Emerging Technologies in the Concrete Industry

ACI Fall 2012 Convention
October 21 – 24, Toronto, ON

Green Cements: Changing the Foundation of the Cement Industry

Largely:
- Activated Fly Ash
- Activated Slag
- Calcium Sulfo Aluminate
- Calcium Aluminate
- Activated Glass
- Geopolymers
- Magnesia Phosphate

Technology Overview

Pozzolan based cement system comprised of a pozzolan powder and proprietary admixtures

Combination produces a dense crystal structure comprised principally of calcium silico-aluminate hydrates

Activated Class C Fly ash

The Chemistry Behind The Approach:
- Dissolution / Retardation of CaO Component
- Soluble Silicates / Aluminates
- Recombination For Desired Chemistry

Cement Science

Raw Material CERATECH Hydrated Cement

James K. Hicks, P.E. Education: B.S., Chemistry, Oklahoma; Graduate School, Business, University of California; Technical diploma, Computer Programming, New Mexico. Developed rapid hardening cements, masonry cements, specialty cements and cement products with over 90% activated fly ash as the main constituent. Developed numerous new cements and associated products for the commercial market. Represents company with leadership roles in ASTM, ACI, USGBC, ICRI, CSI and other organizations. Over 35 years experience in management of cement and concrete product development/technical service, process engineering, marketing/sales engineering, quality assurance/quality control and plant management with such firms as CeraTech, Mineral Resource Technologies-CEMEX, QUIKRETE, Lafarge, Blue Circle and others. Managed and engineered domestic and international cement plants. Developed the first Type IP fly ash - portland cement and product blends in several states beginning in 1973. Earned US and International patents in fly ash-based rapid hardening cements, masonry cements and cement products. Delivered numerous presentations in cement, product technology and process control. P. E. Texas, California.
General Use Cement:

Admixtures:

Base Activators:

Modifiers:

Mechanical:

Compressive Strengths
  30% of 28 Day Strengths in 3 Days
  80% of 28 Day Strengths in 7 Days

Flexural Strengths
  20% of Compressive Strengths

Dimensional:

Length Change
  < 1/16th of an inch over 10 feet

Coefficient of Thermal Expansion
  4.7 x 10^-6

Heat of Hydration
  30% less total heat than OPC

Key Performance Characteristics

Durability:
  - Chemical Resistant
  - Freeze Thaw Resistant
  - Scaling Resistant
  - Abrasion Resistant
  - Corrosion Resistant
  - ASR Resistant

Work-ability

Finish-ability

Pump-ability

Set-ability
Material Technology Value Proposition

- Robust Material System
  - Concrete performance controlled by admixtures
- Cost Competitive
- Sustainable, (Carbon Neutral Cement)
  - Produced from 95% waste material & 5% rapidly renewable resources
- Exceptional Durability
  - Produces an extremely dense cement matrix with low permeability and a discontinuous pore structure
  - No excess calcium hydroxide

Superior Mechanical & Dimensional Properties

- Material is Mixed, Placed and Finished Like OPC
- Drops Into Current Industry Distribution Network

Mix Design

Typical General Use Concrete

<table>
<thead>
<tr>
<th>Component</th>
<th>Spc</th>
<th>lbs/gal</th>
<th>Abs. Volume</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>C Ash</td>
<td>2.720</td>
<td>11.0</td>
<td>2.031</td>
<td></td>
</tr>
<tr>
<td>L Ash</td>
<td>2.720</td>
<td>86.4</td>
<td>696</td>
<td></td>
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<tr>
<td>FA 1500</td>
<td>2.538</td>
<td>10.9</td>
<td>10.390</td>
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<tr>
<td>FA 3500</td>
<td>0.611</td>
<td>0.25</td>
<td>0.513</td>
<td></td>
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<tr>
<td>Water</td>
<td>1.000</td>
<td>45.17</td>
<td>2.383</td>
<td></td>
</tr>
<tr>
<td>HR 350</td>
<td>1.219</td>
<td>51.46/3.78</td>
<td>377</td>
<td>C3 Proprietary</td>
</tr>
<tr>
<td>H 300</td>
<td>1.219</td>
<td>51.46/3.78</td>
<td>482</td>
<td>C3 Proprietary</td>
</tr>
<tr>
<td>Cement 40</td>
<td>64.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AV</td>
<td>6.0 %</td>
<td>11</td>
<td>1.624</td>
<td>SNS Micro air</td>
</tr>
<tr>
<td>Total</td>
<td>405 8</td>
<td>37.000</td>
<td></td>
<td></td>
</tr>
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Strengths:
- 24 hours: 1200 psi
- 2 days: 2100 psi
- 7 days: 3700 psi
- 28 days: 6000 psi

