The Investigation of Nano Silica in the Cement Hydration Process

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AN INVESTIGATION OF NANO SILICA IN THE CEMENT HYDRATION PROCESS

A Thesis
Presented to
the Faculty of Engineering and Computer Science
University of Denver

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Jonathan S. Belkowitz
November 2009
Advisor: Dr. Daniel Armentrout
ABSTRACT

With the advent of nano technology, materials have been developed that can be applied to high performance concrete mix designs. Nano silica reacts with calcium hydroxide (CH) to develop more of the strength carrying structure of cement: calcium silica hydrate (CSH). In this paper, relationships have been developed to distinguish the benefits when using different sizes of nano silica in cement paste. An extensive regime of experimental analysis was carried out to determine the effect of nano silica. Through these experiments the heat of hydration of multiple cement mix designs was measured. After that, the concentration of CH was recorded through X-ray diffraction. Then, the grain structures were examined through scanning electron microscopy. Finally, the compressive strength was determined for each cement paste mixture. Through these experiments it was found that as the silica particles decreased in size and their size distribution broadened, the CSHs became more rigid; this increased the compressive strength.
ACKNOWLEDGEMENTS

The funding by way of materials for this project was generously donated by Eka Chemicals, Chryso Inc., and Cemex. Dr. Daniel Armentrout and Dr. Paul Predecki were instrumental in facilitating experimental apparatus assistance. Lafarge provided laboratory time for sample preparation. Xiaojing Zhu of Materials Data Inc, graciously performed the Rietveld analysis.
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CHAPTER 1 – INTRODUCTION

In the modern age of concrete design, concrete researchers and developers are taking advantage of secondary cementitious materials to give concrete greater strengths. One of the newest technologies to break into the concrete design arena is the use of pozzolanic nano-particles in the concrete matrix. By using pozzolanic nano-particles, the development of the strength bearing crystals of cement paste can be increased/controlled. K. Sobolev, et al. recognized that by using nano-pozzolanic materials, the strength of concrete can be increased (Sobolev 94). The goal of this research was to investigate the effects of nano silica on cement hydration. The investigation was carried out through examinations of: heat change, crystal type and concentration, and change in compressive strength. This research was completed by focusing on a comparison of nano and micron size silica particles and how these affect cement hydration.

Various pozzolanic particles were used throughout the research to determine the advantages of different size particles. Silica Fume, which has been used in the concrete industry since the 1970’s, has been shown to increase the 28 day strength of concrete specimens (Holland 4). Since concrete generates a benefit from silica fume, which is in the micron size range, this research investigates whether or not nano silica will yield better results.
The foundation of this research investigated hydrated cement samples’ change in: heat, crystal concentration, and compressive strength. These properties are dependent on the rate and type of crystal growth. The crystal structures evaluated in this work were the calcium silicate hydrates (CSH) and calcium hydroxides (CH). The first is an amorphous-like crystal (cylindrical) structure that precipitates from solution into a globular mass. The amorphous identification is based on the cylindrical characteristics of the CSH. Due to the amorphous nature of CSH, X-rays will not diffract to give an easily identifiable pattern for measurement. The latter of the two crystals, CH, forms into plate like crystal dwarfing the CSH in cross-sectional area. The CH forms into a more arranged pattern than the CSH when it first precipitates from solution (Bogue, 245). Both phases are necessary in the development of the cement matrix that binds the harder constituents in the concrete.

This research is unique due to the level of examination conducted. Most recently Brian Green from the Army Corp of Engineers has used nano silica to reduce the permeability and increase the compressive strength of concrete (Green 122). The level of investigation of the micro effects with the addition of nano silica was minimal. The intent of this project is to investigate the effects of nano silica on cement hydration in greater detail.
CHAPTER 2 – MATERIALS AND METHODS OF PREPARATION

2.1 – Materials

Five cement paste mixtures were designed, batched, and tested to establish the quantifiable and qualifiable evidence, based on materials properties and proportions, to address the underlying topic of this report. One control mixture, with straight cement, was used in order to have a basis for comparison with a commonly used mix. Four specimens were batched, cast, and tested with different types of silica particles in each mix. Three mixes had nano silica, with three different size distributions, while one of the mixes included fused silica with particles approximately one micrometer in size.

Each of the mixtures were batched keeping all the constituents constant except for the silica. The cementitious material was manufactured at a local cement plant. A Type I/II Portland Cement, with moderate to high alkalis, was used. The High Range Water Reducer (HRWR) was used and the concentration chosen based on the soluble alkali content of the cement. The water-to-cement ratio, paste volume, and the absence of a granular skeleton were chosen based on qualification tests conducted prior to the key experiments. The concentrations chosen were identified as optimal for maximizing compressive strength for the materials used.

Coarse or fine aggregates were not used due to the type of experiments conducted. Both aggregates contained contaminants for crystal qualification and quantification. For compressive tests, finding a source of aggregate with reliable quality control between
samples was difficult. No aggregate was used; only neat cement paste was tested. New mixing methods needed to be developed in order to facilitate neat cement paste mixtures. To ensure that all the constituents were universally mixed, a whipping fixture was used as opposed to a paddle fixture. The whipping fixture was instrumental in combining all the materials with ease. By using the whipping fixture the testing no longer was in accordance with the prescribed ASTM C standard.

The larger silica used, Silica Fume, is a by-product from the production of elemental silicon or alloys containing silicon. The material has been used since the 1970s as a means to reduce permeability and increase compressive strength (Holland 6). It is predominantly comprised of 85% silicon dioxide (SiO\textsubscript{2}) and has an average size of 1.0 µm with a standard deviation of 0.5 µm. The average size and standard deviation is difficult to measure due to the inconsistencies between samples.

