Durability Properties of Blended Portland Limestone Cement Containing Calcium Carbonate Nanoparticles

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ABSTRACT

Durability Properties of Blended Limestone Cement Containing Calcium Carbonate Nanoparticles

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Concordia University, 2021

The use of Portland Limestone Cement (PLC) as a greener alternative to Portland Cement (PC) dates back to 1960s. In Canada, PLC was first introduced in 2008 with the limestone content limit of 15%. While the use of PLC alone in sulfate exposure is prohibited according to CSA A23.1, the limit of 15% is mainly to ensure a suitable level of mechanical and durability performance. Improving the performance of PLC and decreasing its clinker content is very appealing since it can contribute to reducing the carbon and energy footprint of cement industry. Calcium carbonate nanoparticles (NC) have been shown to be effective in accelerating cement hydration in ultra high performance concretes and concretes with high levels of supplementary cementing materials, but their effect on durability has been rarely studied.

In this research, limestone cement was made by blending micro limestone powder with general use cement at 15%, 20%, and 25% content levels. NC was used as an additive at 1%, 2%, 3%, and 4% and heat of hydration using isothermal calorimetry technic was evaluated. Based on the results of this test, 2% addition of NC was selected as the most favorable addition level and was used in mortar samples for further durability investigations. Additionally, the same mixtures were made with the addition of 2% nano silica (NS), which is a one of the most widely-used nanoparticles in cement, in order to put the efficacy of NC in perspective. Several mechanical and durability measures such as compressive strength, volume of permeable voids, sorptivity, bulk electrical conductivity, bulk electrical resistivity, and expansion due to ettringite and thaumasite sulfate attack were studied on mortar samples.

The results showed that 2% NC addition was significantly effective in improving durability of mortar samples. Also, 2% NC addition was found to be more effective than 2% NS addition in improving all of the measures except for compressive strength. Moreover, considering durability performance, it was concluded that, with the 2% NC addition, limestone content limit of 15% can be safely increased to 20% and even to 25% if sulfate resistance is not required.

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1. INTRODUCTION

Concrete is the most widely used construction material in the world. It consists of aggregates and some kind of binder that glues them together. The most commonly used binder for concrete is a cement paste made of water and Portland cement. The Portland cement industry is considered to play an important role in construction throughout the world. However, the cement industry has been criticized because of its two major negative environmental impacts; high CO_2 emission and high energy consumption. Production of each ton of cement releases almost one ton of CO_2 into the atmosphere (Meyer-2009 and Malhotra-1999), and cement industry is responsible for around 8% of global CO_2 emissions (Andrew-2018). The cement industry is also very energy intensive and accounts for 12–15% of total energy consumption in the world (Madlool et al.-2011). Besides optimizing the manufacturing process, one of the main solutions to reduce the environmental impacts and make this industry more sustainable is partial replacement of cement with minerals. Partial replacement of cement with mineral additives improves the sustainability of cement, and depending on the type of mineral and design of the blend, can also be economical and improve the performance of cement.

Limestone, or calcium carbonate, is a cheap and abundant mineral that makes up about 7% of the Earth's crust, and along with clay, shale, and slate, it is one of the main ingredients for producing clinker which will then be pulverized to make cement at cement plants. Therefore, partial replacement of cement with limestone seems to be a feasible idea which is a step towards greener concrete industry. In North America, standards allow additional limestone to be inter-ground with clinker up to 5% of content for regular Portland cement (PC) and up to 15% for Portland-limestone cement (PLC). In Europe, however, there are certain types of limestone cement that contain up to 35% of limestone (EN 197-1:2011).

Limestone is conventionally known to act as an inert filler in the cement paste matrix. However, it has been shown by many researchers that limestone can improve certain properties of concrete at different ages. The effectiveness of limestone in cement highly depends on size distribution of its particles. It has been shown that limestone is especially more effective when its particles are smaller than cement particles (e.g. Sato and Diallo-2010, Camiletti et al.-2012, Vance et al.-2013, and Wang et al.-2018). This effectiveness is considerably higher if the limestone particles are in the form of nanoparticles (Bentz et al.-2012).

Nano Calcium Carbonate (NC) particles can improve the properties of cement mainly by providing nucleation sites for cement hydration (Sato and Beaudoin-2011). This can accelerate the hydration of cement which is why numerous studies have investigated the effect of NC on early age properties of concrete; especially where early age hydration is of importance such as in ultra-high performance concrete or in concrete with high volume of supplementary cementing materials (e.g. Bentz et al.-2012, Shaikh and Supit-2014, and Wang et al.-2014). Any improvement in the early age hydration of cement can also be beneficial to durability of concrete. However, there seems to be a lack of research on the effect of NC on durability properties of concrete.

One of the main reasons for limiting the limestone content in cement by standards is to guarantee a certain level of mechanical and durability properties that may suffer as a result of reducing cement content. High limestone content can lead to lower overall mechanical and durability performance and especially high susceptibility to sulfate attack. Consequently, Canadian standard (CSA A23.1) prohibits the use of limestone cement in sulfate exposures unless it is used along with supplementary cementing materials. NC has shown promising results in improving cement hydration, and it may also help to compensate for the low content of cement when high percentage of limestone is incorporated. This research is an effort to investigate the effect of NC on durability properties of mixtures containing blended limestone cement with different levels of limestone content and also to explore the possibility of exceeding the current 15% limit of limestone content in North America without compromising the durability properties of concrete.

