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# NON-PORTLAND CEMENT ACTIVATION OF BLAST FURNACE SLAG

Anne Oberlink[1], Thomas Robl[2]. [1]Center for Applied Energy Research and [2]Department of Chemistry, University of Kentucky

## Abstract

The purpose of this project was to test a hypothesis of “greener cement” by testing different material mixtures, specifically non-Portland slag activators. By eventually developing “greener cement”, the ultimate goal of a research project such as this, would be to reduce the amount of Portland cement used in concrete, therefore reducing the amount of carbon dioxide emitted into the atmosphere during cement production.

This work deals with a general interpretation of data referencing the behavior of binders free of Portland cement, containing slag with or without bottom ash, activated by calcium compounds or bottom ash. The information found in this paper was collected from experiments regarding calorimetry; simply the release of heat from a particular reaction to the activation energy of particular ratios of material, and mechanical strength determination, together with pH measurement and X-ray diffraction (XRD).

The three main slags used in this project were Euromix (Eurocem) from Europe, Joppa from the U.S., and Orcem from South America. Several different slag activators, in varying ratios, were used over the course of this project, including independent portlandite ($CaOH_2$), independent gypsum ($CaSO_4 \cdot 2H_2O$), a portlandite/gypsum mixture, and various slag/bottom ash mixtures.

The results indicate the possibility of having alkali-activated binders with incorporated slag, and with or without bottom ash, and which have mechanical properties similar to OPC. It was determined that the binder systems can incorporate up to 40% bottom ash without any major influence on binder quality.

## Introduction

There is a growing scientific consensus that the amount of carbon dioxide ($CO_2$) in the Earth’s atmosphere needs to be reduced. Reducing the amount of carbon dioxide in the Earth’s atmosphere would require curbing the growth of $CO_2$ emissions, and ultimately limiting those emissions to a level that would stabilize atmospheric concentrations. [1] One way to limit these emissions to a manageable level would be to limit $CO_2$ emissions on the industrial and production levels. [1]

The cement manufacturing industry is the second largest $CO_2$ producer, only behind the power generation industry, and typically produces about 5% of global man-made $CO_2$ emissions.[2] Half of these emissions typically come from burning fuel, and half of the emissions come from the chemical process, resulting in a 900kg output of $CO_2$ for every 1000kg of cement produced.[1]

As previously mentioned, cement manufacturing releases $CO_2$ in the atmosphere in two main ways: indirectly and directly. [2] The indirect method involves the use of energy. The direct method involves the heating of calcium carbonate ($CaCO_3$), which produces lime ($CaO$) and carbon dioxide ($CO_2$).

Being able to reduce the amount of Portland cement used in concrete with a lower energy/emissions material, such as blast furnace slag, would have a large impact on reducing those emissions. Using slag cement in concrete can greatly decrease the amount of Portland cement typically used for a specific mixture of concrete. [3]

Slag cement can reduce the amount of Portland cement in two ways: direct replacement and reduction in total cementitious material in a mixture. [4] Slag cement is a cementitious material that can help to reduce the amount of Portland cement in a specific concrete mixture. [5] It is also hydraulic cement, meaning that it hardens because of hydration reactions, and can thus replace a higher quantity of Portland cement in concrete compared to other pozzolans [6], such as coal combustion fly ash. [5] Common examples of pozzolans are silica fume, metakaolin, and fly ash. [7,8]

## Research Strategy

By directly and indirectly replacing Portland cement with slag, pozzolans, and other non-Portland additives/activators, it is believed that $CO_2$ emissions can be exponentially decreased.

Calcium sulfoaluminate cements ($Ca_4(AlO_2)_6SO_4$) are typically known as expansive cements, ultra-high early strength cements, and "low-energy" cements, and can be used to try to activate slag.[9] Energy requirements tend to be lower with CSA's because of the lower kiln temperatures required for the reaction, as well as the lower amount of limestone ($CaCO_3$) that is required to be in the CSA mixture.[10] Accordingly, the lower $CaCO_3$ content and the lower kiln temperatures result in a $CO_2$ emission that is about half that of Portland cement.[3,11,12]

