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# Utilization of Coal Combustion By-Products and Green Materials for Production of Hydraulic Cement

James Hicks  
CeraTech, Inc.,  
USA

## 1. Introduction

### 1.1 Condition of highways

The condition of highways is reaching conditions such that immense expenditures are required just to remediate existing conditions. (Floris & Hicks, 2009)

According to the 2005 report card by the American Society of Civil Engineers (ASCE), the state of America's infrastructure has reached alarmingly unacceptable levels which threaten the current lifestyle and standard of living. The average grade for America's infrastructure was D (Poor), requiring an estimated US\$1.6 trillion just to return the infrastructure systems back to a serviceable condition.

Another fact is that US\$9.4 billion a year for 20 years is required to eliminate the deficiencies in the nation's 600,000 bridges, suggests serious systemic problems exist in the construction industry. Society is slowly coming to realize that initial predictions of cement durability may have been excessive and that concrete buildings or structures that last for only 50–70 years may not be cost effective. (Phair, 2006)

Volumes of materials required for the repair of deficiencies are further exacerbated by any new construction required. Much of this will require use of portland cement or other hydraulic cements.

### 1.2 Greenhouse gasses emitted

A large producer of CO<sub>2</sub> emissions is portland cement kilns. For instance, the use of fly ash (a by-product of coal burning in power generation and most common Coal Combustion Products (CCP) in the cement-making process) could reduce substantial amounts of CO<sub>2</sub> emitted by a cement kiln. Worldwide, the production of portland cement alone accounts for 6 to 8 percent of all human generated CO<sub>2</sub> greenhouse gases (Huntzinger, Deborah N. and Eatmon, Thomas D., 2009). Portland cement production is not only a source of combustion-related CO<sub>2</sub> emissions, but it is also one of the largest sources of industrial process-related emissions in the United States. Combustion related emissions from the U.S. [portland] cement industry were estimated at approximately 36 Tg of CO<sub>2</sub> accounting for approximately 3.7 percent of combustion-related emissions in the U.S. industrial sector in 2001 (USGS, 2002).

Extensive research is underway to find more economically feasible alternatives for carbon dioxide capture and storage (CCS). However, until financially and environmentally sustainable alternatives are in use, the byproducts of pulverized coal-based power generation (conventional) will be an issue for decades to come. A successful CO<sub>2</sub> mitigation process presently lies in private-public strategy that combines existing power plants (revamped to capture, geologically store and/or enhance oil recovery), and new ones using more advanced coal power generation technologies like the Integrated Coal Gasification Combined Cycle (IGCC). These approaches alongside proactive regulation could build a relatively sustainable alternative for the future (Floris, Vinio, 2009).

In 2009, a survey of US coal-fired power plants showed production of 122.2 million metric tonnes (t), (134.7 million short tons (st)) of CCP’s (US Energy Administration, 2010). Of this amount, only 22.4 million t (24.7 million st) were used as fly ash in concrete or as a concrete product. The survey reported that more than 71.7 million t (79 million st) of fly ash is still being disposed of in US landfills annually. (ACAA, 2009) Clearly, the use of otherwise waste materials for beneficial use can reduce the need for more landfills and the amount of CO<sub>2</sub> produced.

Coal has been the primary fuel used worldwide in recent times (Figure 1). This has been forecast to continue well into the future.

Not all current power plants will be refurbished as mentioned; yet CCP’s from plants that do not convert to CCS technologies could still be put to good use through innovative ways in order to assist in the decrease of greenhouse gases.

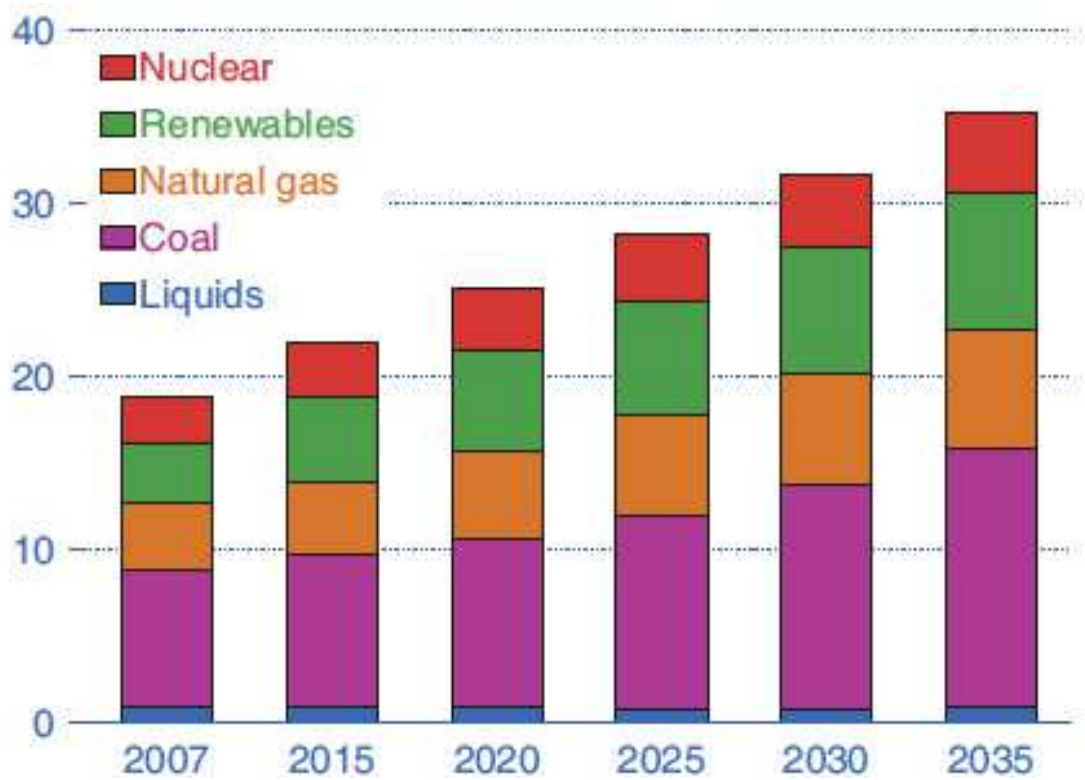


Fig. 1. World net Electricity generation by fuel, 2007-2035 (trillion kilowatt hours) (U. S Energy Administration, 2010)

For instance, fly ash (a by-product that largely ends up in landfills) can substitute for portland cement and improve structural changes to the end product (concrete and others). The use of one unit of fly ash reduces approximately one unit of CO<sub>2</sub> emitted by a cement kiln. Fly ash and other CCP's in the cement-making process could also avoid the use of the high energy requirement and significantly reduce the volume of useable material taken to waste management sites (Floris and Hicks, 2009). The amount of fly ash beneficially used in the United States is illustrated in Figure 2.



