Use of Chemical Admixtures to Modify the Rheological Behavior of Cementitious Systems Containing Manufactured Aggregates

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ABSTRACT

The use of local materials is an important part of sustainability for the concrete industry. The declining availability of aggregate resources in many areas has the potential to result in the use of alternative aggregates of lower quality, which can require higher cementitious materials contents, or the use of aggregates shipped from greater distance. In some markets, manufactured sands are replacing natural sands, which can adversely impact the rheology of cementitious mixtures. The use of certain chemical admixtures has been found to often minimize the need to increase cement and water contents in order to overcome the loss of workability that can accompany aggregate sources which feature flat, elongated, angular, and rough particles. In this study, a wide range of natural and manufactured sands were characterized for gradation, mineralogy, shape, texture, and cleanliness, and also evaluated for their effect on mortar rheology with and without a viscosity modifying type chemical (VMA) admixture. Use of the VMA is shown to mitigate the rheological effect of certain sands, and in some cases can allow for optimizing the mixture to lower paste contents. In the case of polycarboxylate (PCP)-based superplasticizers, attention is drawn to the increased dose required to achieve target workability versus superplasticizers based on naphthalene sulfonate condensate (NSFC) when swellable clays are present in the very fine fraction of certain aggregate sources. The use of sands with higher fines contents are also shown to increase the workability provided the fines are of appropriate quality.

INTRODUCTION

Increasing regulatory pressures coupled with diminishing local availability of naturally occurring sands for use as fine aggregates in the production of concrete has brought about a growing dependency on manufactured sands (Hunt, 2000, McCaig 2002,). Moreover, an economic advantage is often possible when replacing fine aggregates with manufactured sands. Manufactured sands are produced from crushing rock deposits to produce a fine aggregate, which is generally more angular and has a rougher surface texture than naturally weathered sand particles. Furthermore, as much as 20 – 30% of the manufactured sand can be comprised of rock dust or microfines, a by-product of the crushing operation consisting of particles predominately less than 75 μm. While 15-25% microfines may be permitted in some countries such as India, Spain, and Australia (Hunt 2000), fine aggregate gradation limits such as found in ASTM C 33 allow up to 7% finer than 75 μm for some applications assuming the absence of clay or shale (Hudson 1996). To comply with various particle grading standards, the rock dust is removed by washing with water, creating a waste slurry whose accumulation imposes considerable detrimental impact on the aggregate industry.

The workability of concrete mixtures can be reduced when manufactured sands are substituted for naturally sourced fine aggregate, even with the finer than 75 μm fraction controlled. In some cases, the concrete mixture can be more prone to segregation. Furthermore, an increased effort may be required for concrete placement and finishing operations as well as higher pumping pressures. These performance characteristics can be ascribed to increased inter-particle friction, which in turn can be associated with a combination of angular particle shape and rough surface texture (Krinkle 2004, ACI Bulletin E1-1999). These factors can also be responsible for increased void space in the aggregate packing, which will require increased paste content to maintain consistent workability.

One option to overcome the adverse effects that manufactured sands can contribute to concrete mixtures is to increase the paste volume in the form of either higher amounts of cement or cement along with a supplementary cementitious material (SCM). In some cases, especially in the absence of clay-bearing fines, chemical admixtures, especially polycarboxylate-based high range water reducing agents, have been found to be useful to minimize the need for both increased water and paste contents that could be required with manufactured sands (Krinkle 2004).

The dust of fracture microfines created by the crushing of manufactured sand can be used in concrete if they are of suitable quality (Murdock 1960, Ahmed and El-Kourd 1989, Quiroga et al. 2006, Katz and Baum 2006, Koehler and Fowler 2008). In fact, limestone fillers are used successfully in concrete in many parts of the world (Zhu and Gibbs 2005). For example, Quiroga et al. (2006) showed that replacement of natural sand with various manufactured sands of various microfines contents reduced workability—due to shape, grading (including <#200) and cleanliness of manufactured sand. However, the majority of the decrease was apparently attributable to the methylene blue value, indicating the potential presence of clay. The use of manufactured sands with high microfines contents resulted in an increase in compressive strength.

The quality of dust-of-fracture microfines can be evaluated on the basis of size, shape, and cleanliness (Stewart et al. 2006, Koehler and Fowler 2008). The size of these particles are often similar to that of cement, fly ash and slag. The shape characteristics depend on the mineralogy and crushing process and are typically similar to those of the larger sized particles. In some cases the shape characteristic are similar to or better than that of cement or slag. The mineralogy of the microfines is predominantly that of the parent rock, but clay, mica, and other deleterious materials can be concentrated in the microfines fraction. Mica can be detected visually and clay can be identified with the methylene blue test.

