Cement/Fly Ash /Metakaolin Ternary Blends: Effects on Compressive Strengths of Mortars

Billy Wiggins, M.S.
Professional Engineer, Thiele Kaolin Company, Sandersville, Georgia, USA

Khalid Siddiqi, Ph.D.
Construction Department Chair,
Southern Polytechnic State University, Marietta, Georgia, USA

Abstract
The objective of this study is to experiment the possibility of achieving higher compressive strengths and sufficient workability without the use of high range water reducer, in a cement ternary blend containing Metakaolin and fly ash. Metakaolin cement blends provide similar or slightly better hardened concrete properties and better fresh concrete properties as compared to silica fume. Past research indicates that ternary blends of silica fume and fly ash yield a high performance concrete with good early strength age properties and improved workability over concrete containing only silica fume. Concretes containing fly ash and Metakaolin should yield a synergistic ternary system. One important finding was that the most economical blends for strength was a cement/Metakaolin blend with no fly ash. An initial cost was calculated for each mix. The study will benefit concrete mix designers, batching plant owners, and those involved in production and supply of concrete products.

Keywords
Metakaolin, Fly Ash, Ternary Blends, Compressive Strength, Flowability

1. Introduction

Metakaolin (MK), fly ash (FA), and silica fume are Pozzolans. Pozzolans possess little or no cementitious value by themselves but can react with calcium hydroxide in cement to form a binder. In general cases the weak link in concrete is between the aggregate and the cement paste. The Pozzolans create more “paste” and due to the small particle size, Pozzolans act as a micro-filler increasing strength and durability while decreasing permeability.

MK is classified as a Class N Pozzolan (ASTM C618). MK is produced from high-quality kaolin crude clays using state-of-the-art technologies to remove impurities and control particle size. The MK particles are around 1 μm in diameter and are plate shaped. There is a significant amount of published research that exists concerning the effects of MK on high performance concrete (HPC). Common findings in MK studies revealed that there is an increased water requirement and increased strengths similar or slightly better than silica fume. Most concrete blends containing MK include a water reducer for a given slump at
a given water to cement ratio. The fine particle size and platy shape are likely contributing factors for the increased water demand.

Fly ash (FA) is classified as an ASTM C618, Class F or C pozzolan. Fly ash particles can vary from 1 μm to 150 μm in size and are spherical in shape. There are several texts written on fly ash and its effects on concrete mixtures (2, 12, 13). Common findings in studies conducted on FA are decrease in water demand and higher long term compressive strengths. Concrete blends containing Class F fly ashes yield lower early age compressive strengths and higher long term compressive strengths (>90 day) than a comparative control mix. The rate of compressive strength increase is a function of several factors for concretes blended with class F fly ash which include chemical makeup to fineness of grind (12). Better workability of concrete blended with fly ash is attributed to the spherical shape of fly ash. The small glass-like beads tend to “lubricate” the concrete mixture. Silica fume is a by-product in the manufacturing of silicon or ferrosilicon alloy. It is extremely fine with an average diameter of .1 μm which is about 1/100 the size of a cement particle (finer than tobacco smoke particles). Silica fume increases the water demand for a given slump in a concrete mixture. Research indicates that a ternary blend of silica fume and FA result in a mix which requires less HRWR, increased workability, good early age properties, and lower heat rise during curing (4).

2. Research Significance

High-range water reducers (HRWR) are commonly used with silica fume and MK concrete blends (4, 8, 10). HRWR can reduce water content by 12% up to 30% and can increase strengths due to a lower water to cement ratio. HRWR can also cause rapid slump loss. This translates into reduced workability and less time available for placement in the field (10). Water reducers can also cause significant increases in drying shrinkage (10). “Tearing” of the surface while finishing concrete can occur with the use of HRWR (6). MK has been shown to have characteristics that may be more favorable than silica fume. Caldarone’s, Gruber’s, and Burg’s research indicate that MK/cement blends outperform silica fume/cement blends in compressive strength for a given water to cement ratio and the MK/cement blends require less HRWR for a given slump (6). Ding and Li drew the same conclusions on workability; however, compressive strengths were only equal or slightly greater than silica fume. Both research papers allude to the fact that concrete blends with less HRWR may be more economical. MK seems to have advantages over silica fume; therefore it stands to reason that a ternary system containing MK will have advantages over ternary systems with silica fume.

