THE EFFECT OF NANOSILICA ON THE PROPERTIES OF PUMICE INCORPORATED BLENDED CEMENTS

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THE EFFECT OF NANOSILICA ON THE PROPERTIES OF PUMICE INCORPORATED BLENDED CEMENTS

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ABSTRACT

THE EFFECT OF NANOSILICA ON THE PROPERTIES OF PUMICE INCORPORATED BLENDED CEMENT

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Because of the high energy requirement and high CO\textsubscript{2} amount as a waste of burned CaCO\textsubscript{3} present in raw material, Portland Cement production is also responsible from the CO\textsubscript{2} emission among other responsible industries. In order to reduce such an energy consumption, use of portland cement clinker is aimed to be reduced in construction industry. For this aim, use of materials called pozzolan has become widespread.

Through the use of pozzolans, the amount of Portland Cement Clinker in structural concrete can be reduced. Mechanisms of pozzolan in mixtures are reaction of the pozzolan with the product of cement hydration and producing additional products that gives binding property to the paste. However, early age mechanical properties of the mixtures containing pozzolan are lower than that of the mixtures with no pozzolan. So, construction periods can be elongated because of the delays in form removal.

In this research study, early age strength values and some physical/chemical properties of the portland cement, pozzolan, and nanomaterial mixtures at different ratios have been examined on both paste and mortar specimens. Nanosilica and pumice powder have been used as nanomaterial and pozzolan respectively. Early age compressive strength values of the mixtures containing nanosilica have been observed as higher than that of mixtures not containing nanosilica. It is observed that 3% of nanosilica addition increased the early age compressive strength of natural pozzolan blended cements.

Keywords: Portland-pozzolan cement, natural pozzolan, pumice, nanosilica, early age strength.
ÖZ

NANOSİLİKA KULLANIMININ POMZA KATKILI ÇIMENTONUN ÖZELLİKLERİNE ETKİSİ

Dündar, Burak
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Aralık 2016, 90 sayfa


Puzolan kullanımı ile yapısal veya diğer amaçla üretilen bağlayıcı karışmlardaki portland çimentosu miktarı oldukça azaltılabilmektedir. Buradaki mekanizma, çimentosun su ile hidratasyon sonucu ortaya çıkan ürünlerle puzolanın tepkimeye girmesi ile yeni bağlayıcı bileşenlerin meydana gelmesidir. Ancak, puzolanın sonrası etki etmesi nedeniyle puzolan kullanılan karışılarnın erken yaş dayanımları kullanılmayanlarla göre düşük çıkabilmektedir. Bu nedenle, yapıların yapıp süreçleri kalıp sökme sürelerinin uzaması sebebiyle uzayabilmektedir.


Anahtar Kelimeler: Portland-puzolan çimentosu, doğal puzolan, pomza, nanosilika, erken yaş dayanımı.
To my parents,
Bilgin and Hüsamettin Dündar,
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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>ACI</td>
<td>American Concrete Institute</td>
</tr>
<tr>
<td>AP</td>
<td>Artificial Pozzolan</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society of Testing and Materials</td>
</tr>
<tr>
<td>EN</td>
<td>European Norms</td>
</tr>
<tr>
<td>CEMBUREAU</td>
<td>The European Cement Association</td>
</tr>
<tr>
<td>CH</td>
<td>Calcium Hydroxide</td>
</tr>
<tr>
<td>CNF</td>
<td>Carbon Nano Fiber</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nano Tube</td>
</tr>
<tr>
<td>CSH</td>
<td>Calcium Silica Hydrate Gel</td>
</tr>
<tr>
<td>GBFS</td>
<td>Granulated Blast Furnace Slag</td>
</tr>
<tr>
<td>HRWR</td>
<td>High Range Water Reducer</td>
</tr>
<tr>
<td>METU</td>
<td>Middle East Technical University</td>
</tr>
<tr>
<td>MIP</td>
<td>Mercury Intrusion Porosimetry</td>
</tr>
<tr>
<td>MS</td>
<td>Micro Silica</td>
</tr>
<tr>
<td>NC</td>
<td>Nano Calcite</td>
</tr>
<tr>
<td>NF</td>
<td>Nano Ferrite</td>
</tr>
<tr>
<td>NMK</td>
<td>Nano Metakaolin</td>
</tr>
<tr>
<td>NNI</td>
<td>National Nanotechnology Initiative</td>
</tr>
<tr>
<td>NP</td>
<td>Natural Pozzolan</td>
</tr>
<tr>
<td>NS</td>
<td>Nano Silica</td>
</tr>
<tr>
<td>NT</td>
<td>Nano TiO(_2)</td>
</tr>
<tr>
<td>OMMT</td>
<td>Organo-modified Montmorillonite</td>
</tr>
<tr>
<td>OPC</td>
<td>Ordinary Portland Cement</td>
</tr>
<tr>
<td>SCC</td>
<td>Self Consolidated Concrete</td>
</tr>
<tr>
<td>SCM</td>
<td>Supplementary Cementitious Material</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SF</td>
<td>Silica Fume</td>
</tr>
<tr>
<td>SP</td>
<td>Superplasticizer</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray Fluorescence</td>
</tr>
</tbody>
</table>

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CHAPTER I

INTRODUCTION

1.1 General

Concrete is a mixture of Portland cement, aggregate and mixing water generally. For varying purposes some admixtures are also often added to the mixture. These are generally called as mineral admixtures and chemical admixtures. In recent years, nano admixtures are also getting attention in the production of concrete.

Mineral admixtures are used to improve the durability of concrete and to reduce the amount of Portland cement clinker which is relatively expensive and responsible from the CO$_2$ emission among the other responsible industries. Chemical admixtures are generally used to arrange rheological or some mechanical properties of concrete. Nano admixtures are still studied for the aim of determining the advantages.

Utilization of PC alone in a concrete mixture can impose some drawbacks such as high heat of hydration and formation of high amount of calcium hydroxide (CH) which is a threat for durability of concrete. Use of pozzolans as a mineral admixture can help to reduce the heat of hydration and CH content. As Portland cement hydrates, calcium-silica-hydrate gels (CSH) and CH are formed. Pozzolans react with the CH to produce additional CSH which is major binding agent in the concrete. Moreover, heat evolution of pozzolanic reactions is less than cement hydration. Therefore, less heat is generated in the body of concrete mass where excessive heat can be serious problem such as expansion, cracking or loss of design strengths. As pozzolans provide such advantages, they also have some drawbacks. For example, with the use of pozzolan, early age compressive strength generally becomes lower than that of the concrete which includes Portland cement alone as a binding material.
Nano materials, nowadays, are being studied to compensate these drawbacks of pozzolans. They can act as binder, filler or seed for the start of hydration. Because of their quite fine particle size, inter-particle size of CSH gels and capillary voids are expected to be smaller. Until now, although some studies showed that these expectations have been met, there is still need to investigate these materials from many perspectives.

1.2 Objective and Scope

The objective of this thesis is to investigate the effect of nano silica (NS) as nano admixture on some mechanical properties of paste or mortars prepared with pumice incorporated blended cements. Moreover, in order to observe the effect of pumice fineness on the strength development, the same pumice having two different fineness values were used together with NS in blended cement production.

This thesis which is about the nanomodification of pumice blended cement mixtures contains 5 Chapters. First, a brief introduction of the topic is handled in first chapter. Later, theoretical background is explained with the literature review on this subject in the second chapter. In the third chapter, methodology is expressed with the details of materials and techniques used during the experiments. Results of tests and experiments are given and discussed in the fourth chapter. Finally, all study and its results are summarized and some recommendations for further studies are given in the last chapter.
CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Portland Cement

Portland cement (PC) is the binding material used in construction industry and produced from calcareous and clayey materials. These raw materials are calcined together and pulverized to obtain Portland cement. PC has been used for long years. The product of “Portland cement” was first invented by a brick layer Joseph Aspdin in Leeds, England in 1824. The word “Portland” was originated from the stones that were quarried and brought to Leeds from a small island called Portland. This stone seemed like Joseph’s cement. So, the license of this cement was obtained with the name of “Portland cement” (Erdoğan, 2009).

The raw materials of cement are calcareous rock (limestone) and clayey materials. These raw materials are blended in certain proportions according to the design properties. This mixture is calcined to approximately 1400 °C in the rotary kiln after all raw materials are ground. After calcining, clinker is obtained. Cooled clinker is ground with a small portion of gypsum rock. The end product is “Portland cement”.

A typical Portland cement includes some oxides in its form (Table 1). The proportions of these oxides play roles in the formation of the compound compositions in the kiln and the formation of calcium-silica-hydrate gels which are binding agent in the Portland cement pastes, mortar or concrete.
After the calcination of the raw material in the rotary kiln, clinker is produced as an end product. Clinker consists of the compounds (Table 2) originated from the oxides included in raw materials. Most of the mechanical and chemical properties of the concrete are affected by the compound proportions. In the kiln, oxides of the raw materials react together to produce compounds that directly affect the properties of cement. These compounds are mainly tricalcium silicate (C$_3$S), dicalcium silicate (C$_2$S), tricalcium aluminate (C$_3$A), and tricalcium alumino ferrite (C$_4$AF).

### Table 1. Oxides in the Portland cement

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Common Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>Lime</td>
<td>C</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Silica</td>
<td>S</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Alumina</td>
<td>A</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>Iron</td>
<td>F</td>
</tr>
<tr>
<td>MgO</td>
<td>Magnesia</td>
<td>M</td>
</tr>
<tr>
<td>Na$_2$O and K$_2$O</td>
<td>Alkalis</td>
<td>N and K</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>Sulfuric Anhydride</td>
<td>S</td>
</tr>
</tbody>
</table>

### Table 2. Major compounds in a typical Portland cement clinker

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Formula</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium Silicate</td>
<td>3CaO.SiO$_2$</td>
<td>C$_3$S</td>
</tr>
<tr>
<td>Dicalcium Silicate</td>
<td>2CaO.SiO$_2$</td>
<td>C$_2$S</td>
</tr>
<tr>
<td>Tricalcium Aluminate</td>
<td>3CaO.Al$_2$O$_3$</td>
<td>C$_3$A</td>
</tr>
<tr>
<td>Tricalcium Alumino Ferrite</td>
<td>4CaO.Al$_2$O$_3$.Fe$_2$O$_3$</td>
<td>C$_4$AF</td>
</tr>
</tbody>
</table>
Portland cement is the main binder of concrete, which is known as the most widely used construction material in the world. According to the activity report of CEMBUREAU in 2014, 4.3 billion tons of cement was produced in the world. In other words, approximately 600 kg of cement was produced per person in 2014. Turkey had the share with 72 million ton production (Activity Report, 2014).

This huge amount of production brings some environmental concerns. The energy required in the cement production plants is much bigger among the other industries responsible for the CO₂ emission in the world. Intergovernmental Panel on Climate Change says that cement industry is responsible for the CO₂ emission in the world with the share of 7% among other industries in the report on Carbon Dioxide Capture and Storage (Metz et al., 2005). These concerns are tried to be overcome with use of alternative binder materials also called supplementary cementitious materials (SCM). In recent years, research studies on the use of pozzolans in high volumes with cement become popular. However, some drawbacks of use of SCM are still a research topic to solve these problems.

2.1.1 Hydration of Portland Cement

As the desired properties, strength and durability of concrete directly rely on the hydration kinetics of main compounds. Their hydration starts after cement and water are mixed. Each compound produces different product end of the hydration. Degree of hydration also differs from compound to compound.

2.1.1.1 Hydration of C₃S and C₂S

Most of the binding products are created by the hydration of the C₃S (alite) and C₂S (belite). Their products are CSH gels and calcium hydroxide (CH). In addition to this, heat is evolved during the hydration reactions. Hydration reactions can be shown by the following equations below:

\[ 2C_2S + 4H \rightarrow C_3S_2H_3 + CH \]
\[ 2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \]
C₃S₂H₃ is called the tobermorite gel because of its structural similarity to a naturally occurring mineral with this name. This calcium-silica-hydrate gel is simply called CSH gels. CSH is the main agent providing binding and load carrying value to the concrete. Other product CH has little or no contribution to strength. On the other hand, CH can cause serious durability problems during the life time of concrete. While C₃S reacts with water to produce CSH gels even after mixing water added to the cement, C₂S reacts slowly with the water. So, strength contribution rate and heat evolution are less than that of C₃S. Figure 1 illustrates the heat of hydration of C₃S. This heat evolution can be separated into 4 periods: initial reaction, slow reaction, acceleration period, and deceleration period.