This study is concerned with evaluating the interaction of both natural and manufacturing sands with a bio-polymer type viscosity-modifying agent (VMA), a class of admixture finding increased use with angular-shaped fine aggregates. Using yield and viscosity measurements on mortar mixtures, prepared with and without VMA, predictions are attempted to associate the key particle attributes responsible for changes in mortar rheology and the effectiveness of the VMA to maintain mortar workability without altering mixture components. Several examples are also provided to demonstrate how increased use of fines in concrete mixtures with non-optimized aggregate gradations can improve workability. Attention is drawn to a special undesired interaction between polycarboxylate-based superplasticizers and clay-bearing aggregates.

TEST PROGRAM

Seven (7) manufactured and eight (8) natural sands, identified in Table 1, were tested for gradation (ASTM C 33), particle shape and texture (ASTM C 295 petrographic analysis), % finer than 75 µm, and Uncompacted Void Content (ASTM C1252). Mortar mixtures were prepared using the mixture proportions reported in Table 2 with each manufactured and natural sand. Yield and viscosity measurements were performed on the mortar mixtures using a prototype Contec coaxial cylinder rheometer shown in Figure 1. The outer cylinder rotates at a programmable velocity while the inner cylinder is stationary and registers the applied torque from the mortar. By assuming the mortar to flow like a Bingham fluid, the yield value and plastic viscosity are calculated from the slope (viscosity) and yield value (intercept) in a torque-velocity diagram. In this study, focus was mainly on the yield value as it has been shown to correlate inversely with slump.

The performance of PCP and NSFC (naphthalene sulfonate formaldehyde condensate) type superplasticizers with clay-bearing fine aggregate (code RLT) was evaluated using a concrete mixture described in Table 3. The chemical and physical properties of our lab and the RLT sand are summarized in Table 4.

Figure 1. Contec Rheometer

RESULTS

Mortar Rheology

Mortar yield stress results, obtained with the Contec rheometer, were found to correlate well with mortar flow, and thus help to validate measurements with the rheometer (Figure 2). The mortar yield stress results for all the mortar mixtures, prepared at constant w/c and a constant weight of sand either manufactured or natural sand are reported in Figure 3. Mortars prepared with manufactured sands tend to exhibit a higher yield stress versus those mortars with natural sands. However, some overlap in yield stress values suggests other factors must be influencing water demand changes created by the various sand properties. Attempts to further characterize the rheological impact of natural versus manufactured sands by plotting yield stress versus viscosity as shown in Figure 3 could not discern any specific trends

Table 1. Location and Type of Sands

Manufactured Sands (HS)	Natural Sand (NS)	Location
	EN	Standard Sand - Europe
GC-HS	HC-NS	Central California
HSLO-HS	HSLO-NS	Central California
MARI-HS	NS	Arizona
CP-HS	CP-NS	Arizona
BARGE-HS	HV-NS	Southern California
S-HS	DUR-HS	Southern California
D-HS		Illinois
FL-HS	FL-NS	Florida

Table. 2 Mortar compositions with increased paste contents

	Control	Control w/ VMA	Control + 10 % Paste	Control + 20 % Paste	Control + 30 % Paste	Control + 40% paste
Cement	400	400	440	480	520	560
Sand	800	800	800	800	800	800
Water	188	188	207	225	244	263
VMA, % s/s	-	0.0035	-	-	-	-

Table 3. Concrete Composition with Problem Sand "RLT"

Material	Quantity
Lab 170 Cement	415 kg/m^3
"RLT" Sand	650kg/m^3
Coarse Aggregate, 20 mm	795 kg/m^3
Water	245 kg/m^3
W/C	0.59

Petrographic Analysis of Fine Aggregates

All the sand samples were subjected to a petrographic analysis performed according to ASTM C 295 and C 136 Sieve Analysis. Key parameters noted during the examination were mineralogy, shape, texture, and cleanliness, and are reported in Figures 4 and 5 for a pair of natural and manufactured sands, which some concrete producers are known to either blend or use interchangeably. Numerical values, ranging from 1 to 10, were assigned for shape, texture, and cleanliness, where lower the number implies high quality and suitability for concrete manufacture. As expected, the manufactured sands designated with the “HS” code have higher values versus natural sand available from a nearby location.

Correlation of Sand Properties with Yield Stress

In an attempt to identify the sand properties responsible for effecting the workability of mortar and concrete mixtures, the yield stress of mortar mixtures prepared with both natural and manufactured sands were correlated with fineness modulus, percent un-compacted voids, and a combined factor representing the sum of the values assigned for shape, texture, and cleanliness (Figures 6-7). No clear trends were readily evident suggesting that either certain critical sand parameters have yet to be measured, or that a higher level regression-type analysis is required to uncover more complex relationships.