Another strategy to limit the amount of Portland cement used in concrete is to add gypsum ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$) to make "supersulfated cement".[11, 13] Supersulfated cement usually contains about 80% ground granulated blast furnace slag, 15% gypsum or anhydrite, and a small amount of Portland clinker to act as an activator.[13] The addition of gypsum or anhydrite typically produces strength through the formation of ettringite, which imparts a strength gain rate that is similar to a slow-setting Portland cement.[3,14]

A typical way to test all of these different cement mixtures on a small scale is to use calorimetry, the science of measuring the heat of chemical reactions or physical changes of a system.[15] Cementitious mixtures tend to release heat exothermically, at a rate that is proportional to the rate of cement hydration.[16,3]

## Materials Preparation and Testing

The GGBS/non-Portland activator pastes were prepared by using a predetermined percentage of GGBS, a predetermined percentage of non-Portland activator and 50% of the total material's mass of water. This provided a water: cementitious material (w: cm) ratio of 0.5. Orcem, Ecocem (Euromix) and Joppa were the three slags used in the study. The compositions of the slags are listed in Table 1. Each of the hydration experiments has been repeated several times. The amount of materials may have been varied, but the percent basis always remained constant.

To prepare each set of pastes, the GGBS and non-Portland slag activators were weighed and placed into plastic cups with lids specifically designed for the calorimeter. The timer was started on the calorimeter and the appropriate amount of water added to the mixture. The mixture was then stirred thoroughly for 60 s before being placed into the calorimeter to be measured for the next 48 to 72 h. Once the designated time for each run had ended, the hardened paste was removed from the plastic cup and a mineralogical examination of the hardened paste was made by X-ray diffractometry (XRD).

The first set of hydration experiments was prepared using 10, 20, 30, 40, and 50% activator by mass, using pure calcium hydroxide as the non-Portland slag activator. The experiments were carried out in eight-ounce plastic cups with lids. These experiments were run for 48 to 72 h. Table 1 provides the paste compositions for calorimetry experiments using each of the three slags (i.e. each experiment was repeated for each of the slags) and three different activators.

The second set of hydration experiments was carried out on a 40-50% scale, using Ca(OH)2 and gypsum as the additives. These experiments were run for 48 h.
The third set of hydration experiments was carried out in a 40-50% scale, using fluidized bed combustion material (FBC) and gypsum as the additives. These experiments were run for 48 h.

The general procedure consisted of taking the raw, dry slag material (10.0 g) and placing it in a glass jar with the dry activator (Ca(OH)2, and/or gypsum, CaSO4·2H2O**)**. Two steel ball bearings were placed into the glass jar with a lid and blended for exactly one minute. The dry, mixed material was placed into an eight-ounce plastic cup and set on an analytical balance where water (50% of the mass of the dry sample) was added. The calorimeter was started and the wet material was stirred with a glass stir rod for exactly one minute. Excess cement was removed from the sides of the plastic cup. The lid was placed on the plastic cup, the plastic cup was then placed into the calorimeter and the calorimeter lid was closed. Formulations examined by this procedure are listed in Table 1.

| | Paste Ingredients (g) | | | | |
|---|---|---|---|---|---|
| | Slag | $Ca(OH)_2$ | Gypsum | FBC Ash | Water |
| 1 | 10.0 | 1.0 | - | - | 5.5 |
| 2 | 10.0 | 2.0 | - | - | 6.0 |
| 3 | 10.0 | 3.0 | - | - | 6.5 |
| 4 | 10.0 | 4.0 | - | - | 7.0 |
| 5 | 10.0 | 5.0 | - | - | 7.5 |
| 6 | 10.0 | 3.0 | 1.0 | - | 7.0 |
| 7 | 10.0 | 4.0 | 1.0 | - | 7.5 |
| 8 | 10.0 | - | 4.0 | - | 7.0 |
| 9 | 10.0 | - | 5.0 | - | 7.5 |
| 10 | 30.0 | - | - | 12.0 | 21.0 |
| 11 | 30.0 | - | - | 15.0 | 22.5 |

**Table 1: Formulations of slag and activator examined by using calorimetry**

These experiments were all run for 48 h, and Table 2 provides the ingredient proportions for the Ecocem series of experiments.