The nano silica used was separated by size distribution. As per the manufacturer, the nano silica designated 50 has the tightest size distribution. The tightly dispersed particle distribution has a mean size of 5.5 nm and a standard deviation of 1.5 nm. The nano silica designated 8 has a very wide distribution with a mean particle size of 35 nm and a standard distribution that encompasses a range of particle size from 2 nm to 100 nm (Reed 1). Nano silica package 508 is equally divided combination (by weight) of the nano silica package 50 and 8. Refer to Table 1 for a list of the constituents. The nano silica package refers to the size and distribution of a 5% (by weight of cementitious) addition of nano silica.
2.2 – Methods of Fabrication

The method used to fabricate the test samples depended on the experiment conducted. Each experiment was identified as a means of identifying a property of cement hydration. The method of fabrication had to be adapted to each experiment because of instrument limitations and the difficulty of obtaining some of the concrete components. ASTM standards were used wherever possible in the fabrication of the samples. The experiment also needed to be relatively easy to conduct while yielding data pertinent to the topic.

2.2.1 – Calorimetry

For the specimens to be tested for heat signature, ASTM C 31-09 was used in order to have a standardized method for fabrication. The specimens were cast into a 76.2 mm (3 inch) diameter by 152.4 mm (6 inch) length plastic cylinder and then immediately placed into the calorimetric chamber.

2.2.2 – X-Ray Diffraction (XRD)

By diffracting X-rays off a ground sample over a range of angles, an X-ray diffraction pattern was obtained and run through Rietveld Software to compute the concentration of CH per mix. Each mix was cast into a 25 mm (1 inch) by 50 mm (2 inch) by 10 mm (3/8 inch) non-absorbent rubber mold. The specimens were then cured in a 100% humidity chamber at 23 ± 2 °C (73 ± 3 °F). The samples were allowed to cure for 28 days and then were polished to a visually flat surface. The specimens were then cured for another 24 days at the same conditions. In preparation for the XRD tests, the
specimens were then dried in a conventional oven at 52°C (125 °F) for 24 hr. The samples were then lightly ground on a 400 grit SiC sandpaper to remove any surface contamination, prior to being X-rayed.

2.2.3 – Scanning Electron Microscopy (SEM)

For the next stage of testing, each mix design was analyzed under a SEM. By using energy dispersive X-ray spectroscopy (EDX) and high powered magnification, the crystal form and concentration could be investigated. Each mix was cast into a 25 mm (1 inch) by 50 mm (2 inch) by 10 mm (3/8 inch) non-absorbent rubber mold. The specimens were then cured in a 100% humidity chamber at 23 ± 2 °C (73 ± 3 °F). On the 14th day, the specimens were fractured and then allowed to cure at the same conditions for 7 days. The specimens were then dried in a conventional oven at 52 °C (125 °F) for 24 hrs. Each sample was then cooled for 1 hr and finally sputter coated with gold so that the surface was electrically conductive, prior to insertion in the SEM.

2.2.4 – Compressive Strength

Compressive strength was determined by placing a compressive force on a cast and cured cement paste specimens. ASTM C 109-08 was used to cast and cure the specimens. The compressive strength specimens measured 50 mm (2 inch) by 50 mm (2 inch) by 50 mm (2 inch). The cubed specimens were mixed without any coarse or fine aggregate. On the break date, each sample was placed in a closed-loop hydraulic press. The sample was centered onto a machined surface. A compressive force was then applied to the top and bottom surfaces of each cubed specimen until failure.
Table 1 – Cement Paste Mixtures

<table>
<thead>
<tr>
<th>Mix</th>
<th>Water</th>
<th>Cement</th>
<th>Silica</th>
<th>HRWR</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST CMT</td>
<td>133 (224)</td>
<td>425 (716)</td>
<td>0</td>
<td>1.9</td>
</tr>
<tr>
<td>SF</td>
<td>133 (224)</td>
<td>425 (716)</td>
<td>21 (36)</td>
<td>1.9</td>
</tr>
<tr>
<td>8 (nano)</td>
<td>133 (224)</td>
<td>425 (716)</td>
<td>21 (36)</td>
<td>1.9</td>
</tr>
<tr>
<td>50 (nano)</td>
<td>133 (224)</td>
<td>425 (716)</td>
<td>21 (36)</td>
<td>1.9</td>
</tr>
<tr>
<td>508 (nano)</td>
<td>133 (224)</td>
<td>425 (716)</td>
<td>21 (36)</td>
<td>1.9</td>
</tr>
</tbody>
</table>
CHAPTER 3 – CEMENT HYDRATION ANALYSIS

3.1 – Temperature Initiation

The purpose of this section is to identify current theories of the cement hydration process. Each stage of hydration is analyzed later on within this section and in sections to come. The effects of nano and micron silica addition on the analyzed stages will be predicted. The cement strength is based on the reactions between the many phases present and H₂O. The compounds present in the cement before the H₂O is added are available in Appendix A. The development of the crystal structures identified earlier is illustrated through the change in temperature over time, which occurs during the cement hydration process. First the cementitious reactions are analyzed, from initiation to densification. After that the pozzolanic reaction is identified and verified through the literature review. To understand the importance of these reactions, it is first important to identify the stages at which these reactions take place in the heat of hydration process. The entire heat of hydration process is illustrated in Figure 1.