1.1 Research Objectives

In this research, NC powder is used as an additive to blended limestone cement that can potentially improve early age and durability properties of concrete. This research has four main objectives:

1. Finding the favorable amount of NC addition to mortar made from blended PLC

There have been conflicts in the literature regarding the amount of NC that needs to be used in mixtures to improve performance. Some researchers have used amounts of up to 15% (e.g. Sato and Diallo-2010 up to 10% and Camiletti et al.-2012 up to 15%) of NC with respect to binding materials, while some others such as Shaikh and Supit (2014) have found low percentages around 1% of NC to be the most effective. Also, mixing the NC with the rest of the materials has been done differently in various studies. Some researchers have dry-mixed NC powder with cement and some others have used ultra-sonication in water before mixing. Generally, NC particles can bond together and form larger particles that are no longer nano-sized. One way to break this bond is to ultra-sonicate the particles in water and coat them with proper surfactants such as polycarboxylate high range water reducing admixtures to provide stability. Therefore, the first phase of this research is to specify the favorable percentage of NC addition to blended limestone cement mixtures.

2. Investigating the effect of NC additions on early age properties of mortar made from blended PLC

While the effect of NC on early age properties of ultra-high performance concrete and concrete with high SCM contents has been studied, this research will specifically investigate its effect on mortar made from blended limestone cement with different limestone content levels.

3. Investigating the effect of NC additions on durability properties of mortar made from blended PLC

Most studies have used NC in the presence of high volumes of SCM in order to compensate the delay in the early age cement hydration caused by the latter. However, there seems to be a lack of research on the effect of NC alone on improving the durability properties of concrete. It has been shown that NC can act as an accelerator for cement hydration in early ages which can affect the hydrated cement matrix. This may have significant effects on long-term durability properties of concrete which will be studied in this research.

4. Exploring the possibility of increasing limestone content of cement beyond the Canadian standard (CSA A3001) limit of 15%, without compromising durability properties with the help of NC additions

One major reason that North American standards limit the limestone addition to 15% is that high contents of limestone can negatively impact mechanical and durability properties of concrete. Even though using NC as an additive can increase the overall limestone content in cement, it may improve the durability to a satisfactory degree and consequently propose the possibility for incorporating higher limestone contents in PLC in Canada.

5. Comparing the efficacy of nano calcium carbonate with nano silica in cement

Nano silica (NS) is one of the most widely used nanoparticles in cement. In order to put the extent of efficacy of NC particles on different properties of cement paste and mortar made from blended PLC into perspective, NS is also used in this study. For this purpose, in a separate set of similar mixtures, NC is replaced with the same amount of NS and the same testing procedures are performed.

1.2 Outline of the Thesis

This thesis is presented in five chapters. The following is a summary of the contents of each chapter:

Chapter 2 presents a review of the existing literature on the incorporation of limestone in cement. This includes a brief review of Portland cement and Portland-limestone cement, different action mechanisms of limestone powder in cement, and the effect of limestone powder and NC on different properties of concrete. Moreover, a brief review of literature on the effect of NS, which is a widely used type of nanoparticles, on properties of concrete is provided, and a short summary of the gaps in the literature is presented.

Chapter 3 describes the experimental program designed in order to follow the objectives of this research. The materials, mixtures, test procedures and instruments, techniques, and standards are explained in details in this chapter.

Chapter 4 includes all of the test results obtained after performing the experimental program. Each set of test results is presented, analyzed, and thoroughly discussed separately. The results are also compared with findings of other researchers, and where needed, they are combined and discussed with other test results to obtain a better insight into the subject.

Chapter 5 presents the conclusions drawn based on the results of the experimental program and discussions. This chapter also lays out the major contributions of this thesis to the research community and provides possible directions for future work in the field.

2. LITERATURE REVIEW

2.1 Portland Cement

Portland cement is the most common binder used in concrete throughout the world. In cement plants, raw materials are transported from the quarries, crushed, milled, and proportioned based on their chemical composition. The raw materials are generally a mixture of calcareous (calcium oxide) materials such as limestone, chalk, or shells, and argillaceous (silica and alumina) materials such as clay, shale, or blast-furnace slag. The raw materials are mixed and heated in rotary kilns to temperatures over 1450°C. The heat results in chemical reactions between the raw materials, and a stony end-product called clinker is formed. After clinker is cooled down, it is pulverized to a very fine powder to form cement. During this process, 3-5% gypsum, calcium sulfate, is usually added and inter-ground in order to regulate setting time, drying shrinkage, and strength development (Potgieter et al.-2004). Additionally, depending on the type of cement, up to 5% limestone is inter-ground with the clinker. The main reason behind this small limestone addition is reducing the cement consumption and slightly lowering energy requirements while its overall performance is not affected.

