

Understanding the Benefits of High Reactivity Metakaolin

Extraordinary Performance in Concrete, Mortar and Grout

Sharad Mathur, Ph.D.
Group Leader, Product Development
Engelhard Corporation

INTRODUCTION

The purpose of this presentation is to present the unique benefits of high reactivity metakaolin (HRM) in cement-based systems. According to ASTM C618, a variety of naturally occurring materials or their modifications or byproducts can be described as pozzolanic materials. However, the pozzolanic materials differ very widely in their impact on cement-based systems and this is primarily related to their physical and chemical characteristics. Further, a given pozzolan may vary in its effect if its properties are not carefully controlled. This situation primarily occurs with naturally occurring pozzolans and to some extent with byproducts that can be used as pozzolanic materials. HRM, on the other hand, is manufactured with selected naturally occurring kaolin crudes, carefully processed under stringent conditions to result in a reproducible product.

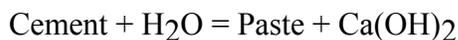
The presentation will cover the following information related to HRM:

1. Typical Manufacturing Process
2. Benefits with Examples
3. How to use HRM

BACKGROUND

Pozzolans are siliceous or siliceous and aluminous materials, which in themselves possess little or no cementitious value, but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.

The above statement can be simply expressed in the following chemical reactions



Calcium hydroxide, which is a byproduct of cement hydration and is part of the paste that glues the aggregate particles, is a “weak link” of any cement-based system for the following reasons.

1. Calcium hydroxide is soluble in water and therefore actually decreases the paste amount thereby leaving behind porosity and a lower density paste.

2. This results in lower strength and opens the system to action of the elements as well as chemicals.
3. Calcium hydroxide after dissolution travels to the surface of the cement-based system and reacts with atmospheric carbon dioxide to form white fluffy deposit better known as efflorescence. Thus it also leads to an unsightly appearance, which needs to be attended to with time and money.
4. Calcium hydroxide reacts with certain aggregates and chemicals to result in alkali-silica reactivity and associated weakening of the cement-based system.

Pozzolanic materials by virtue of the reactions illustrated above convert the calcium hydroxide into cementitious material and therefore lead to improved strength and durability of the cement-based system.

Natural Pozzolans are typically clay-based materials that originate naturally or are modified by thermal activation such as drying or calcination. They vary in chemical composition and physical characteristics such as size and size distribution, surface area, crystallinity, color and therefore result in varying pozzolanic activity, color & performance.

METAKAOLINS AND HIGH REACTIVITY METAKAOLIN (HRM)

Metakaolin is a chemical phase that forms upon thermal treatment of kaolinite. Kaolinite's chemical composition is $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ and as a result of thermal treatment in the range of 400-500°C, the water is driven away to form an amorphous aluminosilicate called metakaolin. The temperature range depends on the kaolin (kaolinite with minor impurities) characteristics such as degree of crystallinity and particle size.

Metakaolin is white in color and acts as a pozzolanic material. The reactivity of the metakaolin may also be affected by grinding to a finer particle size. The purity of the kaolin affects the overall color and reactivity. For example, according to ASTM 618 the minimum amount of SiO_2 , Al_2O_3 and Fe_2O_3 that needs to be present in a class N pozzolan is 70%. Therefore an impure source of kaolin may be used to result in a pozzolanic material that meets the ASTM C618 requirements. The lower amount of siliceous and aluminous material will result in a lesser reactivity, which may be further diminished by a coarse particle size. Also the color will not be white and depending on the impurity type and level may vary resulting in an inconsistent product..

High reactivity metakaolin (HRM) has the highest content of siliceous and aluminous material among the purified kaolins. This is because at least 90% of the product consists of silica and alumina. The HRM is manufactured under controlled conditions to provide consistent product in terms of particle size distribution, surface area, and color and chemical composition. The HRM by virtue of its highest purity is white in color, which is critical to architectural applications. Most importantly, the HRM is thermally activated such that the heat treatment results in maximum pozzolanic activity for the product.

