

Effects of Alternate Cementitious Materials on Compressive Strength and
Environmental Impacts of Cement Mix Designs

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I. Abstract

Specific proportions of Portland cement, fly ash, and blast furnace slag cement mixtures were chosen by a ternary phase diagram to be investigated. By experimental testing and company data history fly ash was limited to not exceed 30% and contribution of Portland cement must be over 50%. Ten chosen mix designs were batched by following ASTM C305-94 and cured for twenty-eight and forty-two days, the extended cure length allows the reaction of pozzolanic material with calcium hydroxide to complete. Compressive strength testing at forty-two days yielded low strength for mix designs with 20% or less Portland cement compared to our 100% Portland cement control. The three mix designs with 30% Portland cement reached the greatest strength of all ternary designs and were averaged to be 1742 psi lower than the 7406 psi control, this is due to the more sufficient amount of calcium hydroxide produced for reacting with the fly ash, compared to the low, 10% and 20%, Portland cement mixes. The ternary design consisting of 30% Portland cement, 20% fly ash, and 50% slag exhibited the highest strength, 5879 psi, 1527 psi below the control. With the cementitious reactions being of greatest significance, SEM analysis was performed on selected mix designs. Images show cementitious reactions as hair like structures throughout the sample, additional observations of un-reacted spherical fly ash particles are present along the fracture area. Fly ash being a low strength contributor, it can be determined as a reason of low strength failure. With use of ternary mix designs environmental impacts are reduced; additionally meeting new California Air Resource board and California Department of Transportation pozzolanic regulations.

II. Introduction

As the second largest carbon dioxide production industry behind power generation, the production of Portland cement creates around one kilogram of carbon dioxide per kilogram of cement. In 2011, 66 billion kilograms of cement were produced creating nearly 60 billion kilograms of carbon dioxide⁶. Alternative cementitious materials, any material having cementing properties or contributing to the formation of hydrated calcium silicate compounds, have been investigated to reduce the environmental impacts of cement in use of concrete. Fly ash, a byproduct of combustion of coal, and blast furnace slag, created from production of iron, are two materials considered for supplementary materials replacing the use of Portland cement. In addition to the two, small amounts of Portland cement will be added to provide a basis of strength for the ternary mixes produced for Graniterock Corporation. Fly ash is categorized as a pozzolanic material, a material that reacts with calcium hydroxide to form compounds possessing cementitious properties. With each mix containing a percentage of Portland cement, 10-30%, various amounts of calcium hydroxide will be produced from the reaction of water and Portland cement, the calcium hydroxide present in the curing mortar will react with the present fly ash to produce additional bonding or gluing. The second material of supplementary consideration, blast furnace slag, is similar in elemental composition to Portland cement. Slag is considered a cementitious material as it is composed mostly of calcium silicate. The use of both supplementary materials and small amounts of Portland cement will additionally decrease landfill accumulation. Nearly 80% of slag is currently utilized in cement mix design, however fly ash contribute small amounts to today's market. On the other hand, 70

to 80% of coal ash products are disposed of in landfills⁴. Thus the incorporation of increased fly ash into my designs gives a possibility of reduction in land fill accumulation. With more companies beginning to utilize increased amounts of supplemented materials, various regulations have been modified for the use of alternate cementitious materials. The California Air Resource Board, CARB, AB32 is requiring a reduced use of Portland cement by 2020. In addition, California Department of Transportation, CALTRANS Section 90, has increased their allowance for pozzolanic materials. Both CALTRANS and CARB will be pushing for reduction in use of Portland cement and increasing the amount of supplementary material being used in future mix designs.

To focus on possible mix designs with the three components, Portland cement, fly ash, and slag, limitations must have been used narrow the proportional possibilities. A ternary phase diagram was implemented to determine the optimal area of focus. Firstly, Graniterock and other concrete providers currently use mix designs with 50% or greater Portland cement in current applications. Having previous performance history on these high Portland cement mixes, I have eliminated the upper half of the diagram and focused my mixes to less than 50% Portland cement contribution (Figure 1).