Fig. 2. CCP Beneficial Use versus production (American Coal Ash Association, 2010)

**2. Waste materials converted into hydraulic cements**

This section provides a brief overview of concretes in which the binder phase is made of materials other than portland cement. The non-portland cement binders discussed here are alkali activated slag and fly ash cements, calcium aluminate cements, and calcium sulfo-aluminate cements. A brief introduction of the recycled glass-based cements and concretes is also provided. It should be mentioned that most of these binder systems have been used for specific applications across the world for several decades. However, recent concerns about the environmental impact of portland cement production have created a renewed interest in these less energy- and CO<sub>2</sub>-intensive binder systems. With energy, resource and infrastructure demands growing in the foreseeable future, a sustainable concrete that is more durable and costs less to maintain, is becoming increasingly desirable (Touzo & Espinosa, 2010).

## 2.1 Alkali activated fly ash concretes

Alkali activated fly ash is a potential substitute for portland cement. Fly ash is mainly composed of glassy alumina ( $\text{Al}_2\text{O}_3$ ) and silicate ( $\text{SiO}_2$ ) phases which can be activated (i.e., dissolved) by a concentrated aqueous alkali hydroxide (e.g.,  $\text{NaOH}$ ,  $\text{KOH}$ ), alkali silicate (e.g.,  $\text{Na}_2\text{SiO}_3$ ), or a combination of these solutions. As the concentration of alumina and silicate species approach saturation in the pore fluid, an amorphous to semi-crystalline inorganic polymer is formed which is called by a common name geopolymer (Davidovits, 1984). This inorganic geopolymer is mainly composed of an alkali (e.g.,  $\text{Na}$ )-alumino-silicate-hydrate gel (in short, NASH) which creates the binding phase; in contrast with calcium-silicate-hydrate (CSH) gel which is the main constituent and binding phase of portland cement concretes (Fernández-Jiménez & Palomo, 2009). In addition to fly ash (both class F and C), geopolymers can be produced using metakaolin.

Alkali activated products can compete with traditional concrete in terms of performance in a wide range of applications including variations in temperatures in use. Depending on the curing conditions and the concentration of activator, alkali activated fly ash can exhibit a wide variety of properties including high compressive strength, low creep and drying shrinkage, acid resistance and fire resistance (Su, M., et. al, 1997).

The spherical shape of fly ash particles is beneficial for reducing water demand and for maximizing particle packing to reduce porosity. On the other hand, alkali activated Class-F fly ash either requires a highly concentrated alkali solution (highly caustic) for activation or high temperature curing to gain sufficient strength. Also, variability in the composition of fly ash can result in significant variability in the performance of concrete produced unless the ash composition is continuously monitored and changes in mixture proportions are made accordingly. These cements have been engineered for use in fast track concrete repairs and construction, conventional paving, walls and concrete block masonry, new construction and repair projects.

Developments in fly ash based cements offers the user a unique set of mechanical and dimensional properties. In addition, they are now competitive in cost to current cementitious product offerings.

These newly developed activated fly ash based products leave virtually no carbon footprint. Updated cementitious binder technology eliminates approximately 0.9 t (1 st) of  $\text{CO}_2$  emitted into the atmosphere per ton of portland cement produced.

Concrete is the most widely used man-made material in the world. In 2008 nearly 2.6 billion t (3 billion st) of portland and hydraulic cement was produced worldwide (PCA, 2009). 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  $1,500^\circ\text{C}$  ( $2,700^\circ\text{F}$ ). Limestone (Calcium Carbonate -  $\text{CaCO}_3$ ) is the principle ingredient of cement. During the portland cement clinker calcining process,  $\text{CaCO}_3$  is changed to  $\text{CaO}$ . This conversion releases one mole of  $\text{CO}_2$  (carbon dioxide) for every mole of  $\text{CaCO}_3$  consumed in the production process. Approximately one ton of  $\text{CO}_2$  is released in the production of one ton of portland cement. In the United States, portland cement production alone constitutes about 2-3 percent of  $\text{CO}_2$  gasses generated annually. Given the impact 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<sub>2</sub> 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. The cements thusly produced develop Calcium Silicate Hydrates (CSH) as shown in Figure 3.