3. Experimental Program

The standard test for compressive strength of hydraulic mortars (ASTM C-109/C 109M-99) was chosen for this experiment. Type I cement, Class F fly ash, Metakaolin, standard lab sand, and deionized water were used to prepare samples. All applicable ASTM standards were followed during testing including C-305-94, C-109/C 109M-99, C-778-99, and C-230-98. The chart below shows the cement recipes and flow properties of the cement mortars with various combinations of cement, MK, and FA measured using the flow table. The Pozzolans were used as a replacement for cement. For each batch of cement flow was checked and water was added or reduced to closely match the flow of the control mix. Each recipe was made twice and flow was checked on each occasion. Samples were cured in a climate-controlled facility in a lime saturated water bath. Compressive strengths were determined for each of the nine blends on a 1, 3, 7, 14, 28, and 56-day curing time. Each compressive strength data point is an average of three samples. The water to cement ratios were recorded based on flowability and fluctuated from the control mix (Mix #1; CM) which had a 0.485 water-cement ratio (W/C).
Table 1: Recipes for Cement Mortar

<table>
<thead>
<tr>
<th></th>
<th>Mix #1(CM)</th>
<th>Mix #2</th>
<th>Mix #3</th>
<th>Mix #4</th>
<th>Mix #5</th>
<th>Mix #6</th>
<th>Mix #7</th>
<th>Mix #8</th>
<th>Mix #9</th>
</tr>
</thead>
<tbody>
<tr>
<td>%MK</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>%FA</td>
<td>0</td>
<td>15</td>
<td>30</td>
<td>0</td>
<td>0</td>
<td>15</td>
<td>10</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>Sand (g)</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
</tr>
<tr>
<td>Cement (g)</td>
<td>740</td>
<td>629</td>
<td>518</td>
<td>703</td>
<td>666</td>
<td>592</td>
<td>555</td>
<td>481</td>
<td>444</td>
</tr>
<tr>
<td>Water (g)</td>
<td>359</td>
<td>345.6</td>
<td>332.1</td>
<td>363.4</td>
<td>368.0</td>
<td>350.0</td>
<td>354.4</td>
<td>336.5</td>
<td>341.0</td>
</tr>
<tr>
<td>Flyash (g)</td>
<td>0</td>
<td>111</td>
<td>222</td>
<td>0</td>
<td>0</td>
<td>111</td>
<td>111</td>
<td>222</td>
<td>222</td>
</tr>
<tr>
<td>Metakaolin (g)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>37</td>
<td>74</td>
<td>37</td>
<td>74</td>
<td>37</td>
<td>74</td>
</tr>
<tr>
<td>W/(C+Pozz) Ratio</td>
<td>0.49</td>
<td>0.47</td>
<td>0.45</td>
<td>0.49</td>
<td>0.50</td>
<td>0.47</td>
<td>0.48</td>
<td>0.45</td>
<td>0.46</td>
</tr>
<tr>
<td>Flow % Increase</td>
<td>0.52</td>
<td>0.50</td>
<td>0.54</td>
<td>0.52</td>
<td>0.53</td>
<td>0.48</td>
<td>0.44</td>
<td>0.45</td>
<td>0.41</td>
</tr>
</tbody>
</table>

4. Test Observations And Results

The water requirement of MK and FA that yield similar flow to the control mix was determined for individual batches before ternary blends were made. It was found that the FA required 75% of the water that was needed for an equal mass of cement for a given flow. Similarly, the MK required 125% of the water that was necessary for an equal mass of cement for a given flow. These percentages were used for all the blends to determine the amount of water required for a given recipe. The results for compressive strengths versus curing time are shown on the graph below.
5. Discussion Of Test Results

The 10% MK blend yielded the highest compressive strengths across the board with only a slight change in the water to cement + pozzolan ratio (W/C+P). At the 7-day break the 10% MK average compressive strength exceeded the CM by 15%; 4688 psi compared to 4070 psi. At the 28-day break the 10% MK boasted average break strength of 6128 psi compared to 4652 psi for the CM. The 10% MK had an average 56-day compressive strength of 7236 psi, which is about a 37% increase from the compressive strength of 5279 for the CM. The 5% MK blend broke at 4135 psi on day 7 and 5759 psi on day 28. The blends with MK and 15% fly ash exceeded the control mix break strength between day 7 and 28. The 10%MK/15%FA yielded average 28-day breaks of 5648 psi; the 5%MK/15%FA yielded average 28-day break strengths of 5131 psi. Fly ash without MK in the mixture did not exceed the break strengths of the control mix; however the gap between the curves grows narrower as time passes. This is a typical property of fly ash and if data had been gathered for 90 days and beyond it would be expected that fly ash would eventually surpass the control mix. As predicted the MK boosted early strengths for each concentration of fly ash blended cement and continue to yield higher strengths in the time period tested in this study.