![Figure 1](image_url)

*Figure 1. Rate of C₃S hydration as a function of time given by isothermal calorimetry measurements (Bullard, 2011)*

### 2.1.1.2 Hydration of C₃A and C₄AF

C₃A and C₄AF are very similar according to their hydration process. C₃A reacts with water immediately after mixing to produce some alumino oxides. Rapid hydration of C₃A results in early stiffening of the cement paste. This is called “flash set”. The
reason why gypsum rock is added to the clinker after formation in the kiln is the prevention of flash set. With the rapid reaction of $\text{C}_3\text{A}$, great heat is evolved. $\text{C}_3\text{A}$, gypsum rock and water may transform to two different products as shown below:

\[
\begin{align*}
\text{C}_3\text{A} + \text{C}\overline{\text{S}}\text{H}_2 + 10\text{H} & \rightarrow \text{C}_4\text{A}\overline{\text{S}}\text{H}_{12} \\
\text{C}_3\text{A} + 3\text{C}\overline{\text{S}}\text{H}_2 + 26\text{H} & \rightarrow \text{C}_6\text{A}\overline{\text{S}}_3\text{H}_{32}
\end{align*}
\]

$\text{C}_4\text{A}\overline{\text{S}}\text{H}_{12}$ is called calcium alumino monosulfohydrate which is not stable in the presence of additional gypsum and moisture. This additional gypsum may come from internal or external sources during the life time of concrete. When additional gypsum reacts with $\text{C}_4\text{A}\overline{\text{S}}\text{H}_{12}$ more $\text{C}_6\text{A}\overline{\text{S}}_3\text{H}_{32}$ formation takes place in the concrete body. $\text{C}_6\text{A}\overline{\text{S}}_3\text{H}_{32}$ is commonly called as “ettringite”. When ettringite forms, a great expansion occurs. If this expansion occurs while mixture is still plastic, there exists no problem. However, with the presence of further gypsum, formation of ettringite in the concrete body can cause serious cracking. This reaction can be shown below:

\[
\text{C}_4\text{A}\overline{\text{S}}\text{H}_{12} + 2\text{C}\overline{\text{S}}\text{H}_2 + 16\text{H} \rightarrow \text{C}_6\text{A}\overline{\text{S}}_3\text{H}_{32}
\]

2.1.2 Products of Hydration of Portland Cement

At the end of all hydration processes of main compounds, there exist new products in the hardened cement paste. These are CSH gels, CH, monosulfohydrates, and ettringite except voids and unhydrated cement particles. CSH is poorly crystalline, nearly amorphous material. Molecular size of CSH is 1000 times smaller than that of a Portland cement particle. It occupies approximately 60% by volume of cement paste (Raki et al., 2010). CH does not contribute to strength but it arranges the pH balance in the hydrated cement paste. It is in crystalline form. The share of CH in the cement paste can be achieved to 20%. Other products monosulfohydrate and ettringite has the share of 20% in the paste. Ettringite can be eventually transformed into monosulfate. Likewise, monosulfohydrate can transform into ettringite in the presence of gypsum and moisture. This would be a reason to make concrete vulnerable to the harmful environment effects (Mehta and Monteiro, 2006). Besides these, there are also unhydrated cement particles in the microstructure of cement.
paste. This depends on the particle sizes of cement used. Firstly, finer particles react with water. Bigger particles may not have reacted with water completely. Figure 2 illustrates relative rate of formation of the hydration products in the paste.

![Diagram illustrating the formation of cement hydration products in the cement paste (ACI 225R-99)](image)

**Figure 2.** Diagram illustrating the formation of cement hydration products in the cement paste (ACI 225R-99)

### 2.2 Pozzolans

Pozzolan is defined by ACI 116R, “a siliceous or siliceous and aluminous material, which in itself possesses 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.” Pozzolans generally includes high amount of silica and alumina. In addition to this, they usually include small amounts of iron oxide, calcium oxide, magnesium oxide and alkalis.

According to their contribution to the mechanical properties of concrete like producing CSH gels and strength gain, pozzolans are characterized by pozzolanic
activity. As the pozzolanic activity is higher, the type of pozzolan is inferred as being a good pozzolan to be used in concrete mixture. Pozzolanic activity of a pozzolan depends on the content of “SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$” in its composition, the degree of amorphousness of its structure, and the fineness of its particles (Erdoğan, 2009).

2.2.1 Natural Pozzolans

Natural Pozzolan is defined as in the ACI232.1R:

“...either a raw or calcined natural material that has pozzolanic properties (for example, volcanic ash or pumicite, opaline chert and shales, tuffs, and some diatomaceous earths).”

Natural pozzolans (NP) react immediately with the CH. There is a rapid decrease in the CH amount in the paste. Secondly, there exists a formation of CSH gels. When compared to the mixtures with Portland cement alone, there will be more CSH and less CH in the hydrated cement pastes including NP. In addition to the increased CSH gels, there will also be mechanical and chemical durability advantages with the use of NP.

NP is generally used directly without any process like calcining. However, in order to make use of pozzolanic activity of NP, they are usually interground with the clinker for a certain period of time required for achieving to the intended fineness level. Elimination of calcining process provides a more anti-pollutionist solution to the concrete industry. Obtaining NP and using it in concrete as replacement for Portland cement, will decrease the CO$_2$ emission from production of unit concrete. Therefore, carbon footprint of cement can be reduced with the use of natural pozzolans.

Some mechanical and chemical properties of NP directly affect the properties of concrete. Particle size distribution, particle shape, density, and chemical composition influences the properties of fresh and hardened concrete. Because of the finer particle sizes and high surface area water requirement will be higher according to that of PC alone mixtures. Moreover, use of natural pozzolan can help to reduce bleeding
problem in fresh state. Typical NPs and their chemical analysis are summarized in Table 3 (Tokyay, 2016).

Table 3. Typical chemical analysis of some natural pozzolans (Tokyay, 2016)

<table>
<thead>
<tr>
<th>Type</th>
<th>Reference</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>CaO</th>
<th>MgO</th>
<th>Na2O</th>
<th>K2O</th>
<th>TiO2</th>
<th>SO3</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyroclastic (Incoherent)</td>
<td>Costa and Massaza (1974)</td>
<td>53.08</td>
<td>17.89</td>
<td>4.29</td>
<td>9.05</td>
<td>1.23</td>
<td>3.08</td>
<td>7.61</td>
<td>0.31</td>
<td>0.65</td>
<td>3.05</td>
</tr>
<tr>
<td></td>
<td>Takemoto and Uchikawa (1980)</td>
<td>71.77</td>
<td>11.46</td>
<td>1.14</td>
<td>1.10</td>
<td>0.54</td>
<td>1.53</td>
<td>2.55</td>
<td>0.14</td>
<td>-</td>
<td>6.50</td>
</tr>
<tr>
<td></td>
<td>Meral (2004)</td>
<td>76.57</td>
<td>9.99</td>
<td>0.96</td>
<td>0.51</td>
<td>0.03</td>
<td>-</td>
<td>5.58</td>
<td>-</td>
<td>0.04</td>
<td>5.23</td>
</tr>
<tr>
<td>Pyroclastic (Coherent)</td>
<td>Eroğdu (1996)</td>
<td>48.52</td>
<td>17.49</td>
<td>7.80</td>
<td>7.84</td>
<td>1.41</td>
<td>5.20</td>
<td>3.10</td>
<td>2.02</td>
<td>0.29</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>Meral (2004)</td>
<td>76.57</td>
<td>9.99</td>
<td>0.96</td>
<td>0.51</td>
<td>0.03</td>
<td>-</td>
<td>5.58</td>
<td>-</td>
<td>0.04</td>
<td>5.23</td>
</tr>
<tr>
<td></td>
<td>Eroğdu (1996)</td>
<td>48.52</td>
<td>17.49</td>
<td>7.80</td>
<td>7.84</td>
<td>1.41</td>
<td>5.20</td>
<td>3.10</td>
<td>2.02</td>
<td>0.29</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>Massaza (2004)</td>
<td>54.68</td>
<td>17.70</td>
<td>3.82</td>
<td>3.66</td>
<td>0.95</td>
<td>3.43</td>
<td>6.38</td>
<td>-</td>
<td>-</td>
<td>9.11</td>
</tr>
<tr>
<td>Clastic (Diatomaceous Earth)</td>
<td>Johansson and Andersen (1990)</td>
<td>75.60</td>
<td>8.62</td>
<td>6.72</td>
<td>1.10</td>
<td>1.34</td>
<td>0.43</td>
<td>1.42</td>
<td>-</td>
<td>1.38</td>
<td>2.15</td>
</tr>
<tr>
<td></td>
<td>Mielenz et al. (1950)</td>
<td>85.97</td>
<td>2.30</td>
<td>1.84</td>
<td>-</td>
<td>0.61</td>
<td>0.21</td>
<td>0.21</td>
<td>-</td>
<td>-</td>
<td>8.29</td>
</tr>
<tr>
<td></td>
<td>Tonak (1995)</td>
<td>84.24</td>
<td>4.75</td>
<td>0.91</td>
<td>0.94</td>
<td>0.26</td>
<td>0.15</td>
<td>0.25</td>
<td>-</td>
<td>0.09</td>
<td>8.47</td>
</tr>
<tr>
<td></td>
<td>Aruntaş et al. (1998)</td>
<td>88.32</td>
<td>3.47</td>
<td>0.48</td>
<td>0.42</td>
<td>0.26</td>
<td>0.17</td>
<td>0.28</td>
<td>0.18</td>
<td>-</td>
<td>5.84</td>
</tr>
</tbody>
</table>

2.2.2 Artificial Pozzolans

Fly ash (FA), condensed silica fume, granulated blast furnace slag (GBFS), burned clay, and rice husks ash can be accepted as examples of artificial pozzolans (AP). Their difference from NP is being obtained with use of artificial processes except grinding. Almost all AP are exposed to some sort of a heat process. Although that heat process takes place in the formation of AP, they are still anti-pollutionist solution to the concrete industry since they are generally by-product of several industries.
AP differs from NP according to their chemical compositions, particle sizes, molecular structures or mode of production. FA, GBFS, and silica fume (SF) are the most widely used APs.

2.2.3 Pozzolanic Reaction

In a cement paste, when the pozzolanic material exists in finely divided form, some chemical reactions will start in the presence of water. For a while, there is only cement hydration producing CSH gels and CH. After formation of CH, siliceous portion of pozzolan reacts with CH. So, additional CSH gels are obtained and already present CH is reduced with the pozzolanic reaction as shown below:

\[
\begin{align*}
2C_2S + 4H & \rightarrow C_3S_2H_3 + \text{CH} \\
2C_3S + 6H & \rightarrow C_3S_2H_3 + 3\text{CH}
\end{align*}
\]

This retardation of obtaining CSH gels may result in low compressive strength in early ages of concrete, and of course there would be less heat of hydration. This may be an advantage for the cases where low heat of hydration is desired, but especially in projects where rapidity is important this retardation becomes a serious problem. Therefore, this study focuses on this problem coming from the use of pumice as a mineral additive in the Portland cement composites.

In the past studies, the various effects of pozzolanic reactions can be seen. Turanlı et al. (2005) used volcanic tuff in various proportions and examined mechanical properties of cement pastes and mortars. According to the test results, final setting times of blended cement with replacement of 35% and 45% were increased substantially. Similarly, heat of hydration was decreased with use of pozzolan (Figure 3). According to the XRD analysis applied after 90 days of hydration of samples of blended cement with 55% addition of volcanic tuff, CH was not observed. All blended cements showed a great resistance to sulfate attacks and alkali-silica reactions.
2.2.4 Pumice

Pumice is one of the ancient construction material with its light-weight, porous structure, high isolation capacity and high pozzolanic activity. In ancient Rome and Greek periods, pumice was used widely and the structures created with pumice are still stable.

Pumice is called as ponza in Italian, bimsslein in German, pomza in Turkish. The pumice is also called as pumatic in the literature. It is pyroclastic type natural pozzolan (Table 3). The material is called as pumice if it is in form of gravel or bigger particle sizes. It is called as pumicite if it is in sandy form or smaller particle sizes (Gündüz, 1998). A typical view of pumice is demonstrated in Figure 4.

Pumice is used in most industries such as construction, textile, agriculture and chemical. The pumice is most widely used by the construction industry both in Turkey and the world. Although, Turkey has a big portion of pumice reserves of the world, it is not used effectively. The share of 40% of 18 billion ton of pumice reserves in the world exists in the Turkey (Gündüz et al., 2005).
The extent of pumice use in construction industry can be summarized as; producing lightweight building components, prefabricated building components, lightweight plastering, roof covering and decorative elements, and lightweight concrete. Pumice is used as an aggregate in production of lightweight concrete. Because of the porous structure of pumice aggregate, concrete made with it would have a low density (Figure 5). In addition, it is also used as a pozzolanic mineral admixture when it is in a finely divided form to replace Portland cement portion in the cement paste.