Table 4. Sieve Analysis, Specific Gravity, Absorption, Mineralogy, and Methylene Blue Value for Lab and RLT Sands

Cumulative % Retained on Sieve Size, mm	**Lab Sand**	**RLT Sand**
4.75	0	5
2.36	7	21
1.18	32	35
0.60	61	50
0.30	80	65
0.15	95	81
0.075	99.6	90.5
Pan	100	100
Bulk Specific Gravity	2.62	2.32
Fineness Modulus	2.75	2.57
Absorption Capacity (%)	0.6	3.0
BET Total Surface Area, m^2/g	8.2	32.0
Ratio Surface Area to Lab Sand	1.0	3.9
XRD /Microscopic Analysis **Amorphous silica** **Clay**	-	High + + +
Methylene Blue Value		
Bulk Sand	<0.01	1.30
-0.075 mm	0.096	3.00

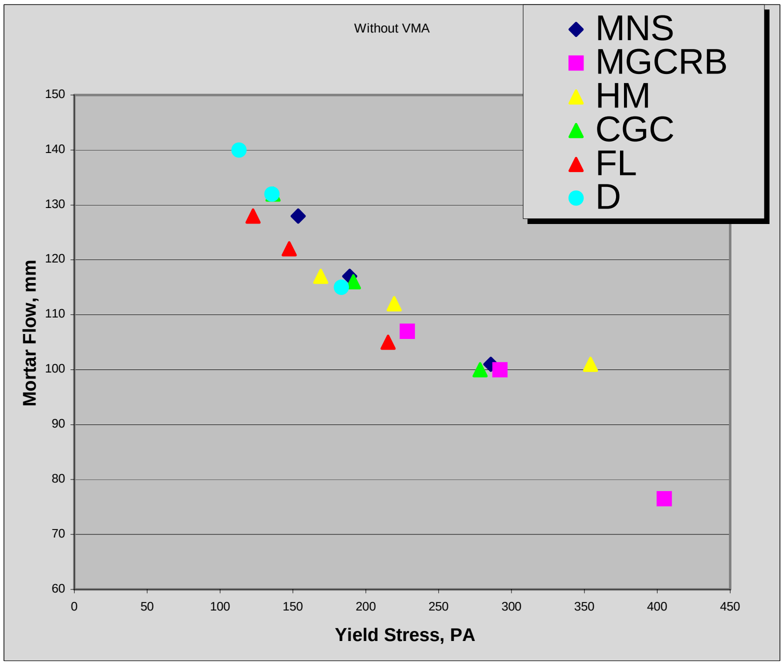

Figure 2. Correlation of Mortar flow with Yield Stress

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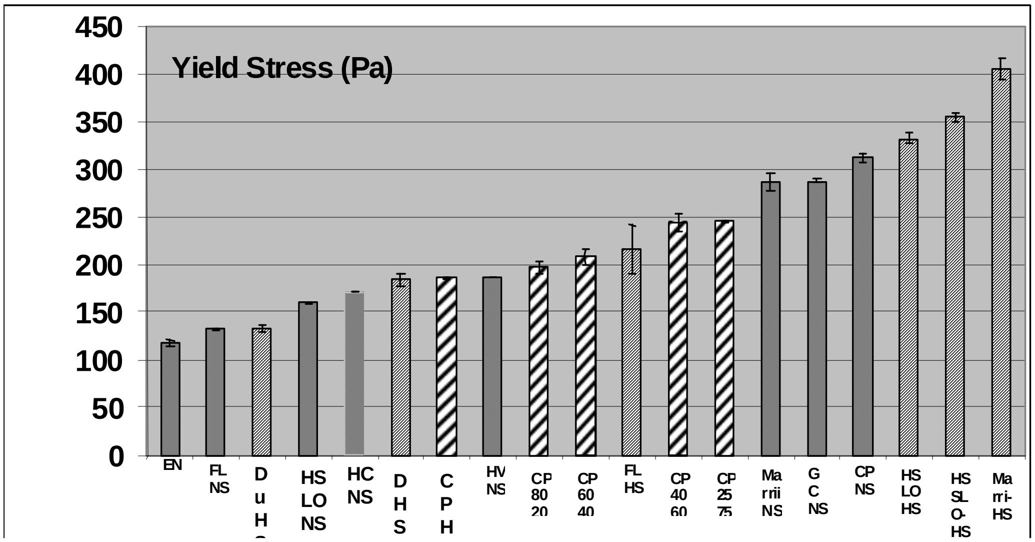
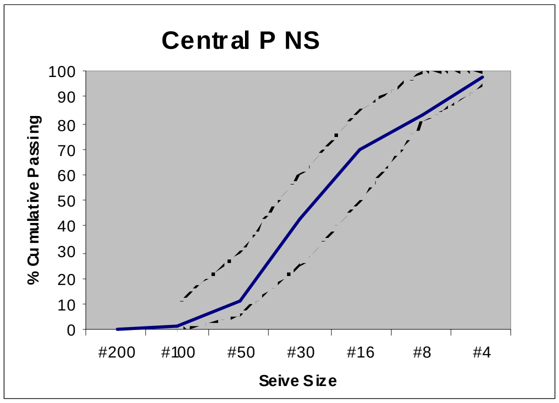
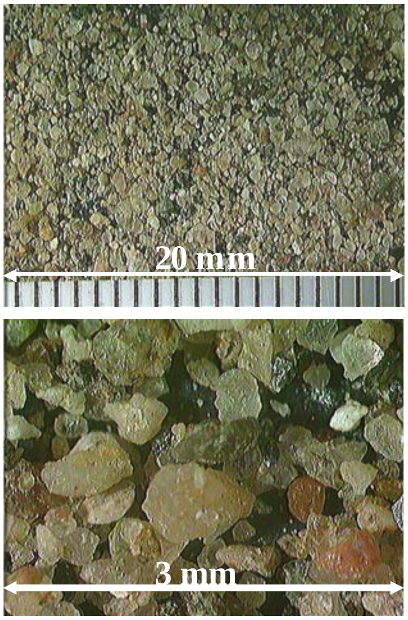