3.2 – Stage 1, Mixing

When powdered cement is mixed with H₂O, exothermic hydration reactions begin to take place. In Stage 1, Mixing, the tri-calcium aluminate (C₃A) reacts with H₂O to form calcium aluminate hydrate (ettringite) in the cubic (C₃AH₆) or the hexagonal (C₄AH₁₂) crystalline structures shown in Figure 2 and documented in chemical Formula
1. Table 2 defines the abbreviated compounds in the discussed formulas. Along with the production of ettringite, there is an initial precipitation of CH. These two crystalline compounds, in combination, form (over time) a surface layer, which acts as a diffusion barrier to H₂O, covering the cement particles, approximately 10 nm thick (Neville 14). The initial release of energy from these reactions causes a spike in the temperature of the mix during Stage 1. The temperature change during mixing was measured. It was found that the temperature of the constituents before and after mixing did not change by more than 2° F. Even though some of the chemicals begin to react during mixing and energy is added by mixing, the temperature change was small and could be neglected in comparison to the heat of reaction which occurred after mixing.

\[
3\text{CaO}.\text{Al}_2\text{O}_3 + 6\text{H}_2\text{O} \rightarrow 3\text{CaO}.\text{Al}_2\text{O}_3.6\text{H}_2\text{O} \quad (1)
\]

3.3 – Stage 2, Dormancy

In Stage 2, Dormancy, the surface layer that begins to coat the cement particles is a diffusion barrier to H₂O. As the surface layer grows in thickness, it slows the ingress of H₂O thereby, decelerating the hydration reactions. Within the diffusion barrier, the reaction rate is maintained until the free H₂O approaches exhaustion; the coating over the cement particle becomes thicker; and the rate of reaction decreases to a point where the crystal production approaches a period of dormancy or when the development of crystals steadily approaches dormancy.

As the cement hydration process continues, more H₂O reacts with the tri-calcium silicates (C₃S) to form CH and CSHs. A principle that has been commonplace to
describe the concept of hydration, was developed by Le Chatllier. He recognized in 1881 that, “calcium silicates do not hydrate in the solid state but the anhydrous silicates probably first pass into solution and then react to form less soluble hydrated silicates which separate out of the supersaturated solution” (Spinks 26). Neville supports this declaration showing that the CSH forms from solution after the CH separates out (Neville 16). Formula 2 documents the reactants and products from this initial reaction of H₂O and C₃S are the compounds which make up the principal reactant in Stage 2.

\[
2(C₃S) + 6(H₂O) \rightarrow CSH + 3CH \quad (2)
\]

C₃S react before di-calcium silicates (C₂S). The reality of this process is diagnosed from the differences in the properties of both crystals. C₃S forms a crystal with an average cross-sectional size of 35 µm while C₂S is rounded with an average cross-sectional size of 25 µm. It has been found that the concentration of the C₃S exceeds the C₂S, making up approximately 70% and 5% of the cement particle, respectively (Neville 14). In conjunction with a smaller size distribution, the C₂S can be found in the form of nests or clusters included in the C₃S. The greater availability of C₃S over C₂S ensures an earlier reaction time in the presence of H₂O. Finally, due to its geometry (hexagonal-like) and larger size, the C₃S will have more surfaces to facilitate initial reaction with H₂O when compared to the rounded structure of the C₂S (Gartner 28). Reaction time is based on surface area, so the C₃Ss larger surface area reacts faster than the C₂S.
3.3.1 – Breaking the Dormancy

CH has the greatest potential for growth and solubility in the presence of H₂O, recognized by W. Michaelis in 1893 (discussed later) and governed by Formula 2 (Neville 34). The CH crystal can form into a myriad of shapes to include: plate-like, hooded, and fractured. An example of a plate-like CH crystal is shown in Figure 2. The CH crystals grow to the point where they will break through the H₂O diffusion barrier covering the cement particles. Once the surface layer is broken, H₂O can react with the remaining unhydrated cement and more crystals develop. The reaction products in Formula 2 release heat to the surroundings to increase the temperature and transition from Stage 2, Dormancy to Stage 3, Hardening/Acceleration.

3.4 – Stage 3, Hardening/Acceleration

During Stage 3, the CH grows within the cement paste, impregnating itself within the webbed network of the other crystal formed, CSH. In 1893 W. Michaelis stated that the CH will give the cement paste its initial strength. Michaelis maintains that after the CH precipitates, the solution left over is supersaturated with CSH. As the compounds combine, the H₂O in this supersaturated solution is expended. The CSHs harden and grow into globular masses with successive layers. The CSH has two distinct forms, which are categorized by whether they are developed early or late (Mindess 16). These CSHs give the concrete its compressive strength. The early CSHs are the impure form of the crystal like structure. While maintaining more strength than the CH, the early and late CSH, are developed in a H₂O filled spaced. The H₂O in the liquid phase is decreased
when it is incorporated into the reaction of the cementitious compounds. As the H₂O level decreases the CSHs start to develop into the microstructure to increase the ability to bear compressive loads.

3.4.1 – CSH, Early

Layering of the CSHs are shown in Figure 3. These successive layers are saturated with H₂O at early stages of hydration. Once the CSHs surface area starts increasing, the free H₂O not bonded to the cement particle will migrate toward this increased area of said hydrate. As the water is absorbed by the unhydrated cement, the CSH gel dries. As the gel dries, the CSH starts to harden. Upon drying the CSHs will arrange themselves into clay-like sheets. The orientation of the CSH structure represents the structural integrity as well as the fragility from voids pictured in Figure 3.

Throughout the structural web, there is a myriad of pore types and sizes. A listing of pore types and sizes is shown in Table 3. These pores, if filled, can offer more resistance to compressive loads. This phenomenon is applied and discussed in later sections of this report.