2.2 Portland-Limestone Cement

In the past few decades, sustainable development has become an important concern in many industries and the cement manufacturing industry is no exception. As mentioned before, the cement industry is responsible for around 8% of global CO_2 emission (Andrew-2018) and 12-15% of global energy consumption (Madlool et al.-2011). The CO_2 emission of cement production is the result of fuel combustion and limestone calcination in the kiln. One of the best solutions to making the cement industry greener and more sustainable is reducing the clinker portion of Portland cement. This can be achieved mainly by partial replacement of cement with supplementary cementing materials (SCMs) or mineral additives. SCMs such as natural pozzolans, slag, fly ash, silica fume, and metakaolin are reactive materials that can improve mechanical and durability as well as fresh properties of concrete. Moreover, some SCMs are by-products of other industries that are generally considered waste and often end up in landfills. Therefore, their consumption enhances the sustainability of those industries as well.

Limestone, however, is generally known to be an inert material which does not have cementing properties like other SCMs. As explained, limestone is one of the main raw materials for manufacturing cement which is why cement plants are always located close to limestone quarries (Tennis et al.-2011). This makes it an appealing replacement for cement that can significantly reduce the environmental impact of cement industry. In a study done by Schmidt et al. (2010), three different cement plants in Germany were investigated for their CO_2 emission. They reported 15% reduction of CO_2 emission by replacing 15% of clinker with limestone.

Portland-limestone cement (PLC) is produced either by blending limestone powder with Portland cement (PC) or inter-grinding limestone with clinker in cement plants. Due to its lower CO_2 emission and energy consumption, this type of cement is increasingly used in the world. Most standards allow up to 5% limestone content in PC and anything above that can be classified as PLC.

In Europe, PLC has a very long history going back to the 1960s and is currently used more than any type of cement in the European Union (Hooton et al.-2007). The European standard (EN 197-1) allows up to 35% limestone content for certain types of cement. Cement containing limestone was first introduced by EN 197-1 in 1987 as a new type of cement called PKZ which consisted of 15 ± 5% limestone and 85 ± 5% clinker (Schmidt-1992). Because of the increasing use of limestone cement in Europe in the following years, the European standard (EN 197-1) in 2000 introduced different types of Portland-limestone cement allowing the replacement of Portland cement with limestone powder up to 35% by weight. Due to the poor performance of Portland-limestone cement against sulfate attack, all European countries have specified certain limitations for its usage in sulfate exposures. The Thaumasite Expert Group (TEG) in the UK for example states "those cements in which the amount of limestone filler can range from 6% to 35%, should not be permitted in conditions where sulfate concentrations in the groundwater are in excess of 0.4 g/L" (Crammond-2003).

In North America, the Canadian standard CSA (Standard specifications for Portland cement) has allowed using up to 5% limestone as filler in General Use (GU) cement since 1983. In 2008, CSA A3001 (CSA-2008b) introduced a new category of cement as Portland-limestone cement (GUL) which can contain up to 15% limestone. In practice, GUL has 12% to 13% limestone content in Canadian cement plants (Hooton et al.-2010). In the United States, the use of limestone powder as filler in cement was first allowed up to 5% by ASTM in 2004 (ASTM C150). In 2012, ASTM C595 introduced Portland limestone cement with up to 15% limestone content while not allowing its use as moderate or high sulfate resistant cement.

Many other major countries have also studied and practiced the production and use of PLC. Similar to North America, Australia and New Zealand have allowed the use of 15% limestone in specific types of cement (Schneider et al.-2011). Mexico has defined blended cements that may contain 6% to 35% limestone, and South Africa follows the European standard (EN197-1) with regards to the definition of PLCs (Tennis et al.-2011).

High contents of calcium carbonate (limestone) in cement makes it susceptible to sulfate attack. Therefore, the use of PLC without supplementary cementing materials in sulfate exposures is generally not allowed by current standards. Since limestone is mostly inert and acts as a filler in cement, in addition to poor performance against sulfate attack, mechanical and durability properties of cement with high content of limestone may also suffer. That is why in order to guarantee certain levels of mechanical and durability properties in concrete, the North American standards do not allow more than 15% of limestone content in cement, and cement plants usually grind PLC to sizes finer than PC in order to improve its reactivity.

2.3 Limestone's Action in Cement Paste

As mentioned, limestone is generally an inert material in cement, and its main action is as a filler that can potentially fill up the voids in the cement matrix. However, many researchers have concluded that limestone can have other action mechanisms in cement which, depending on the size of limestone particles, can be significant (e.g. Wang et al.-2018, Lothenbachet al.-2011, Deschner et al.-2012, Scrivener et al.-2015, Berodier and Scrivener-2014). These action mechanisms are categorized as filler effect, nucleation effect, dilution effect, and chemical effect.

2.3.1 Filler Effect

The filler effect is mainly dependent on the size and amount of the limestone particles and their ability to fill the voids in the cement matrix. De Schutter (2011) investigated the packing density of cement containing limestone and slag and concluded that when limestone particles are coarser and comparable to the size of cement particles, the packing density is lower. Whereas, packing density is higher when limestone particles are finer than cement because they can easily fill the voids. Cyr et al. (2006) also found better compressive strength and durability when fine limestone was added to cement.