Figure 3. Yield measurement of mortar mixtures prepared with natural and manufactured sands as well as blends of both sands. Manufactured sands tend to produce higher yield stress versus natural sands.

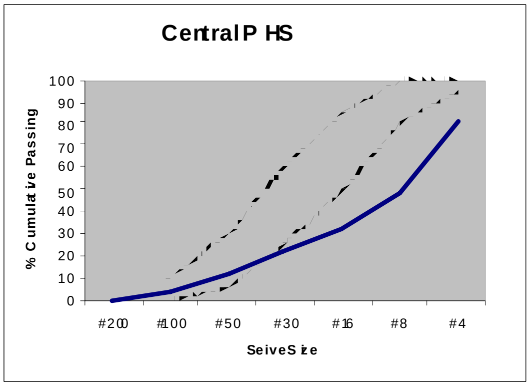


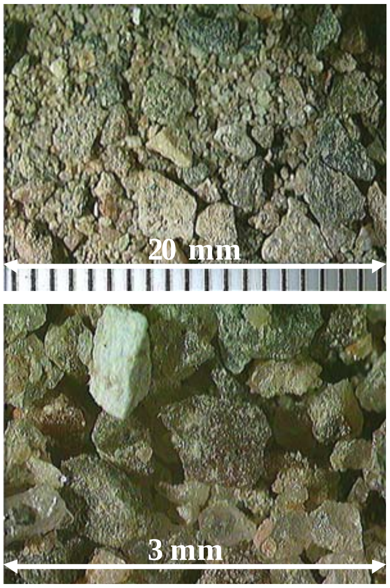


Mineralogy: : Medium to fine river gravel / sand of mixed lithology with some micas

Shape: 3 Elongated and Equant
Texture: 4 Sub Angular
Cleanliness: 1 Clean
STC Factor: 8

Figure 4. Petrographic Analysis of natural sand HSLO





Mineralogy: : Medium to fine well graded sand of mixed lithology with little to no micas.

Shape: 3 Elongated and Equant
Texture: 3 Sub Angular to sub rounded
Cleanliness: 4 Dirty
STC Factor: 10

Figure 5. Petrographic and sieve analysis of harsh sand CP.

Probing Interaction of Sand–Type Using VMA Modifying Agent and Cement Paste

With the measured sand properties providing limited predictive information concerning mortar workability, changes in mortar rheology as a function of VMA addition and increased paste content were next evaluated. Mortar mixtures described in Table 2 were prepared with each of the natural and manufactured sands identified in Table 1. In addition, the control mixture with the manufactured sand was dosed with 0.003% VMA actives by weight of cement (% s/s). Yield stress was measured for the mixtures. A sample plot of the yield stress as a function of increasing cement paste is shown in Figure 11. Interestingly, the pair of selected manufactured and natural sands, exhibit a similar drop in yield stress with increasing paste content. In the case of the VMA-treated mortar containing the manufactured Mari-HS sand, a 75 Pa drop in yield stress was observed. Extrapolating the lower yield stress to the yield stress-cement paste plot, the VMA appears to have the potential of lowering the paste content by about 12% without altering the yield stress.

In Figure 12, the reduction in paste content observed with the addition of 0.003% s/s VMA to 11 mortar mixtures prepared with the various manufactured sands. Interestingly, the sands appear to have quite a diverse response to the VMA additive, exhibiting a six (6)-fold change in yield stress.

Increasing the paste content of the control mortar mixture had a similar effect on yield stress compared to the VMA (Figure 13). Once again, the mortar mixtures prepared with the various manufactured sands exhibit a different response to added paste content expressed as percent reduction in yield stress normalized for percent cement paste added.