3.4.2 – CSH, Late

The other type of CSH formed is the late or outer product. This product will be a more pure and denser version of the previous CSH. The density and therefore ability to resist compressive loads increases as the hydration products increase. In Stage 3 the majority of the CSH form from the C₃S, while only a small trace of C₂S reacts (Neville
15). In other words, Stage 3 will primarily have early calcium silica hydrate and trace amount of late CSH.

3.4.3 – CSH Growth

When the C\textsubscript{3}S reacts with H\textsubscript{2}O and starts to produce the CSH structures, these crystals grow out of the C\textsubscript{3}S grain as well as into the grain. As the hydration process continues, the CSHs will form a thick coating around the C\textsubscript{3}S grains. This diffusion barrier densifies over time. The diffusion reaction slows down as the barrier becomes thicker. This is when the hydration of the C\textsubscript{3}S has a propensity to approach completion (Mindess, 64). As the reaction of C\textsubscript{3}S slows, the reaction of C\textsubscript{2}S increases. The slowing down or deceleration is the next stage of cement hydration.

3.5 – Stage 4, Deceleration

The reaction of the C\textsubscript{2}S develops slowly due to its aforementioned properties. By way of its slower reaction, the C\textsubscript{3}S will release less heat to the surroundings when compared to the C\textsubscript{3}S. From previous sections it was mentioned the C\textsubscript{2}S yields growth of late CSH. Therefore, as the propensity for C\textsubscript{2}S to react increases, so does the concentration of late CSH. For this reason, the heat from the C\textsubscript{2}S formation is difficult to measure. The heat balance of the whole process is dominated by the reaction of C\textsubscript{3}S. Table 4 lists the heat exchange for both formations (Mindess 65). Based on these observations, the temperature curve in Stage 4 decreases. Even though the reaction of the C\textsubscript{2}S is slower and releases less energy, the reaction yields less CH and a denser CSH. That is the CSH developed has less CH and pores. This generated CSH crystal can resist
more compressive loads than the former. The reaction for the C\textsubscript{2}S and H\textsubscript{2}O is shown in Formula 3.

\[ 2(C\textsubscript{2}S) + 4(H\textsubscript{2}O) \rightarrow CSH + CH \quad (3) \]

3.6 – Stage 5, Densification

In Stage 4, the C\textsubscript{3}S reactions started declining. Stage 5, Densification illustrates this drop of the C\textsubscript{3}S reactions and therefore, energy/temperature exchange. The heat of hydration curve, shown in Figure 1 illustrates this heat plateau or Stage 5. There is a small temperature gain from pozzolanic and cementitious (C\textsubscript{2}S) reactions. These reactions release less energy than earlier reactions. This phenomenon is illustrated in Table 4. Due to the lower energy output there is a smaller temperature change. Currently, the software used will not recognize this temperature change. Even though this temperature change is not recognized, these exothermic reactions still occur. Stage 5 of the cement hydration process will continue as long as H\textsubscript{2}O and sufficient reacting compounds are present. Therefore, the longer a sample is allowed to cure with silica and H\textsubscript{2}O present, the higher the concentration of CSH.

3.7 – Pozzolanic Reactivity

In addition to the cementitious reactions in Formula 2 and Formula 3, a pozzolanic reaction occurs with the addition of silica. The Silica Fume Association stipulates that a pozzolanic material will not gain strength when mixed with H\textsubscript{2}O while a cementitious material will hydrate and gain strength (Holland 4). The pozzolanic material assists in the development of CSH through a pozzolanic reaction with the CH.
Formula 4 illustrates the reaction of the CH and silica. The CH will not be totally consumed by this reaction.

\[
\text{SiO}_2 + \text{CH} \rightarrow \text{CSH} \quad (4)
\]

3.7.1 – Pozzolanic Benefits Identified

Through a great deal of experimentation and analysis, D.P. Bentz highlighted three significant benefits involved when using a micrometer size silica based or pozzolanic material (Bentz 365).

3.7.1.1 – Packing Efficiency

The first benefit, which is based on the particle size, shows that the silica packs more efficiently, than the cement particles, in the interfacial transition zone (ITZ). The ITZ is the region where the aggregate surface meets the cement matrix. Normally the amount of cement paste at the ITZ is less than that in the body of the specimen. This is known as the wall effect. The reduction in cement paste is due to the increased surface area at this ITZ between the aggregate and the cement paste. By limiting the paste, it is desirable to ensure that the paste that is available contains a more homogenous mixture of silica and cement paste. This contributes to a larger amount of pozzolanic reactivity. The silica enriched cement at the ITZ region [cement paste in the case of this project] is denser than the cement paste in the body of the concrete. The hydration of the densified paste improves the bonding of the aggregate into the hydrated cement matrix. This improves compressive strength.
3.7.1.2 – Porosity Reduction

The second factor is that there will be a reduction of the porosity in the hydrated cement paste. By reducing the porosity, more material is deposited to resist compressive loads. Balaguru and Chonge recognized the potential to increase compressive strength by impregnating nano materials between the CSH crystals. This densification of pores with the CSH structure increases compressive strength (Balaguru 23).