Filling up the voids by the limestone particles can also affect the microstructure of concrete. Liu and Yan (2008) saw a more refined pore structure in their mortar samples that contained fine limestone powder compared to the ones with plain PC. In another study, Senhadji et al. (2014) found the mean pore size of their plain PC mortar samples and mortar samples with 10% fine limestone powder to be 60 nm and 31 nm respectively which implied the effectiveness of limestone powder in refining the pores. Other researchers have also confirmed that the refining effect of limestone powder could be improved by using finer limestone (Bederina et al.-2011 and Shu-hua & Shu-hua-2010).

2.3.2 Nucleation Effect

The nucleation effect of limestone is by far the most noticeable effect of fine limestone powder in concrete and is the main incentive for using NC particles. Soroka and Stern (1976) first reported nucleation or seeding effect of limestone powder in cement. Generally, fine limestone particles provide a nucleation site for formation of calcium silicate hydrates (CSH) during normal cement hydration which can improve the rate and degree of cement hydration. Many other researchers have confirmed this finding over the years.

The effectiveness of limestone powder depends on its amount, particle size, and surface structure. Numerous studies have shown that finer limestone particle are more effective in improving cement hydration (e.g. Camiletti et al.-2012, Sato and Diallo-2010, Vance et al.-2013, and Wang et al.-2018). This is mainly because C-S-H absorption capacity of limestone particles increases as its particle size decreases. Bentz et al. (2015) reported that acceleration ability of fine limestone in cements also depends on the type of polymorph. They tested mixes with two of the most common naturally occurring crystal forms of calcium carbonate; i.e. calcite and aragonite. They concluded that calcite provides favorable surfaces for nucleation of C-S-H whereas aragonite does not. This could be attributed to the different surface structures of calcite and aragonite in aqueous solutions. Rode et al. (2009) saw that the surface of calcite is composed of a planar configuration of Ca and O atoms, which is similar to the CaO layers in C-S-H. In another study, Araki et al. (2012) found Ca atoms on the surface of aragonite while they detected no O atoms. As a result, it can be concluded that the surface of calcite is more conductive for the formation and growth of early age hydration products than the surface of aragonite.

2.3.3 Dilution Effect

Since only a small fraction of limestone may take part in the chemical reactions and limestone does not have cementitious or pozzolanic properties, cement replacement with limestone increases the free water that can react with cement particles at the same water/binder ratio. This phenomenon is referred to as the dilution effect which results in higher degree of cement hydration (Cyr et al.-

2006, De Schutter-2011, and Deschner et al.-2012). Consequently, the extent of the dilution effect mainly depends on the amount of limestone present in the cement.

In cement hydration, when coarse limestone powder is used which minimizes the nucleation effect of limestone particles, the dilution effect becomes the major influence on the heat of hydration. In this case, the overall heat of hydration is still lower than that of plain cement paste. In other words, the dilution effect of limestone is not negligible, but it is usually not significant enough to compensate for the lower hydration heat as a result of lower cement content (Tikkanen et al.-2014 and Thongsanitgarn et al.-2014).

2.3.4 Chemical Effect

As the size of limestone particles decreases, its dissolution in the water in cement paste increases. This is especially true for fine limestone powder and nano limestone. As a result of limestone dissolution, the concentration of carbonate ions in the pore solution increases, and they can react with alumina from C_3A and C_4AF in cement as well as SCMs to form carboaluminate (Kakali et al.-2000, Menéndez et al.-2003, and De Weerdt et al.-2011). Therefore, the chemical effect of limestone highly depends on the fineness of its particles and the alumina content of cement and the SCMs that may have been used with cement. When SCMs are not present, due to the limited alumina content in cement, the chemical effect of limestone is negligible. However, if SCM's such as slag with high alumina contents are used, the formation of carboaluminates can stabilize the existing ettringite and prevent its decomposition into monosulphate. This can result in reduced porosity (Kakali et al.-2000, Menéndez et al.-2003, and De Weerdt et al.-2011). The dissolution of calcium carbonate in water is extremely low, but it will be intensified if the calcium carbonate particles are in the form of nanoparticles. Through the reaction of alumina from C_3A and carbonate ion to form carboaluminates, some of the C_3A that would participate in ettringite sulfate attack would be unavailable which may reduce the susceptibility of concrete to ettringite sulfate attack.

2.4 Effect of Micro Limestone Particles on Early Age Properties of Concrete

The four different action mechanisms of limestone in cement discussed in Section 2.3 can also display themselves in the early age properties of concrete. The filler effect and dilution effect seem to be more important for properties of concrete in the first few minutes and hours after mixing such as workability and bleeding. The nucleation effect and chemical effect seem to be mainly contributing to the setting time and heat of hydration.