| | Paste Ingredients (g) | | | | | |
|---|---|---|---|---|---|---|
| | Ecocem Slag | Anhydrite | FBC Ash | OPC | CSA Cement | Water |
| 1 | 10.0 | - | - | - | - | 5.0 |
| 2 | 5.0 | - | - | 5.0 | - | 5.0 |
| 3 | 5.0 | - | - | - | 5.0 | 5.0 |
| 4 | 5.0 | 1.0 | - | - | 4.0 | 5.0 |
| 5 | 5.0 | 2.0 | - | - | 3.0 | 5.0 |
| 6 | 5.0 | 3.0 | - | - | 2.0 | 5.0 |
| 7 | 5.0 | 5.0 | - | - | - | 5.0 |
| 8 | 5.0 | - | 5.0 | - | - | 5.0 |

**Table 2: Paste compositions for calorimetry experiments**

The general procedure used for compressive strength testing was accomplished by following ASTM standard C109, where water was added to a stainless steel mixing bowl. A mixture of slag and FBC ash was added to the water in the mixing bowl. The mixer was started and mixed at low speed for 30 s. Sand was added slowly over a 30 s period, while mixing at low speed. The mixer was stopped, changed to medium speed and allowed to mix for another 30 s. The mixer was stopped again and the mortar was allowed to stand, covered, for 90 s, scraping down the side of the bowl during the first 15 s. The mixing of the mortar was finished by mixing for additional 60 s at medium speed. A flow test of the mixed mortar was completed using ASTM standard C-1437-01.

## Test Results

A range of compositions was used to determine the amount of calcium hydroxide used to get the maximum heat release and hydration. In figure 1, it was shown that the 40% Ecocem (Euromix) /Ca(OH)2 mixture released the most heat in 48 h.