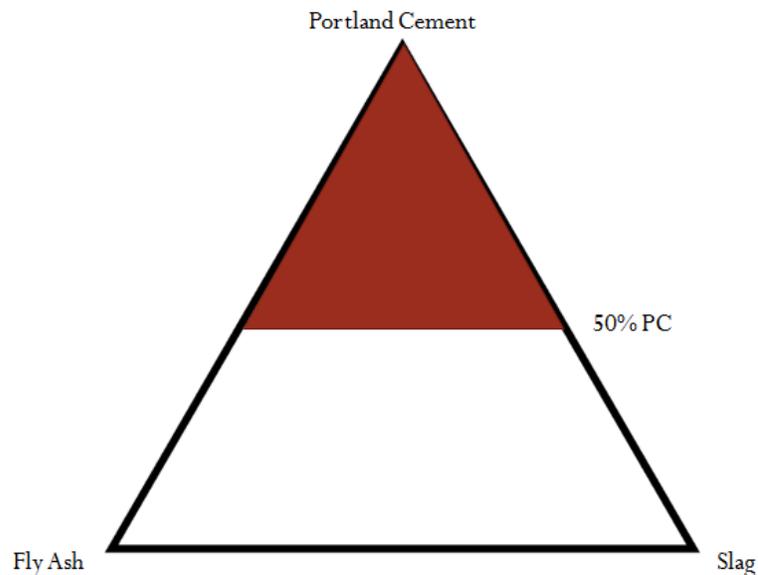


Figure 1. Elimination of high Portland cement mix designs due to current usage and previous research.

Secondly, experimental testing between Portland cement and increasing amounts of fly ash was previously conducted. Compressive strength results show a decrease in strength when greater than 30% fly ash is incorporated into the mix. Thus, the elimination of greater than 30% fly ash was placed onto the diagram (Figure 2).

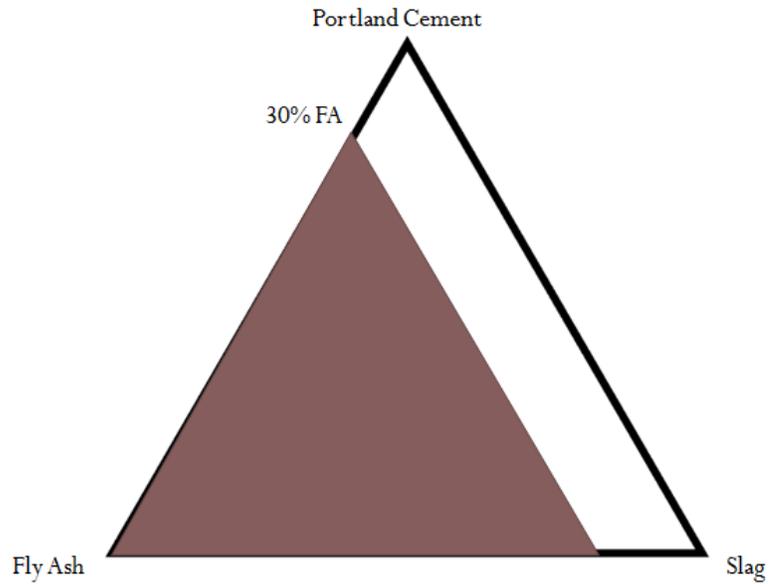


Figure 2. Higher amounts of Fly ash within the design would result in lower compressive strength, thus removing the area from focus.

With a reduced area, a final assumption was made to determine the exact proportions of the three components used in the possible ternary mix designs. Prior testing showed a ternary mix with 70% Portland cement replacement exhibited acceptable compressive strength after a curing compared to a 100% Portland cement control. With all reasons for area reductions a final ternary diagram was created and nine proprietary ternary cement mixes were created for Graniterock (Figure 3).

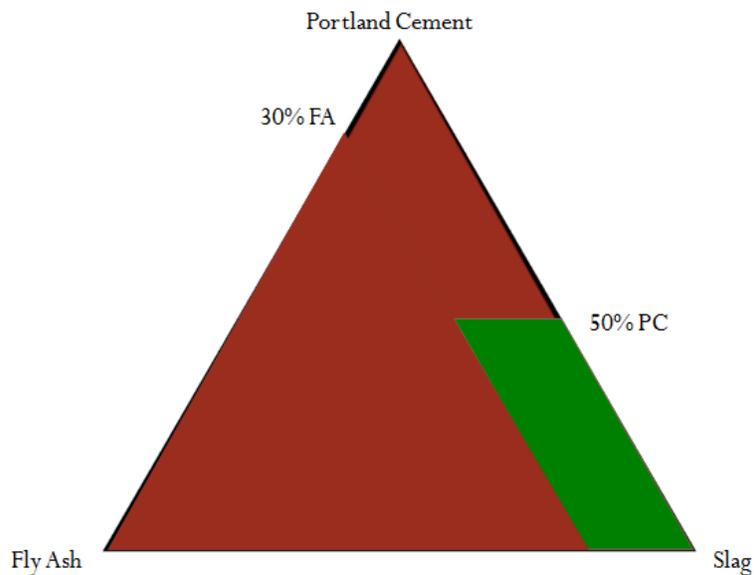


Figure 3. Placing all limitations together a much smaller area of focus was examined for Graniterock cement mix possibilities.