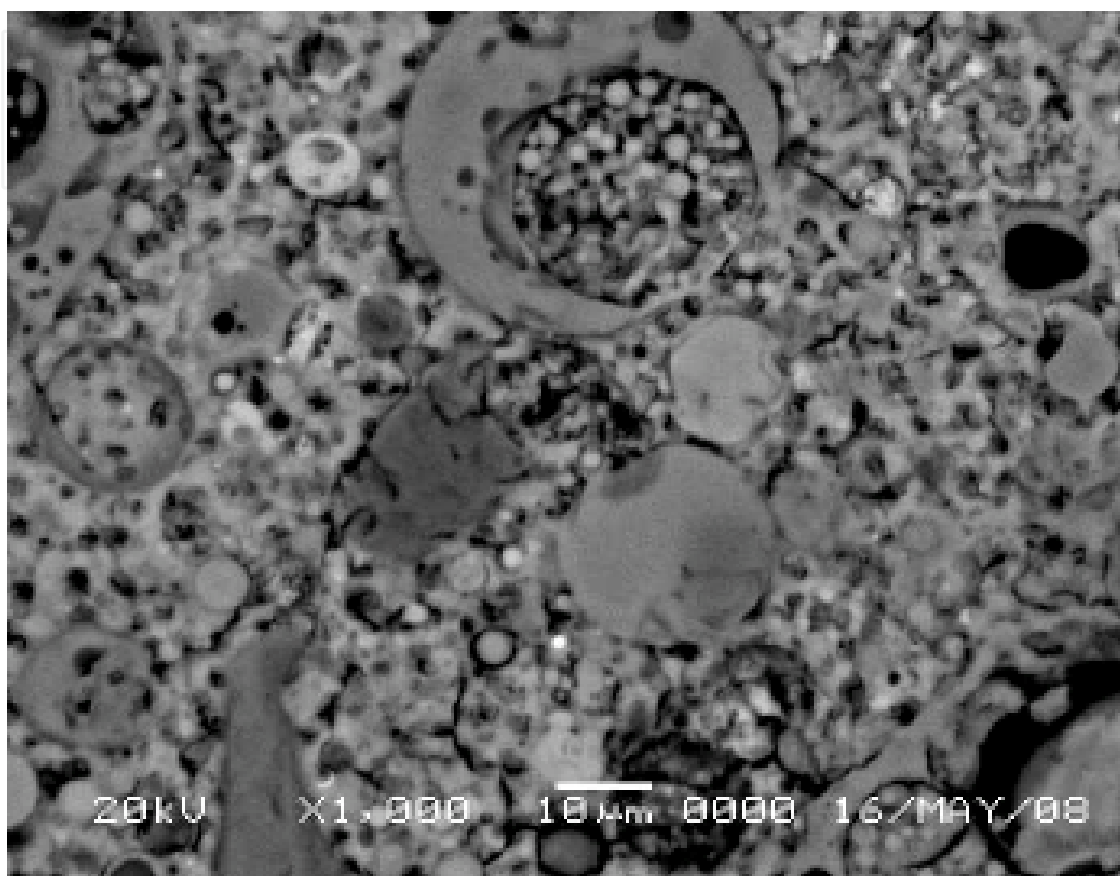


Fig. 3. Micrograph of CSH Formation in Activated Fly Ash Cement, sample age is 14 months from addition of water. (James K. Hicks, et. al., 2009).

Portland cement has long been used in standard building materials. 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. In the past, at times the modified formulations have worked at cross purposes, so that a cement formulation that initially cures more rapidly results in a final product with a lower ultimate strength, while the higher late 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, US Patents. (Davidovits,

1982). 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 always provide the types of strengths sought in a concrete composition. Furthermore, geopolymers typically require post reaction thermal processing for up to 24 hours in order to achieve desirable strengths.

Below is a recent historical summary of earlier versions of pozzolan based cements:

- Alkali activation of solid, non-portland cement precursors (usually high-calcium slags) was first demonstrated in reasonably modern times by Purdon in 1940, and was developed on a larger scale primarily in Eastern Europe in the succeeding decades, (vanDeventer, Jannie S.J. et. al, 2010)
- 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 product 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, Hicks and others. There were some drawbacks 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 28 MPa (4,000 psi) at 4 hours, the release strength necessary for prestress work, have been sought.

### 2.1.1 The new generation of cement technology

This new generation of fly ash based 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 construction cementitious repair, product and paving 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.

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

Key to green cement development was creating a material matrix that had a very dense crystal structure eliminating the movement of water and other chemicals through the

material matrix; water being the catalyst for many of the reactions that occur in the concrete matrix.

This is accomplished through the simultaneous dissolution and retardation of the Calcium Oxide phase to solubilize both the silicate and aluminate amorphous phases. The minerals recombine to the desired structure providing desired mechanical and dimensional properties. Thusly, pozzolanic materials are modified with chemicals to produce the desired structure. They are characterized by a very dense crystal structure exhibiting the optimum chemical ratio of calcium to silicates to aluminates. The micro pore structure is very small, greatly limiting the movement of liquids within the material matrix.

The crystal structure of portland cement is dominated by Tricalcium Silicate ( $C_3S$ ) and Dicalcium Silicate ( $C_2S$ ) components producing a crystal structure that is not as dense leading to relatively a large voids structure within the material matrix. The chemical and mineralogical improvements, coupled with the much higher fineness of pozzolan based cements ground leads to much lower porosity in the concrete. The lower porosity provides for very low water to cementitious ratios and improved durability factors.

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

The improved activated hydraulic 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 mixed, single component activated, turnkey concrete, mortar or grout with flexible working times from 15 minutes to three hours. The products were engineered to allow for mixing, hauling, 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 17 MPa (2,500 psi) in as little as 60 minutes supported by bond strengths of over 21 MPa (3,000 psi) and flexural strengths over 10 MPa (1,500 psi) 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 epoxy resins are contained.

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



- Rapid Repair
- Ready Mix including paving
- Volumetric mixer concrete and mortar
- Concrete block/grout/mortar
- Precast
- High Temperature Resistant Materials such as that being placed in Figure 4.
- Chemical Resistant Materials



Fig. 4. Construction of base for a heat treating facility in Houston, Texas. Cycling of temperatures caused severe breakdown of conventional concrete, (James K. Hicks, et. al., 2009).