Manufacturing Process of High Reactivity Metakaolin

The manufacturing of HRM is optimized for cement-based systems to provide maximum benefits in terms of pozzolanic reactivity, white color and needs of the application such as minimal rebound for shotcrete.

The kaolin is selectively mined for particle size distribution, morphology and chemical composition. The crude kaolin is dispersed into a slurry form and pumped to the manufacturing site to be processed to:

- (i) Remove impurities to provide consistent color
- (ii) Create desired particle size distribution for reactivity and application needs, and
- (iii) Provide optimal thermal treatment for maximizing pozzolanic activity.

The particle size distribution of pozzolan is important both for the fresh properties of cement-based systems as well as the speed of pozzolanic reaction. Coarser particle size distribution will result in lower water demand owing to a lesser surface area and therefore a more flowable cement-based system for the same water/cementitious ratio. However the low surface area also results in a slow speed of reaction and therefore the strength gain expected occurs at a slower rate. Thus a lower early strength and most likely lower hardened structure strength will be obtained with a coarse particle size distribution of pozzolan. Additionally, the chemical resistance and permeability may be lower than the system with a fine particle size distribution pozzolan.

The crude used in the production of HRM is centrifuged to appropriate particle size and since the crude is selectively mined for particle size distribution, the particle size distribution of HRM is consistent from lot to lot. The centrifuged product goes through impurity removal steps such as magnetic separation and chemical bleaching to facilitate a consistently white color HRM product. The HRM undergoes optimal thermal treatment in a calciner such that the product exhibits the same maximum pozzolanic activity.

Typical Properties of High Reactivity Metakaolin (HRM)

- $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 90\%$
- White in Color
- Specific Gravity: 2.5
- Particle size less than fly ash (FA) and greater than silica fume (SF)

From a quality standpoint, HRM is a consistent product because of controlled manufacturing with respect to

- Chemical Composition
- Particle Size Distribution
- Pozzolanic Reactivity
- White Color

BENEFITS OF HRM IN CEMENT-BASED SYSTEMS

HRM can provide a variety of benefits in a number of cement-based systems such as:

- Ready-Mixed Concrete
- Glass Fiber Reinforced Concrete (GFRC)
- Oil Well Cements
- Precast Concrete
- High Performance Grouts, Mortars, Stuccos and Plaster

Typical benefits provided by usage of HRM are:

- Workability Enhancement
- Increased Strength
- Reduced Permeability
- Increased Chemical Resistance
- Ability to Color Match and Produce High Performance Architectural Products
- Additional Enhancement of Other Pozzolans

We will present examples to illustrate the benefits listed above by HRM.

HRM Workability Enhancement

The workability enhancement due to HRM means the following:

- Increased “Creamy” Texture for Flatwork, Masonry, etc. Metamax produces a cohesive mixture that is described by finishers as “buttery” or “creamy”. Although the mixture seems “tighter” when formulated correctly, the mixture flows well with minimal effort when moved by trowel.
- Reduced Rebound in Shotcrete with Good Finishability using HRM. The cohesiveness of the mixture minimizes rebound but the shear thinning nature of the mixture allows pumpability and ease of troweling.
- Improved Consolidation in Precast & Ready-Mixed Concrete. Mixtures containing Metamax due to the cohesiveness imparted by the latter are less sticky to the form, move easily under vibration without segregation and are self-leveling.

HRM, in comparison to other admixtures such as silica fume result in lesser usage of High Range Water Reducer (HRWR) and Air Entraining Agent (AEA). This is illustrated by way of the following “REALCRETE” mixture design (Table 1) where the HRM was substituted for SF in Ready Mix application. The design shows lesser amount of HRWR and AEA required with HRM when compared to the mixture with silica fume and similar fresh concrete properties (Table 2).

Table 1. Concrete Mixture Design with additional HRM or SF.