The main chemical composition of pumice can be encountered as 60-75% SiO$_2$, 13-17% Al$_2$O$_3$, 1-3% Fe$_2$O$_3$, 1-2% CaO, 7-8% Na$_2$O-K$_2$O and trace amount of TiO$_2$ and SO$_3$ (DPT, 2011). Because of its high SiO$_2$ content and amorphous structure, pumice is an appropriate pozzolanic material. It provides more economic and ecologist concrete production. In the literature, use of pumice as pozzolanic mineral admixture widely becomes a topic of many researches.

Hossain (2003) examined cement based and lightweight concrete based properties of pumice. In this research, pumice was used as both mineral admixture in the powder form and coarse aggregate for the lightweight concrete production. As a SCM, pumice was added to cement with the ratios of 0% and 25%. As a coarse aggregate, it was used with various ratios between 0 to 100%.

Figure 4. Typical view of pumice (Wikipedia, 2006)
2.3 Nanotechnology in Civil Engineering

The term nanotechnology implies atomic and molecular scale production of constructions, materials and some items. This provides measuring, prediction or monitoring in a scale of nano-materials. In recent years, nanotechnology can be seen in varying industries such as electronic, bio-mechanic, or mechanical engineering. This technology can also be seen in the construction industry nowadays. With the use of some nanomaterials, mechanical properties of concrete is being tried to be efficient.

U.S. National Nanotechnology Initiative (NNI) defines the word nanotechnology as:
- Nanotechnology covers the research and technology progresses at the 1 nm to 100 nm range.
- Nanotechnology creates and uses structures that have novel properties because of their small size.
- Nanotechnology builds on the ability to control or manipulate at the atomic scale.
In order to understand nanotechnology better, it can be given as a good example that the specific human hair strand is approximately 80,000 nm in width. Another example can be the difference between the radii of a small mill and the world. If we assume the radius of a toy marble as 1 nm, the radius of the world would be 1 m. These materials having nano-scale particles are called “nanomaterial” or “nanoparticle” (Birgisson et al., 2012).

Nanomaterials can be divided into two types: non-intentionally made nanomaterials and intentionally made nanomaterials. Non-intentionally made nanomaterials indicate the materials naturally occurring in the environment without any process by human activity (proteins, viruses etc.). Intentionally made nanomaterials are accepted as the materials obtained by any kind of processes of human activity. Nanotechnology is about only intentionally made nanomaterials (Filipponi et al., 2007).

Nano phases of materials differ from their bulk phases. Their mechanical properties such as strength, melting, yielding etc. are different because of the molecular attractions and external forces. In the nano scale, gravitational forces are accepted as negligible because of low mass of particles. There exist electromagnetic forces as dominant force. This force determines the molecular behavior of materials. Electromagnetic forces are attraction or repulsion force between objects and depend on their charges. Furthermore, nanoparticles have very large surface areas. This results in chemical reactivity of material. All these nano scale properties play important role influencing macroscopic level. So, with this technology it is possible to change nature of materials in various industries. Such that, if atoms will be able to be bound and formed into new formation molecules with the control of computers, diamond base materials from coal atoms, computers smaller than bacteria or more complex structures will be possible to be achieved (Phoenix et al., 2003).

### 2.3.1 Production

Nanotechnology considers two types of production techniques: top-down and bottom-up approach. Powdered form materials having nano scale particle sizes, can
exhibit very different behavior than the same material having greater particle size (macro-scale). In order to obtain specific behavior of these nanoparticles, not only particle sizes should be ensured as in nano scale, but also these particles should be dissolved in the solution homogeneously without flocculation (agglomerate). This homogeneous dissolution is the most critical process of nanomaterial production without flocculation of these materials produced with the several techniques such as gaseous phase condensation, liquid phase precipitation, sol-gel technique and hydrothermal synthesis (Tsuzuki et al., 2004).

2.3.1.1 Bottom-Up

Bottom-up approach resembles the producing nanomaterial atom by atom. This approach is also called self-assembly. This production generally occurs naturally with biological processes (Figure 6). DNA double helix can be given an example of this approach. In this technique, sub-units or atoms get into together spontaneously and in the regular formation to produce nano scale material (Filipponi et al., 2007).

Bottom-up production is classified according to the phase of the material. These are gaseous phase technique, liquid phase technique and solid phase technique (Kayır et al., 2010).

![Figure 6. Schematic of bottom-up and top-down approach (Filipponi et al., 2007)](image-url)
2.3.1.2 Top-Down

Top-down approach resembles producing nanomaterial from the bulk mass of this material. This method disperses the bulk structure and builds the new nano-structure. This method does not examine the atomic scale formations. The advantages of this method are being inexpensive, large scale process capacity, and possibility to achieve 2-20 nm particle sizes. Disadvantages of the method are producing irregular nanoparticles, introduction of defects, and mixing some impurities from balls or other milling agents. Beside the ball mill technique, other technique is the photolithography.

2.3.2 Nanomaterials used in Construction Industry

Construction industry among other industries follows the recent development of nanotechnology and tries to implement the development into itself. Use of nanoparticles in construction materials is getting popular day by day. With the use of nanoparticles, not only properties of material such that strength, durability but also photo-catalytic (Lackhoff et al., 2003), sensation to stress changes (Hui et al., 2004) properties would be gained to the concrete body. In recent years, many studies focusing on nanomaterials in construction materials have been conducted.

Nanotechnology taking place in the literature of concrete and other cement base composites can be categorized into four groups: investigation and modification of nano-structure of CSH gel, providing controlled release of chemical additives into concrete mix, cement based composites including carbon nano-tubes, and cement systems including nanoparticles (Raki et al., 2010).

There are a lot of studies known on nanomaterials providing strength (Campillo et al., 2007), more durable concrete (Cardenas et al., 2006), self-cleaning, stainless, anti-microbial concrete (Lackhoff et al., 2003), anti-fog property and sensing property (Hui et al., 2004). Nanoparticles influence the cement hydration in varying ways in cementitious systems. They act as a seed catalyzing start of hydration. Also, they can provide greater particle packing with decreasing pore ratio in the concrete.
By means of the smaller particle size of nanoparticles, pores in nanoscale dimensions can be eliminated.

Concrete is a brittle material and it is probable to form cracks. Cracks start from the nano-scale dimensions. Then these cracks get bigger and bigger. So, this formation results in micro-cracks and macro-cracks. The last few years, microfibers are started to be used in order to eliminate the micro-cracks to get bigger macro-cracks. However, formation of nano-cracks cannot be eliminated by this solution. In this point, nano-scale solutions should be investigated. Nanoparticles can stop the transformation of nano-cracks to micro-cracks by producing additional CSH gels and providing greater particle packing.

The effects; acceleration of hydration of cement grains, increasing the degree of hydration at a certain age, increasing early age strength while improving the micro-structure of hardened system at early ages were proved by researches in the literature. (Raki et al., 2010; Lee and Kurtis, 2012) These effects of nanomaterials have importance for potential of solving early age strength reduction problem of mixtures containing cement clinker and high volume mineral admixture. Therefore, CO₂ emission coming from Portland cement production can be eliminated by using nanomaterials. Nonetheless, there are still drawbacks needing to be investigated such as high water demand, high energy required for dispersion of nanoparticles. So, further studies should be conducted on these problems.

In order to take advantage of nanomaterials, having knowledge of challenges for the application of them in cement based system is important. The first challenge is to produce nano-size particles used in mixtures. The other drawback is the heat of hydration. Due to high specific surface areas the nanoparticles are very reactive and causes high amount of heat of hydration. However, despite this high heat evolution, reduction of cement portion in the mixes with mineral admixtures provides less heat of hydration ultimately. Nevertheless, in order to take control, some organic or inorganic chemical additives can be used.
2.3.2.1 Nano CaCO$_3$

CaCO$_3$ (calcite or calcium carbonate) can be found in marble, chalk, limestone or it is produced intentionally and artificially. Nano calcium carbonate is produced with CH in deionized water solution and CO$_2$ as raw materials in a gas-liquid-solid reactant system (Pour and Moghadam, 2014). The reaction equation can be shown as:

$$\text{Ca(OH)}_2(\text{solid}) + \text{CO}_2(\text{gas}) + \text{H}_2\text{O(liquid)} \rightarrow \text{CaCO}_3(\text{solid}) + 2\text{H}_2\text{O(liquid)}$$

Nano calcite (NC) may have average particle diameter as 15-40 nm. Correspondingly, the specific surface area can reach to almost 24-32 m$^2$/g (Liu et al., 2012). Scanning electron microscope (SEM) images of nano and micro CaCO$_3$ (MC) particles are shown in Figure 7. (Raki et al., 2010) According to that case study, while the average particle diameter of the micro CaCO$_3$ was approximately 5 to 20 μm, that of nano calcite is about 50 to 120 nm.

![SEM image of (a) MC and (b) NC (Raki et al., 2010)](image-url)
NC is one of the newly researched nanomaterial as a construction material. There is limited knowledge about NC in the literature. Until now, the research studies on hydration ratio, setting time, early age compressive strength value and heat of hydration properties of NC particles were conducted.

MC was used as accelerator for the early age strength development before. Although calcite usage was first applied as filler to replace cement or gypsum, the results of several studies showed that calcite have a great effect on the compressive strength development in early ages with increasing rate of hydration. In a recent study, this effect of finely ground calcite was verified (Ramachandran and Zhang, 1986). According to the results, calcite was very effective in increasing the compressive strength in early ages. The higher the calcite amount, the higher was the rate of hydration. This effect was especially on C₃S. This effect of calcite with the developments in the nano science built up passion on researchers to study nano effect of calcite.

![Graph](image.png)

*Figure 8. Rate of heat development of blended cement pastes with OPC, FA, MC and NC measured by calorimeter (Sato et al., 2007)*
In a study, different cement pastes with addition of FA as SCM and with NC were investigated. Figure 8 shows the rate of heat development of four different samples. These values were measured by the conduction calorimeter. The heat development of the ordinary Portland cement (OPC) and FA blend with 50% replacement is much lower than that of 100% OPC (sample 1). When MC was added to the blended cement with 50% replacement (sample 3), a slight acceleration was monitored compared to sample 2. When NC particles were used in sample 4, the rate of heat development was significantly accelerated. This means an increase in early age strength (Sato et al., 2007).

### 2.3.2.2 Carbon Nano Tubes

The most commonly used nano tubes are carbon nano tubes (CNT), discovered by the Japanese Scientist Sumio Iijima in 1991 (Iijima, 1991). After a short time, in order to produce bulk amounts of CNT, arc-evaporation systems were built. These nanotubes were the multilayered CNT. CNT are obtained from graphene sheets (Figure 9).

*Figure 9. Schematic view of single wall and multiwall CNT (Iijima, 1991)*
In addition to CNT, there are also nano-test tubes, nano-fibers, and nano-horns. Nano-horns are in conic shapes and single walled. They have significant catalytic and adsorptive capacities. Nano horns are foreseen as super material that is used in fuel cells. Nano test tubes are generally used in medical fields as being filled with biological materials such as biological molecules. Nano fibers could become the ultimate carbon nano fibers because of their stiffness, very high strength, purity, and aspect ratio (Belaguru and Chong, 2006).

CNT and Carbon Nano Fibers (CNF) have potential for being used as nano reinforcements in cement based composites. CNT and CNF show excessive strength with elastic modulus of the range of TPa and tensile strength in the order of GPa. They have useful chemical and electronic properties (Srivastava et al., 2003; Salvetat et al., 1999; Ajayan, 1999). Concrete has a brittle structure because of its low tensile. There are several ways to overcome this problem. Some types of fiber are used to increase tensile strength and to improve durability. CNT connect two cracked cement hydrates face with high bond strength. They provide a load transfer in tension as acting as a bridge between cracked surfaces. (Makar, 2005; Li et al., 2005).

In the literature, it is possible to see that tensile and flexural strength of cement based composites can be raised up by the help of CNT with low ratios (e.g., 0.025 % by weight of cement). It is also pointed out that with low concentration of CNT (e.g., 1% by weight of cement) compressive strength of composites can be increased (Mann, 2006).