Some of the more specific examples descriptions are:

- Rapid repair products all have cementitious components greater than 90 percent 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 (See Table 1). 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 (See Table 2). Slump control can be adjusted to range from roller-compacted concrete (RCC) to a self-consolidating concrete (SCC).

| Property   | As Packaged<br>4 in. x 8 in. cylinders | Test Method         |
|--|--|---------------------|
| <b>Compressive Strengths, psi (MPa)</b>  |  |                     |
| <b>2 hours</b>   | <b>2820</b> (19.4)                     | <b>ASTM C 39</b>    |
| <b>1 day - 24 hours</b>  | <b>6115</b> (42.2)                     | <b>ASTM C 39</b>    |
| <b>7 days</b>  | <b>9345</b> (64.4)                     | <b>ASTM C 39</b>    |
| <b>28 days</b>   | <b>10,510</b> (72.5)                   | <b>ASTM C 39</b>    |
| <b>Flexural Strength, psi (MPa)</b>  |  |                     |
| <b>1 day - 24 hours</b>  | <b>690</b> (4.8)                       | <b>ASTM C 78</b>    |
| <b>7 days</b>  | <b>945</b> (6.5)                       | <b>ASTM C 78</b>    |
| <b>28 days</b>   | <b>1405</b> (9.7)                      | <b>ASTM C 78</b>    |
| <b>Splitting Tensile Strength, psi (MPa)</b>   |  |                     |
| <b>28 days</b>   | <b>590</b> (4.0)                       | <b>ASTM C 496</b>   |
| <b>Bond Strength, psi (MPa)</b>  |  |                     |
| <b>1 day - 24 hours</b>  | <b>1960</b> (13.6)                     | <b>ASTM C 882</b>   |
| <b>7 days</b>  | <b>2745</b> (18.9)                     | <b>ASTM C 882</b>   |
| <b>Rapid Freeze Thaw Resistance</b> (Durability Factor - Retained percentage of Dynamic Modulus) |  |                     |
| <b>300 cycles</b>  | <b>100%</b>                            | <b>ASTM C 666A</b>  |
| <b>Scaling Resistance, lbs/ft<sup>2</sup> (kg/m<sup>2</sup>)</b>                                 |  |                     |
| <b>50 cycles</b>   | <b>0</b>                               | <b>ASTM C 672</b>   |
| <b>Modulus of Elasticity, msi (GPa)</b>  |  |                     |
| <b>28 days</b>   | <b>5.2</b> (35.1)                      | <b>ASTM C 469</b>   |
| <b>Coefficient of Thermal Expansion, in/in/°F</b>  |  |                     |
| <b>28 days</b>   | <b>1.32</b>                            | <b>AASHTO TP 60</b> |
| <b>Length Change, % of total length</b>  |  |                     |
| <b>28 days soak / 28 days dry</b>  | <b>-0.052 / -0.041</b>                 | <b>ASTM C 157</b>   |

Table 1. Characteristics of an activated pozzolan cement fast return to service ready mixed concrete. Source, CeraTech, Inc.

| Property   | <sup>1</sup> Rapid Set | <sup>1</sup> Standard Set | Test Method              |
|--|------------------------|---------------------------|--------------------------|
| <b>Compressive Strengths, psi (MPa)</b> <small>4 in. x 8 in. cylinders</small>                   |                        |                           |                          |
| <b>6 hours</b>   | <b>3500</b> (24.1)     | <b>NA</b>                 | <b>ASTM C 39</b>         |
| <b>24 hours</b>  | <b>3604</b> (24.9)     | <b>2497</b> (17.2)        | <b>ASTM C 39</b>         |
| <b>3 day - 72 hour</b>   | <b>4502</b> (31.0)     | <b>4193</b> (29.0)        | <b>ASTM C 39</b>         |
| <b>7 days</b>  | <b>6487</b> (44.7)     | <b>5998</b> (41.3)        | <b>ASTM C 39</b>         |
| <b>28 days</b>   | <b>8511</b> (58.7)     | <b>8502</b> (58.6)        | <b>ASTM C 39</b>         |
| <b>Flexural Strength, psi (MPa)</b>  |                        |                           |                          |
| <b>7 days</b>  | <b>510</b> (3.5)       | <b>485</b> (3.3)          | <b>ASTM C 78</b>         |
| <b>28 days</b>   | <b>650</b> (4.5)       | <b>630</b> (4.3)          | <b>ASTM C 78</b>         |
| <b>Splitting Tensile Strength, psi (MPa)</b>   |                        |                           |                          |
| <b>28 days</b>   | <b>720</b> (5.0)       |                           | <b>ASTM C 496</b>        |
| <b>Rapid Freeze Thaw Resistance</b> (Durability Factor - Retained percentage of Dynamic Modulus) |                        |                           |                          |
| <b>300 cycles</b>  | <b>100%</b>            |                           | <b>ASTM C 666A</b>       |
| <b>Scaling Resistance, lbs/ft<sup>2</sup> (kg/m<sup>2</sup>)</b>                                 |                        |                           |                          |
| <b>50 cycles</b>   | <b>0</b>               |                           | <b>ASTM C 672</b>        |
| <b>Abrasion Resistance, Depth of wear, millimeters @ 28 day</b>                                  |                        |                           |                          |
| <b>0.14</b>  |                        |                           | <b>ASTM C 944 (2005)</b> |
| <b>Modulus of Elasticity, msi (GPa)</b>  |                        |                           |                          |
| <b>28 days</b>   | <b>5.00</b> (34.0 )    |                           | <b>ASTM C 469</b>        |
| <b>Coefficient of Thermal Expansion, in/in/°F</b>  |                        |                           |                          |
| <b>28 days</b>   | <b>4.6</b>             |                           | <b>AASHTO TP 60</b>      |
| <b>Length Change, % of total length</b>  |                        |                           |                          |
| <b>14 days</b>   | <b>0.04</b>            |                           | <b>ASTM C 157</b>        |
| <b>Creep (365 days)</b><br>(μ Strain / psi)  |                        |                           |                          |
| <b>Creep Coefficient</b>   | <b>1.91</b>            |                           | <b>ASTM C 512</b>        |

Table 2. Characteristics of an activated pozzolan cement fast return to service ready mixed concrete. Source, CeraTech, Inc.

- 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. 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 35 MPa (5000 psi) in compressive strength in 24 hours.



Fig. 5. Marine Corps Engineers training for fast track construction and repair prior to deployment. Marine Corps Base Concrete Installation, (James K. Hicks, et. al., 2009).