	Control	+10% HRM	+10% SF
Type I cement, lb	658	656	658
HRM, lb	0	66	0

SF, lb	0	0	66
Coarse Aggregate, lb	1745	1744	1745
Fine Aggregate, lb	1240	1150	1156
Water, lb	268	263	264
HRWR, oz/yd ³	65	115	179
AEA, oz/yd ³	10	9	13.5

Table 2. Fresh Concrete Properties based on design in Table 1.

	<i>10% HRM 10% SF</i>		
	<i>Control</i>		
Slump, inches	6¼	4¾	4½
Air Content, %	6.3	6.2	6.2
Initial Set Time, hrs	4.8	4.2	4.1
Temperature, °F	74	80	80

Increased Strength with HRM

This is a typical benefit of pozzolanic reaction as a result of converting the calcium hydroxide, which does not contribute to the strength of the paste, to cementitious products. For the mixture design mentioned above, Figure 1 compares the strength achieved due to presence of HRM and SF.

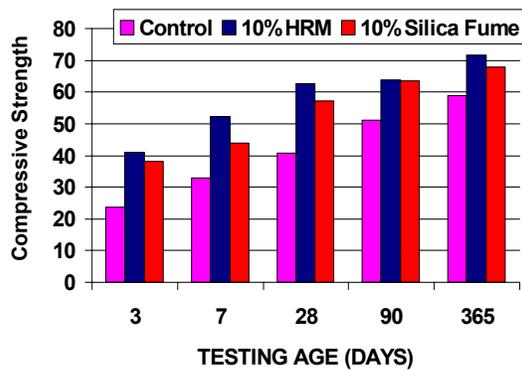


Figure 1. Comparison of compressive strength with time for HRM and SF with the mixture design in Table 1.

It is clearly seen from Figure 1 that although both HRM and SF result in early age strength increase, HRM provided slightly better results. The large increase in strength with HRM and SF with respect to the control is partly due to a lower water/cementitious ratio with the former.

Reduced Permeability with HRM

Calcium hydroxide, if left untreated in the paste, may solubilize and migrate to the surface resulting in increased porosity and permeability of the paste. However, the high speed of pozzolanic reaction with HRM results in stabilization of calcium hydroxide as cementitious products and therefore, reduced porosity and permeability. This reduced permeability is effective against penetration of ionic species such as chloride ions, which negatively impact the steel reinforcement in concrete.

Table 3 shows the mixture design that was used to test the permeability of chloride ions in concrete with two different levels of HRM. In this case HRM substituted for part of the cement.

Table 3. Summary of Mix design and Fresh properties.

Mixture	1	2	3
w/cm	0.40	0.40	0.40
OPC	100%	92%	88%
HRM	0	8%	12%
OPC (kg/m ³)	380	350	334
HRM (kg/m ³)	-	30	46
Coarse Agg. (kg/m ³)	1100	1100	1100
Fine Agg. (kg/m ³)	655	647	641
Water (kg/m ³)	152	152	152
25 XL Water Reducer (mL/100kg)	325	325	325
SPN Superplasticizer (mL/100kg)	400	600	800
Micro Air Entrainer (mL/100kg)	40	40	40
Slump (mm)	135	125	200
Air Content (%)	9.5	7	6
Fresh-Concrete Density (kg/m ³)	2275	2353	2424

It is clearly seen from Figure 2 that the chloride migration is significantly reduced with adding HRM and further reduced with higher levels of HRM.