After construction and curing of the multiple variations of ternary mixes the compressive strength results will indicate performance properties compared to those of a 100% Portland cement control.

III. Procedures

Prior to construction of the ternary cement cubes, a standard deviation test was done to examine the variation in compressive strength results due to the mixing procedure. A series of cubes consisting of 100% Portland cement were batched and cured for seven days. Before testing for compressive strength each individual cube was measured and weighed to compare density between the samples. The compressive strength of the cubes was measured and the standard deviation was noted.

Following ASTM C305-11¹ nine 2"x2" cubes were batched for each of the nine proprietary mix designs, in addition a set of nine 100% Portland cement control cubes were batched. At twenty-eight days of curing in a 75 degree Fahrenheit 100% humidity environment three cubes of each of the nine separate ternary mix variations along with the control were broken and measured for compressive strength. After forty-two days of curing, in the same environment, the remaining six cubes of each combination were broken. All cubes were measured against a 100% Portland cement mix and compressive strength was recorded in psi. Fracture surfaces were observed to be along outside of cubes. The cubes were placed in individual plastic bags to preserve state of being for future observations.

The Scanning Electron Microscope was used to observe reaction properties along the fracture surface. The SEM was set to low vacuum mode with an additional secondary electron detector added to the aperture. Specimens sprayed with dust-off to ensure a clean surface. Observations and images were produced using the specimens set at a five millimeter working distance with a spot size of 3.5 to 4.

IV. Results

The compressive strength at twenty-eight days and forty-two days was not statistically different. The original hypothesis of the reaction between the Fly Ash and calcium hydroxide from the cement creating a higher strength ternary mix compared to the control was not achieved. Looking at a larger sample size data was taken from the forty-two day strength. Figure 4 shows the trend in decreasing strength with increased amounts of supplementary material.

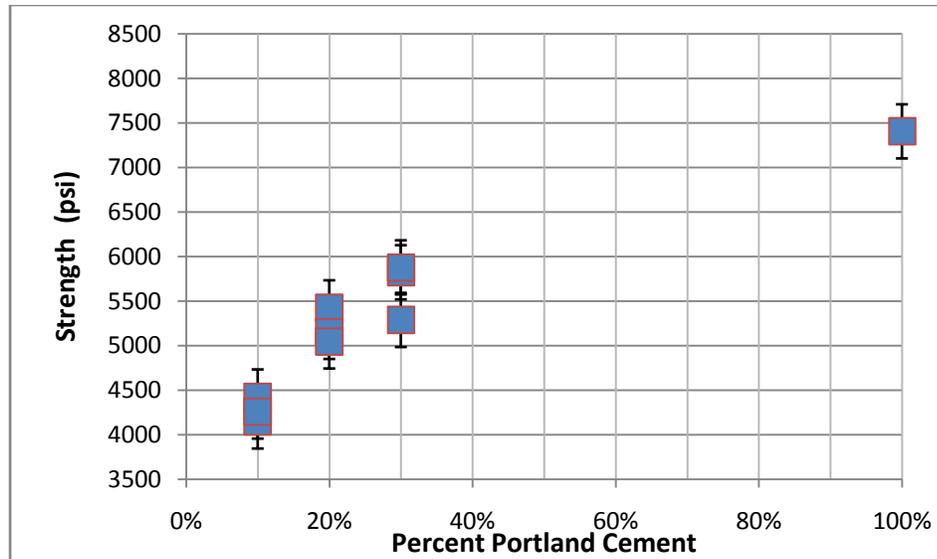


Figure 4. Compressive strength of ternary cement mix designs exhibit lower compressive strength.

Categorizing concrete can be done in various ways. Graniterock created their categories by low, medium, and high strength. Although I conducted research on mortar when aggregate is added to produce concrete the strength can be best estimated to 1000 psi lower than the mortar cubes. Creating a simple pass fail table, the ternary mixes were categorized, Table I.