2.4.1 Workability and Bleeding

Current literature shows that effect of limestone on early age properties of concrete can depend on the particle size distribution of limestone relative to the cement particles. Generally, water absorption of particles depends on their surface area; higher surface area results in higher water absorption capacity in the paste. In addition to the filler effect and dilution effect that influence workability, the surface morphology of limestone particles can also severely impact workability and flowability of concrete. Some researchers detected an angular and rough surface morphology for their limestone which can lead to reduced workability (e.g. Alyamaç and Ince-2009, Cam and Neithalath-2010, Mohammed et al.-2013, and Thongsanitgarn et al.-2014). However, Sua-Iam and Makul (2013), observed a spherical morphology for their limestone powder particles which can improve workability.

Conflicting results are reported on workability of concrete as a result of limestone powder incorporation in cement. Kanazawa et al. (1992), Sua-iam and Makul (2013), and Derabla and Benmalek (2014) have reported increased workability and bleeding due to limestone incorporation in cement while many other researchers have found that addition of limestone to cement can increase the water demand and consequently reduce workability and bleeding especially for finer limestone (e.g. Moir and Kelham-1999, Ghezal-1999, and Nedhi-2000). This conflict may also suggest that for a specific type of limestone with certain particle size distribution and surface morphology, there may be an optimum limestone amount with regards to workability and bleeding (Yahia et al.-2005).

The source from which the limestone comes can also affect the surface morphology of its particles and consequently affect the workability of concrete. Felekoglu (2007) compared the effect of limestone quarry waste and the limestone produced by direct grinding on self-compacting concrete. Figure 2.4.1 shows the SEM images of the two types of limestone in his study. The figure shows that the surface of the limestone from quarry waste was rough and porous, whereas the surface morphology of ground limestone powder was smoother. Quite expectedly, the use of limestone quarry waste resulted in reduced workability, and ground limestone powder resulted in improved workability.

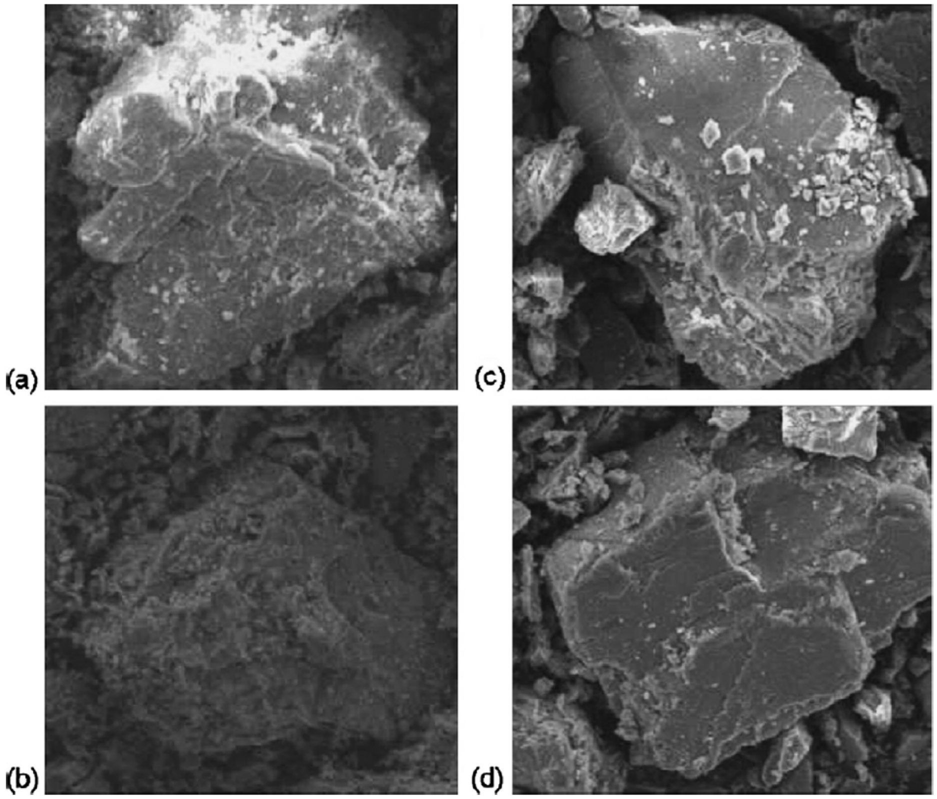

Figure 2.4.1: SEM images of limestone quarry waste (a, b) and directly ground limestone (c, d) (Felekoglu-2007)

2.4.2 Setting Time and Heat of Hydration

Most researchers have found that fine limestone addition can shorten the setting time and increase the rate and degree of hydration (e.g. Hooton et al.-2007 and Mounanga et al.-2011). The finer the particles, the more pronounced this effect will be. As mentioned earlier, fine limestone particles act as nucleation sites for C-S-H formation, and as the particles get finer this effect becomes more pronounced. On the other hand, higher amounts of limestone lead to a more pronounced dilution effect. As a result, free water for cement hydration increases which in turn improves the rate of hydration. Vance et al. (2013) compared the heat of hydration of plain OPC paste and OPC with 10% replacement of cement with limestone powder. They used three different limestone powders with median particles sizes of 0.7, 3, and 15 μm for the 10% cement replacement. The heat of hydration diagram is shown in Figure 2.4.2. The figure shows that the main peak of hydration of the sample containing the finest limestone powder (median particle size of 0.7 μm) was 15% higher than the peak of hydration of OPC paste. The figure also shows that the main peak was shifted 25% to the left; i.e. 25% earlier. Since the limestone particles are very fine, the chemical effect of limestone is increased which is why the second peak of the graph is more pronounced as a result of carbonaluminate formation (also referred to as the secondary ettringite formation). As the particle size of limestone powder increases, the main peak of hydration and its onset time and the second peak become more similar to those of the OPC paste curve.