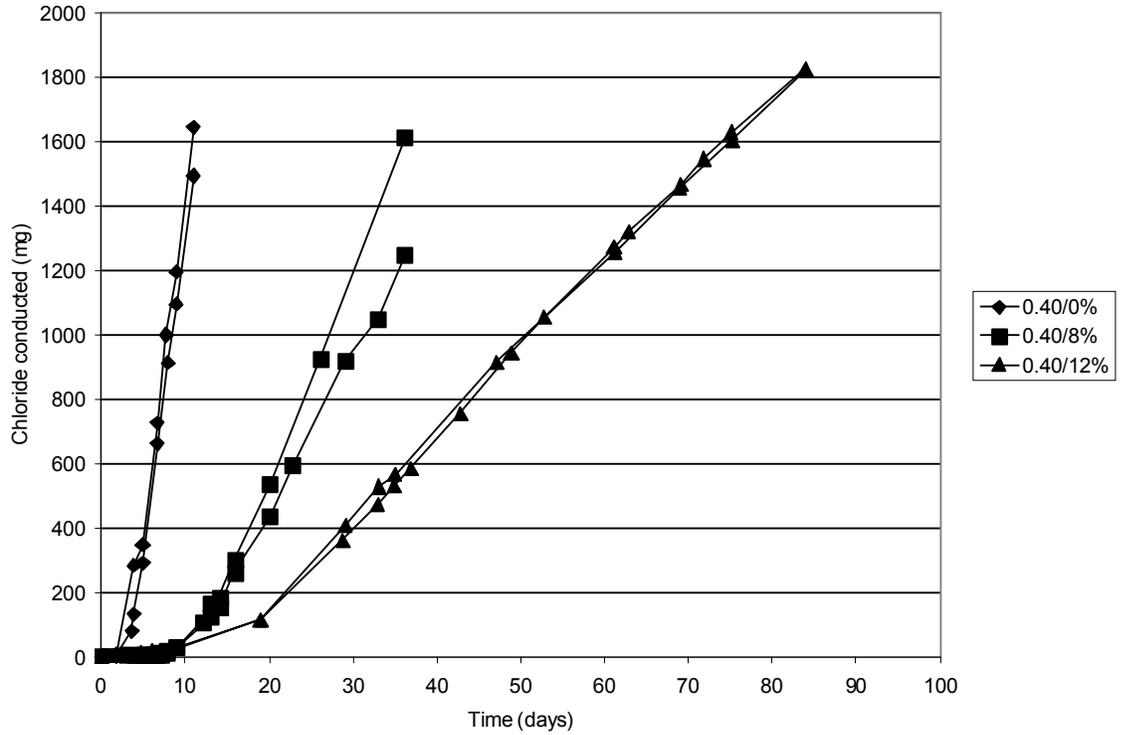


Figure 2. Effect of HRM addition on Chloride Migration

Another example to illustrate the reduced permeability due to HRM is presented in a Grout application. In the design mixture no water reducer was used and water to cementitious ratio was maintained constant by replacing a portion of the cement with the HRM. The workability of the mix was not adversely influenced. Since the w/cm ratio was constant the gain in strength with HRM is not as dramatic (see Figure 3) as we saw in Figure 2.

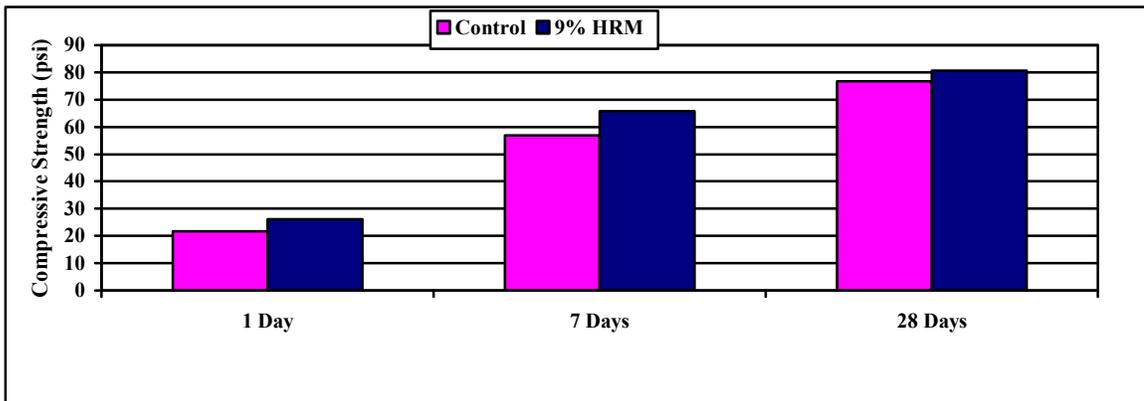


Figure 3. Compressive strength improvement in a grout formulation by replacement of cement with HRM.