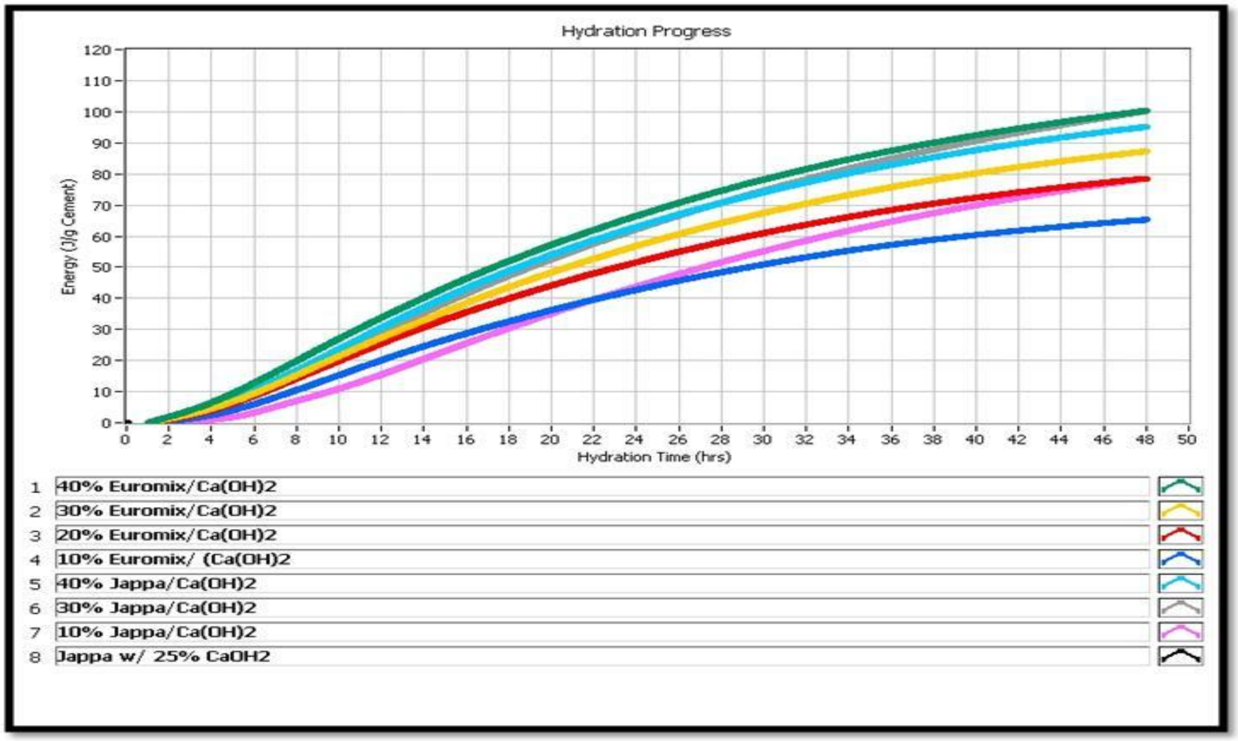

**Figure 1: Effect of $Ca(OH)_2$ concentration on slag hydration progress**

Based on the data in figure 1, the percentage of calcium hydroxide was then increased for the Ecocem (Euromix) and Joppa slags, while the Orcem was sampled. The run time was increased from 48 h to 72 h to allow for maximum hydration. As shown in figure 2, for the Joppa and Ecocem slags, 50% $Ca(OH)_2$ increased the total energy because of a more complete hydration and the formation of ettringite. For the Orcem/$Ca(OH)_2$ slag, the 40% $Ca(OH)_2$ (gray line, hidden underneath the red line) showed the greatest amount of heat release when compared to the other percentages of Orcem tested.

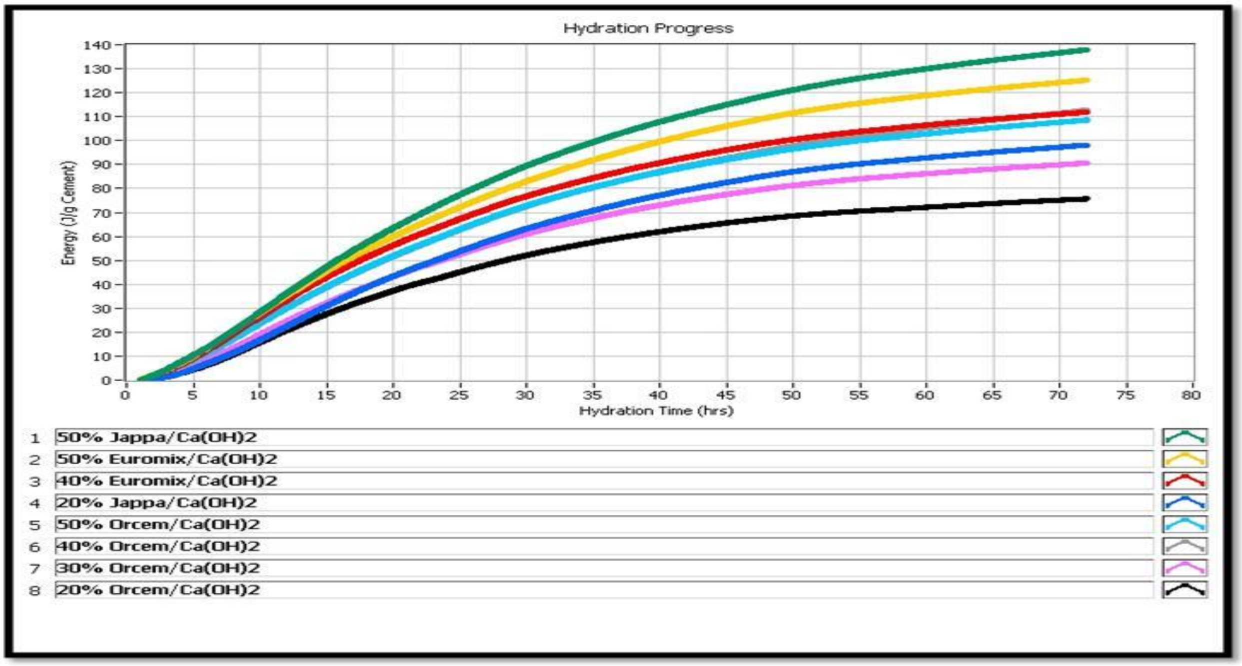

**Figure 2: Hydration progress with Ca(OH)2**

Based on the calorimetry data, it was determined that 40-50% $Ca(OH)_2$ was the optimal range at which to work. Once the maximum percentages were established, additional products, like gypsum, were added to the mixtures.