In another research, the addition of CNT (up to 0.02 %) to blended cement and nano metakaolin (NMK) mortar increased the compressive strength. The increase in compressive strength by use of CNT with the ratio of 0.02 % was 11% higher than that of blended mortar containing only 6% NMK. However, as the ratio of CNT increases (e.g. 0.1 %), compressive strength decreases (Morsy et al., 2011).

Macro-fibers and microfibers have been studied in cementitious system by some researches. It was proved that they acting as bridge with load transfer mechanism can delay crack propagation (Makar, 2005). Although, they delay the cracking, they do
not stop the beginning of cracking. CNF can help in this point to prevent nano-cracks initiation by setting a bond with cement hydration products. In a research study, in order to increase flexural strength of cement base composite significantly, optimum CNF amount was found as 0.048% by weight of cement (Metaxa et al., 2010). It was also noticed that homogeneous distribution of CNF is common concern to achieve these advantages. Manzur and Yazdani (2010), in their study, examined mixing techniques and workability issues of cement mortar with different types of multiwall CNT. They tried the sonication mixing technique. They claimed that in order to achieve high compressive and tensile strength, mixing water and CNT should be mixed by sonication through at least 5 min.

The reason why uniform distribution is difficult is strong van der Waals force among nano-fibers (CNT and CNF). Use of SP is suggested to overcome dispersion problem. The nano-fiber can be uniformly distributed in water with the help of ultrasonic process and admixture. Nevertheless, even use of SP in water-nano-fiber solution does not ensure uniform distribution. It is also suggested that highly dispersible nano-fibers should be used to achieve more uniform distribution in paste (Nasibulina et al., 2010).

2.3.2.3 Nano TiO$_2$

Titanium dioxide (TiO$_2$) is another type of the nanomaterials used in construction industry. It is in white powder form and used for generally reflective purposes. Nano TiO$_2$ (NT) is applied generally outdoor surfaces; unlink the organic ingredients in coating, flying organic pollutants, and bacterial substances. There exist severe catalytic reactions. From this point, NT is utilized outdoor surfaces with its self-cleaning property. It collects all the pollutants coming from outside or interior of the cover, on the surface, and when rain water attaches the surface washes them off. Furthermore, because of its white color, resulting concrete is also white in color; and NT with its hydrophilic property retains the concrete clean and white (Srivastava et al., 2011).
There are commercially available cements and concretes containing NT in Turkey, Japan and Europe. They are used generally for the covering purposes in the building and sometimes for concrete pavements. The performance of NT based concretes can be tested with ultraviolet light representing natural light levels. Self-cleaning property of NT based products were studied by Enea and Guerrini (2010). They examined the performance of mineral pigments containing NT in varying colors. These pigments were mixed with hydraulic lime and cement. The mixtures were applied as building covers and exposed to several tests. They put forth that covering material containing these pigments can provide better maintenance for especially historic buildings and better reduction capacity of pollution to covering in urban environments.

### 2.3.2.4 Nano Fe₂O₃

Another nano material providing compressive and flexural strength increase with the particle size about 30 nm is nano Fe₂O₃ (NF). It has also property of stress sensing in the body of concrete. This property was investigated with the changing electrical resistance of cement mortar specimens including NF. It was observed that as the load applied was increased, a change in electrical resistance was monitored (Li et al., 2004). Especially, with 5% NF addition, significant observation was obtained. The electrical resistance was seemed to be decreased, while compressive strength was increasing. From this point of view, concrete including NF can be accepted as self-sensing concrete determining its own compressive strength level. This outcome can be a starting point for innovated building industry to get rid of embedded sensors for the aim of instant structural health monitoring (Birgisson et al., 2012).

In a research study, the effect of NF on concrete specimens has been studied (Nazari et al., 2010). According to the results, compressive strength could be increased significantly with addition up to 2% NF in to cement. It was found that optimum NF amount was 1% by weight of cement. As the cement replacement with NF was increased, workability of fresh concrete was seemed to be influenced negatively. It was originated with the high specific surface area of nano material. This negative effect can be overcome with use of SP.
2.3.2.5 Nano Clay

Montmorillonite is the raw material of nano clay. This clay mineral occur flatty in nature. Each flat plate is in approximately 1 nm. Montmorillonite is water soluble, i.e. hydrophilic. Main constituents are SiO$_2$ and Al$_2$O$_3$ in clay (Patel, 2012).

Nanotechnology uses also clay as nanomaterial for obtaining self-consolidating concrete (SCC) in slip form paving. In order to achieve self-consolidating level, mix should be workable enough. Beside workability, stiffness of the fresh mix is expected to be good as being stand without formwork. So, in slip form paving it is desired to obtain concrete having slump value less than 5 cm. In ordinary slip form pavements, concrete is exposed to an internal or external vibration process for better consolidation. However, there may exist anomalies such as segregation, surviving large trapped voids or undesirable particle packing. These may be caused by incorrect vibration frequencies or by mix design properties. In literature there are several studies (Shah et al., 2008; Tregger et al., 2010) that show that there is no need for the vibration process in slip form pavements. The main difficulty in development of SCC is necessity to obtain both fluid and very stiff fresh concrete. The solution of this problem relies on changing the microstructure for great particle packing, using adequate admixture and controlling rheology. Above studies showed that using small amount (%1 by weight of cement) nano clay and Class C FA helped to obtain intended flowability and stiffness during the placing and compacting of concrete mix. The shape and surface smoothness of nano-modified concrete was observed as better than that of ordinary SCC concrete specimens.

Some other studies showed that nano clay has the potential to eliminate chloride penetration, to reduce permeability and to improve mechanical properties of concrete (Kuo et al., 2006; Chang et al., 2007; He and Shi, 2008; Morsy et al., 2009). As a kind of polymer and clay composite, organo-modified nano clay was employed as filler and reinforcement in cement mortars (Kuo et al., 2006). Other type of nano-clay (Montmorillonite) cannot be used as directly as reinforcement because of its hydrophilic structure. Water dissolves the Montmorillonite as infiltrating between the silicate sheets of clay. This causes expansion and harmful durability problems.
Organo-modified montmorillonites (OMMT) can be employed to increase strength and decrease permeability. With a small amount of OMMT (less than 1% by weight of cement) can help to reduce permeability 100 times lower. These nanoparticles place around capillary pores and prevent aggressive chemicals and pore solutions from diffusing in hydrated structure. Decreased porosity can be also seen in Mercury Intrusion Porosimetry (MIP) results. In the presence of 0.4 and 0.6% of nano-clay in cement paste, 13.24% of increase in compressive strength and 49.95% decrease in coefficient of permeability were observed (Chang et al., 2007).

In the literature, it is also possible to see another type of nano clay named “nano-sized smectite clays” acting as nucleation unit for formation of CSH gels (Kroyer et al., 2003; Lindgreen et al., 2008).

2.3.2.6 Nano Silica

In the last decade, beside carbon nano tubes, nano titanium, and nano alumina nano SiO$_2$ (NS) has become another popular topic of nanotechnology. In fact, NS is mostly studied nanomaterial, because hydration mechanism of NS in concrete is still not well known. Nowadays, researchers are studying NS with the awareness of improvement effect of NS on mechanical and permeability properties of cement based composites including NS as mineral admixture.

Micro silica (MS) and nano sized silica can fill the voids between cement particles. With optimum mix design, denser mixes with low water demand can be achieved. Denser hydrated pastes have less porosity, so compressive strength can be higher. Beside physical effect, NS has greater pozzolanic activity than that of MS or SF. So, high performance concrete can be produced in the presence of these two effects of NS (Zapata et al., 2013). The key parameter to achieve these advantages is homogeneous dispersion of NS particles into cement paste. Unless NS particles are not distributed homogeneously, there will be voids and weak zones in the hydrated structure.
The hydration rate can be increased by use of NS. When NS contacts with cement particles, there exists $\text{H}_2\text{SiO}_4^{2-}$ and this output reacts with \( \text{Ca}^{2+} \) present in the paste to create additional CSH (Figure 10). These additional CSH are solved in water and fill the voids between the cement particles and caused denser CSH formation. This effect is named as seeding effect. Additional CSH formation not only takes place among cement particles but also takes place in other type of voids. Thus, a great number of seeds accelerate the hydration of cement paste. In the literature, there exist several studies that exhibit the accelerated hydration and early CH formation by adding NS into cement composites (Senff et al., 2009; Land et al., 2012; Ltifia et al., 2011; Madani et al., 2012).

![Reaction kinetics of cement based composites including NS](image)

The summaries of the research studies on NS use in cement based composites in the literature can be listed as above. In these studies, mechanical and micro structure properties were analyzed with the use of NS and other nano materials. Researchers revealed that mechanical performance and micro structure properties of the samples including NS even in small amounts (1-5%) has improved significantly (Li et al., 2004; Zhang and Li, 2011). The results showed that NS acted as filler and triggered the mechanism that improving the microstructure. So, void ratio was seen as decreasing with the use of NS. They also examined the effect of homogeneously dispersion of NS and noticed that homogeneously dispersion was very efficient to
achieve these advantageous effects of NS. They also proposed the necessity of carrying out further studies on finding optimum mix proportion of NS.

Luciano et al. (2009) focused on the rheological properties of cement pastes including NS. In the presence of 2.5% NS in the paste with fixed values of water to cementitious material ratio and fixed SP amount, a great decrease was observed in the lubricating water in the paste. NS affected the cohesiveness of the paste as enhancer, so, decrease in spread diameter of mortar samples on the flow table was observed. They also reported that dormant period is reduced by adding NS. With 2.5% NS addition, setting time was reduced 60% and the duration to maximum hydration temperature was decreased 52.3%. Moreover, CH formation was observed with the X-ray diffraction (XRD) test results. According to these test, CH formation was started already after 9 hr. This duration was much less than that of mixtures without NS.

Beside the mechanical properties, physical and microstructure properties of concrete including NS were examined in the literature with varying tests such as water absorption, permeability, porosity, calorimetric analysis, thermos-gravimetric analysis and XRD. Use of NS was revealed as reason of decreasing detrimental pores. So, decrease in porosity and water adsorption was identified as effects of NS (Nazari and Riahi, 2010).

The effect of NS on the heat of hydration of cement pastes is significant. According to the results in the literature, the formation time of primary and secondary peaks coming from calorimetric test results of mixtures containing NS is significantly lower than only cement mixtures (Stefanidou et al., 2012). This effect can be linked through the acceleration mechanism of NS in the hydration process. According to the thermogravimetric analysis (TGA) results in the high temperatures, mixtures containing NS loose more mass than mixtures without NS. This means there had been existed more hydration products in mixtures containing NS. Moreover, by the SEM observations researchers realized that NS particles had formed into seed form that creates crystal shape structure around themselves by the hydration. They claim
that this homogeneously distributed tight micro structure originated from NS particles provide high compressive strength to concrete.

2.3.3 Hydration Mechanisms of Nanomaterials

A large knowledge on the behavior of concrete has been developed over the past 150 years (Mehta, 1986). With widely usage of nano materials in concrete composites, hydration mechanism of nano-cement composites has become curiosity in literature. The following steps that we saw from cement hydration mechanism help to understand the hydration of nano-cement composites (Balaguru and Chong, 2006):

- 1 mm$^3$ of cement releases about 2 mm$^3$ of volume after the hydration is completed.
- There exist three main components: Calcium Silicate Hydrate (CSH), Calcium Hydroxide (CH) and Calcium Sulfo-Aluminates (ettringite or CS). CSH covers 50 to 60% of total volume of hydrated structure whereas CH and Calcium Sulfo-Aluminates take the 20 to 25% and 15 to 20% respectively.
- CSH sheets are less than 2 nm in size. The voids between the CSH sheets differ from 0.5 to 2.5 nm. CSH particles coming in together to form a mass can reach 1 to 100 nm. Spacing between the particles in a mass differs from 0.5 to 3 nm.
- The surface area of CSH varies 100 to 700 m$^2$/g and the predominant strength of CSH is van der Waals forces.
- The other product CH has a typical width approximately 1000 nm.
- Calcium Sulfo-Aluminates have striped type structure and they are unstable.
- Adsorbed water can exists in hydrated cement paste. About 1.5 nm thick (nearly 6 molecules of water) can be connected by hydrogen bonding. Most of this water can evaporate with drying at regular relative humidity.
- Capillary voids vary from 10 to 1000 nm in size. Pore size can reach maximum 100 nm in an ideally hydrated cement paste with optimum water cement ratio.
- The small hydration products including CSH, calcium aluminate hydrates and calcium sulfo-aluminates present great surface areas. They have great
adhesive capability. They hold aggregate particles and un-hydrated cement particles.