3.7.1.3 – CSH Gel Densification

The silica used, in this project, pozzolanically reacts with the CH that grows in these interstitial voids. The tendency for CH follows the predisposition recommended by Mindess, et al, which stipulates that CH crystals will grow in the interstitial space in the body of the hydrated cement (Mindess 69). In the presence of H₂O, the CH crystals are soluble. In 1979 P. Christensen, et al discovered through optical microscopy that CH redeposits in cracks, cavities, and pores of a sample (Christensen 138). By use of electron microscopy, R. Berger found that within the pores and capillaries of the CSH networks were impregnated CH grains (Berger 320). As the recrystallized CH disperses in solution it will combine with the available nano silica. This silica will react with the CH to form CSHs to increase the density of the porous CSH structure. The CSH gel produced with silica addition decreased the chloride ion diffusivity through the sample by 25 times when compared to conventional CSH gel. This effect is caused by an increased concentration of a more pure CSH with fewer voids.
Figure 1 – The Heat of Hydration Type I/II Cement (Mindess 73)

Figure 2 – Hydrated Cement Sample
Table 2, Abbreviated Compounds (Neville 11)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tri-Calcium Silicate</td>
<td>$C_3S = 3\text{CaO} \cdot \text{SiO}_2$</td>
</tr>
<tr>
<td>Di-Calcium Silicate</td>
<td>$C_2S = 2\text{CaO} \cdot \text{SiO}_2$</td>
</tr>
<tr>
<td>Tricalcium Aluminate Phase</td>
<td>$C_3A = 3\text{CaO} \cdot \text{Al}_2\text{O}_3$</td>
</tr>
<tr>
<td>Ferrite Phase</td>
<td>$C_4AF = 4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$</td>
</tr>
<tr>
<td>Calcium Silicate Hydrate</td>
<td>$\text{CSH} = \text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Calcium Hydroxide</td>
<td>$\text{CH} = \text{CaO} \cdot \text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>
Table 3 – Classification of Pore Sizes in Hydrated Cement Pastes (Mindess 75)

<table>
<thead>
<tr>
<th>Designation</th>
<th>Diameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capillary Pores</td>
<td>10,000 - 50 nm</td>
<td>Large Capillaries (Macropores)</td>
</tr>
<tr>
<td></td>
<td>(10 - 0.05 μm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50 - 10 nm</td>
<td>Medium Capillaries</td>
</tr>
<tr>
<td>Capillary Pores</td>
<td>10 - 2.5 nm</td>
<td>Small Isolated Capillaries (Small Mesopores)</td>
</tr>
<tr>
<td></td>
<td>2.5 - 0.5 nm</td>
<td>Micropores</td>
</tr>
<tr>
<td></td>
<td>≤ 0.5 nm</td>
<td>Interlayer Spaces</td>
</tr>
</tbody>
</table>

Table 4 – Heats of Hydration of the Cement Compounds (Mindess 64)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H ) (J/g) for Complete Hydration</th>
<th>Pure Compounds</th>
<th>Cement(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_3S \rightarrow C_3S.H + CH )</td>
<td>~380</td>
<td>520</td>
<td>480</td>
</tr>
<tr>
<td>( C_2S \rightarrow C_3S.H + CH )</td>
<td>~170</td>
<td>260</td>
<td>225</td>
</tr>
<tr>
<td>( C_2A \rightarrow C_4AH_{12} + C_3AH_6 )</td>
<td>~160</td>
<td>.</td>
<td>-</td>
</tr>
<tr>
<td>( \rightarrow ) ettringite</td>
<td>900</td>
<td>880</td>
<td>-</td>
</tr>
<tr>
<td>( \rightarrow C_3AH_6 )</td>
<td>1670</td>
<td>1670</td>
<td>-</td>
</tr>
<tr>
<td>( \rightarrow ) monosulfoaluminate</td>
<td>1150</td>
<td>1140</td>
<td>1170</td>
</tr>
<tr>
<td>( C_4AF \rightarrow C_3(A,F)H_6 )</td>
<td>420</td>
<td>420</td>
<td>-</td>
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</table>

\(^a\)These values should be negative since they refer to exothermic reactions, but they are customarily written without the negative sign.

\(^b\)One-year-old paste assumed to be completely hydrated

\(^c\)Individual contributions determined by multiple linear regression analysis
4.1 – Calorimetry

Temperature is one of the key indicators that enable prediction of dormancy and strength development per concrete mix design. When a nano sized particle of a pozzolanic material is introduced in the mix, the temperature of the hydration process should increase. The temperature increase should take place in Stages 3 and 4 for the nano silica. This affect is due to the availability of silica at the nano scale, specifically, the greater surface area of silica to react pozzolanically. The silica fume (SF) mix will have a delay due to the time it takes to react with the larger silica. The heat from the SF pozzolanic reaction will be in Stage 5. From the calorimetry conducted it is expected that the cement mixtures will yield faster initiating and greater temperatures in the following mixture order: Mix 8, Mix 508, Mix 50, Mix SF, and Mix ST CMT because the smaller silica particles will react quicker.

4.2 – XRD

Because of CSH amorphous makeup, radiation will not diffract into measurable peaks for counting/measuring purposes. Although there wasn’t a way to determine the concentration of CSH directly, the amount of CH could be used to determine the CSH concentration indirectly. The concentration of CH could be determined qualitatively
through obtaining an XRD pattern of from a concrete sample and then quantify the CH phase concentration using the Rietveld method.

Larsen investigated and analyzed the production of CH based on changing cement and admixture. Through his findings in 1961, it was determined that the concentration of CH, commonly known as Portlandite, can be used to quantify the CSHs formed in the same specimen (Larsen 36). There should be a decrease in the amount of Portlandite in a given specimen based on addition of silica and maximum nominal size of the graded silica. As CH decreases, CSH increases and so should compressive strength.

The percentage of Portlandite found in the five mixes in order from least to greatest (to be tested after 28 Days of curing in a 100% RH room) should be: Mix 8, Mix 508, Mix 50, Mix SF, and Mix ST CMT.