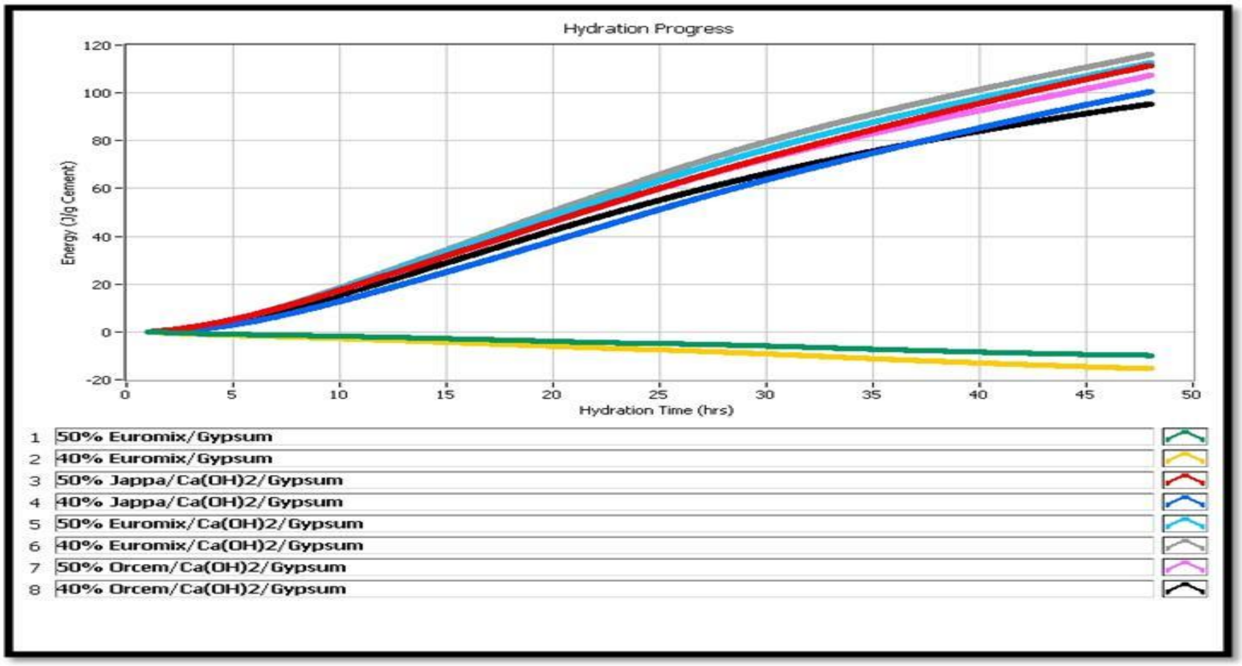

**Figure 3: Hydration progress with Ca(OH)2 and gypsum**

Once the ideal percentage of activation material was determined, the $Ca(OH)_2$ was replaced with FBC spent bed material, or “bottom ash”, to observe the extent of activation, or hydration.