Among the general construction and precast benefits are:

- 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. These are placed with a conventional batching and mixer system.
- 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.
- 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 °C) for 300 cycles. This result 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 Joint Strike Fighter.

- **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 69 MPa (10,000 psi) in 24 hours, and up to 152 MPa (22,000 psi) 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.
- **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 over 14 to 69 MPa (2,000 to 10,000 psi) using conventional concrete block manufacturing facilities, techniques, and cement percentages equal to those used by conventional cement. (Hicks, et. al., 2009)

Notes:

1. Strength development and working times can be adjusted by varying the cement ratio and by use of various proprietary activator admixtures.
- Rapid Set Test results based on 846 lbs. of cement per cubic yard mix design and Fast Set Activator.
  - Standard Set Test results based on 564 lbs. of cement per cubic yard mix design and Fast Set Activator.

## 2.2 Alkali Activated Slag cements

An alkali activated slag (AAS) concrete is one in which the binder phase is made of ground granulated blast furnace slag (GGBFS), water, and an alkali activator which triggers the chemical reactions involving dissolution of slag and polymerization of calcium-silicate and aluminum-silicate phases which serve as the binder. These systems contain no portland cement. Although slag is cementitious and can self-activate, the reaction is typically slow and requires external activators to enhance reaction rates and form stronger products. Sufficient alkali content is also necessary for the development of significant strength. Since slag is deficient in alkalis, these have to be supplied externally. These alkali-activated slag systems also appear in the literature with a variety of names such as alkali-activated cements (Palomo & López dela Fuente, 2003), and alkali-slag cements (Roy, D.M. 1999).

The most commonly used alkaline activating agents are sodium hydroxide (NaOH) and sodium silicate ( $\text{Na}_2\text{SiO}_3$ ), also known as water glass, or combinations of these (Shi & Day, 1996), (Krizan & Zivanovic, 2002). A variety of industrial by-products containing alkalis and sulfates such as cement kiln dusts are also equally effective in activating slag (Chaunsali & Peethamparan, 2010). Among the activators used, water glass is widely reported to give rise to rapid hardening and high compressive strengths (Oh et. al. 2010). The main hydration product in AAS systems is calcium silicate hydrate (C-S-H) with a low Ca/Si ratio regardless of the type of activator used (Song, et. al., 2000). The morphology of the hydration products changes with the activator and other hydration conditions. Hydrotalcite (magnesium-calcium aluminate hydrate:  $(\text{M},\text{C})_4\text{AH}_{13}$ ) and minor amounts of strätlingite ( $\text{C}_2\text{ASH}_8$ ) are also found in AAS.



Alkali-activated slag displays very good strength (Atis, et. al, 2000), durability (Fernández-Jiménez & Puertas, 2002), and a variety of other potentially valuable characteristics such as fire and waste water resistance. However, shorter setting time, increased shrinkage, and difficulties with safe handling of the liquid water glass outside the laboratory have limited its use (Shi, et. al., 2006). Sodium silicate with higher modulus (i.e., silica-to-alkali ratio) can often alleviate some of these problems.

Supersulfated slag cement is an example of a cement that has used ettringite in combination with CSH as the main binding phase to a relative degree of success. Supersulfated slag cements consist mostly of granulated blast-furnace slag, gypsum or anhydrite with a small amount of lime or Portland cement to catalyse the chemical reaction. Although, they exhibit slow strength development and may undergo deleterious carbonation reactions, they still have significant application potential.

More research is needed to modify the early age properties of the alkali activated slag concrete. The low CO<sub>2</sub> emission rate and the low embodied energy of AAS, as slag being a commercial by-product, compared to traditional portland cement are primarily attributed to the absence of high temperature clinkering processes involving a large amount of fossil fuel-derived energy. While the use of alkaline hydroxide or silicate activating solutions rather than water does reintroduce some greenhouse costs, the overall beneficial effects due to widespread use of alkali activated slag is expected to be highly significant.

### 2.3 Calcium Aluminate Cements

Calcium aluminate cements (CAC's) are a special class of cement containing primarily aluminates and calcium. Small amounts of ferrite and silica are also typically present. 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 (Scrivener & Capmas, 1998, Juenger, et.al. 2010). The manufacturing process of CAC's generates significantly less CO<sub>2</sub> than the ordinary portland cement (OPC); roughly on the order of 50% less (Juenger, et.al. 2010), Gartner, E. (2004). However there is slightly more grinding energy required (than OPC) due to the increased strength of the clinker less (Juenger, et.al. 2010, Scrivener & Capmas, 1998).

The most widely discussed and controversial aspect of CAC's is a process referred to as conversion. Conversion is a process where metastable hydrates (CAH<sub>10</sub> and C<sub>2</sub>AH<sub>8</sub>) formed at low and moderate temperatures (T=5 to ~70°C) convert to stable hydrates (C<sub>3</sub>AH<sub>6</sub>) 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. The hydration process of CAC's is thus highly temperature dependant and the time spent during hydration within specific temperature ranges will dictate the type and amount of metastable and/or stable hydrates formed (Scrivener & Capmas, 1998).

Several building collapses in the 1970s were attributed to CAC conversion, and many structural codes subsequently banned the use of this material. Since this time, intensive research has provided a greater understanding of CAC chemistry and behavior. Furthermore, a report by the Concrete Society (Palomo & López dela Fuente, 2003) revisited these landmark collapses and revealed that improper structural detailing, a lack of understanding about CAC properties and not following manufacturers' guidance had lead to the majority of the structural failures. Improved guidance for predicting long-term properties and a better scientific understanding of the material has seen resurgence in interest and use of this alternative cementitious binder (Juenger, et.al. 2010).

There are several recommendations that have been employed to keep the strength lost during conversion to a minimum. This includes keeping the w/cm below 0.40 and including a minimum cement content of 400 kg/m<sup>3</sup> ( Concrete Society Technical, 1997, Fentiman, C. et.al. , 2008).