4.3 – SEM

When investigating the cured samples under the SEM in secondary electron mode, an image of the crystal forms can be captured. With the addition of silica, the type and population of CH will change. As the size of the silica particles increase, the amount of CH will increase. The CH found should be in an eroded form, reminiscent of crystals that dissolved in solution and transformed to CSH. As for the control mix with only straight cement, the CH will cover a larger area.

4.4 – Compressive Strength

From the samples to be tested, the strength of early specimens (1 - 7 day) will be dependent on the concentration of CSH, produced from $C_3S$, $C_2S$, and CH
(pozzolanically transformed). Mix 8 will have a considerably higher resistance to compressive loads due to the early CSHs formed. The contributions of early strength for all three mixes can be attributed to the cementitious and pozzolanic reaction but is also credited to the packing density of the larger nano particles found in the subsequent nano silica packages Mix 50 and Mix 508. For this reason, Mix 508, (combination of 8 and 50) will have a higher early strength than Mix 50. This increase in strength is due to the higher packing density from the greater size distribution of Mixes 8 and 508 that is absent in Mix 50.

Packing density is dependent on the size distribution of the nano particles left over from the reaction when a sample is tested. Larger particles in the mix that had not completely dissolved in solution will reduce porosity in the pores/capillaries of the CSH gel by packing into these voids. In doing so, the density of the CSH will increase in the plastic form and convert into a denser compressive bearing structure after hydration. The SF mix will also find some contribution to early strength but not as great as the strength developed from the CSHs formed in the nano mixes. Finally, the ST CMT mix compressive strength will fall below the previous mixes discussed in that the benefits from earlier pozzolanic reaction and packing density will not be present.
CHAPTER 5 – EXPERIMENTAL RESULTS AND INVESTIGATION

5.1 – Calorimetry

The heat of hydration curves determine the exothermic energy developed by the reaction of the cementitious and pozzolanic materials. Generally, an increase in CSH development will generate a higher heat of hydration. This increase in heat generation will represent a higher strength development (Mindess 65). A calorimetric chamber was used to store and record the change in temperature over time.

The calorimetric tests were conducted to characterize the heat of hydration curve differences. These differences were based on the constituents used in each mix. Figures 4 through 8 illustrate the change in temperature over a 49 hr period for each mix design.

5.2 – XRD

The data that was collected from the XRD qualified some of the phases that represented a larger population of the sample. Once the data was collected, it was run through Rietveld Software to quantify the population of each phase. Table 5 documents the changing CH (Portlandite) content for each specimen. Mixes are listed in Table 5 in the measured order of increasing concentration of CH.
5.3 – SEM

The SEM images were obtained to gain a real time representation of the effect of the nano particles on the hydrated cementitious samples. The object of this portion of the project was to recognize a tangible change in the amount of crystals formed. Figures 9 through 13 show the change of crystal forms from mix to mix. The crystals in question are CH and CSH. Observations of the prepared samples exposed the changing density/porosity of crystal forms. The grain structures were very similar between mixes except when identifying the CSH between the mixes with different nano-silica particle size distributions. Figure 14 shows the CSHs in Mix 8 while Figure 15 shows the CSHs in the Mix 508.

5.4 – Compressive Strength

The compressive strength tests were run as a method of quantifying the macro effects of the nano-particles. In the Appendix B a table is given listing values from averaged compressive strength tests from pairs of samples. Failure of a given specimen was characterized by a significant loss of material from the sample accompanied by the inability of the specimen to support 80% of the maximum load for an extended period of time. Figure 16 documents the stress and cure time relationship for the compressive stress tests on the mix designs used.
Figure 4 – Heat Signature, Mix ST CMT

Figure 5 – Heat Signature, Mix SF
Figure 6 – Heat Signature, Mix 8

Figure 7 – Heat Signature, Mix 50
Figure 8 – Heat Signature, Mix 508

Figure 9 – SEM of CH and CSH, Mix ST CMT
Figure 10 – SEM of CH and CSH, Mix SF

Figure 11 – SEM of CH and CSH, Mix 8
Figure 12 – SEM of CH and CSH, Mix 50

Figure 13 – SEM of CH and CSH, Mix 508
Figure 14 – SEM, CSHs from Mix 8

Figure 15 – SEM, CSHs from Mix 508
Figure 16 – Averaged Compressive Strength Data

Table 5 – Percentage of CH (Portlandite)

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Calcium Hydroxide ($\sim \pm 2%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>22.7%</td>
</tr>
<tr>
<td>SF</td>
<td>23.9%</td>
</tr>
<tr>
<td>508</td>
<td>24.9%</td>
</tr>
<tr>
<td>ST CMT</td>
<td>27.4%</td>
</tr>
<tr>
<td>50</td>
<td>27.5%</td>
</tr>
</tbody>
</table>
CHAPTER 6 – DISCUSSION

6.1 – Calorimetry

When comparing the predicted versus actual values for temperature, the governing feature was based on the particle size and distribution of the silica. The calorimetry data in Figures 4 through 8 validated that as the silica distribution incorporates smaller nano silica, there will be an earlier and greater heat generation. The ST CMT mix in Figure 4, which had no additional silica did not benefit from pozzolanic activity but served as a means of comparison. The mixture with SF, Figure 5, showed signs of delayed hydration. This same mix showed an increase in temperature later on after all the other mixes had reached a temperature plateau, indicating that the larger silica particles were still reacting after the nano particles.