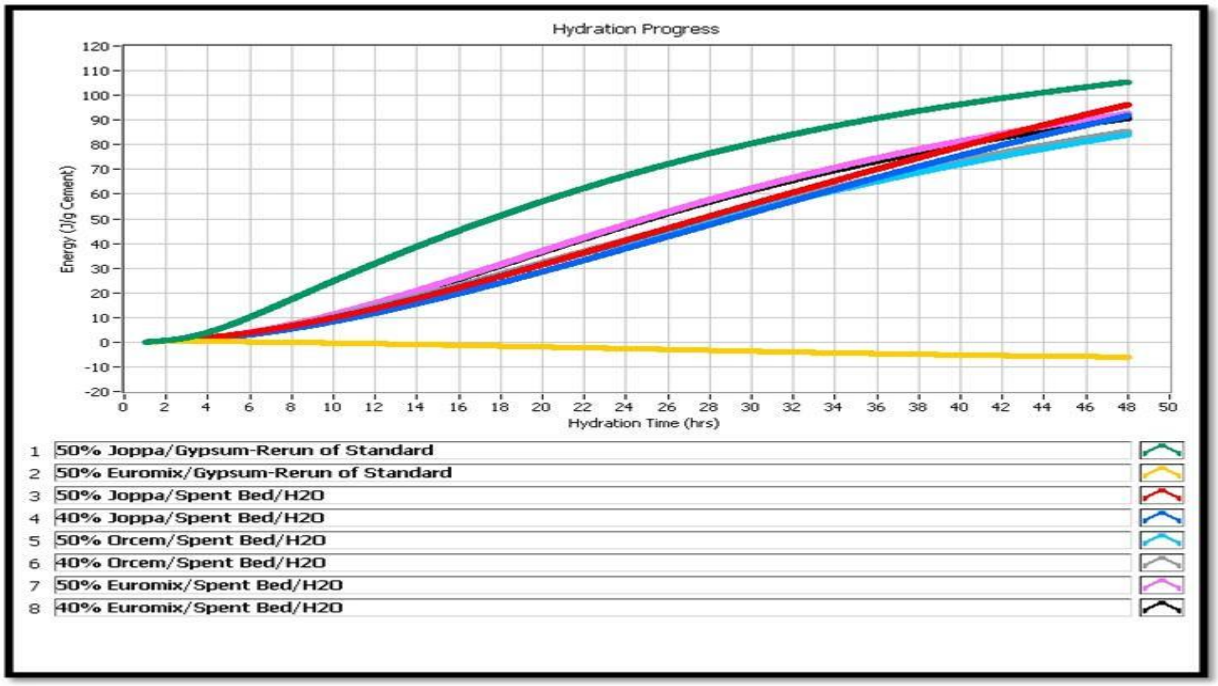

**Figure 4: Hydration progress with Ca(OH)2 and gypsum**

The FBC was then replaced with CSA (calcium sulfoaluminate cement, $Ca_4(AlO_2)_6SO_4)$) cement as the activator. The CSA cement and the Ecocem (Euromix) slag were tested to determine the amount of activation upon the addition of CSA and anhydrite ($CaSO_4$).

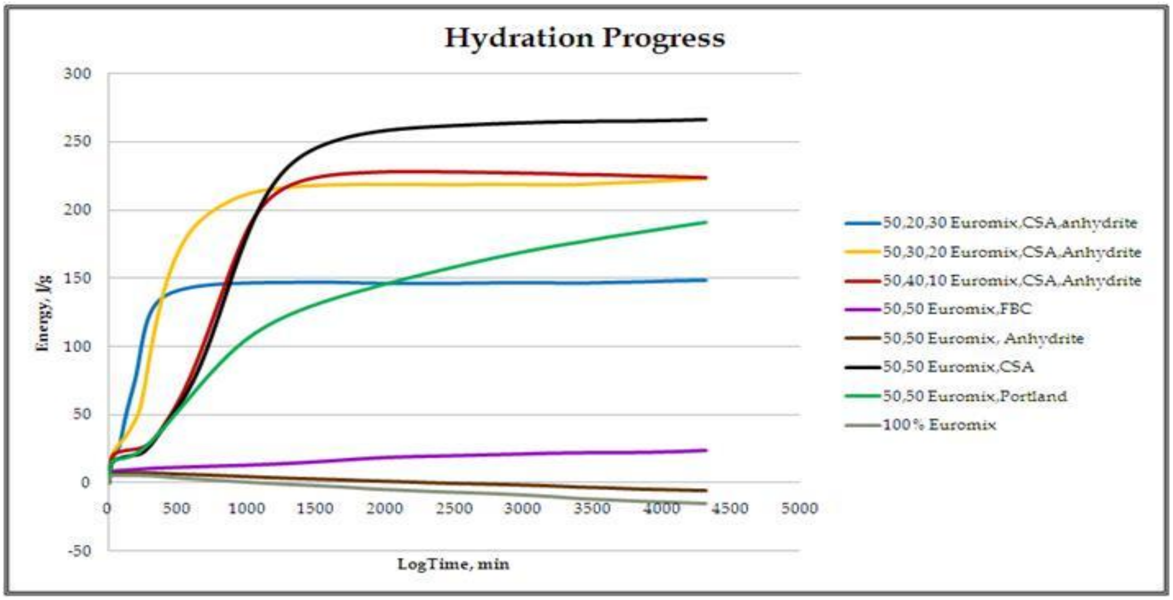

**Figure 5: Hydration progress with CSA**

As seen in figure 5, the addition of CSA and anhydrite to the Ecocem (Euromix) slag resulted in a substantial heat release, compared to slag without CSA and anhydrite.