To understand if the yield stress reductions observed by both the addition of VMA and increased paste content have a similar mechanism in reducing the increased frictional particle-to-particle forces associated with manufactured sands, the change in yield stress produced by the VMA was correlated to the ratio of percent change in yield stress to percent added paste (Figure 15). A somewhat unexpected qualitative trend suggests that sands with a low to moderate yield stress response to the VMA have a high response to increasing cement paste. This could possibly be explained by the proposed mechanisms illustrated in Figure 16, where the increased paste content enables more significant particle-to-particle separation under various degrees of shear, whereas the effect of VMA on yield stress is probably more shear history dependent.

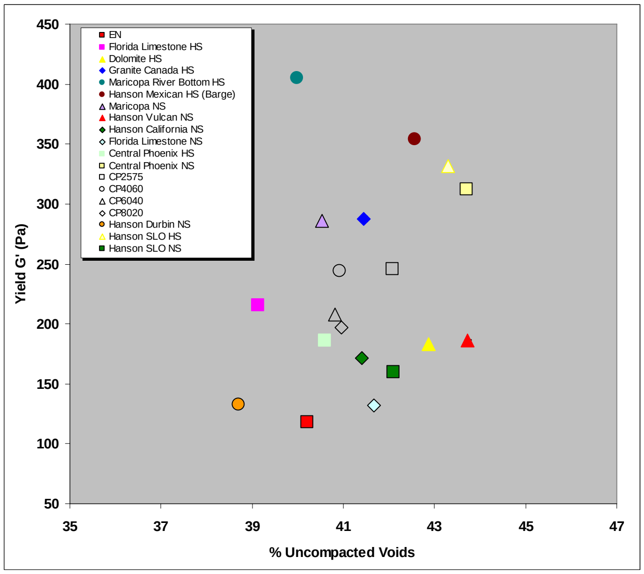


Figure 6. Correlation of Yield Stress versus % Uncompacted Voids.

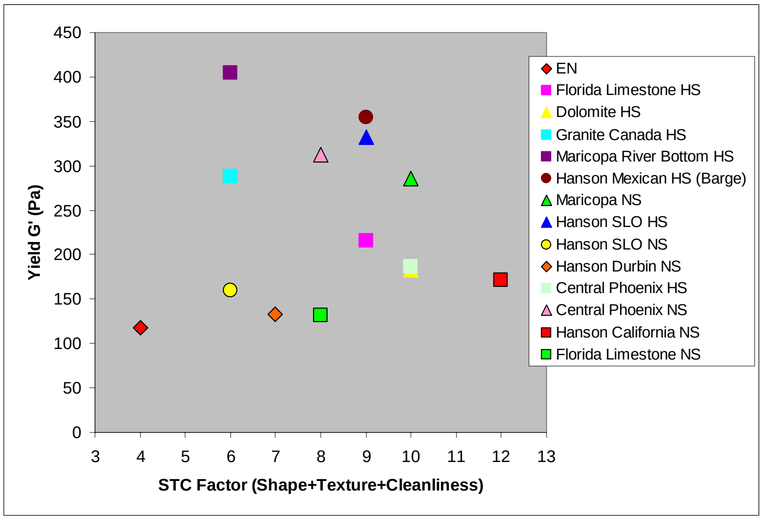


Figure 7. Correlation of yield stress with combined aggregate properties of shape, texture, and cleanliness.

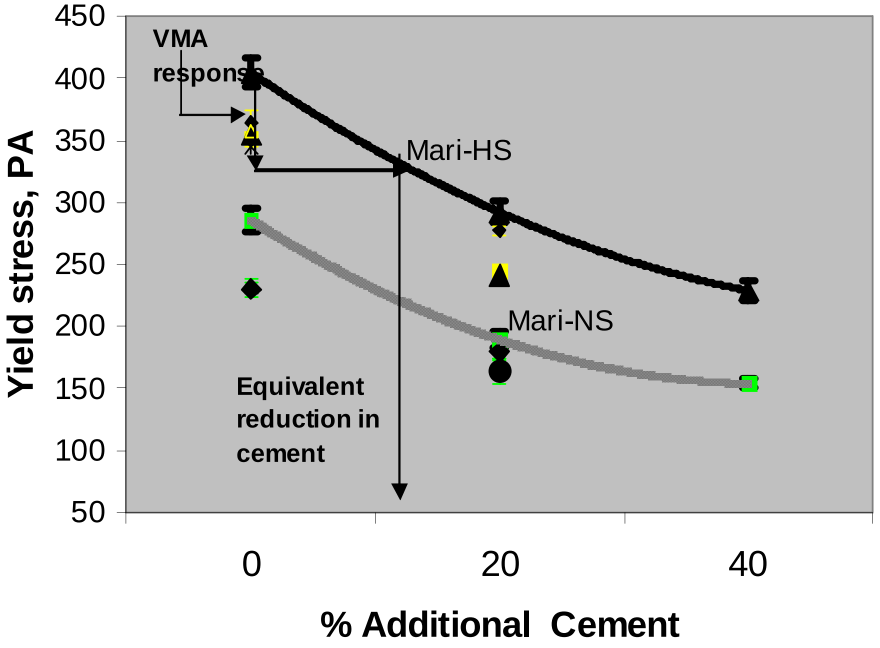


Figure 8. Change in mortar yield as a function of VMA and cement paste addition for mortar mixtures prepared with natural and manufactured sands.