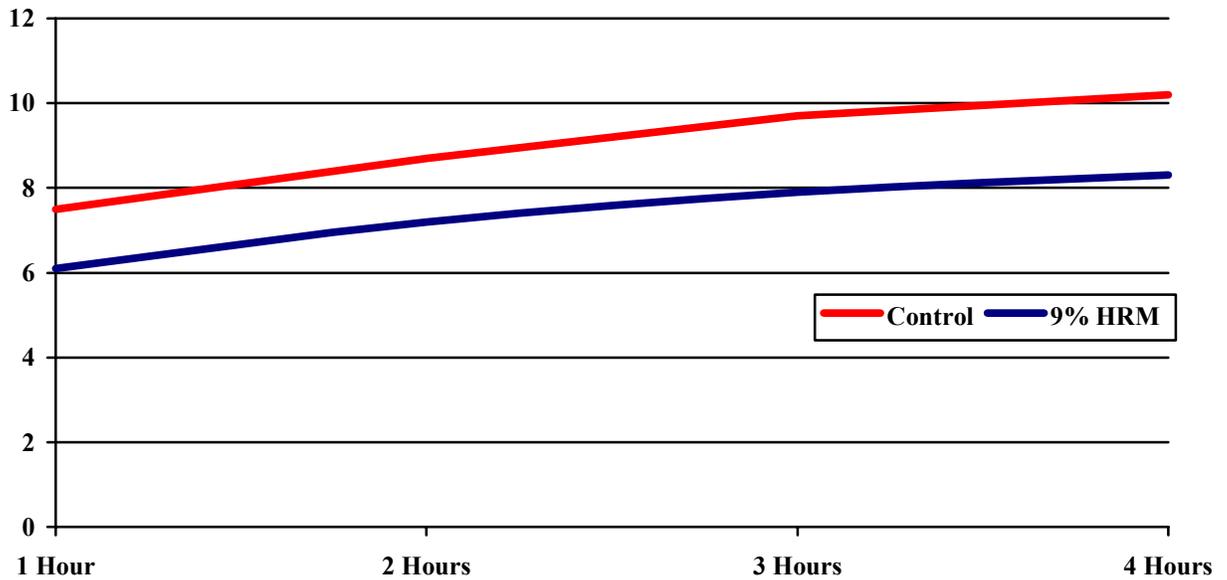


Figure 4. Effect of HRM on water absorption in a grout formulation.

It is clearly seen that the presence of HRM leads to less water absorption indicative of lower porosity and permeability of the grout.

Increased Chemical Resistance with HRM

The pozzolanic reaction with calcium hydroxide also results in reduced Alkali Silica Reactivity (ASR) through binding of alkali in the cementitious products. The reduced porosity and permeability also help in improving the chemical resistance by increasing the time for the chemical to reach the aggregate particles.

Figure 5 illustrates the impact of HRM on ASR due to reactive aggregates as measured by the CAN/CSA A23.2-14A (similar to ASTM C1293). Clearly, with 15% or higher levels of HRM, the 2 year expansion was reduced by over 80% and less than the CSA limit of 0.04%.