## Compressive Strength Results

The next main step was to look at the mechanical strength of the non-Portland cement. Using the data from the calorimetric experiments, it was determined that when mixed with FBC, there was not a great difference in activation between the 40% and 50% slag/FBC (bottom ash). The 40% mixture was easier to work with, so the cubes made for determination of mechanical strength were a 40% mixture of slag and FBC (bottom ash).

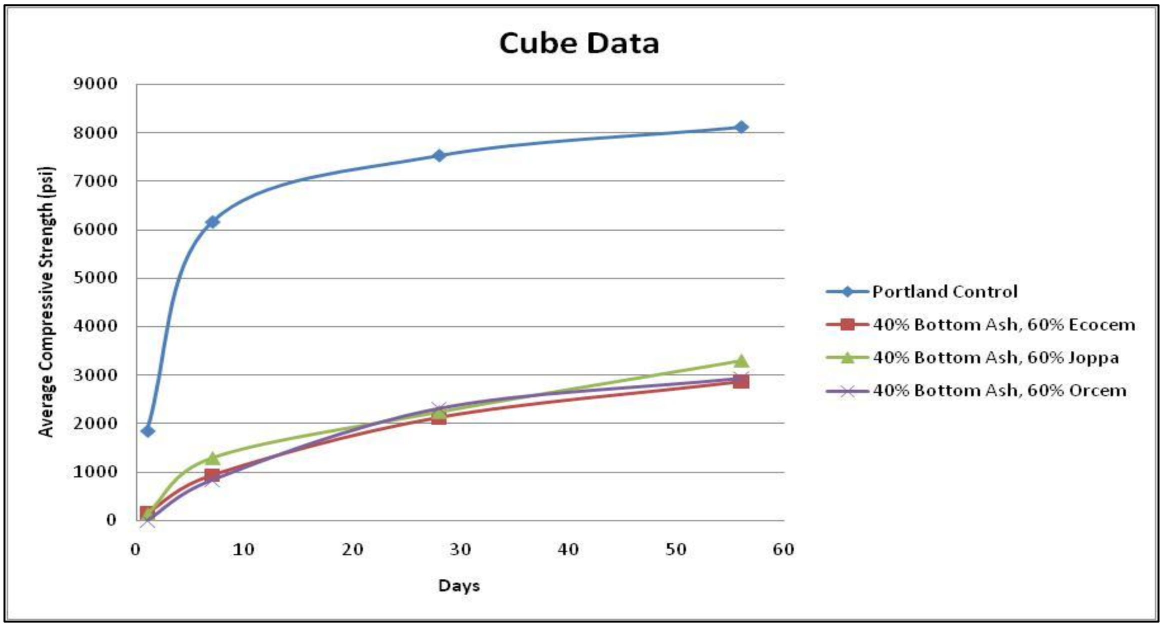

**Figure 6: Cube Data with Slag and Bottom Ash**

One of the main goals of this research project was to produce a “greener” cement by testing different material mixtures, specifically non-Portland slag activators. The strength of cements derived from slag mixtures is substantially less than that of the Portland control, and although the slag/FBC (bottom ash) mortars made may not be able to be used in a structural application, they would be able to accommodate everyday uses. These slag/FBC (bottom ash) materials have a zero carbon footprint, and can be very useful as sidewalks, floors, etc. All three of the slag/FBC (bottom ash) cements are very close in strength.

Another way to develop “greener” cement is to decrease the amount of Portland cement, used in typical formulations, by direct replacement of the cement with a byproduct or several byproducts. Pozzolans, such as metakaolin, can impart high strength to mortar and concrete and can also substantially improve durability. Metakaolin, a dehydroxylated form of the clay mineral kaolinite ($Al_2Si_2O_5(OH)_4$) and is prepared by heating kaolinite to temperatures of 500-800°C.[19] It is a highly reactive aluminosilicate pozzolan that when hydrated in the presence of alkali, forms a strong slow-hardening cement. [17,18] Metakaolin can be used to replace Portland cement in concrete by 8-20%, and usually exhibits similar strengths to Portland cement concrete.[19]