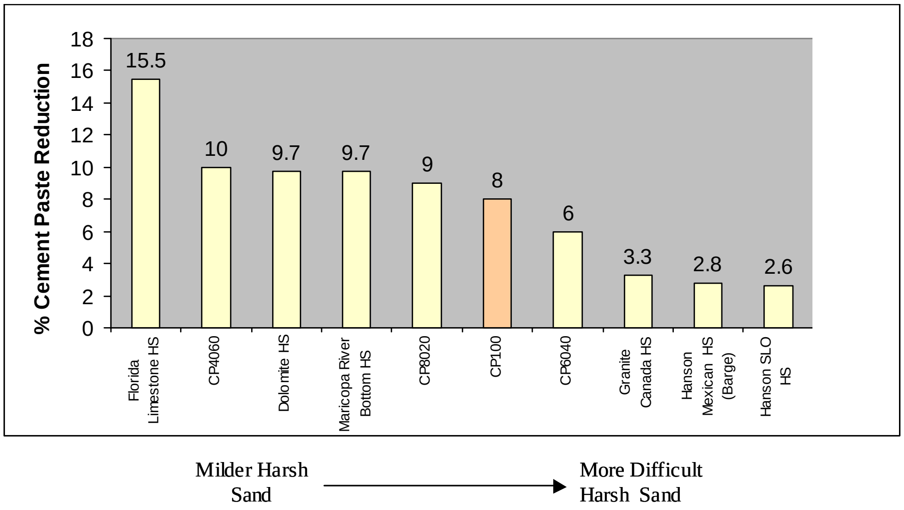


Figure 9. Reduction in cement paste content with 0.003%VMA s/s at constant yield stress.

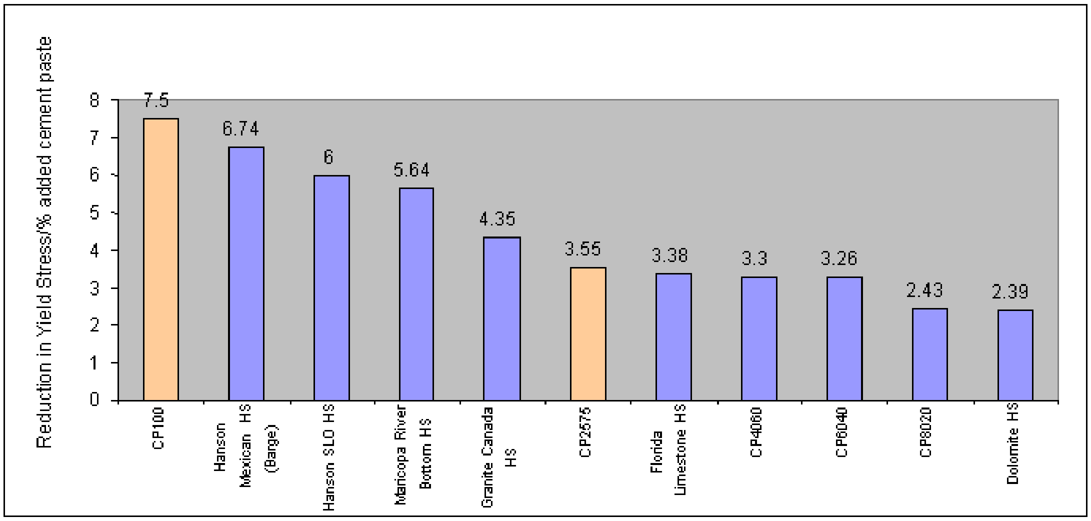


Figure 10. Reduction in Yield stress as a function of added cement paste.

