboratory concrete trials

Thermal profile testing for evaluation of materials and optimization of proportions

- Approach: lab mixtures of the paste fraction of concrete mixtures to evaluate performance influences of multiple variables (materials and proportions), one change at a time
  - Set time effects
  - Relative hydration efficiency
  - Potential for incompatible behavior
  - Early strength performance, via compressive tests
- Advantage: dozens of variables evaluated in a few hours, optimizing proportions for concrete trials

Equipment for thermal measurement testing

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<tr>
<th>Inexpensive temperature sensors and loggers</th>
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<th>Manufactured and adapted equipment</th>
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Data collection setups used for presented data

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<th>Laboratory paste mixtures produced for mix design optimization</th>
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Hydration and thermal profile indications

The temperature history of the first few hours of hydration (thermal profile) serves as a record of relative C3A and C3S hydration rates and the interaction of CaSO4 (gypsum).

- Initial C3A hydration
- Dormant period from interaction of CaSO4 with C3A
- “Main Peak” - C3S hydration
- Approximate timing of initial set of concrete
- 50% fraction” indicator used as a setting time reference

Applications of thermal measurement testing

- Performance evaluation, troubleshooting, & QC tool for concrete & other cementitious mixtures:
  - Setting time trends due to changes in SCM’s, admixtures, dosages, project field temps
  - Evaluation / selection of cements, SCM’s, admixtures
  - Checking for incompatibility potential of combinations
  - Qualifying a new mix design under field extremes
  - Evaluating material source variability or new sources
  - Substitute (w/ care…) for C 403 set time test, field or lab
  - Troubleshooting field or product problems

- Cement production QC uses:
  - Sulfates optimization, sulfate balance checks – effects of new fuels or raw materials, gyp sources, mill temps, etc.
  - Evaluation of setting time trends with SCMs & admixtures

Thermal profile testing ≠ calorimetry…

…but can be used for many of the same applications.

- TAM Air isothermal calorimeter
- Isothermal calorimetry

Example – thermal profiles used to evaluate setting influences of admixtures & dosages

- Increased WR dose vs. separate retarder

Sulfate-balance “incompatibility” evaluation

Simplest way to evaluate sulfate adequacy for a mixture of materials

- 5-paste mixtures using the same cement sample with 25% C ash & incremental sulfate demand via admixture dosage adjustments

Incompatibility more common with high SCM mixtures

- Some SCM’s, especially Class C fly ash, especially some sources
- Admixtures (almost all of them, some way more than others)
- Admix dosage rates (higher rates of many relatively inoffensive products can drive sulfate demand)
- Hot weather (higher mix temps = lower sulfate solubility)
- Cements that are marginally sulfated or have less soluble sulfate forms, with any combination of sensitive materials
- The most common culprit: combinations of the above
Mixture development & optimization process

- Materials selection – avoiding incompatibility influences, maximizing synergies, minimizing retardation contributions
- Screening tests with lab paste, thermal profiles & strengths:
  - Establishment of performance targets via reference mixes
  - Effects of increasing SCMs to proposed levels
  - W/cm adjustments with admixtures to restore early strengths
  - Compensating for retardation effects with accelerators
  - Sulfate balance checks at field temps
- Concrete trials & final mix refinement
- Additional adjustments, if needed, for changing temps

Materials selection – cement

- Desirable characteristics:
  - Good synergy with SCMs
  - Good sulfate balance trends, amply sulfated
  - Relatively short setting times, high early strengths

Materials selection – water reducing admixtures

- Desirable characteristics:
  - Higher range water reduction capability, dosage flexibility
  - Minimal retardation influences

Materials selection – SCMs

- Desirable characteristics:
  - Minimal incompatibility impact!
  - At left, thermal profiles and 1-day strengths comparing 3 different SCMs (C ash, F ash, and slag cement) in moderate sulfate demand mixtures, with incremental replacement rates.
  - A single sample of Type I/II cement was used, w/cm = 0.40, upper-limit dosage of Type A/D admixture, 32°C (90°F) mix and cure temps.
  - C ash mixtures suggest problems at higher replacement rates.
  - Slag cement may be most likely for very high replacement rates.

Performance of traditional low-SCM mixtures

- "Reference" mixtures to establish performance targets for mix development
- 15% C ash, 15% F ash, 30% slag cement with mild WR dosages
- For these examples, criteria to be based on these mixtures (green bands), 50% fraction thermal set indications and 1-day strengths in bar charts

Effects of SCM replacement rate increased to 50%

- Same temps & admix dosages, with the addition of an F ash mix w/ A/F WR
- Set time with F ash and A/F WR driven by admix
- Good set performance with slag and F ash + A/F
- C ash set time goes quite long (indication of potential issues)
- 1-day strengths all now unacceptable
- Next: use admixtures to restore adequate 1-d strengths, then adjust set
Effects of lower w/cm using HRWR dosages

- Lower w/cm needed to restore early strengths. A/F WR dose increased.
- All 1-day strengths now marginally acceptable, slag mix healthiest.
- 60% replacement mix with slag added, still acceptable strength.
- All set times now unacceptable, need help from accelerators (esp. C ash).
- Next: establish needed NCA dosages to restore set (further improve 1-d).

Compensating for delayed set with accelerating admix

- All mixtures repeated with varying & incremental dosages of non-chloride accelerator (NCA).
- Moderate dosages restore acceptable set for F ash and slag.
- NCA less effective with C ash and seems to create sulfate balance issues (incompatibility) at higher dosages (in pursuit of restored set).
- 1-day strengths benefit from NCA.

Sulfate balance evaluation of the C ash mix

- An affected mixture using NCA repeated with incremental CaSO4 additions.
- Profile shapes and 1-day strengths improve with additions, but not set time.
- Confirms sulfate balance issues.
- C ash not considered a candidate for 50% replacement mix design.
- Lower replacement mix could be developed.

Verification of proportions at extreme field temps

- F ash and slag mixtures with same A/F dose & max NCA dose repeated at highest envisioned concrete field temps: 36ºC (96ºF) mix and cure temps.
- No sulfate balance issues indicated; NCA dosages could be reduced.
- OK to proceed to trial concrete mixtures.

Temperature Influences

Two different mix / cure temp ranges: 70ºF and 93ºF.

4 paste mixtures, same materials and proportions for each temp range series:

- 100% OPC, no WR, w/cm = 0.45
- 25% C ash, no WR, w/cm = 0.45
- 25% C ash, 4 oz/cwt WR, w/cm = 0.46
- 25% C ash, 6 oz/cwt WR, w/cm = 0.46

WR admix is a high sulfate-demand Type A/D with a recommended dosage range of 3-6 oz/cwt on total cementitious content.

Note that higher temps alone drive incompatible behavior in the mixtures with both ash & WR.

Summary and conclusions

- Higher SCM mixtures for applications sensitive to setting and early strength performance are achievable.
- Thermal profile & compressive strength testing of lab paste mixtures can help screen & optimize performance, eliminating most required concrete batches and significantly reducing necessary lab time.
- Strategies for optimizing performance with admixtures include:
  - Lower w/cm with HRWR for required early strength.
  - Use of accelerating admixtures, if needed, based on testing.
  - Dosage refinements for specific performance and temps.
- Sulfate balance checks and seasonal effects can be evaluated using similar mixture sets.
- Next step – trial concrete mixtures, refinements of proportions for specific requirements or temp changes.
Questions?

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