Since the heat of hydration of cement is an indication of C-S-H formation as the main source of strength in concrete, any changes in the heat of hydration in the first minutes and hours after mixing can potentially affect the setting time. The chemical effect of limestone which is represented by the second peak in the hydration diagram occurs after the setting time of concrete. The filler effect of limestone generally only affects the workability and porosity of concrete. Therefore, the effect of limestone on the setting time of concrete can be mainly attributed to the nucleation and dilution effect. The nucleation effect highly depends on the fineness of limestone particles. When the limestone is very fine, its nucleation effect leads to significant acceleration of early age hydration reactions resulting in a shortened setting time (e.g. Sato and Beaudoin-2011). However, if the limestone powder is coarser, for example a median particle size of 4 μm (De Weerdt et al.-2011) or 16 μm (Bentz-2010), the acceleration in the hydration and its consequent short setting time is not observed. It has also been shown that high contents of limestone (generally beyond 15%), even if the particles are fine enough to accelerate the hydration reactions, can delay the setting time of concrete (Meddah et al. 2014).

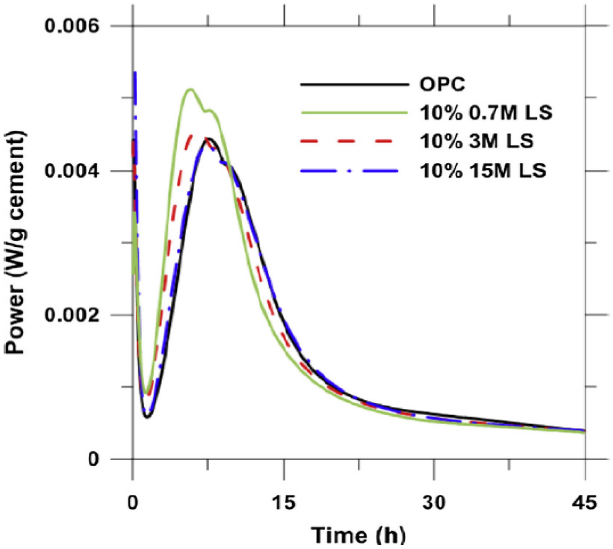

Figure 2.4.2: The effect of particle size of limestone powder on the heat of hydration of cement paste (Vance et al.-2013)

2.5 Effect of Micro Limestone Particles on Mechanical and Durability Properties of Concrete

Compressive strength of concrete containing limestone as a replacement for cement depends on the particle size of limestone and its content. As discussed in Section 2.3.1, when limestone particles are finer than cement particles, they can fill the voids between the cement particles and improve the overall packing density of cementitious materials. Moreover, fine limestone powder can improve the hydration of cement through nucleation. It is needless to say that if compressive strength is improved, other mechanical properties of concrete such as tensile strength, flexural strength, and elastic modulus will generally be improved.

Bosiljkov (2003) saw improved compressive strength in the self-compacting concrete when ultra-fine limestone powder was incorporated. In another study on self-compacting concrete, Ghafoori et al. (2016) used three limestone powders with median particle size of 5, 10, and 20 µm. They found the that for the same limestone content, finer limestone resulted in higher compressive strength. However, when large amounts of limestone are incorporated in cement, researchers have reported reduced compressive strength. An example would be the work of Ramezanianpour et al. (2009) where the compressive strength of mortar containing 0, 5, 20, and 35% limestone as replacement for cement was monitored over time. Their results are presented in Figure 2.5.1 and show that increasing limestone content consistently reduced the compressive strength of mortar samples at all ages. Since the same limestone was used in all samples, the reduction in compressive strength is clearly the result of lower hydration products due to lower cement content when limestone content is increased. Similar results were seen in the work of Sezer (2012) and Meddah et al. (2014).

Overall, only ultra-fine limestone may be able to improve compressive strength of concrete, and since high limestone content usually results in reduced compressive strength, there seems to be an optimum amount of limestone content with regards to compressive strength. Depending on the particle size distribution of limestone, its source, and the type of concrete where it is used, the optimum amount limestone can be different. For example, Livesey (1991), Schmidt (1992), and Sprung (1991) reported the optimum limestone content for compressive strength to be 5, 10, and 15%, respectively.