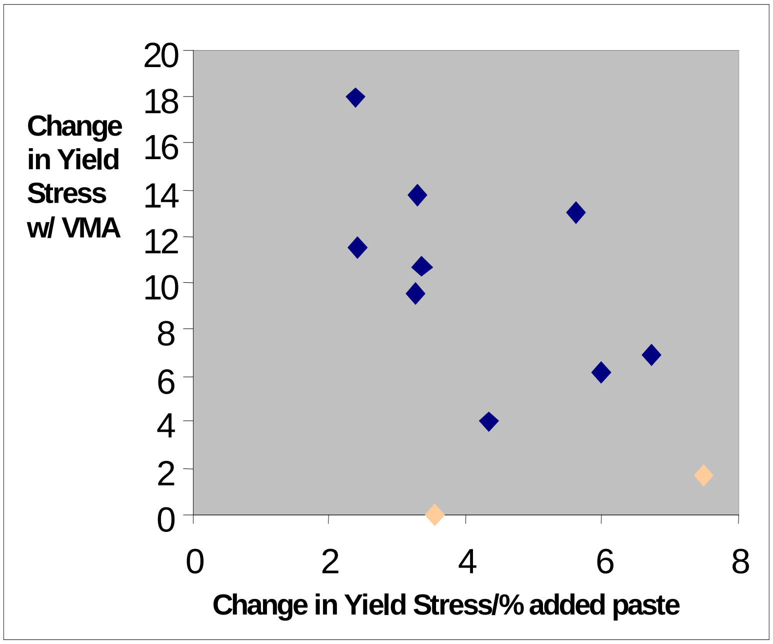


Figure 11. Correlation of VMA and cement paste additions on yield stress of mortar with various harsh sands. Sands with low response to VMA appear to respond well to added cement paste.

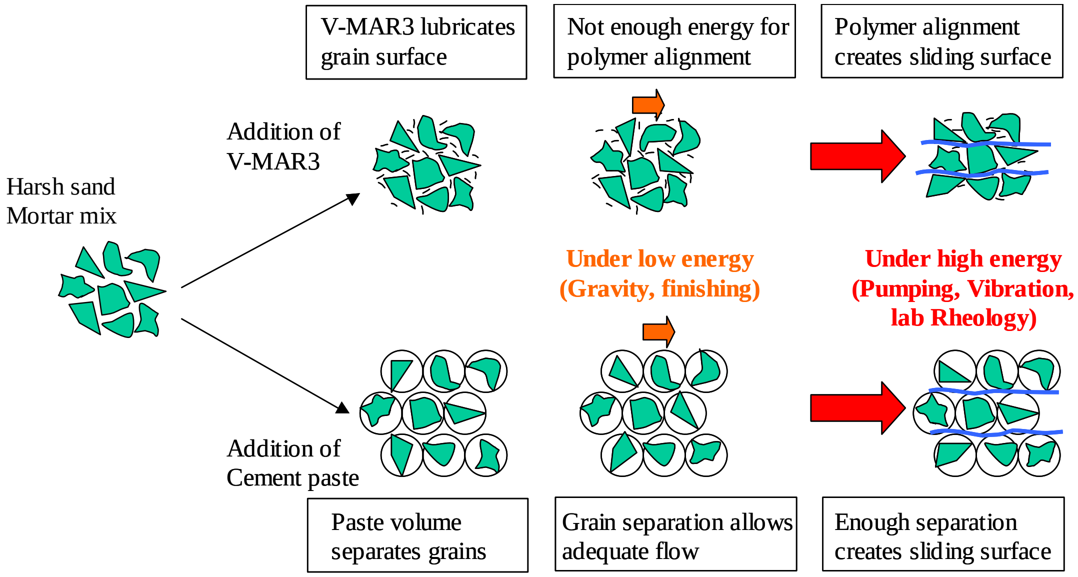


Figure 12. Mechanism of yield stress reduction as a function of VMA and cement paste additions.

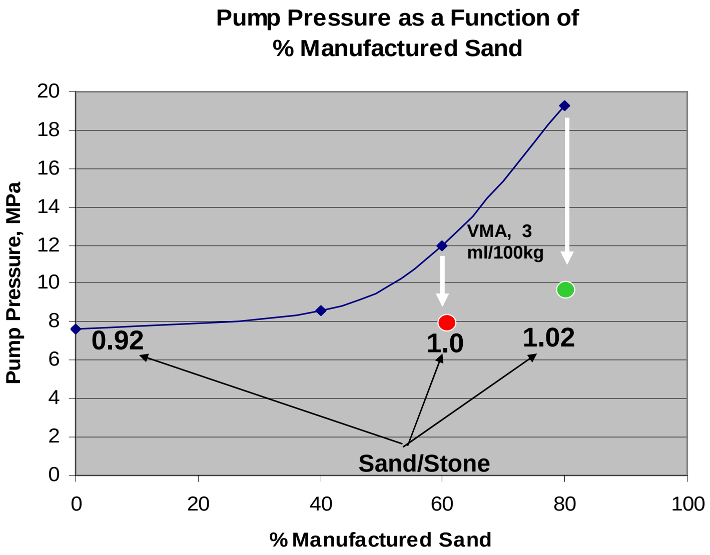


Figure 13. Effect of Manufactured Sands and VMAs on Pumping Pressure. Mix **Design, kg/m3: Cement 248; Fly Ash 65; Water 178 – 186; WRA 260 ml/100 kg Slump, 115-127 mm**

Impact of Manufactured Sands and VMA on Pumping Pressure

The lubricating effect that VMAs can impart to particle surfaces has been found beneficial for reducing the yield stress and viscosity of cementitious mixtures, especially those containing manufactured sands. One application that can take advantage of these improved rheological parameters is pumping concrete. Pumping pressures as a function of increasing manufactured sand content are shown in Figure 13. With the addition of a VMA, the increased pressure observed with up to 80% manufactured sand content can be reduced to pressures corresponding to a 20/80 natural/manufactured blend.