The MK used in this experiment did not significantly change the W/C+P. As a rule of thumb when water to cement ratios are between .45 to .58 a decrease of .01 will increase the 28 day compressive strength by 100psi and vice versa when Pozzolans are not present. The w/c ratio versus strength is more complex with additives than for normal concrete mixes. Interestingly the highest W/C+P yielded the highest compressive strength when 10% MK was added versus the lowest ratio yielded the lowest break strength when 30% FA was present. The MK paste had a creamy smooth texture which was as easy to finish even in comparison to straight fly ash blends.
<table>
<thead>
<tr>
<th>%MK</th>
<th>Mix #1 (CM)</th>
<th>Mix #2</th>
<th>Mix #3</th>
<th>Mix #4</th>
<th>Mix #5</th>
<th>Mix #6</th>
<th>Mix #7</th>
<th>Mix #8</th>
<th>Mix #9</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
</tr>
<tr>
<td>0.05</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
</tr>
<tr>
<td>0.1</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
</tr>
<tr>
<td>0.3</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
<td>2035</td>
</tr>
</tbody>
</table>

The chart above lists the cost for each blend made and a ratio of cost to 28 day compressive strengths. The mix costs are based from individual material costs in the middle Georgia area March 2003. The costs used are $7.00 per ton for sand, $70.00 per ton for cement, $35 per ton for FA, and $400 per ton for MK. As a rule of thumb in a pure cement blend the cost of concrete is directly related to compressive strength (if 3000 psi concrete cost $30 per yard then 4000 psi concrete cost $40 per yard). The last row on the chart ratios the costs for each blend to the control mix. A ratio greater than 1.0 indicates that the blend may have an economic advantage over the control mix, depending on what structural factors are being considered.

6. Conclusion

An obvious synergy for the paste or hardened cement was not found in this research. This can be seen by comparing the flow properties of the ternary blends with the binary blends containing only one of the two Pozzolans. The binary cement mortars containing either MK or FA yielded flow increase between 50 to 54%. However, the ternary cement mortars containing both MK and FA yielded flow increase between 41 to 48%. Clearly, the addition of FA to a cement/MK mix did not yield any improvement for the flow property of the cement mix. It is apparent that MK had better characteristics by itself than it did in combination with fly ash. The Cement/MK/ FA ternary blends behaved as predicted; the results were similar to blends of cement, silica fume, and fly ash. It must be indicated that other fly ashes might yield different results based on chemical composition and fineness of grind. This is true for the MK as well. Different grades of MK can yield different results in concrete. There are also several properties of concrete that were not considered in this experiment; however, in general design cases strength is a top consideration for the engineer as workability is to the constructor.

Just as strength and workability are not the only factors that are considered in a concrete, initial cost is not the only economic factor for choosing a building product. However, initial cost does need to be investigated and in this experiment the lowest dollar to compressive strength was found in the 5% MK mix. A 5% MK blend yielded a 4% cost advantage in comparison to the CM. The 15% FA blend is the second most economical blend with a 2% advantage over the CM. Since MK yields a higher strength concrete at a lower cost per compressive break strength in comparison to a CM it is likely that MK could be used commonly in concrete mixes and not just in special applications especially when the added benefits of increased durability, lower permeability, less bleed water, and lower drying shrinkage are considered.
7. Acknowledgements

This research was supported by Thiele Kaolin Company of Sandersville, Georgia. The authors acknowledge ZZ Zhang of Thiele Kaolin for advisement through the research process. The authors also acknowledge Bearings and Drives of Sandersville, Georgia for their support with testing equipment.

8. References

ACI Committee 301, 2001. *Specifications for Structural Concrete*. American Concrete Institute, Detroit, MI, ACI 301-99

ACI Committee 232, 2000. *Use of Fly Ash in Concrete*. American Concrete Institute, Detroit, MI, ACI 232.2R-96

ACI Committee 232, 2001. *Use of Raw or Processed Natural Pozzolans in Concrete*. American Concrete Institute, Detroit, MI, ACI 232.1R-00

ACI Seminar, 2002. *Supplementary Cementitious Material*. American Concrete Institute, Atlanta, GA., November 2002

ACI Seminar, 2001. *Practical Concrete Materials*. American Concrete Institute, Atlanta, GA., October 2001