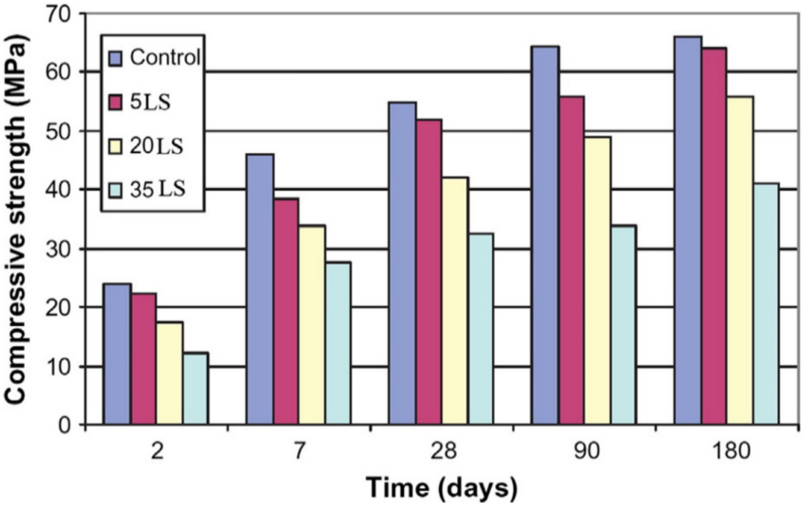

Figure 2.5.1: Effects of limestone content on the compressive strength of mortar samples at different ages by Ramezanianpour et al. (2009)

Current literature generally shows that up to 15% of limestone content in cement does not have a significant impact on most durability measures. However, there seems to be a consensus on the negative effect of higher limestone contents on durability of concrete. This could be attributed to the lower overall quality of concrete due to lower amounts of hydrated cement. Lack of hydrated cement in ordinary concrete can result in higher porosity and permeability that can severely reduce the durability.

It has been shown that replacing small amount of cement with limestone powder can reduce chloride permeability of concrete. Gesoglu et al. (2012) replaced cement with 5, 10, and 20% of limestone powder and conducted Rapid Chloride Permeability Test (RCPT) according to ASTM C1202. Their results showed that at all the three levels of limestone content, the total charge passed through the concrete samples were lower than the concrete with just PC. They justified this improvement by attributing it to the filler effect of limestone powder. Li and Kwan (2015) discussed that the pore structure of concrete in their study was refined as a result of filler and nucleation effect of fine limestone incorporation. They tested samples with 4, 8, and 12% limestone content and compared their RCPT results to the control sample. Their RCPT results are presented in Figure 2.5.1 and show that at every w/c, the increasing limestone content has led to lower charge passed through concrete. Tsivilis et al. (2000) also performed RCPT according to ASTM C1202 on 28-day old samples. Their results, presented in Table 2.5.1, show that increasing limestone content up to 15% does not significantly affect chloride permeability, but in higher limestone contents, the negative effect is noticeable. Other researchers such as Alunno-Rossetti and Curcio (1997) and Bonavetti et al. (2000) also reported higher chloride ion penetration in PLC as opposed to PC.

Table 2.5.1: Chloride permeability of concrete with limestone addition (Tsivilis et al.-2000)

Limestone, %	0	10	15	20	35
Fineness, m^2/kg	260	340	366	470	530
Mortar: strength at 28 days (MPa)	51.1	47.9	48.5	48.1	32.9
Concrete: W/CM	0.70				0.62
Concrete: strength at 28 days (MPa)	31.9	27.4	27.3	28	26.6
Concrete: RCPT (Coulombs)	6100	5800	6000	6400	6600

Gonzales and Irassar (1998) and Irassar et al. (2000 and 2005) compared length change of mortar bars made of three cements with 0, 10, and 20% limestone in 5% sodium sulfate solution to study their sulfate resistance. They found that samples with 20% limestone addition had more expansions compared to the others. In a review of sulfate attack in cement, Irassar (2009) concluded that PLC is more vulnerable to sulfate attack than PC especially in cold temperatures (under 15°C). Resistance of concrete to freeze/thaw cycles, deicer salt scaling, and carbonation also highly depend on permeability of concrete, and may suffer in cements with high limestone contents.

Sorptivity or rate of water absorption is an important durability measure which indicates how fast water or potentially solutions containing deleterious ions can travel through concrete using the capillary action. When limestone particles are smaller than cement particles, they can fill up the voids and improve the packing density, and consequently reduce sorptivity. Gesoglu et al. (2012) found that the sorptivity of concrete was lower when 5, 10, and 20% of cement was replaced with limestone powder. They concluded that adding LS to replace cement could reduce the sorptivity coefficient. Chen et al. (2014) also reported reduced sorptivity due to the filler effect of limestone when 4 or 8% of cement was replaced with limestone powder. Their results are shown in Figure 2.5.2.