The mix which incorporated a smaller particle size and therefore greater surface area to pozzolanically react, illustrated in Figure 6 (Mix 8) and Figure 8 (Mix 508) gives evidence of early reactivity. The wider distribution of these two nano silica packages contributed not only a greater amount of surface area due to the smaller sizes for early effects but also allowed for more silica to be available for later pozzolanic reactivity. This is evident in the longer time it took for the heat signatures to reach a temperature plateau. Mix 50 in Figure 7, with a tighter distribution, had a slower heat initiation than Mix 8 and 508. Mix 50 had the lowest average size; the size of these particles did not initiate pozzolanic reaction as fast as Mix 8 and 508. Both Mix 8 and 508 nano silica
packages had smaller particles with a greater surface area for reaction. These two nano silica packages also had a wider distribution of sizes. A well graded mixture of sizes can mix throughout covering more surface area of cement paste than a narrow distribution of sizes. For greater temperature gain, it is important to have not only the smallest particle but a well graded envelope of sizes. All three nano-silica mixes took a longer time to reach a heat plateau then the control mix, Figure 2 (ST CMT). This initiation of a temperature plateau can be attributed to the nano silica still available for pozzolanic reaction beyond the diffusion barrier.

6.2 – XRD

The documented XRD data in Table 5 validates the prediction that an inclusion of silica generates CSH production. The control or ST CMT mix gave a baseline to evaluate the micron silica and nano silica addition. Larsen recognized that the CH concentration is inversely related to CSH production. By increasing the production of CSH, less CH will be available for diffracting X-rays. As the silica size increases, the early production of CSH, from pozzolanic reaction reduces. This phenomenon captured in Table 5, documents the change of CH percentage for the mixes that contained nano silica packages. Mix 8, which had the smallest nano silica and a large distribution, had the least CH. This concept refers back to the greater surface area well graded size distribution can cover and react with, compared to a narrow distribution of sizes. As Larsen suggested, the smaller particle size and greater surface area reacted with CH in solution to produce more CSH. Less CH was available for diffraction. As particle size and distribution decreased, the CH concentration increased. Mix 508 and then 50 which
had larger particle sizes and tighter distributions had higher concentrations of CH indicative of less pozzolanic reactivity. Mix 50 which had the narrowest sized distribution had a CH concentration greater than the ST CMT mix. This suggests the importance of a wider distribution. The SF mix demonstrated how a wider distribution can have similar benefits to the nano silica mixes.

When reviewing the tabulated XRD data in Table 5, it was found that the SF produced less CH then the mixes with the nano particles. This could be due to the time at which the samples were tested. All mixes were cured for 52 days and then dried for 1 day before testing. As shown from the temperature curves in Figures 4 through 8, the SF mix was showing signs of significant heat exchange. Due to the SF size, the silica will not be readily available (compared to the nano silica) for pozzolanic reaction. Therefore the reduction in CH could be attributed to the later pozzolanic effects in Stage 5, where the nano silica could have been used up at this point. It was originally predicted that the Mix SF would produce more CH than all the nano-silica mixes. The lower value of CH can be attributed to a wider distribution of sizes that the SF has as compared to all three nano packages. Where the nano silica reacts rapidly in the presence of CH in solution, the SF reacts over an extended period of time. This extended period of reaction is a direct result of the time it takes for the CH in solution to absorb into the larger silica particle. All the samples were given a long time to cure. This cure time in conjunction with available silica could have facilitated CH conversion. In addition to these possible explanations for the low CH concentration in the Mix SF, the Rietveld analysis of the SF containing sample was probably unreliable because of an unidentified phase or phases.
(possible carbon or silicon) in the diffraction pattern. There was an insufficient number of peaks from this phase (or phases) to allow Rietveld analysis.

6.3 – SEM

All predictions and scenarios developed for the SEM were verified. The images collected and incorporated are not necessarily representative of the whole sample. Each sample was investigated to find any irregularities inconsistent with this project. The images reflected the change in structure of the highlighted crystals, CH and CSH. By viewing the crystallographic environment it was possible to understand why there was an earlier peak in the temperature profile for the smaller nano packaged mixes. Through use of EDX in conjunction with SEM it was possible to confirm the developed crystals in the images.

The control mix (ST CMT) showed a presence of CH that over-shadowed the development of CSH in Figure 9. The center of the image is dominated by the congestion of CH. The CSH looks porous and is littered with CH crystals. As the silica was added, the CH concentration lessened or was only visible in an eroded form embedded in CSH structural webs. From Figure 10 for the SF mix, the CH is still visible as the principal crystal in the shape of a wall overshadowing the CSH.

As the silica size decreased, the CSH was found to be more organized. Mix 8 yielded a grouping of CSH that formed into a network. The CH for Mix 8, pictured in Figure 11, can be seen as a small deposit in the CSH structure. The CSHs, shown in Figure 12 for Mix 50, also showed organization that was not present in the ST CMT and
SF mix; allowing for a greater resistance to compressive loads. Finally, Mix 508 gave way to a concentration of CH that was embedded beneath CSH structures.

For the smaller nano packaged mixes, the CSH concentration was greater and had a denser structure. The CH was difficult to find in concentration. As the nano particles decreased in size, larger CH became scarcer within the body of the specimen. The form of the CSH produced from the nano particles was visually more stable than the sample viewed for the ST CMT and SF mix. By magnifying the CSH structure until individual crystals were visible, the source of the benefit to CSH structure is apparent. Figure 14 (Mix 8) shows that with a smaller nano particle it is possible to generate a CSH that has a larger diameter. As silica size increased, the CSH crystal decreased in diameter. This phenomenon is visible when comparing Figure 14 to Figure 15 (Mix 508). The larger the silica particle, the smaller the diameter of the CSH, as shown in Figure 15 (Mix 508).

