Utilization of Recovered Materials for High Quality Cements and Products

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ABSTRACT:

CeraTech, Inc. has advanced the state of the art in reactive pozzolanic cements for use in most cement and concrete markets. The result is an enabling technology that utilizes a very large percentage of coal fly ash to produce a high performance family of cements. This cement technology can be used as a direct replacement for portland cement in most concrete, mortar or grout applications, thereby reducing the consumption of portland cement and the associated greenhouse gases generated from that manufacturing process.

The production of activated fly ash cements generates virtually no “carbon footprint". In contrast, portland cement production generates approximately 1 ton of CO_2 for each ton of clinker produced. These green cements and resulting products are comprised of more than 90% sustainable industrial waste stream materials. They are manufactured via a simple low energy, powder blending process. This revolutionary green cement technology possesses exceptional mechanical performance characteristics highlighted by rapid strength development properties. The highly reactive nature of the cement matrix allows for a broad range of mix designs as low as 3,000 psi (21 MPa) to over 12,000 psi (69 MPa) compressive strength at 28 days with nominal cementitious content per cubic yard of concrete. Moreover, this activated fly ash cement is mixed, placed and finished like standard cement concrete. Resulting products can be effectively placed in ambient temperatures ranging from 30°F (-1.1° C) to 120°F (48.9° C). Post placement temperature rise is minimal and less than most other hydraulic cements and their products.

INTRODUCTION

Concrete is the most widely used man-made material in the world. In 2007 nearly 3.05 billion tons of portland and hydraulic cement was produced worldwide. The production of cement - the main active ingredient of concrete - accounts for 5 to 10 percent of all anthropogenic carbon dioxide emissions; a leading greenhouse gas involved in global warming. Cement production generates carbon-dioxide emissions because it requires fossil fuels to heat the powdered mixture of limestone, clay, ferrous and siliceous materials to temperatures of 2700° F (1,500 ºC) Limestone - Calcium Carbonate ($CaCO_3$) - is the principle ingredient of cement.[1] During the portland cement clinker calcining process, $CaCO_3$ is changed to CaO. This conversion releases one mole of CO_2 (carbon dioxide) for every mole of $CaCO_3$ consumed in the production process. Approximately one ton of CO_2 is released in the production of one ton of portland cement. In the United States, portland cement production alone constitutes about 2-3% of CO_2 gasses generated annually[2].

Given the impact that portland cement production has on the environment, it is incumbent on concrete manufacturers to actively pursue immediate programs and/or practices that reduce the generation of CO_2 emissions. The concrete industry shouldn't consider this obligation a negative, however, because this responsibility also brings the opportunity to develop innovative technological advances in both material and a production processes.

HISTORICAL

Portland cement has long been a standard building material. Over the years, various modifiers have been developed for cement formulations to provide particular properties or advantages, such as more rapid curing, compatibility with and resistance to certain materials, and varying strengths, etc. Frequently, the modified formulations have worked at cross purposes, so that a cement formulation which initially cures more rapidly results in a final product with a lower ultimate strength, while the higher strength portland cement formulations frequently cannot be demolded for substantial periods of time because there is not sufficient early strength.

Over the past thirty years, scientists have pursued various methods to produce a class of fly ash based cement known as geo-polymers. These early precursors to present products were found - even though mineral in composition - to provide many of the properties of molding resins, such as epoxies and polyurethanes. Some geopolymeric cementitious products are in used still today in various parts of the world. Such geopolymers are described and claimed, for example, in U.S. Pat. Nos. 4,349,386 and 4,472,199, each in the name of Joseph Davidovits.[3] These geo-polymers are primarily composed of silicas and aluminas, mixed and reacted in particular ways to provide the desired structure. While, in general, these geopolymers are perfectly adequate for the purposes intended, as such, they do not provide the types of strengths sought in a cement composition.[4] Furthermore, geopolymers require post reaction thermal processing for up to 24 hours in order to achieve desirable strengths.

Earlier versions of pozzolan based cements:

1970's: Geo-polymers from fly ash, cements high in Al-Si. J. Davidovits makes references to their use in historical construction techniques.