- With the presence of nano additives there exists pozzolanic reaction and seeding property for CSH formation (Figure 10). These reactions reduce capillary voids and consume CH to transform into CSH.
- Particle size affects the heat of hydration dramatically. While Blaine fineness of ordinary cement is around 320 m²/kg, surface areas of nano additives vary from 25 m²/g to 500 m²/g.
- The zone where active hydration takes place is around 2000 nm thick (Figure 11). Because of the high surface area and their small particle sizes nano additives fill into the gel layer. They start and accelerate the hydration by seeding effect. They also accelerate pozzolanic reaction where mineral additive is present.
- With the accelerated hydration mechanism, heat of hydration can raise again a certain amount (Figure 8).
- Higher early age compressive strength is obtained by the acceleration effect of nano materials.

![Details of hydrating cement grain at nano-scale](image)

*Figure 11. Details of hydrating cement grain at nano-scale (Balaguru and Chong, 2006)*
2.4 Research Studies on Nanomodification of Blended Cements in Literature

Energy consumption in cement industry compels the material science to achieve a more environmentally friendly production steps. For this aim, varying kinds of mineral admixtures are intended to be replaced with cement in concrete mix designs. However, mineral additives come together with several disadvantages. In the last decade, these disadvantages are being overcome with use of nanomaterials. So, there exist many studies analyzing effects of nanomaterials on performance of concrete containing mineral admixtures. In terms of performance criteria, mostly used and most effective nano additive is seemed to be NS. Thus, the literature review focuses mostly on NS addition to the blended cements.

Hou et al. (2013) have tried to add FA and NS both separately and together. When these additives were added to cement separately, FA decreased early age strength compared to control specimen, and NS increased the early age strength. When these additives with high FA proportion were added to the mix together, decrease in early age strength with FA addition was observed as being overcome with accelerating effect of NS on hydration.

Other researchers studying combined effect of FA and NS examined the hydration kinetics and saw that formation of peaks on the heat of hydration graph were observed as being achieved earlier (Said et al., 2012). TGA results show that FA and NS combination increased the CH consumption significantly. Moreover, MIP test results showed that NS addition even in small proportions had a great effect on pore structure and total pore volume. This inference has been supported with chloride ion penetration tests. According to the results, permeability and transmission through concrete body was almost eliminated.

In some other studies, GBFS and NS were used as combination. Researchers focused on hydration, setting time, strength gaining, and other mechanical properties of blended cements (Zhang and Islam, 2012; Nazari ve Riahi, 2011). Lag duration in hydration of blended cement containing only GBFS is shortened by use of NS. As being in the use of FA, NS increases the CH consumption amount and rate in use of
GBFS in concrete. Thus, similarly with FA-NS combination, NS increases the CSH amount in the hydrated matrix and increases the compressive strength of concrete, especially in early ages. Heikal et al. (2013) have also seen that 3-4% NS addition into the blended cement with 45% GBFS was observed as giving the optimum mechanical properties. According to the results, increasing NS amount decreased both free lime formation and pH value. Furthermore, 4% NS addition showed increases in both compressive and flexural strength. However, NS addition more than 4% ended the strength increase and started to decrease strength values.
CHAPTER III

EXPERIMENTAL PROGRAM

3.1 General

In order to investigate the effect of nano silica (NS), fineness and replacement rate of pumice on some mechanical properties of pumice incorporated blended cements, test procedures listed in this chapter were planned to be conducted. For this aim, an experimental program has been developed. According to the program, firstly, optimum NS ratio has been determined in preliminary experimental testing. After this stage, final test program was planned on a large frame.

3.1.1 Materials

This study focuses on the tests made on mortar and paste specimens. So, materials used are cement, pumice, nano silica (NS) as cementitious materials, sand, and mixing water. All the materials having binding properties were subjected to several tests for their chemical and physical characterization. Chemical analysis was conducted as X-ray fluorescence (XRF) and spectrophotometer according to the standard TS EN 196-2 (Table 4). As the physical analysis, particle size distribution of these materials and Scanning Electron Microscope (SEM) images of NS were obtained. All these tests were handled at R&D Institute of Turkish Cement Manufacturers Association (T.C.M.A.).

Portland cement was obtained from the plant of ÇİMSA Company in Ankara. Portland cement is labeled as CEM I 42.5R according to the TS EN 197-1.
Table 4. Chemical composition of cementitious materials used

<table>
<thead>
<tr>
<th></th>
<th>CEM I 42.5R</th>
<th>Pumice (Coarse)</th>
<th>Pumice (Fine)</th>
<th>Nano SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOI</td>
<td>5.12</td>
<td>4.27</td>
<td>4.31</td>
<td>-</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>18.63</td>
<td>61.99</td>
<td>62.27</td>
<td>99.17</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>4.55</td>
<td>15.58</td>
<td>15.70</td>
<td>0.38</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>3.05</td>
<td>4.91</td>
<td>4.94</td>
<td>0.04</td>
</tr>
<tr>
<td>CaO</td>
<td>62.74</td>
<td>1.41</td>
<td>1.18</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>1.58</td>
<td>0.19</td>
<td>0.18</td>
<td>0.21</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>2.66</td>
<td>0.08</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.26</td>
<td>6.21</td>
<td>6.09</td>
<td>0.09</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.53</td>
<td>4.81</td>
<td>4.63</td>
<td>-</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>-</td>
<td>0.30</td>
<td>0.30</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>0.0474</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Pumice was obtained from the region of Van-Erciş. In this thesis, two different pumice having different particle sizes with different grinding duration were handled to observe the effect of particle size of mineral admixture in the cementitious system. Coarser pumice was ground throughout 250 minutes in the rotary mill by suppliers. Finer pumice has the grinding duration of 500 minutes. Their particle size distribution and their comparison with Portland cement and nanomaterial can be seen in Figure 12. Their chemical analysis results are almost similar.

NS was obtained commercially. The particle size distribution test result above is not reliable for the NS. In the test nano particles can flocculate, so mean particle size can be larger than actual size.
All the experiments were conducted on mortar or paste specimens. So, only fine aggregate which is obtained from Set Cement Company, Trakya Factory was used. The reasons why this sand was selected are to provide same particle size distribution and particle surface texture for all mixtures and to eliminate possible differences in the mechanical and mineralogical properties of specimens caused by difference in properties of different sands. CEN standard sand is rounded in shape and produced from natural silica sand. According to the TS EN 196-1, silica content should be 98% at least, and particle size distribution should comply with the chart shown in Table 5.

Use of NS is known to decrease the workability of mixtures significantly. Therefore, in order to improve the workability of mixtures, Glenium 51, high range water reducing admixture (HRWR – polycarboxylate ether as an active ingredient with 1.1 specific gravity and 40 % solid content) produced by BASF Construction Chemicals was used.
Table 5. Particle size distribution of CEN reference sand according to TS EN 196-1

<table>
<thead>
<tr>
<th>Square Mesh Dimension (mm)</th>
<th>Cumulative Retained (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>0</td>
</tr>
<tr>
<td>1.60</td>
<td>7±5</td>
</tr>
<tr>
<td>1.00</td>
<td>33±5</td>
</tr>
<tr>
<td>0.50</td>
<td>67±5</td>
</tr>
<tr>
<td>0.16</td>
<td>87±5</td>
</tr>
<tr>
<td>0.08</td>
<td>99±1</td>
</tr>
</tbody>
</table>

As mixing water, tap water of METU Materials of Construction Laboratory was used.

3.1.2 Preliminary Experimental Testing

In order to determine the optimum NS ratio, uniaxial compressive strength tests were conducted. For this reason, a test set was created as summarized in Table 6. The initiated pumice ratios planned to be tested were 15, 30, and 45% by weight of cement and the one aim of the study was to determine the effect of fineness of pumice (ground for 250 min (coarser) and ground for 500 min (finer)) on some mechanical and microstructural properties of cementitious composites. So, this preliminary test was carried out with blended cement with coarser pumice with 25% replacement. NS was added in 1, 2, 3, 4, and 5% ratios to the mixtures containing 30% pumice. There was also a control mix containing only 25% coarser pumice (Table 6).
Table 6. Mix proportions of preliminary test samples

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Cement (%)</th>
<th>Pumice (Coarse) (%)</th>
<th>Nano SiO₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>75.0</td>
<td>25.0</td>
<td>-</td>
</tr>
<tr>
<td>1% Nano SiO₂</td>
<td>74.2</td>
<td>24.8</td>
<td>1.0</td>
</tr>
<tr>
<td>2% Nano SiO₂</td>
<td>73.5</td>
<td>23.5</td>
<td>2.0</td>
</tr>
<tr>
<td>3% Nano SiO₂</td>
<td>72.8</td>
<td>24.2</td>
<td>3.0</td>
</tr>
<tr>
<td>4% Nano SiO₂</td>
<td>72.0</td>
<td>24.0</td>
<td>4.0</td>
</tr>
<tr>
<td>5% Nano SiO₂</td>
<td>71.2</td>
<td>23.8</td>
<td>5.0</td>
</tr>
</tbody>
</table>

The tests were carried out in accordance with the Turkish Standard TS EN 196-1 and ASTM C109. Mixture ratios, fix w/cm value were set according to TS EN 196-1, mixing, molding and curing were carried according to the ASTM C109. For all six mixture proportions, similar mixture proportions were selected. For each mix design of mortars, 450 g cementitious material (75% of PC and 25% of pumice powder), 1350 g CEN standard sand, and 225 g water were proportioned for the test samples. To provide an optimum workability, 7 g HRWR was added to each mixture to provide a similar microstructure due to the addition of HRWR.

**Mixing Procedure:**

NS addition to the mortar specimens (1, 2, 3, 4, and 5 % by weight) was provided by the ultrasonic mixing technique (homogenizer) in the mixing water. The device used during this procedure is Sonics Vibra Cell VCX 600 Ultrasonic Homogenizer with Probe 600 Watt (Figure 13).

All mixtures were mixed with standard mixer. First, mixing water of the samples including NS went through the process of homogenizing for homogeneous distribution of NS to the water. Homogenizing duration was selected as 5 min based on the applications in literature (Manzur and Yazdani, 2010; Yeşilmen et al., 2015).
All of the mixing water was mixed with the NS addition by homogenizer. At the fourth minute, dry mix (sand, Portland cement, and pumice) was prepared and mixed for 1 min in the mixer bowl at a low speed. Then, mixing water including NS was added to the dry mix. After mixing water was added, entire mixture was mixed for 1 min with slow speed, and 2 min with fast speed. HRWR was added to entire mixture after 1 min slow mixing. Entire mixture was mixed with HRWR only for the last 2 min of fast mixing.

After all mortar mixtures were prepared, they were molded into 50*50*50 mm cubic molds. Molding and placing the mortars were performed according to ASTM C109. Molded mortars were placed into the curing room having 95±3 % relative humidity.

Mortar specimens were removed from the mold 24 h after mixing. Unmolded specimens were placed into water tank for being cured. Water cured specimens were exposed to uniaxial compressive strength test at the ages of 2 and 7 days (Table 7).
Table 7. Uniaxial compressive strength test results of the 50*50*50 mm mortar cube specimens

According to compressive strength test results, increase in compressive strength was observed in all NS additions at both ages. However, most significant increase was seen in the results of the specimen including 3% NS by weight of PC (Table 7). With addition of 3% NS, 38.4% increase in compressive strength at the age of 7 days and 36.6% increase at the age of 2 days were observed.

Finally, decisive and optimum NS content was accepted and considered as 3% by weight of PC. Because, this point was accepted as the best decisive point showing the effect of NS on blended cement with pumice with different replacement ratios and different particle sizes, in the remaining studies, 3% NS addition was only used.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Specimen No.</th>
<th>2 Days Result</th>
<th>7 Days Result</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#1</td>
<td>#2</td>
<td>#3</td>
</tr>
<tr>
<td>Control</td>
<td>13.1</td>
<td>14.4</td>
<td>12.7</td>
</tr>
<tr>
<td>1% Nano SiO2</td>
<td>16.1</td>
<td>16.5</td>
<td>17.8</td>
</tr>
<tr>
<td>2% Nano SiO2</td>
<td>18.0</td>
<td>15.8</td>
<td>17.5</td>
</tr>
<tr>
<td>3% Nano SiO2</td>
<td>17.4</td>
<td>19.5</td>
<td>17.9</td>
</tr>
<tr>
<td>4% Nano SiO2</td>
<td>17.9</td>
<td>18.1</td>
<td>18.3</td>
</tr>
<tr>
<td>5% Nano SiO2</td>
<td>16.1</td>
<td>18.0</td>
<td>16.3</td>
</tr>
</tbody>
</table>
3.1.3 Final Test Program

The mix proportions were designed at 3 different mineral admixture groups with two different fineness values and a control sample with/without nano admixture. The aim of the program is both to determine the effect of NS on the cementitious composites including pumice as mineral admixture with different ratios, and to observe differences in mechanical properties of composites with the different mineral admixture ratios and with different fineness. Besides these, control samples with only cement and with NS addition were also designed for observing the effects of both mineral and nano additives (Table 8). Therefore, the main parameters are fineness of pumice, replacement ratio, and presence of NS.