## 2.4 Calcium sulfoaluminate (CSA) cements

Calcium Sulfo-Aluminate Cements or ettringite cements are a type of high alumina cement that first came to prominence in the 1970s. To form calcium sulfoaluminate clinker, limestone, bauxite, and gypsum are mixed and heat fired in rotary calcining kiln. Commercial sulfoaluminate clinkers developed by the Chinese predominantly consist of  $C_4A_3S^-$  (55–75%) (also known as Klein's compound) and  $\alpha-C_2S$  (15–25%). The remaining phases present are  $C_{12}A_7$ ,  $C_4AF$  and  $CaO$ , but  $C_2AS^-$  and  $CS^-$  are considered deleterious and, therefore, undesirable. Belite ( $C_2S$ )-rich sulfoaluminate cements are preferred to alite ( $C_3S$ )-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<sub>2</sub> being generated from the reaction of formation of  $C_2S$  compared to  $C_3S$ . Belite-based sulfoaluminate cements are also preferred for certain performance reasons, since cements containing larger quantities of  $C_2S$  than  $C_3S$  are less permeable as well as being more resistant to chemical attacks and smaller drying shrinkage. On the other hand, large proportions of  $C_2S$  do reduce the rate of strength evolution and setting point but the presence of calcium sulfate and calcium sulfoaluminate more than compensate for this deficiency.

Sulfoaluminate cements may be defined by the compositional system of  $CaO-Al_2O_3-SiO_2-Fe_2O_3-SO_3$ . Strength and material performance rely heavily on the specific composition and phases present. The bonding phases within sulfoaluminate cements consist predominantly of ettringite, monocalcium sulfo-aluminate hydrate, ferrite and alumina gel. Calcium aluminates such as  $C_3AH_6$  and  $C_4AH_{13}$  have been observed in some instances.

To date, studies on the durability of these cements have been promising. Typically, sulfoaluminate cements are used where rapid setting, early strength or shrinkage compensation is required. They also have the advantage that their long-term strength and durability can exceed that of Portland cement. These cements have seen widespread and high volume use as bridge decks, airport runways, patching roadways etc. where rapid setting is required.

Approximately 81,000 t of CSA Cement was produced in 1996 in the US alone, but it has been used even more in Japan and China to construct bridges and buildings. Production now exceeds 106 tonnes per year. However, rapid setting and expansive cements are inappropriate for certain building engineering applications. Since the hydration of belite-sulfoaluminate cements at ambient temperatures leads to the formation of ettringite as the major phase, the cements may be susceptible to degradative problems associated with carbonation, delayed ettringite formation as well as thaumasite attack. So if the setting time is to be properly regulated, special activators must be added to reduce the setting rate. Further research is ongoing in this area to widen the potential use of sulfoaluminate cements.

Significant environmental advantages exist in using sulfoaluminate cements. The calcium sulfoaluminate clinker ( $C_4A_3S$ ) generates the least amount of  $CO_2$  per g of raw material as by-product of its reaction of formation. This makes it extremely attractive. Furthermore, the calcining of the raw materials for clinker formation occurs at temperatures (1160–1200°C) much lower than those used for firing Portland cement clinker (1450°C). Another environmental advantage of the manufacturing process of belite-rich sulfoaluminate clinkers is that it can utilize industrial by-products with high sulfate content. For example, fluidized bed combustor (FBC) fly ash, blast furnace slag, low-calcium fly ash or flue gas desulfurization (FGD) sludge can be utilized to manufacture belite-rich sulfoaluminate clinkers, whereas they could not be used in the manufacture of Portland cement clinker, which limits the  $SO_3$  content to 3.5% dry weight. Energy savings also occur in the grinding of the clinker compared to Portland cement, since the low firing temperatures result in a clinker, which is generally softer.

Another advantage of calcium sulfoaluminate cements is that it can use gypsum to form hydration products which have not undergone any heat treatment in a kiln. This results in a considerable energy saving.

Utilization of sulfoaluminate cements in both China and Japan is now becoming so widespread that they may almost be referred to as a commodity material, particularly in China. In Europe and North America, its utilization has largely been restricted to high early strength, self-stressing or shrinkage applications. Sulfoaluminate cements could potentially become a major large-scale alternative to Portland cement, however their classification has largely been restricted to certain geographic regions with different climatic and economic conditions. As for alkali-activated cements, a significant disadvantage of sulfoaluminate cements has been the confusing nomenclature and lack of international consensus as to standards and names.

Calcium sulfoaluminate (CSA) cements are receiving increasing examination from the cement industry and researchers as a lower-energy, lower- $CO_2$  alternative to portland cement. Such cements are not new; they contain as a primary phase Ye'elimite ( $Ca_4Al_6SO_{16}$ ; or  $C_4A_3S$  in cement chemistry notation), which was used by Alexander Klein in the 1960s as an expansive additive to portland cement and is sometimes called Klein's compound (Klein, A. 1966). The Chinese have been industrially producing these cements since the 1970s and their annual production may exceed 1 million tons (Glasser & Zhang 2001). CSA cements are used for some structural applications, but they are especially well-suited for precast and cold-weather applications which take advantage of the rapid strength gain of these materials (Quillin, 2001). Their mechanical properties and durability are reported to rival portland cement (Mehta, 1980), but much work is needed to fully vet the long-term material performance.

CSA cements lack standardized composition or performance criteria. They are distinguished by the presence of  $C_4A_3S$  as the primary cementing phase, belite ( $C_2S$ ) as a secondary phase, and the absence of alite ( $C_3S$ ). Other phases that are commonly present include  $C_4AF$ ,  $C_2AS$ ,  $CA$ , and  $CS$ , and gypsum is added for hydration control as in portland cement. Because ettringite is the primary reaction product of  $C_4A_3S$  with gypsum and water, these cements can exhibit rapid setting, rapid strength gains, and expansion. However, these properties can be controlled through manipulating the composition of the cement and through the addition of chemical retarders. Mechanical properties and dimensional stability similar to portland cement can be achieved (Juenger & Chen, 2011, Sharp, 1999).