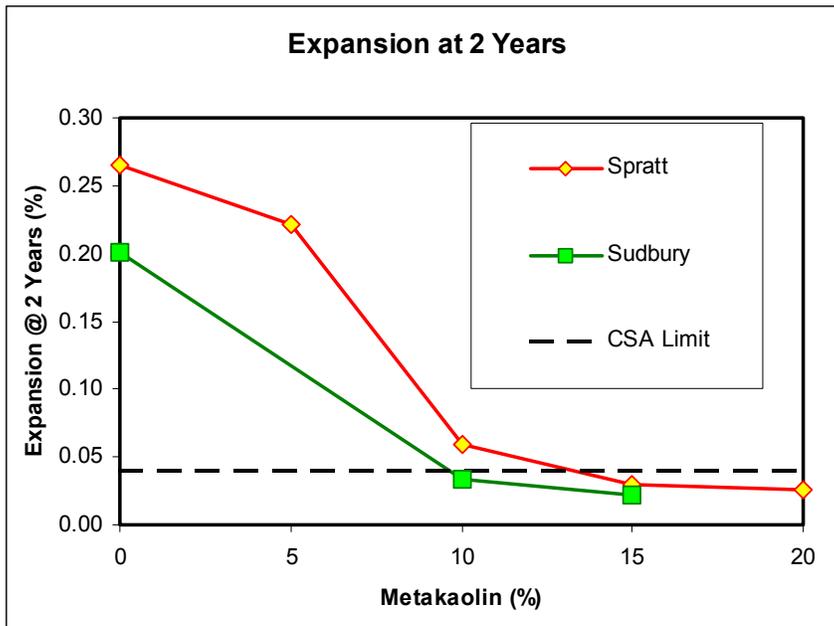


Figure 5. Effect of HRM on ASR.

Benefits due to White Color of HRM

The white color of HRM provides a distinct advantage over SF and FA as it does not darken or change the color of white cement and/or pigmented systems. Figures 6 and 7 illustrate the preservation of white color and ability to color match respectively with HRM. These figures also show that SF and FA clearly are at disadvantage in ability to maintain the white color or show the intended pigmentation.