Table I. Concrete Strength Classification for Ternary Mix Designs

Percent Supplemental Replacement (%)	Low Strength 2000-3000 psi	Medium Strength 3000-5000 psi	High Strength > 5000 psi
90	Pass	Fail	Fail
80	Pass	Pass	Fail
70	Pass	Pass	Fail

The ternary mix designs all meet minimum strength requirements for low strength concrete, used in applications such as sidewalks. Both the 70 and 80 percent supplemental materials however could be used in structural applications, medium strength concrete. Applications such as support columns, foundations, walls, etc. Lastly none of the mix designs were strong enough for high strength applications.

With the fractured samples retrieved, various ternary mix designs showed non-uniform reactions along the surfaces examined. Examining a 100% Portland cement, Figure 5, you can see uniform reaction along the entire fracture surface.

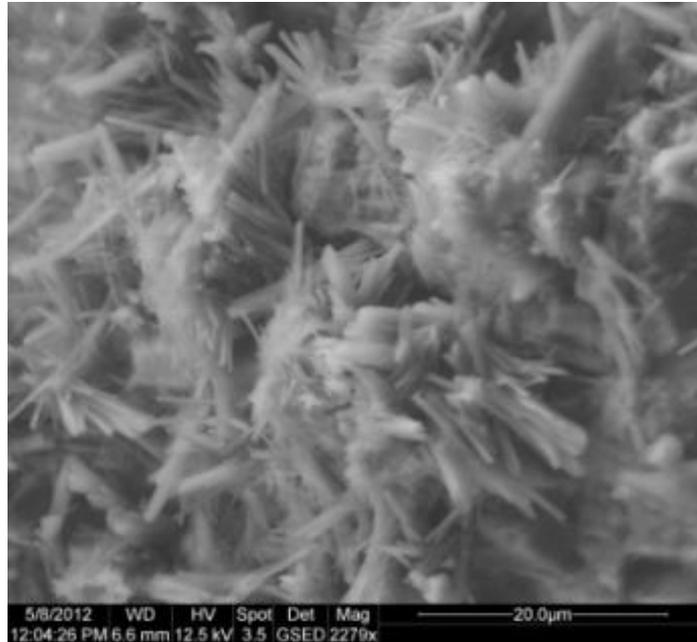
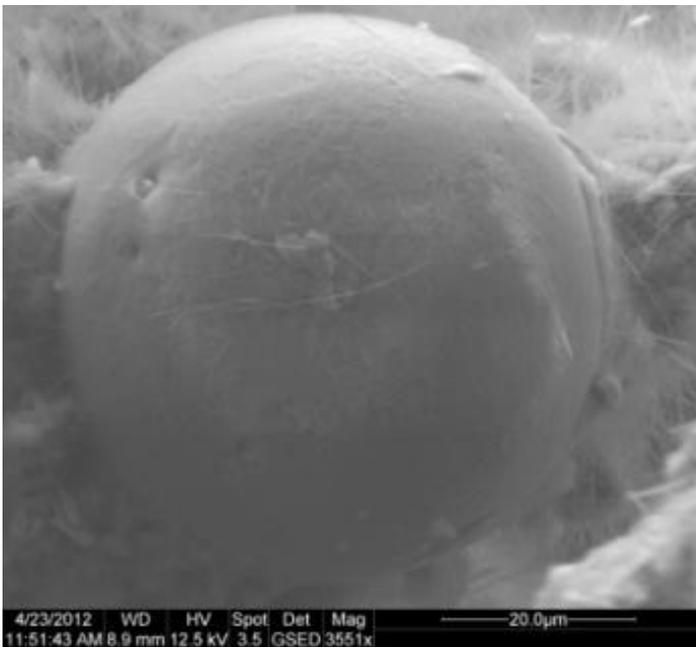
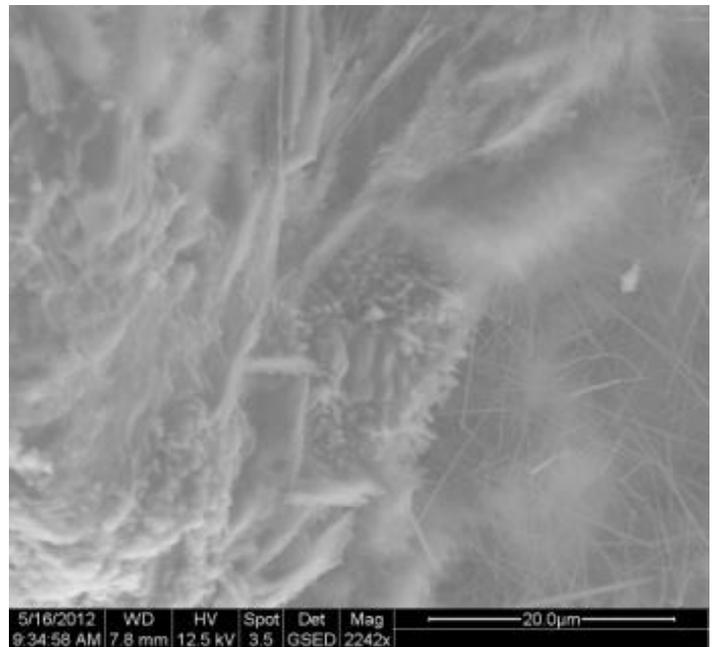


Figure 5. SEM analysis of Portland cement control samples.