The reputation of CSA cements as environmentally-friendly comes from reductions in energy use and  $CO_2$  emissions during manufacturing. CSA clinkers can be made at lower kiln temperatures than portland cement clinkers ( $1250^\circ C$  instead of  $1350-1450^\circ C$ ), and are more porous and friable, thereby requiring less energy for grinding (Shi, et. al, 2005, Rajabipour, et. al, 2010). The lime ( $CaO$ ) content of  $C_4A_3S$  is low (36.7 wt.%) compared to that of  $C_3S$  (73.7 wt.%); therefore much less limestone is calcined in the production of CSA cements, leading to lower  $CO_2$  emissions. CSA cements may be able to reduce limestone use by 40% and energy by 25% compared to OPC (Sharp, 1999). One of the primary challenges facing the widespread adoption of CSA cements, aside from further knowledge of its material properties, is the cost of raw materials. The high alumina content demands the use of bauxite as a raw material, which is not widely available and is expensive. Alternatively, the high sulfur and iron (if  $C_4AF$  is included) contents allow for the use of many types of industrial by products as raw materials, reducing the cost of the clinker, both in terms of the economy and the environment (Palou & Majling, 1995, Phair 2006).

## 2.5 Magnesia based cements

Magnesia cements are a range of cements based on magnesium oxide ( $MgO$ ) as the key reactive ingredient. The first type of magnesia cement was developed by Frenchman Stanislas Sorel in 1867 and is now referred to as Sorel, magnesite or magnesium oxychloride cement (Phair, J.W. 2006). Sorel cement was produced initially by the combination of magnesium oxide with concentrated aqueous magnesium chloride. This results in a hardened cement paste consisting of four main bonding phases:  $2Mg(OH)_2 \bullet MgCl_2 \bullet 4H_2O$ ,  $3Mg(OH)_2 \bullet MgCl_2 \bullet 8H_2O$ ,  $5Mg(OH)_2 \bullet MgCl_2 \bullet 5H_2O$  and  $9Mg(OH)_2 \bullet MgCl_2 \bullet H_2O$ . It was soon discovered, however, that the magnesium oxychloride phases are not stable after prolonged exposure to water, and will leach out in the form of magnesium chloride or magnesium hydroxide. As a consequence, Sorel cement has found limited application in the building and construction industry despite demonstrating other properties that are far superior to those of Portland cement. For instance, it has high fire resistance, low thermal conductivity, high abrasion resistance, high transverse and crushing strengths and does not require wet curing. Various additives are being investigated to improve its water resistance although no spectacular discovery in this area has been made yet.

With time, a variety of other magnesia cements have been developed based on permutations of magnesium oxide as the binding phase with varying levels of success. Magnesium oxysulfate cements, formed by the reaction of a magnesium sulfate solution with magnesium oxide, have similar properties to magnesium oxychloride cements. Again, they have good binding properties and combine well with a variety of inorganic and organic



aggregates such as sand, marble flour, gravel, saw dust and wood flour to produce a cement with high early strength. Poor weathering resistance, however, is again the main drawback for this type of cement.

Another analogue is magnesia phosphate cements, which can be 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 ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ).

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.

More promising magnesia cements that have recently attracted considerable interest from industry have been magnesium carbonate or magnesite cements (Harrison, 2003). The bonding phase for these cements includes magnesium hydroxide and magnesium carbonate. In the presence of accelerating additives (such as  $\text{KNO}_3$ ,  $\text{Fe}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ ,  $\text{CaCl}_2$ , etc.) magnesium oxide will undergo hydration to form magnesium hydroxide, or brucite, which is considerably less soluble than portlandite ( $\text{Ca}(\text{OH})_2$ ), the calcium analogue. Brucite can then react in the presence of sufficient carbon dioxide and a calcium source to form magnesite, hydromagnesite and calcium magnesium carbonate or dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ). These carbonates add strength to the binding phase, and in being relatively insoluble and fibrous in structure, have the ability to form a better network nanostructure than observed for calcium carbonates.

The presence of the accelerator also serves to increase the setting time making the long-term strength gains comparable to that of Portland cement. (Harrison, 2003). Typically, magnesia carbonate cements can be formed when magnesia is in the presence of considerable quantities of waste materials or traditional pozzolans, provided sufficient brucite, carbon dioxide and accelerators are present.<sup>131</sup> Such waste materials include fly ash, slag, silica fume, silica flour, mine tailings, sewerage ash etc.

The possibility also exists for adding magnesium oxide to ordinary portland cement, yielding more durable composite cement. This may be achieved by promoting the reaction of portlandite with pozzolans, thereby allowing brucite to replace it and sequester excess alkali. This is an advantageous scenario since brucite is some 100–1000 times less soluble than portlandite. ( $\text{Ca}(\text{OH})_2$   $K_{\text{SP}} = 5.5 \times 10^{-6}$ ,  $\text{Mg}(\text{OH})_2$   $K_{\text{SP}} = 1.8 \times 10^{-11}$  at  $25^\circ\text{C}$ ). The main environmental advantage associated with magnesia carbonate cements is that the starting material, magnesia, is readily obtained from the calcining of magnesite. The process of magnesite decomposition occurs at temperatures around  $400^\circ\text{C}$  less than that of limestone so it requires considerably less energy to manufacture. However, the reaction for formation of magnesia results in the emission of considerable amounts of  $\text{CO}_2$ , which slightly offsets the gains achieved in the lower energy requirements for processing magnesia. Nevertheless, the carbonation reaction resulting in the formation of the main bonding phase from magnesia can consume atmospheric  $\text{CO}_2$ . This suggests that such cements could in fact act as carbon sinks, acting to favorably reduce greenhouse gas emissions. However, this



reaction is slow since it is diffusion controlled, so the useful lifetime of the cement would probably be exceeded before complete carbonation could occur. Theoretically, since magnesium carbonate is the main binding phase, these cements are also readily recyclable.