6.4 – Compressive Strength

The compressive strength results in Figure 16 confirmed the hypothesis developed based on nano silica size and distribution. For the early strength the ST CMT and SF mixes did not resist as great a compressive force as the nano silica mixes. With a wider gradation of sizes, the pore density, which acted as a weak link, was reduced. The nano silica is able to pack into the voids to give more resistance to compressive forces. As the silica size increases, as in the SF and ST CMT mix, there is less packing efficiency and therefore less compressive strength. The SF mix had a considerably lower early strength which can be attributed to the water that was intended for hydration was hindered by the
silica fume. This is supported by the low heat of hydration in the initial stages of hydration.

As particles are reduced in size, more surface area for pozzolanic reaction is available irrespective of the stages of cement hydration. With the onset of a higher concentration and more pure form of the CSH, there will be a final higher compressive strength when compared to those mixes without nano silica. From Figure 16 it is evident at 7 days that as the silica particle reduced in size, the CSH development was improved to resist higher compressive forces. The SF mix showed improvement in strength which is credited to the addition of silica and therefore pozzolanic activity. Mix 8 had the greatest strength at this point which is indicative of the CSH production with the smaller nano silica size and the widest size distribution. Mix 508 started showing signs of CSH production from the smaller particle size as in Mix 8. Finally, Mix 50 did not have a dramatic increase in strength, as the 508, due to the absence of the smaller nano silica.

The 28 day strengths from Figure 16, the mixes with SF, 50, and 508 leveled off most likely due to the exhaustion of nano silica, in the nano silica mixes and the initiation of reaction of the micron size silica from the SF mix. For Mix 508 and 50, the nano silica reaction slows due to a reduction in effective surface area. The SF mix shows a dramatic increase in strength which can be ascribed to the initiation of pozzolanic activity. Mix 8 exhibited the greatest increase in strength from the greater concentration of nano silica for converting CH to CSH. Finally, the ST CMT mix showed the least strength development. This lack of increased strength exemplifies the benefit of the addition of silica and more importantly nano silica.
CHAPTER 7 – CONCLUSIONS

From the experiments performed, it was validated that as the silica decreases in size and increases in size distribution, a number of properties begin to improve. Because the silica is on the nano scale, the crystal development becomes dependent on the availability of reactive silica surface area. When the silica diameter increases, the rate of early pozzolanic reaction decreases. Both nano and micron size silica particles were added at the same concentration. The nano silica was more effective, due to exposed surface area, in reacting pozzolanically. The micron silica would only react as silica became available. As the CH reacts with exposed micro silica, more silica will become exposed and ready to pozzolanically react. This phenomenon was shown through the early heat signature in the nano-silica mixes. If allowed to cure for an extended period of time the unhydrated silica will eventually pozzolanically react with the CH in solution, reducing CH concentration, increasing the concentration of the CSH structure and thereby increasing compressive strength. This observable fact was documented in the XRD and the compressive strength data. Finally, this report highlighted the experiments used and illustrated that by using nano silica with a wide distribution it is possible to generate a microstructure that can support a greater compressive load.


Balaguru, P., and Chong, K. Nanotechnology and Concrete: Research Opportunities. ACI SP-2008.


Christensen P. Structural and Ingredient Analysis of Concrete – Methods, Results, and Experience. Nordisk Betong. 1984.


# APPENDIX A

## CEMENT MILL TEST REPORT

Cement Identified as:

- **Plant**: CEMEX Lyons Cement
- **Location**: Lyons, CO
- **Production Dates**: Beginning: May 1, 2009, Ending: May 31, 2009

### STANDARD CHEMICAL REQUIREMENTS (ASTM C114)

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<th>Type II</th>
<th>ASTM C1157 SPEC.</th>
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<td>Silicon Dioxide (SiO₂), %</td>
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<td>20.2</td>
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<td>Aluminum Oxide (AI₂O₃), %</td>
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<td>Maximum</td>
<td>5.0</td>
<td>Maximum</td>
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<td>Ferric Oxide (Fe₂O₃), %</td>
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<td>Maximum</td>
<td>5.0</td>
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<td>Calcium Oxide (CaO), %</td>
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<td>Magnesium Oxide (MgO), %</td>
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<td>Maximum</td>
<td>6.0</td>
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<td>Sulfin Trioxide (SO₃), % **</td>
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<td>Maximum</td>
<td>3.5**</td>
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<td>Loss on Ignition (LOI), %</td>
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<td>Alkalies (Na₂O equivalent), %</td>
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<td>Tricalcium Silicate (C₃S), %</td>
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<td>Tetracalcium Aluminate (C₃A), %</td>
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<td>Minimum</td>
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<td>Ternary Aluminate (C₄AF), %</td>
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<td>(C₃S + 4.75C₃A) or (C₄AF + C₂F), %</td>
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<td>C₂O₂, %</td>
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<td>Heat of Hydration @ 7 day (Kcal/kg)</td>
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### PHYSICAL REQUIREMENTS

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**Note 1**: ASTM C150 allows for additional expansion as measured by ASTM C1030 does not exceed 0.005%.  
**Note 2**: Heat of hydration is provided for information only

CEMEX hereby certifies that this cement meets or exceeds the chemical and physical Specifications of:

- ASTM C150 - 07 for Type I Portland Cement
- ASTM C150 - 07 for Type II Portland Cement
- ASTM C1157 - 02 for Type GU Hydraulic Cement

By: [Signature]

**Anand Krishnan**  
Quality Control Manager  
CEMEX - Lyons Cement Plant

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### APPENDIX B

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