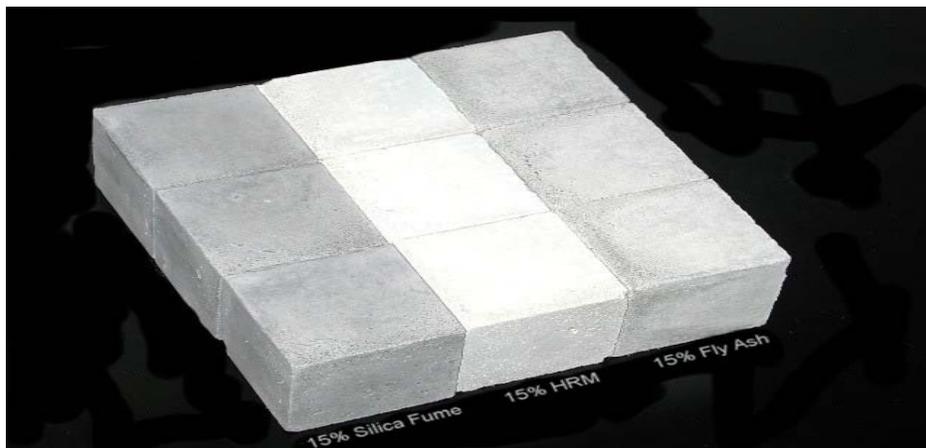


Figure 6. Mortars containing WPC with 15% SF, HRM and FA

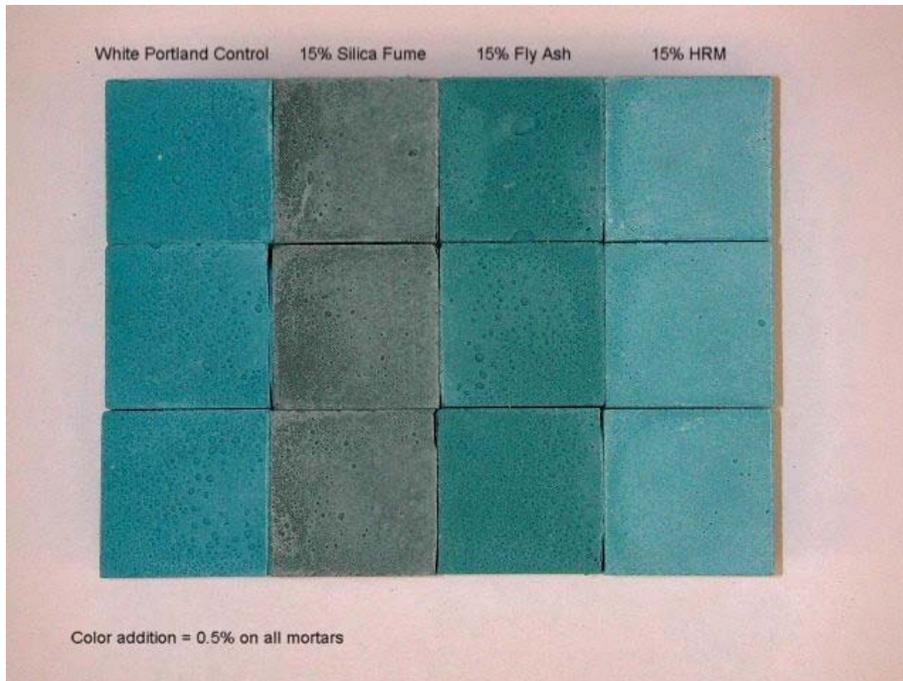


Figure 7. Addition of pigment (bright blue in this case) to WPC can only be matched by HRM and not SF or FA.

In architectural products HRM also provides the following benefits:

- Increases the workability and durability of the fresh mixture
- Reaction with calcium hydroxide helps reduce efflorescence
- Consistent white color of HRM can increase reflectivity versus other alternatives

Examples of architectural applications are :

- A. Swimming Pool Plaster:
- B. High Durability Structures – parking garages, bridge decks/overlays, industrial floors, specialty precast pieces and spun piles.
- C. GFRC – thin casting to bring out intricate details

In case of swimming pool plasters HRM provides following specific benefits:

- Reduced permeability
- Improved chemical resistance
- Improved trowelability
- Reduced mottling
- Control of spot-etching

In case of GFRC following specific benefits are obtained with HRM usage:

- Increased Production
- Durable (Retains Toughness)
- Improved Surface Appearance
- Less Chipping of Delicate Pieces
- Improves Bonding of Fibers

Improvement in Performance of Other Pozzolans and Specialty Cements with HRM

Pozzolanic reaction of HRM can supplement other slower reacting products such as FA and Ground Granulated Blast Furnace Slag (GGBFS). This approach may be useful to obtain the needed improvements with minimal cost. Also HRM can be successfully used in specialty cements such as oil-well and shrinkage-compensating.

To illustrate the benefit of using FA and HRM together rather than just FA, the following concrete design mixture was formulated.

Table 4. Concrete Mixture proportions

	<i>FA</i>	<i>HRM Addition</i>	<i>Additional FA</i>
Type I cement (lb.)	500	500	500
Class F FA (lb.)	100	100	145
HRM (lb.)	0	45	0
Fine Aggregate (lb.)	1340	1340	1340
Coarse Aggregate (lb.)	1740	1740	1740
Type A water reducer (oz.)	15	15	15
Air-entraining agent (oz.)	5	9	9
Type F HRWR (oz.)	33	97	61

Table 5. Fresh Concrete Properties with FA, HRM and additional FA.

	<i>FA</i>	<i>HRM Addition</i>	<i>Additional FA</i>
Slump (in.)	6½	6¼	7
Air (%)	7.4	7	7.4
Unit Weight (lb/ft ³)	141.1	142.3	142.7

The compressive strength data in Figure 8 below shows that addition of HRM leads to a significant improvement over just FA alone and even when additional FA is added to have the same cementitious content as with HRM addition, the gain in strength is marginal only. Thus a better value may be obtained with additional HRM rather than FA.