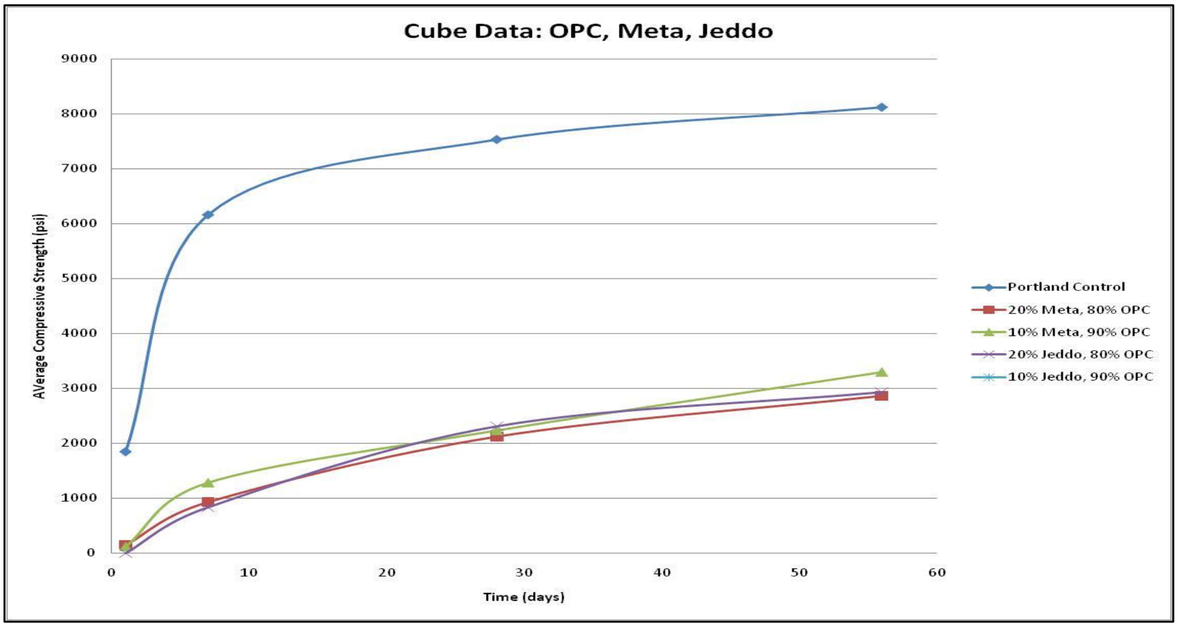

**Figure 7: Cube Data with Metakaolin and Jeddo**

## Summary/Future Works:

Our test results have confirmed some advantageous properties of ground granulated blast furnace slag-based cementing materials, as well as pozzolan materials.

The three representative ground granulated blast furnace slag cements used in these experiments, Joppa, Ecocem, and Orcem, were well activated by a number of additives. The most surprising result was the hydration of the Joppa slag and gypsum on its own, which was shown to take place because of the high pH of the Joppa slag. All three GGBSs were well activated by bottom ash. The use of bottom ash is important because the use of a byproduct that typically ends up in landfills or holding ponds, not only helps to improve the environment, but also helps to accomplish the original goal of this experiment, which was to reduce the amount of $CO_2$ being emitted into the atmosphere by cement manufacturing.

Strength testing was a very important characterization method for the GGBS materials. The majority of the slag mixtures showed positive qualities overall. The slow development and low final strength of the GGBS materials compared to Portland cements may make them unsuitable for some structural applications, but are found to be very useful in everyday applications like sidewalks and floors.

The total replacement and partial replacement of Portland cement in mixtures should be tested in future experiments. Although the GGBS strength was much lower than the OPC, a material made completely out of byproduct, with a zero carbon footprint, has been made and would be able to accommodate everyday applications. The results from replacing specific amounts of Portland cement showed good strength data, and may be considered more for structural applications.

The main goal of this project was to test non-Portland slag activators with the bigger picture of developing "greener" cement. This was accomplished by producing a material made completely from byproduct waste material. Ground granulated blast furnace slag was activated with fluidized bed combustion material (bottom ash), and this material is carbon neutral and can be used in many commonplace applications.

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