As opposed to portland cements, which cannot be easily reheated to regenerate the original starting materials (calcium carbonate and clinker), the formation of magnesia from the magnesium carbonates should be much easier. The utilization of secondary materials such as fly ash and slag is routine in the cement industry but it is the chemistry of the bonding phases that is more important. Significantly, magnesium hydroxide is less alkaline than calcium hydroxide and, therefore, has a considerable reduction in potential problems later on. It has been reported that the addition of the accelerator allows the cement to overcome many of the problems associated with magnesia oxychloride cements. As a result, magnesium carbonate cements exhibit greater resistance to acids and are a less corrosive substrate that is stable in moist environments.

While magnesia carbonate cements are still in the developmental stages, there are a few downsides. For instance, despite the fact that filler materials such as industrial by-products are reasonably cheap and inexpensive to obtain, acquiring magnesium carbonate is generally more expensive than calcium carbonate and harder to find. With increasing demand, however, it is possible that the prices could dramatically drop. The technology, to some civil engineers, may also be regarded as unproven. A range of concerns still surround the material such as the load-bearing performance, long-term dimensional stability, freeze-thaw resistance, creep under load as well as a host of basic characteristics such as heat output during hydration, porosity/permeability relationships and fire resistance. However, magnesia carbonates and OPC/ magnesia carbonate composite cements are the most likely large-scale magnesia cement alternatives to portland cement.

## 2.6 Recycled glass-based cements and concretes

The main incentive behind using post-consumer recycled glass (e.g., bottles, windows) in concrete is the prohibitive costs of shipping recycled glass from collection points to remelting facilities that manufacture new glass products. As of 2003 in the U.S., about 600,000 tons/year of “recycled” glass is landfilled or stockpiled in hopes that future technologies would allow a profitable use of this material (Reindl, 2003). Pulverized glass can be used in concrete as fine aggregates or as cement replacement. Aggregate applications are more developed and have been commercialized in the U.S., U.K., and Australia. Desirable strength and workability of concretes containing glass sand have been achieved by proper mixture proportioning (Polley, et.al, 1998). The main challenge on the use of these materials is the alkali-silica reaction (ASR) of glass particles leading to cracking and deterioration of concrete. However, ASR has been successfully controlled by (a) use of fly ash, (b) use of glass finer than #50 sieve (0.3 mm) (Jin, et.al., 2000), or (c) annealing crushed glass before use in concrete (Rajabipour, , et. al., 2010).

In comparison, the use of glass powder as a cementitious material is in its infancy. 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

Shao, et. al., 2000, Shi, et. al, 2005). Fineness of glass powder has a significant impact on its reactivity; glass finer than  $38\mu\text{m}$  satisfies the strength activity index of ASTM C 618 ( $\text{SAI} > 75\%$  at 7 days) and can be classified as a Type N pozzolan (Byars, et. al., 2004, Shao, et. al., 2000). By further increasing glass fineness and/or heat curing, concretes with 3-day strengths surpassing that of OPC concrete can be prepared (Shi, et. al, 2005). In addition, fine glass powder ( $< 10\mu\text{m}$ ) can mitigate the alkali-silica reaction generated by glass aggregates or other natural reactive aggregates (Shayan & Xu, 2006).

### 3. Conclusions

Despite all global warming concerns and being in the midst of a financial crisis, an approximate growth of 30-50 percent of coal power generation is expected between Years 2007 to 2025. The installed capacity would jump to approximately 2.1 million MW. Initial estimates were even higher but the US and Europe are scaling back due to strong environmental pressures. China alone would add approximately 350,000 MW during this period while India would follow with more than 100,000 MW.

It is essential to emphasize that the use of CCP could make key reductions in  $\text{CO}_2$  emissions by using byproducts to make cement, substituting for portland cement in concrete, and reducing energy given the energy-efficient nature of concrete structures. It is important to point out that the CCP option is only available for pulverized coal plants. IGCC units follow a different technique and do not produce any cementitious materials as by-products.

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 high calcium 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. See Figure 5.

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.

It is important to note that although the environmental and even economic benefits from using CCP's are apparent, they are still under-utilized. The American Coal Ash Association reported that less than 40 percent of CCP are used. The Association only reports affiliated utilities. The authors estimate that less than those amounts are currently used and end up in landfills, creating a burden to the environment and the economy of different enterprises.

We all need to understand that we must adopt sustainable energy policies to avoid endangering energy security and control carbon emissions. Without any intervention,  $\text{CO}_2$  could increase 42.4 gigatons in 2035 from 29.7 in 2007 (EIA, 2010). This increase is a real and immense challenge that has to be managed promptly.

#### 4. References

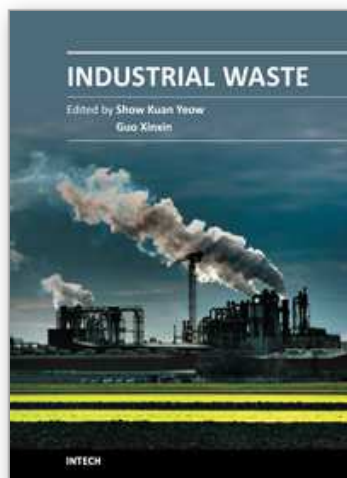
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This book is intended to fulfil the need for state-of-the-art development on the industrial wastes from different types of industries. Most of the chapters are based upon the ongoing research, how the different types of wastes are most efficiently treated and minimized, technologies of wastes control and abatement, and how they are released to the environment and their associated impact. A few chapters provide updated review summarizing the status and prospects of industrial waste problems from different perspectives. The book is comprehensive and not limited to a partial discussion of industrial waste, so the readers are acquainted with the latest information and development in the area, where different aspects are considered. The user can find both introductory material and more specific material based on interests and problems. For additional questions or comments, the users are encouraged to contact the authors.

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Unit 405, Office Block, Hotel Equatorial Shanghai  
No.65, Yan An Road (West), Shanghai, 200040, China  
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元  
Phone: +86-21-62489820  
Fax: +86-21-62489821

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