1980's: Activated fly ashes blended with cement, e.g. mostly two step mixes unconditionally require addition of the activator at the jobsite.

1990’s through mid-decade beginning in 2000: Development of one step mixes, activator in package or cement. The cementitious compositions typically consisted of harsh acids and bases such as citric acids (pH ~ 2.2) and alkali metal activators including alkali hydroxides (pH ~12-14) and metal carbonates (pH ~ 11.6). These included patents by Gravitt, Kirkpatrick, Styron, and others. There were some draw backs to these materials. The prior art required acid -base reactions. These reactions sometimes were non-uniform and difficult to control.

The art has needed and continued to seek a hydraulic cement composition, which provides for utilization in standard situations, while providing both a high early strength and an ultimate, very high strength. In particular, compositions having a minimum strength of 4,000 psi (28 MPa) at 4 hours, the release strength necessary for prestress work, have been sought.

THE NEXT GENERATION CEMENT TECHNOLOGY

This new generation of pozzolanic cements offers the user a unique set of mechanical and dimensional properties competitive in cost to current cementitious product offerings, providing the user with a value added alternative solution for today’s most challenging repair and construction applications. The technology is built around a highly flexible chemistry that allows for the inclusion of a wide array of waste materials as part of its binder matrix, establishing it as a truly green sustainable construction material with unique performance and application advantages,

THE APPROACH

This new green cement technology is based upon an all pozzolanic cement design that requires no portland cement in its matrix. Through a detailed study of various types of pozzolanic chemistry and reactive pozzolanic-based cement pastes, key aspects of the mineralogy have been identified for determining the usefulness of various pozzolanic sources as high performance cements, including non acid-alkali activated, fly ash-based.

Having developed a technique to “fingerprint” pozzolanic raw materials as well as a “road map” of good pozzolanic sources, the new approach is able to maintain quality assurance on product lines using a broad array of ash-based pozzolanic sources, and blends of sources.

The cement technology is the principal backbone chemistry for a range of product offerings from small area repair packaged goods to new construction concretes. Products from the non acid alkali activated cements were developed specifically to satisfy user or application performance requirements. Each product is water activated, single component, turn key concretes with flexible working times from 15 minutes to three hours. The products were engineered to allow for mixing, placing and finishing using standard industry equipment and practices. The products were designed for applications where speed, strength and durability were desirable performance characteristics. Compressive strengths of more than 2,500 psi (17 MPa) in as little as 60 minutes supported by bond strengths of over 3,000 psi (21 MPa) and flexural strengths over 1,500 psi (10 MPa) in 7 days frame the technology's mechanical properties. Dimensional stability is highlighted by shrinkage of less than 0.04% length change in 28 days.

Principle benefits of this new class of products include:

- Non shrink
- Exceptional sustained bond strengths (slant shear and direct tension)
- Low coefficient of thermal expansion
- Modulus of elasticity consistent with portland cement concrete
- Low permeability
- High resistance to freezing and thawing
- High resistance to scaling
- High resistance to sulfate and chemical attack
- Exceptional durability
- Placement temperature tolerant
- No portland cement is needed
- No epoxy resins are contained

PRODUCTS AND MARKETS

Specific areas of products developed meeting objective criteria fall into several areas:

Departments Of Transportation / Department Of Defense Applications;

Figure 1. Marine Core Air Base Concrete Installation

- Rapid Repair

Rapid repair products all have cementitious components greater than 90% coal ash, and contain no portland cement. Based upon the size of the repair, products range in working time from 15 to 45 minutes, offering return to service ranging from 1 to 4 hours. All products can be mixed with conventional mixing equipment and placed like portland cement products, however without the requirement of bond coats.

- Ready-mix truck delivery

For large placements such as roadway slabs, ash-based pozzolanic cements have been adapted to ready-mix batch plant/transit truck mixing and placement. These products are able to be site activated (up to 4 hours transit time), and adjusted to placement times from 1 to 3 hours. Return to service can be achieved in as little as 6 to 12 hours. Slump control can be adjusted to range from roller-compacted concrete (RCC) to a self-consolidating concrete (SCC).