As can be seen in Table 8, pumice was tested with 3 different ratios 15, 30, and 45%. Preliminary compressive strength test was carried out with 25% mineral addition with coarser pumice and NS in different ratios (1-5%). According to the results, 3% NS addition was found to be the most effective on compressive strength test results. Therefore, NS amount was fixed as 3% for all mix proportions.

The amount of ingredients seen in Table 8 was calculated according to standard mix proportioning and standard w/cm ratio given in TS EN 196-1. Amount of chemical admixture was found as 7 g as optimum value in the preliminary compressive strength test. For some tests such as determining heat of hydration, paste samples were prepared without any sand and chemical admixture.
### Table 8. Mix Proportions of the Final Test Program

<table>
<thead>
<tr>
<th>Control</th>
<th>15% Mineral Additive</th>
<th>30% Mineral Additive</th>
<th>45% Mineral Additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement (%)</td>
<td>Pumice (Fine) (%)</td>
<td>Pumice (Coarse) (%)</td>
<td>Nano SiO₂ (%)</td>
</tr>
<tr>
<td>100% (450 g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>97% (436.5 g)</td>
<td>3% (13.5 g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>85% (382.5 g)</td>
<td>15% (67.5 g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>82% (369 g)</td>
<td>15% (67.5 g)</td>
<td>3% (13.5 g)</td>
<td></td>
</tr>
<tr>
<td>85% (382.5 g)</td>
<td>15% (67.5 g)</td>
<td></td>
<td>3% (13.5 g)</td>
</tr>
<tr>
<td>82% (369 g)</td>
<td>15% (67.5 g)</td>
<td>3% (13.5 g)</td>
<td></td>
</tr>
<tr>
<td>70% (315 g)</td>
<td>30% (135 g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>67% (301.5 g)</td>
<td>30% (135 g)</td>
<td>3% (13.5 g)</td>
<td></td>
</tr>
<tr>
<td>70% (315 g)</td>
<td></td>
<td>30% (135 g)</td>
<td></td>
</tr>
<tr>
<td>67% (301.5 g)</td>
<td></td>
<td>30% (135 g)</td>
<td>3% (13.5 g)</td>
</tr>
<tr>
<td>55% (247.5 g)</td>
<td>45% (202.5 g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52% (234 g)</td>
<td>45% (202.5 g)</td>
<td>3% (13.5 g)</td>
<td></td>
</tr>
<tr>
<td>55% (247.5 g)</td>
<td>45% (202.5 g)</td>
<td></td>
<td>3% (13.5 g)</td>
</tr>
<tr>
<td>52% (234 g)</td>
<td>45% (202.5 g)</td>
<td>3% (13.5 g)</td>
<td></td>
</tr>
</tbody>
</table>

#### 3.1.4 Sample Notations

According to the mix design, all samples including different ingredients with different proportions were entitled as seen in Figure 14.
3.2 Test Procedures

Preliminary experimental tests were conducted for determining test mix proportions. After deciding the mixing techniques and replacement rate of NS, workability (flow table) test, flexural and compressive strength test, heat of hydration analysis, XRD analysis and thermogravimetric analysis were conducted for the final mixtures. Preliminary experimental tests were carried out in Gazi University Material of Construction Laboratory. All remaining parts of the study were carried out in METU Materials of Construction Laboratory.
3.2.1 Preparation and Curing

The mixing procedure was a little different from the standard ASTM C305. The same mixing procedure with the preliminary experimental testing (section 3.2.1) was conducted while test specimens were prepared.

The prepared mortar was molded into prism molds having dimensions of 40*40*160 mm. After the molding stage, specimens were placed in curing room that has 95±3% humidity. Moreover, wet fabrics were also spread on the specimens (Figure 15). 24 hr later, specimens were demolded and immersed into lime saturated water tanks.

Figure 15. Molded mortar samples (a) and curing technique (b)

3.2.2 Consistency

The mortars prepared for the compressive strength test were tested also for workability on the flow table. These tests were carried out according to the standard
ASTM C1437-13. According to the standard, a flow mold was placed on the flow table. Placement was executed in two layers. The flow mold was centered on the flow table, then mortar was poured into the mold till 25 mm thickness and then mortar was tampered 20 times. After that, mold was filled entirely with the mortar and tampered as again 20 times. After mold was filled with mortar, mortar was cut off to a plane surface with a spatula. Then, mold was wiped carefully. Finally, table was dropped 25 times in 15 s immediately after removal of mold. After spreading finished, two perpendicular diameters were measured and their average diameter was taken as slump flow diameter.

### 3.2.3 Strength

In order to determine compressive strengths of mortar specimens, two broken pieces of specimens broken in the flexure (ASTM C348) were used. Both flexure and compressive strength tests were carried out with the universal testing machine (UTM) (Figure 16) in the materials of construction laboratory of METU. The loading rate was 1.5 kN/s.

![Figure 16. Assembly of flexural and compressive strength tests. (a) Flexural test specimen, (b) splitted specimen, (c) compressive test specimen, (d) test device screen](image-url)
For each mix proportions, prepared specimens at the ages 2, 7, 28 and 90 days were tested under compressive strength test after broken in flexure. As compressive strength test sample, both pieces can be used unless the piece was less than 65 mm in length. So, one of the pieces which is taller than other and not having any detectable deflection was used in compression.

UTM device gives the compressive load and compressive strength values simultaneously. The approach that helps to reach strength value is given in the standard ASTM C349. The dimensions of the plate that crushes the broken pieces are 40*40 mm. The area which is exposed to compression load is 1600 mm$^2$. The device calculates the compressive strength value as ultimate force divided by the surface area according to the standard:

$$f = \frac{P}{A}$$

f: Compressive Strength (MPa)
P: Force (N)
A: Area (mm$^2$)

Each sample having different mix proportions were tested 3 times with 3 different samples. Recording differing by more than 10% from the average value of all 3 tests were omitted. When two of three reading differed from the average, retest was applied.

3.2.4 Heat of Hydration

The heats of hydration of all mixtures designed were observed by the calorimeter device in Material of Construction Laboratory in METU. The brand of device is called Tam Air Calorimeter. Operating temperature range of Tam Air Calorimeter is 5-90$^\circ$C. There exist eight Calorimetric Channels. This allows 8 observations simultaneously.

Eight calorimetric channels are combined together to form a calorimeter tool (single heat - sink block) embedded in a temperature controlled air thermostat. Each
calorimetric channel is designed as two sections; one section for the sample and the other section for a reference. The Figure 17 illustrates this twin configuration.

![Diagram of twin configuration of one of eight calorimetric channels](image)

**Figure 17. View of twin configuration of one of eight calorimetric channels (TAM Air Calorimeter Manual, 2007)**

During measurement, the sample and reference materials are held in 20 ml volume ampoules. Solids, liquids or slurries may be studied. In this study, slurry based mixtures was tested. The calorimeter block as well as the ampoule holders is made of aluminum, which has been anodized to withstand corrosion. Measurements are recorded continuously and in real time through an eight-channel data logger, which is connected to a computer (Figure 18).
Each calorimetric channel is constructed in twin configuration with one side for the sample and the other side for a static reference. Each calorimeter operates using the heat flow principle. Heat created by any physical or chemical reaction in the sample will flow rapidly to its surroundings.

Within each calorimetric channel, there are two heat flow sensors—one under the sample and one under the reference. The main route for heat exchange between the sample and its surrounding is through the heat flow sensor. The flow of heat, caused by the temperature gradient across the sensor, creates a voltage signal proportional to the heat flow (TAM Air Calorimeter Manual, 2007).

The eight twin calorimetric channels are held together in the calorimeter block. The sample and the reference calorimeters of each channel are accessed from above for loading through inlets marked A and B on the insulated thermostat lid. The ampoule
holding the sample is placed inside A, and the reference ampoule into side B. The difference in heat flow between the sample and the reference is monitored, i.e., side A minus side B. Thus, an exothermic process in side A (the sample) results in positive heat flow values.

### 3.2.5 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) method relies on the principle of diffraction of X-ray within characteristic order created by atomic pattern of specific crystalline phase of a material. This diffraction profiles for each crystalline phase specifies a crystal like a fingerprint. XRD method does not demolish the sample and it provides an analysis for samples even in much small amounts. For the aim of observing completeness of hydration and quality and quantities of hydration products, hydrated cement paste samples were ground into the powder form. These samples were then analyzed representing all mixture proportions (Table 8). Each sample was prepared at the ages 2, 7, 28 days.

XRD analysis was conducted with the device named as Olympus BTX II Benchtop in Material of Construction Laboratory in METU. The BTX II has the capability to realize XRD and XRF analysis for powder samples. XRD range of the device is 5 - 55° 2Ø. It can provide an accuracy provided by the large and expensive lab machines. Sample preparation is very simple with approximately 20 mg sample and finer than 150 µm particle sizes.

### 3.2.6 Thermogravimetric and Differential Thermal Analysis

Thermogravimetric (TGA) and differential thermal analysis (DTA) was conducted with Perkin Elmer Diomand TG/DTA device at İzmir Institute of Technology (İYTE) Center for Material Research. The TGA/DTA system provides the flexibility of DTA with the capabilities of the TG analysis technology, giving proper information for samples in the temperature range from 25-1200 °C. The simultaneous TGA/DTA system can be used for such applications as oxidation, heat resistance, and amount of bound water, compositional analysis and the measurement
of ash content in a sample. By this test results, bound water, CH, and CaCO₃ amounts in the paste samples were obtained.

As the result files of TG/DTA analysis, heat flow vs. sample temperature and weight of sample vs. sample temperature graphs can be obtained (Figure 19). The fluctuation in the heat flow vs. sample temperature gives the idea about the ratio of CH and CaCO₃ in the paste sample. The four readings (degrees) on the first graph is read as shown in Figure 19. The first couple of temperature degrees (~415-475 °C) show the decomposition of CH in the structure of paste sample. By the same way, second couple of temperature degrees shows that CaCO₃ in the paste sample decomposed between these two degrees. The difference between two weight readings according to these temperatures from the second graph gives the weight of water of CH and weight of CO₂ respectively.

While temperature is increasing, initial weight of sample decreases step by step. First, bound water evaporates after 100-105°C. Theoretically, difference between the weight reading at the temperature 105°C and initial weight gives initially existing bound water amount.

Approximately, at the degrees between 400-500°C Ca(OH)₂ decomposes into H₂O and CaO. The weight difference along these temperatures (exact values are read from the fluctuations on the graph) gives the resolving H₂O amount separated from Ca(OH)₂. From this calculation Ca(OH)₂ composition can be detected by multiplying water amount by 4.11 which is the ratio of atomic mass of calcium hydroxide and water.

At the same way, approximately at the degrees of 650-700°C CaCO₃ decomposes into CO₂ and CaO. The weight difference along these temperatures (exact values are read from the fluctuations on the graph) gives the resolving CO₂ amount separated from CaCO₃. From this calculation CaCO₃ composition can be detected by multiplying CO₂ amount by 2.2727 which is the ratio of atomic mass of CaCO₃ and CO₂.
Figure 19. Calculation of ratio of CH and CaCO$_3$ in the paste sample from the outputs of TGA (a)/DTA (b) analysis
CHAPTER IV

RESULT AND DISCUSSION

4.1 General

In this section test results obtained from the experimental studies are reported. The outcomes are finally discussed and compared with the similar studies in literature.