Influence of Clay-bearing Sands on Polycarboxylates

In a prior study, Jeknavorian (2003) has reported on the relative dosage-to-slump response for NSFC and PCP-based superplasticizers as a function of aggregate mineralogy comprised of swellable clays, namely, smectites such as sodium montmorillonite. Such clays, when initially wetted by the mix water, can expand, and in such altered forms can adsorb polycarboxylate-based comb-type polymers, rendering this family of superplasticizers less effective in providing the intended slump increase or water reduction (Figures 14 and 15). This effect is far less prevalent with NSFC.

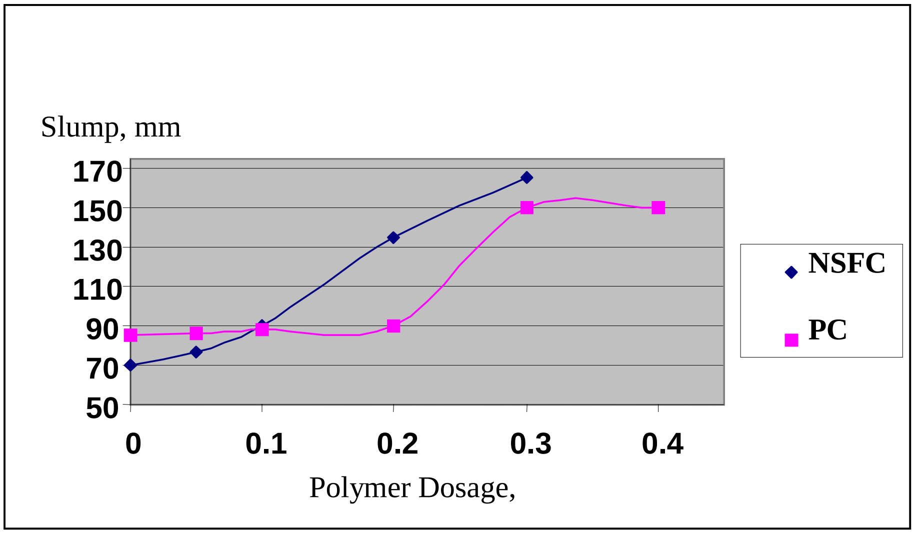


Figure 14. Dose-Slump Response for PCP vs NSFC Superplasticizers in Concrete with RLT Sand and Lab Cement 170

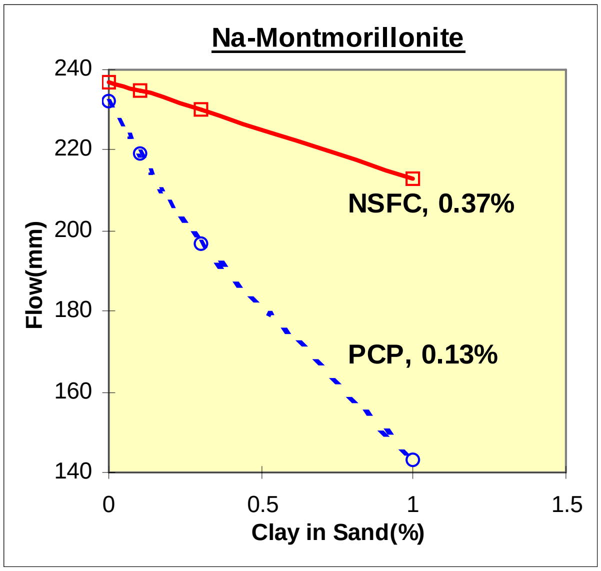


Figure 15. Relative change in Mortar Flow as a Function of Increasing Clay Content in Lab Sand.

CONCLUSIONS

Rheology measurements were found to be a useful to differentiate the effect that different natural and manufactured sands can have on the workability of mortar mixtures. Despite significant characterization of the various sands, no simple correlation was identified to associate sand properties with effect on yield stress. A multiple regression analysis might possibly provide a predictive relationship between some set of physical parameters associated with manufactured sands and mortar and concrete workability. Moreover, changes in yield stress of a control mortar mixture batched candidate sands, and subsequently modified either by the addition of a VMA or increased paste content, could have some potential use for concrete producers as a means of predicting the need for a change in mixture proportions to assure adequate placing and pumping operations.

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