- Volumetric mobile mixer use

The volumetric pozzolanic product utilizes the same backbone chemistry as the rapid repair products. For larger placements that also require fast return to service, the pozzolans have been adapted to work in a volumetric mixer, allowing from 20 to 50 minutes of placement time, with return to service in as little as 1 hour depending upon the user requirements.

General construction and precast;

- Ready-mix

For vertical construction markets, including columns, flooring, and tilt-up construction, ash-based pozzolanic cements have been adapted to perform as self-consolidating concrete (SCC). These products permit easy pumping and long working times, yet can suspend aggregate, provide sufficient placement time, and offer early return to service.

- Volumetric

As with DOT and DOD applications, the principal benefit of volumetric placement is the ability to place larger volumes while still taking advantage of the quick return to service. One version of this product can be used as a flowable grout capable of providing up to three hours of working time, yet providing up to 5000 psi (35 MPa) in compressive strength in 24 hours.

- Concrete block/grout/mortar

The non acid-alkali activated fly-ash based pozzolanic cements have also been optimized to product both normal strength and high strength concrete masonry units (CMUs). Products have been able to achieve strengths ranging from 2000 to 10,000 psi (14 to 69 MPa) using conventional concrete block manufacturing facilities, techniques, and cement percentages equal to those used by conventional cement.

• Precast

Additional benefits of non acid-alkali activated ash-based pozzolanic cements also extend to precast concrete applications. Higher strength precast components can be developed, offering the ability to strip molds much earlier than with cement based concrete. This ability permits faster turn-around and throughput to the manufacturer.

SPECIALTY APPLICATIONS

• High Temperature Resistant Materials

A unique benefit of ash-based pozzolanic cements is their high temperature resistance capabilities. Ash-based cements are naturally refractory given their amorphous glass chemistry. Coupled with other high-temperature admixtures, these products are the only materials that have passed Mach 1 shock testing at 1700°F (927 ºC) for 300 cycles. This has qualified the material for use as a run-up and takeoff pad for current emerging vertical takeoff aircraft (VTOL) including the AV-8, V-22 Osprey, and the new Joint Strike Fighter.

Figure 1. Construction of base for a heat treating facility in Houston, Texas. Cycling of temperatures caused severe breakdown of conventional concrete.

• Armor and Protective Materials

Non acid-alkali activated fly ash-based pozzolanic cements are not only able to achieve high-early strength, but very high strengths overall. In one development area, a class of cements has been developed capable of achieving over 10,000 (69 MPa) psi in 24 hours, and up to 22,000 psi (152 MPa) within 28 days. These products are in development with the US Army Corps of Engineers as a field emplaced armor material capable of withstanding both blast and fragment penetration.

CONCLUSIONS

These cutting-edge, next-generation “green” non acid-alkali activated fly-ash based pozzolanic cements provide the construction a value added alternative to traditional cement product offers. The extent of engineering that has been done with the product offers widest range of end-use applications from any pozzolan, removing it from its previous limited use as a short-life rapid repair product only. Moreover, the amount of research that has been conducted on understanding fly-ash chemistry and mineralogy has extended the ability to use a much wider range of class C coal ash while maintaining predictable product performance. These truly green building materials are comprised largely of renewable, recyclable or reusable resources. They are the only cements in the world whose chemical matrix is comprised of more than 95% waste materials.

This new generation of all ash-based pozzolanic cements also furthers the ability to utilize green building technology for the widest range of end-use markets, including most DOT, DOD, and building construction market applications while meeting International Building Code and ASTM Standards.

REFERENCES

[1] The Nano Secret to Concrete, Prachi Patel-Predd, HYPERLINK "http://cee.mit.edu
[2] The Ready Mixed Concrete Industry LEED Reference Guide, Ready Mixed Concrete (RMC) Research Foundation and the Cement Association (PCA), 2006
[3] Davidovits, Science, What is a Geo-polymer, July, 2008
[4] Report to Congress entitled, "Study on Increasing the Usage of Recovered Mineral Components in Federally Funded Projects Involving Procurement of Cement or Concrete to Address the Safe, Accountable, Flexible, Efficient Transportation Equity Act: A Legacy for Users." , Stephen-L. Johnson, UNITED STATES ENVIRONMENTAL PROTECTION AGENCY, June 2008