4.1.1 Slump Flow Test

The properties of consistency of all designed mixes are presented in Table 9. These values significantly differ from each other according to presence of nano silica (NS) in the mixture. As seen from Table 9, NS decreases workability significantly. To improve the workability of mixtures, same amount of high range water reducing admixture (HRWR) was used for all mixtures. This chemical admixture affects the microstructure of mixtures including entraining air bubbles. Because of the aim of similar mixture proportions and microstructure other than NS and pumice additions, chemical admixture amount was set to a constant value for all mixture. As a result of this action, flows of mixtures without NS were at the levels of 140-150 %. Besides, mixtures containing NS can achieve at the levels of flow of 75-100 %. Control sample with NS (100C-3NS) has the flow value of 110% while flow values of test samples containing pumice and NS are lower than 100%. The reason for that is not only existence of mineral admixture which is another reason for water demand increase. This is for existence of NS having high surface area.
Table 9. *Flow values of mixtures (%)*

<table>
<thead>
<tr>
<th></th>
<th>0% NS Addition</th>
<th>3% NS Addition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fine Pumice</td>
<td>Coarse Pumice</td>
</tr>
<tr>
<td>Control</td>
<td>150</td>
<td>110</td>
</tr>
<tr>
<td>15% Replacement</td>
<td>150</td>
<td>85</td>
</tr>
<tr>
<td>30% Replacement</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>45% Replacement</td>
<td>150</td>
<td>80</td>
</tr>
</tbody>
</table>

4.1.2 Flexural Strength

The results of the flexural strength test conducted according to ASTM C348 are listed in Table 10. The flexural strength values of four different ages; 2, 7, 28, and 90 days are reported in this table. Reference mixtures with/without NS and with/without pumice were also produced for control purpose.

According to the results, a significant difference is observed in early age strengths. Pumice addition decreased strength especially at early ages. Besides, NS addition seems to be like compensator for this early age strength decrease.

**Effect of NS addition:**

For the early age results (2 days) differences are considerable. While flexural strength contribution of NS with 15% pumice added mixtures is around 20%, these value is around 25% for 30% pumice mixtures and 30% for 45% pumice added mixtures.

The most significant increase was observed in the 30% fine pumice replacement with 3% NS addition (30PF-3NS) and 45% fine pumice replacement with 3% NS addition (45PF-3NS). There is 20.7% increase in flexural strength with NS addition to 30PF at the age of 90 days. The increase in the ratio of the flexural strength of 45PF-3NS at the age of 90 days is 14.4%. Although there exist small increases in 90 days results of other mixtures, these differences are negligible.
Table 10. Flexural strength of 40\(*\)40\(*\)160 mm prism specimens

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Flexural Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 days</td>
</tr>
<tr>
<td></td>
<td>MPa COV (%)</td>
</tr>
<tr>
<td>100C</td>
<td>5.6 7.4</td>
</tr>
<tr>
<td>100C-3NS</td>
<td>5.9 8.6</td>
</tr>
<tr>
<td>15PF</td>
<td>5.1 5.0</td>
</tr>
<tr>
<td>15PF-3NS</td>
<td>6.0 2.9</td>
</tr>
<tr>
<td>15PC</td>
<td>4.9 7.4</td>
</tr>
<tr>
<td>15PC-3NS</td>
<td>5.7 4.0</td>
</tr>
<tr>
<td>30PF</td>
<td>3.9 0.0</td>
</tr>
<tr>
<td>30PF-3NS</td>
<td>5.0 2.8</td>
</tr>
<tr>
<td>30PC</td>
<td>4.2 2.8</td>
</tr>
<tr>
<td>30PC-3NS</td>
<td>4.9 4.3</td>
</tr>
<tr>
<td>45PF</td>
<td>3.2 0.0</td>
</tr>
<tr>
<td>45PF-3NS</td>
<td>3.9 5.1</td>
</tr>
<tr>
<td>45PC</td>
<td>2.9 0.0</td>
</tr>
<tr>
<td>45PC-3NS</td>
<td>3.9 2.6</td>
</tr>
</tbody>
</table>

**Effect of replacement ratio of pumice:**
At the later ages (28 and 90 days), there is slight differences between the results of mixtures with 15, 30, and 45% pumice. Besides, at the ages 2 and 7 days, the strength values incrementally decreases with increasing replacement ratio. When the 2 days strength results are compared with the results of the control mixture (without pumice and NS), 9.1%, 28.6%, and 42.9% decreases are observed with 15, 30, and 45% replacement ratios of pumice, respectively.
Effect of fineness of pumice:
According to the results, even though the fine pumice incorporated mixtures seem to have higher flexural strengths when compared to the coarse pumice incorporated mixtures, this change is not that significant.

4.1.3 Compressive Strength

Compressive strength values of the specimens prepared at the ages 2, 7, 28, and 90 days was measured according to the standard ASTM C349 (Table 11). The effect of HRWR on the compressive strength test results was eliminated by keeping the HRWR amount constant.

Table 11. Compressive strength of mixtures at different ages

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Compressive Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 days</td>
</tr>
<tr>
<td></td>
<td>MPa</td>
</tr>
<tr>
<td>100C</td>
<td>30.0</td>
</tr>
<tr>
<td>100C-3NS</td>
<td>31.6</td>
</tr>
<tr>
<td>15PF</td>
<td>22.8</td>
</tr>
<tr>
<td>15PF-3NS</td>
<td>28.1</td>
</tr>
<tr>
<td>15PC</td>
<td>23.1</td>
</tr>
<tr>
<td>15PC-3NS</td>
<td>27.4</td>
</tr>
<tr>
<td>30PF</td>
<td>16.4</td>
</tr>
<tr>
<td>30PF-3NS</td>
<td>20.6</td>
</tr>
<tr>
<td>30PC</td>
<td>16.3</td>
</tr>
<tr>
<td>30PC-3NS</td>
<td>20.3</td>
</tr>
<tr>
<td>45PF</td>
<td>11.6</td>
</tr>
<tr>
<td>45PF-3NS</td>
<td>13.9</td>
</tr>
<tr>
<td>45PC</td>
<td>11.3</td>
</tr>
<tr>
<td>45PC-3NS</td>
<td>13.6</td>
</tr>
</tbody>
</table>
Three different parameters were tested throughout experimental program; amount and fineness of pumice, and NS. Therefore, two control mixtures both without any pumice and one with NS were also prepared. As seen from Table 11, the effect of fineness of pumice was not significant because of the similar compressive strength values obtained from the similar mixtures with different pumice fineness. Therefore, as representative test mixtures, only mixtures including fine pumice are taken into the consideration during the discussion section. Moreover, in order to better understand the results shown in the Table 11, results are grouped and analyzed in accordance with testing ages:

2 Days Test Results:

According to the results after 2 days moist curing, compressive strength values of all mixtures having NS are higher than that of mixtures without NS. The most significant increase in compressive strength is observed from the mixtures with 30% pumice (Figure 20). In terms of relative replacement ratio of pumice, a great reduction is observed with an increase in the replacement ratio. Compared to the control mixture (100C), 24%, 45%, and 61% reduction in compressive strength values are observed for 15PF, 30PF, and 45PF mixtures, respectively. This situation is created by the delayed hydration rate of pozzolanic reactions. In this point, NS is seen to be effective to compensate for the strength loses with the use of pumice at early ages. By the use of NS, the reduction of strength decreased to the level of 6%, 31%, and 53% for 15PF, 30PF, and 45PF mixture, respectively. However, the most significant compensation is observed in 15PF and 30PF.

Another remarkable point is that NS addition closes the gap between 2 days compressive strengths of 100C and 15PF, which are in the levels of 30.0 MPa, 28.1 MPa, respectively.
Figure 20. Test results of specimens at the age of 2 days

7 Days Test Results:

Similar to the 2 day results, compressive strength values of mixtures containing NS are greater than that of mixtures without NS. Compared to the other tested ages, effect of NS addition is the highest at the age of 7 days. While strength of control mixture (100C) is increased 10% by use of NS, strengths of all three blended test mixtures are increased 29-30% by use of NS (Figure 21).

As a hydration product of C₃S and C₂S, calcium hydroxide (CH) formation remarkably takes place in cement paste. Pumice reacts with CH to perform pozzolanic reaction. In addition, NS as a very fine reactive powder also reacts with CH to create additional CSH gels (Said et al., 2012). Because of its quite small particle size, NS also acts as filler material that decreases porosity. This binary reaction provides a significant increase in compressive strength. Similar to that of 2
days age, with NS addition compressive strength value of 15PF can almost reach to the strength level of control mixture (100C).

![Figure 21. Test results of specimens at the age of 7 days](image)

**28 Days Test Results:**

Unlike the early ages, 28 days strength differences between the mixtures with and without NS are quite limited. While there is an almost 12% increase with the use of NS in the mixtures with 15% pumice (15PF and 15PF-3NS) couple, no significant contribution with the use of NS is obtained in mixture with 30% pumice addition. As in the 15PF mixtures, the use of NS increases the compressive strength of 45PF with the level of 21%.
As can be seen from Figure 22, compressive strength of 15PF-3NS is almost similar to that of 100C. This means at the age of 28 days, strength loss due to the use of pumice as pozzolanic material can be overcome with use of 3% NS at low replacement rate of pumice. Furthermore, 33% decrease caused by use of 45% pumice (45PF) can be reduced to 19% by the use of 3% NS (45PF-3NS).

**90 Days Test Results:**

When the test results measured at different testing ages are compared, slight improvements were observed after the testing ages of 28 days. It is important to note that compressive strength values of mixtures without NS are greater than that of mixtures containing NS except 45PF-3NS mixture. According to the Figure 23, these differences can be neglected because of the slight differences between with and without NS mixtures (the greatest difference is 4.9% for 45PF and 45PF-3NS).
mixtures). This situation can be linked to the early age effect of NS. NS is seen to be effective in early ages. At later ages after 28 days, contribution of NS to the strength is seen to be diminished.

Therefore it can be stated that NS is very effective in especially increasing hydration rate at early ages, not in increasing ultimate strength. So, this shows that aim of using NS should be to obtain high early age compressive strength value when using moderate or high content of pumice as pozzolan.
Figure 24 is summarizing the NS effect on the compressive strength of blended cements at four different curing ages. According to the figure, most significant effect is seen at seventh day. A similar improvement can be seen at second day. After seventh day, this improvement rate starts to decline, and finally NS contribution to the compressive strength of blended cements stops at 90 days.

### 4.1.4 Heat of Hydration

Rate of heat of hydration of pastes prepared according to the designed mixtures are shown in Figures 25-27.

As shown in figures, hydration rates and kinetics of pastes are changing in different patterns and scales according to fineness and proportion of pumice and presence of NS. For better understanding, these analysis results are shown in 3 grouped figures according to different pumice proportions. Control pastes with and without NS
(100C and 100C-3NS) are shown in all figures with black and grey color. Only pumice groups (fine or coarse) are shown in red and blue color, and pumice with NS groups are shown in faded red and blue color.

According to the figures, with NS effect on hydration kinetics, peaks are observed to be increased significantly. This may be related to the compressive strength contribution of NS. More heat coming from NS addition shows that more hydration products were produced in a shorter time compared to the pastes without NS. The accelerating effect of NS on pozzolanic reactions and hydration of PC is seen even in these graphs. While blended cements without NS are hydrating slowly and evolve lower heat, blended cements with NS hydrate faster and more productive.
Figure 25. Heat of hydration curves of 15% pumice replacement couples with/without NS and control mixtures.
Figure 26. Heat of hydration curves of 30% pumice replacement couples with/without NS and control mixtures
Figure 27. Heat of hydration curves of 45% pumice replacement couples with/without NS and control mixtures
Moreover, as pumice proportion increases, peak levels and total heat evolved are decreased (Figure 28). The slow rate of hydration of blended cements with high proportions is confirmed even in calorimeter analysis.

Finally, although there is not significant difference between two different pumices fineness, finer pumice pastes are seen as evolving a little more heat compared to coarse pumice pastes (Table 12).
4.1.5 X-Ray Diffraction (XRD)

The effect of curing time up to 2, 7, and 28 days on the hydration characteristics of paste samples can be seen from XRD patterns shown in Figure 29, 30, and 31. XRD patterns show peaks of portlandite, ettringite and CaCO$_3$ as well as anhydrous phases. Because of similarity of XRD patterns of pastes including finer pumice powder, only pastes including coarser pumice powder are shown and discussed in this section.

2θ values measured by the XRD device at the peak regions were examined and compared to the values in the literature (Luciano et al., 2009; Babu, 2013; Jumate et al., 2012). According to the literature, 2θ values approximately 9° and 23° coincide to ettringite formation; 18°, 28°, 34°, 47°, and 54° coincide to CH; 32°, 33°, 41°, 42°, and 51° coincide to C$_3$S and C$_2$S; and 29° coincides to CaCO$_3$.