On the contrary, when samples contained supplemental materials the fracture surface was observed non-uniform. Un-reacted fly ash particles were found, Figure 6a, along with visual uneven distribution of the reactions, Figure 6b.



A.



B.

Figure 6. On the left, the presence of a non-reacted fly ash particle could have lead to low strength fracture. On the right, the widespread distributions of hair like reactions.

V. Discussion

Based on compressive strength results it is proven that mix designs utilizing supplementary material are not as strong as 100 percent Portland cement mixes. However, results do indicate that the supplementary material do provide some strength. In collaboration with Dr. Michael Taylor, if you were to conduct additional testing with an increasing amount of an inert substance, such as sand, as filler; with decreasing Portland cement, the 30, 20, and 10 percent Portland cement mixes would exhibit lower strength than what was observed with the addition of fly ash and slag⁵. If this is indeed true, it proves that the reaction between fly ash and calcium hydroxide must have taken place and both the slag and fly ash are not just space fillers, they do exhibit reactivity.

During examination of the fracture surfaces, the reaction of 100 percent Portland cement was most notable. SEM analysis is a fairly new way to examine cement and it is not common within the industry. With little history and background it was difficult to determine exactly what the images were composed of. There are two theories behind the reaction processes. One explanation, by Neville, is that the formation of crystals occurs in sheets³, the water being encased by the cement. This however does not seem to be the case shown in my images, the only possibilities to agree with the sheet theory is that I would be looking at the cross section of one of the sheets or they are thin and possibly wrapped up into a roll like shape. Discussing the possibilities with Dr. Taylor, he had his own theory. The hydration reaction begins at a cement particle, when water is added the reaction continues to grow outward, creating an elongated needle or hair like structure⁵. This seems to match the SEM images closer than the sheet theory presented by Neville. Additional support for the reaction shape is the thickness of the hairs or needles. At high magnification the needles are seen to be thin and orientated in various directions and lengths, unlike the more organized sheets.

Imaging of a high slag concentration mix produced possibilities of smaller needle like reactions. Slag being similar elemental composition to Portland cement its reaction with water would be similar. However, the small needles may be due to the smaller initial particle size of slag compared to larger Portland cement.

Examining additional areas along the fracture surface the presence of unused Fly ash particles were common within the mixes. Figure 6 showed a complete spherical particle unreacted along the surface, along with areas in which clusters of particles were present. The fly ash can exhibit poor adhesion and a possible area where fracture can occur. Additionally, small areas which looked like holes were noticed. During the compressive testing the high stress on the weaker particles split the particle in half, producing an image where the portion of the fly ash was still adhered to the fracture surface.

All ternary samples subjected to SEM analysis demonstrated visual non-uniformities along the fracture surface. As technology grows, further examination of cement by SEM or other means will be conducted. As for now, observations and possible reasoning is the best approach for understanding the reaction of cement at the fracture surfaces.

With environmental concerns within the scope of this project it was determined that the use of fly ash in cement mix design will reduce landfill accumulation. With limiting my mixes with a maximum of 30 percent fly ash the reduction is not as large as I would have liked. However, for low strength applications, further testing with higher amounts of fly ash may result in enough strength to meet performance requirements. With high strength applications being less abundant than low and medium strength applications the incorporation of supplemental materials will still result in met specifications for the desired application and reduce the amount of unused materials.

VI. Conclusions

Examining the use of Fly ash and blast furnace slag as cement replacement for Graniterock the experimental was deemed a success. Concluding results have led Graniterock to further investigate the use of ternary cement mix designs.

1. Compared to control, mix designs with supplemental material have lower compressive strength.
2. Visible non-uniformity of reactions on fracture surface led to poor adhesion
3. Mix Designs with up to 90 percent supplemental material can be achieved and used for engineering applications.
4. Use of increased supplemental material has the potential to reduce carbon dioxide and landfill accumulation.

VII. References

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