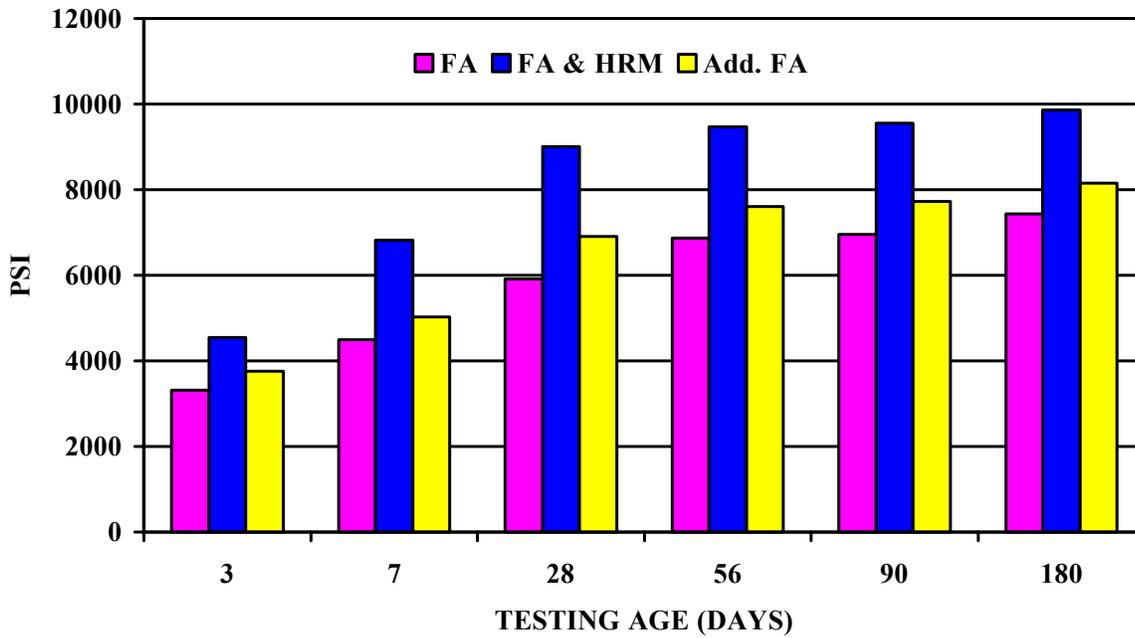


Figure 8. Increase in compressive strength with HRM compared to FA as well as additional FA.

The reduction in permeability with HRM is also higher than with FA alone or additional level of FA added to match the amount of cementitious material in the mixture (see Table 6).

Table 6. RCPT with FA, HRM and additional FA.

Mixture Design	Coulombs Passed
Fly Ash	2500
FA + HRM	800
FA + FA	1500

HOW AND WHEN SHOULD HRM BE USED?

The recommended amount of HRM varies based upon application & need. In general, 10% by mass of cement for increased strength and reduced permeability, which translates to 10 pounds of HRM for every bag of cement. The amount of HRM needs to be increased to 15-20% for improved chemical resistance & Alkali-Silica Reactivity (ASR) Control. This means, for a mixture containing five bags of cement one bag of HRM (55 pounds) may be added. Further, adjustments may be required in formulation such as change in water-reducer and air-entraining agent levels as shown in examples previously.

Unlike cement, HRM has an unlimited shelf life as long as it is kept dry. Direct moisture will not cause HRM to react, but may produce lumps of material to form that may decrease the dispersion in a mixture.

For Bagged Products dry HRM can be added while blending in cement. For Ready-mixed or Precast Plants HRM can be batched after cement at ready-mix plant or to the back of the Ready-mixed truck after the concrete has been batched. In any case, the HRM should be added before superplasticizer addition.

The finer particle size distribution of HRM than cement results in a higher water demand and the best way to offset the higher water demand is to increase the amount of water reducer as we saw in an earlier example. In case no other additives are being used, then the minimal amount of water should be added to maintain workability. As pointed out earlier, workability should not be assessed by the appearance of the mixture in the mixing equipment where it would look like a cohesive mass and need of more water. Workability should actually be assessed by troweling some of the mixture.

Finally, proper application and finishing techniques are still required with the usage of HRM just as without HRM.

SUMMARY:

HRM is recommended because of the following **benefits** in a number of cement-based systems.

- Excellent Workability
- Architecturally Appealing - No Darkening or changing of Color
- Increased Strength
- Reduced Permeability
- Control of Alkali-Silica Reactivity
- Enhancement of Lower/Slower Reactivity Materials - Fly Ash, GGBS

All the above listed benefits translate to the following **value** from HRM to the end-user.

- Increased Service Life
- Improved Performance
- Improved Appearance

- Increased Productivity