Mix Design

Typical Specialty Use Concrete

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<td>55.5</td>
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<td>FA 3500</td>
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<tr>
<td>Component C</td>
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<td>0.04</td>
<td>0.319</td>
<td>C1 Proprietary</td>
</tr>
<tr>
<td>FA 5000</td>
<td>0.611</td>
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Strengths:
- 24 hours: 2100 psi
- 2 days: 3500 psi
- 7 days: 6050 psi
- 28 days: 8000 psi

Case Study - Roller Compacted Concrete (RCC)

SAVKO Columbus, Ohio

Case Study - Highway Full Depth Slab Replacement

VDOT Richmond, VA
Other Major Green Cements

- Calcium Sulfo Aluminate (CSA)
- Calcium Aluminate (CA)
- Activated Glass (AC)
- Magnesia Phosphate
- Geopolymers

Commercial sulfoaluminate clinkers developed by the Chinese predominantly consist of $\text{C}_4\text{A}_3\text{S}^-$ (55–75%) (also known as Klein’s compound) and $\text{C}_2\text{S}$ (15–25%). The remaining phases present are $\text{C}_1\text{S}_7$, $\text{C}_4\text{AF}$, and $\text{CaO}$.

Belite ($\text{C}_2\text{S}$)-rich sulfoaluminate cements are preferred to alite ($\text{C}_3\text{S}$)-rich, since belite-based cements can be formed at around 1200 °C, as opposed to 1400 °C for the alite cements. This equates to an energy savings of 20% during manufacture (Popescu, et al.) and results in less CO$_2$ being generated from the reaction of formation of $\text{C}_2\text{S}$ compared to $\text{C}_3\text{S}$.

Cements containing larger quantities of $\text{C}_2\text{S}$ than $\text{C}_3\text{S}$ are less permeable as well as being more resistant to chemical attacks and smaller drying shrinkage.
CAC's were invented in the early 1900's to resist sulfate attack. CAC's are inherently rapid hardening and can be rapid setting, adjustable with appropriate chemical admixtures. These cements are often used in refractory applications, building chemistry and rapid repair, rehabilitation and construction of concrete flatwork (e.g. sidewalks, overlays and full-depth pavement construction).

The rapid hardening properties, resistance to sulfate attack and alkali-aggregate reaction and abrasion resistance make these cements desirable in a wide-range of special applications. The manufacturing process of CAC's generates significantly less CO2 than the ordinary portland cement (OPC); roughly on the order of 50% less. The most widely discussed and controversial aspect of CAC's is a process referred to as conversion. Conversion is a process where metastable hydrates (CaH10 and C2AH8) formed at low and moderate temperatures (T=5 to ~70°C) convert to stable hydrates (C3AH6) formed at high temperatures (T>70°C). This process leads to an increase in porosity and subsequent decrease in strength. Conversion is an inevitable process and must be accounted for when designing the concrete mixture.

Magnesia phosphate cements:

Synthesized by reacting magnesium oxide with a soluble phosphate (e.g. ammonium phosphate). In essence, this is an acid-base reaction between the phosphate acid and the magnesium oxide to form an initial gel that crystallizes into an insoluble phosphate, mostly in the form of magnesium ammonium phosphate hexahydrate (NH4MgPO4·6H2O).

Magnesia phosphate cements are characterized by very high early strength and rapid setting, which makes them useful as a rapid patching mortar. It can also bind well to a wide variety of aggregates and substrates. Unlike magnesium oxychloride and oxysulfate cements, this cement has good water and freeze-thaw resistance and is, therefore, amenable to a wide variety of applications. A major drawback, however, is the expensiveness of phosphate, which confines its application to niche areas.

Recycled Glass-based Cements and Concretes:

Due to a high concentration of amorphous silica (>70% wt.) soda-lime glass can react pozzolanically with portlandite in a glass-portland cement system and produce low Ca/Si C-S-H. At moderate (up to 30%wt.) replacement levels of OPC, glass powder has been found to improve compressive strength beyond 28 days; however, early strengths can be reduced when using the same w/cm. Fineness of glass powder has a significant impact on its reactivity; glass finer than 38µm satisfies the strength activity index of ASTM C 618 (SAI>75% at 7days) and can be classified as a Type N pozzolan. By further increasing glass fineness and/or heat curing, concretes with 3-day strengths surpassing that of OPC concrete can be prepared. In addition, fine glass powder (<10µm) can mitigate the alkali-silica reaction generated by glass aggregates or other natural reactive aggregates.