### Table 12. Total heat evolved at the ages of 24 h and 72 h

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Total Heat Evolved (J)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 h</td>
<td>72 h</td>
<td></td>
</tr>
<tr>
<td>100C</td>
<td>917.0</td>
<td>1165.6</td>
<td></td>
</tr>
<tr>
<td>100C-3NS</td>
<td>1184.6</td>
<td>1757.2</td>
<td></td>
</tr>
<tr>
<td>15PF</td>
<td>843.2</td>
<td>1087.1</td>
<td></td>
</tr>
<tr>
<td>15PF-3NS</td>
<td>1128.4</td>
<td>1712.1</td>
<td></td>
</tr>
<tr>
<td>15PC</td>
<td>782.1</td>
<td>1000.0</td>
<td></td>
</tr>
<tr>
<td>15PC-3NS</td>
<td>1022.6</td>
<td>1510.5</td>
<td></td>
</tr>
<tr>
<td>30PF</td>
<td>696.8</td>
<td>950.0</td>
<td></td>
</tr>
<tr>
<td>30PF-3NS</td>
<td>881.8</td>
<td>1318.9</td>
<td></td>
</tr>
<tr>
<td>30PC</td>
<td>680.3</td>
<td>861.7</td>
<td></td>
</tr>
<tr>
<td>30PC-3NS</td>
<td>893.5</td>
<td>1320.0</td>
<td></td>
</tr>
<tr>
<td>45PF</td>
<td>561.3</td>
<td>760.7</td>
<td></td>
</tr>
<tr>
<td>45PF-3NS</td>
<td>791.6</td>
<td>1181.4</td>
<td></td>
</tr>
<tr>
<td>45PC</td>
<td>577.3</td>
<td>729.4</td>
<td></td>
</tr>
<tr>
<td>45PC-3NS</td>
<td>845.2</td>
<td>1254.6</td>
<td></td>
</tr>
</tbody>
</table>
According to the figures, OPC–Pumice–NS composite cement pastes (15PC-3NS, 30PC-3NS, 45PC-3NS) exhibit lower intensity of portlandite peaks in comparison with those of related OPC-Pumice composites. This is due to the higher pozzolanic activity of NS than that of Pumice. Therefore, the rate of lime consumption and that of CSH production increase in the presence of NS. C₃S and C₂S intensities are clearly seen as decreasing by the increasing curing age. With the increasing age of hydration, CaCO₃ amount is seen to be decreased by the consumption of CH in pozzolanic reactions.
The quite remarkable point is lower intensity of CH in the 45PC-3NS paste at all ages. When compared, CH intensity is quite lower than that of other pastes. This gives idea about the advantages of this mixture in several probable durability problems.

Hydration accelerator effect of NS can be also seen in Figure 29 and 30. According to the Figure 31, C₃S and C₂S intensities of pastes with NS are lower than that of pastes without NS. This relation can be also seen in 7 days results of 30PC-3NS and 45PC-3NS. This can be explained by consumption of C₃S and C₂S to produce additional CSH.
Figure 31. XRD patterns of paste samples at the age of 28 days

4.1.6 Thermogravimetric Analysis

CH, CaCO$_3$, and bound water in CSH gel amounts in hardened cement pastes were determined with TGA-DTA analysis at the ages 2, 7, and 28 days. The results are shown in Figures 32, 33, and 34.
Figure 32. CH portions of pastes at the ages of 2, 7, and 28 days.
Figure 33. \( \text{CaCO}_3 \) portions of pastes at the ages of 2, 7, and 28 days.
Bound water portions of pastes at the ages of 2, 7, and 28 days

Figure 34. Bound water portions of pastes at the ages of 2, 7, and 28
As discussed before, fineness of pumice is not an effective parameter in compressive strength results. Therefore, only results of coarse pumice test groups are represented below. According to the comparison of results shown in figures, the following observations are made:

- CH amounts are decreasing with an increase in the pumice amount in the paste simply because of the reduced C₃S and C₂S amounts. With increasing curing age, CH amount of pastes with low pumice content (15PC, 15PC-3NS) increases gradually. However, with increase in age, CH amount decreases dramatically in high amount of pumice pastes (30PC-3NS, 45PC, 45PC-3NS), except 30PC. This is related to the amount and rate of pozzolanic reactions that consumes CH produced at early ages.

- In all test groups, NS addition decreases the CH amount in the pastes at all ages for all replacement levels. In early ages, NS acts as a nucleation site for the production of additional CSH gels. This effect relatively decreases the ratio of CH in the paste. In later ages, NS acts as a pozzolan and contributes to the pozzolanic reactions with consumption of CH.

- In both early and later ages, CaCO₃ amount is seen to be lower in higher pumice content test groups. Especially, in later ages this drop becomes significant in 45% pumice replacement test group.

- With the effect of NS, consumption of CaCO₃ up to 28 days is seen to be more significant in itself.

- Bound water of highly replaced blended cements at the earlier ages is lower and at the later ages is higher. As pumice content increases, bound water amount is seen in uptrend with increasing curing age.

- Except 15% replacement group, 30% and 45% replaced blended cement groups with NS addition contain quite large amount of bound water at the later ages. This situation shows the contribution of NS to the hydration process. The plenty of bound water in these ages (7 and 28 days) depends on both delayed pozzolanic activity of pumice and combined (seeding for CSH formation and pozzolanic activity) effect of NS.
CHAPTER V

SUMMARY AND CONCLUSION

5.1 General

The effects of nano silica (NS) on hydration trend and other properties of blended cement with different ratios and different fineness were examined physically and chemically by various tests and analysis. The results of these tests and analysis can be summarized as:

1. All the experiments were conducted on mortar or paste specimens. Beside, ordinary portland cement (CEM I 42.5R), two different pumices with two different fineness, commercially obtained NS, CEN standard sand, and high range water reducing admixture (HRWR, Gelnium 51) were used to produce test samples and specimens. HRWR was used for recovery of workability loss related to use of NS. In order to obtain more uniform dispersion of NS particles to the paste ultrasonic homogenizer was used.

2. In mix design, 3 main parameters were used: two different pumices with different fineness, 3 different pumice replacement ratios, and presence of NS (3% by weight). The w/cm ratio, cm/sand ratio, and HRWR amount were fixed for all mix designs.

3. In order to determine optimum NS ratio, preliminary uniaxial compressive strength test was conducted. This test designed with coarse pumice with 30% replacement ratio and various NS ratios (1-5% by weight). According to the results, the most significant compressive strength increase is obtained with 3% NS addition. With the addition of NS by 3%, 38.4% increase in compressive
strength at the age of 7 days and 36.6% increase at the age of 2 days are observed. So, 3% NS was selected for the further detailed of study.

4. No significant differences are observed in terms of compressive strength results with the use of pumices with different fineness values. Therefore, additional grinding process is not required to improve strength performance.

5. According to the flow test results, use of NS is reducing the consistency of mortar mixtures significantly. Flows of mixtures without NS are at the levels of 140-150 %. On the other hand, mixtures containing NS can achieve at the levels of flow of 75-100 %.

6. NS addition seem to improve the flexural strength of blended cements. On the other hand, addition of pumice decreases the flexural strength. With the increase in pumice replacement rate, further reductions in flexural performances are observed. With comparison of 2 days results to that of the control mixture (100C), 9.1%, 28.6%, and 42.9% decrease in flexural strength values are obtained with the 15, 30, and 45% replacement ratios of pumice, respectively. According to the 2 days results, while flexural strength contribution of NS to 15% pumice mixtures is around 20%, this value is around 25% for 30% pumice mixtures and 30% for 45% pumice mixtures.

7. According to compressive strength test results, early age strength values of high content pumice mixtures are quite lower than that of control mixture and mixtures with 15% pumice content. NS seem to improve the early age strength problem. Most impressive effect of NS is seen at 7 days of age results. NS addition provided 29% increase in compressive strength of all of the three blended cement mortars including fine pumice (Figure 23). The upcoming finding here is that NS is very effective in especially increasing hydration rate, not in increasing ultimate strength. So, this shows that aim of using NS should be to obtain high early age compressive strength value when using moderate or high content of pumice as pozzolan.
8. With NS effect on hydration kinetics, peaks are observed to be increased significantly (Figure 27-29). While blended cements without NS are hydrating slowly and evolve lower heat, blended cements with NS hydrate faster and more productive. Moreover, as pumice proportion increases, peak levels and total heat evolved are decreases (Figure 30).

9. XRD results have shown that portlandite intensities of all pastes with NS are lower than pastes without NS. According to the results, CaCO₃ amount was seen to be decreased with increasing curing time. The CH amount was seen as quite low in the 45PC-3NS paste. Lower C₃S and C₂S intensities of pastes with NS showed and supported the accelerating effect of NS in hydration of pumice blended cement.

10. According to the Thermogravimetric analysis, the most remarkable point is that NS addition decreases the CH amount in the pastes in all ages for all replacement levels. In early ages, NS acts as a seeding point for production of additional CSH gels. This effect relatively decreases the ratio of CH in the paste. In later ages, NS acts as a pozzolan and contributes to the pozzolanic reactions with consumption of CH. Except 15% replacement group, 30% and 45% replaced blended cement groups with NS addition contain quite large amount of bound water at the later ages.

To sum up, NS was found to be effective to recover compressive strength loss of blended cements in early ages. Even with a small amount of NS (3%) results in significant mechanical and chemical improvements. However, homogeneous dispersion is the key point to achieve all the positive effects of NS.

5.2 Recommendations for Further Studies

According to the outcomes of this research, the following studies recommended for the future researches:
1. Other type of nanomaterials such as nano CaCO$_3$, CNTs, or CNFs can be examined in high content pozzolanic cementitious composites with various ratios.

2. While adding nanomaterials to the mixtures, mixing procedure can be changed and examined for the case of homogeneous dispersion in the mix. Mechanical and chemical properties of design mixes can be observed.

3. NS addition to the blended cement can be tested with other standard test methods such as Mercury Intrusion Porosimetry (MIP), setting time and Scanning Electron Microscopy (SEM).

4. Durability properties such as permeability, alkali silica, freezing and thawing, abrasion and sulphate resistances of designed mixes used in this research can be examined.
REFERENCES


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APPENDIX A

PREPARING THE CALORIMETER SAMPLES AND REFERENCE SAMPLE

For the test of heat of hydration, isothermal calorimeter was used. The device takes measurement from the test sample put in a glass ampoule with comparison to the reference sample heat capacity. The ratio of water to cementitious materials by weight was taken 0.5 as constant for all test mixtures. Pastes tested were prepared in the ampoules. The total mass of each paste was 7.5 g; water was 2.5 g constant, cement-pumice-NS amounts were 5 g in total. NS was added initially to the mixing water and water-NS solution was prepared in another container with ultrasonic homogenizer. After water of water-NS solution was added to the ampoule with the help of a syringe, paste was mixed with a special needle. Immediately after mixing procedure, test ampoule was placed into the test cell in the body of calorimeter.

Before test ampoule was prepared, reference sample was prepared in another ampoule. It is recommended in the manual of calorimeter that heat capacity of test sample and reference sample should be identical. Thus, in order to achieve same heat capacity of test sample, any material whose heat capacity is known can be used in a certain amount calculated proportionally. For this purpose, quartz sand was used as reference material.
APPENDIX B

AN EXAMPLE OF CALCULATION OF REFERENCE SAMPLE

For determining the amount of reference sample, amounts and heat capacities of ingredients should be known. According to the averages of heat capacity values taken from literature:

<table>
<thead>
<tr>
<th>Material</th>
<th>Average Heat Capacities</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>750</td>
<td>J/kg.K</td>
</tr>
<tr>
<td>SiO₂</td>
<td>705</td>
<td>J/kg.K</td>
</tr>
<tr>
<td>Pumice</td>
<td>1088</td>
<td>J/kg.K</td>
</tr>
<tr>
<td>Water</td>
<td>4180</td>
<td>J/kg.K</td>
</tr>
</tbody>
</table>

For each designed mix, total ingredient amounts multiplied by heat capacities should be equal to reference amount multiplied by heat capacity of reference sample. In order to illustrate, calculation of one of the designed mix 30PF-3NS can be taken as an example:

\[
(C_p(\text{water}) \times W_{\text{water}}) + (C_p(\text{cement}) \times W_{\text{cement}}) + (C_p(\text{pumice}) \times W_{\text{pumice}}) + (C_p(\text{NS}) \times W_{\text{NS}}) = (C_p(\text{quartz}) \times W_{\text{quartz}})
\]

\[
W_{\text{quartz}} = \frac{4180 \text{J/kg.K} \times 2.5 \text{g} + 750 \text{J/kg.K} \times 3.35 \text{g} + 1088 \text{J/kg.K} \times 1.5 \text{g} + 705 \text{J/kg.K} \times 0.15 \text{g}}{705 \text{J/kg.K}} = 12.47 \text{ g}
\]

Reference sample amount were calculated with this formulation for all other designed mixes.