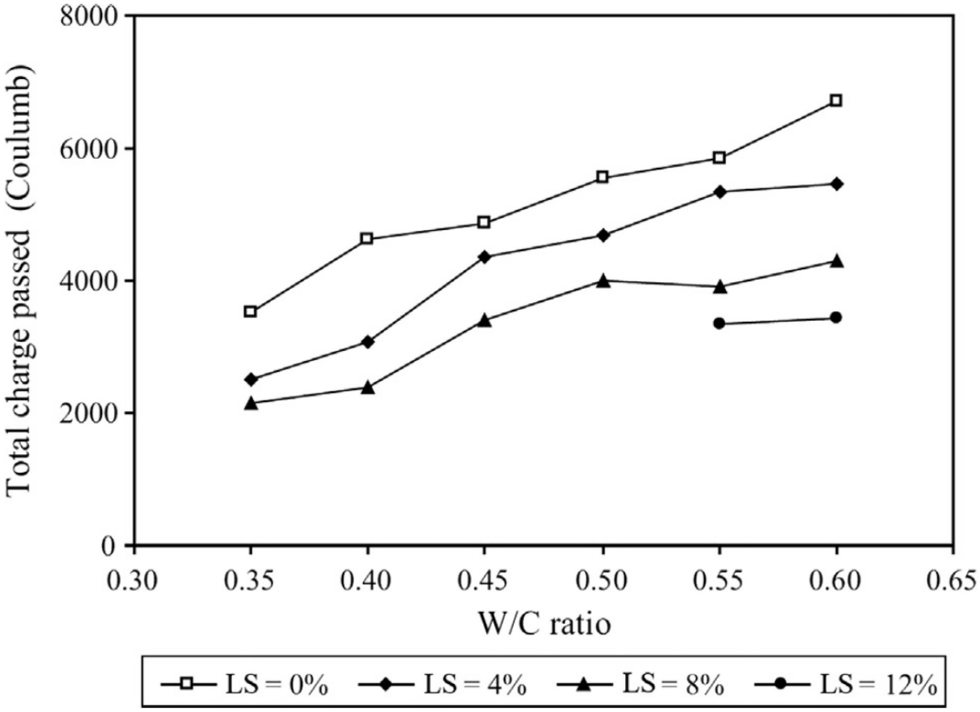

Figure 2.5.1: Effect of w/c and limestone content on RCPT results (Li and Kwan-2015)

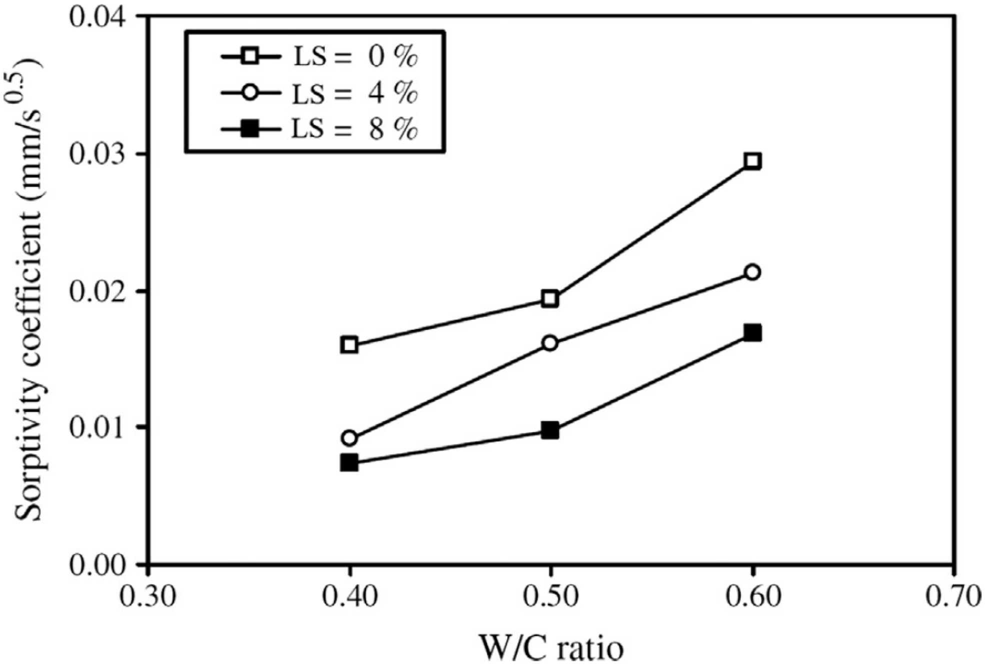

Figure 2.5.2: Effect of limestone content on sorptivity of concrete (Chen et al.-2014)

Sulfate resistance is another important durability property of concrete. Sulfate ions that penetrate concrete react with calcium hydroxide to form gypsum. Gypsum will then react with C_3A and form ettringite. Gypsum and especially ettringite are larger in volume than the reactants, and their formation can cause cracks and deformations in concrete. Therefore, the cement with higher C_3A content is generally more susceptible to sulfate attack. Sulfate attack has been widely studied, and its effects are well known. As an example, Tosun-Felekoğlu (2012) measured the expansion of mortars made with two types of cement; one with 4.59% C_3A content and one with 11.25% C_3A content. He found significantly larger expansions in mortar bars with higher C_3A content. Schmidt et al. (2008 and 2009) also confirmed the higher susceptibility of cement with higher C_3A content to sulfate attack.

Another type of sulfate attack happens when sulfate ions in the presence of carbonate ions and water react with the C-S-H gel and form thaumasite which is non-cohesive and results in disintegration of cement paste and concrete. A very important source of carbonate ions is calcium carbonate (limestone) in the cement. Therefore, higher limestone content severely increases the susceptibility of concrete to sulfate attack. This is why the Canadian standard does not allow the use of limestone cement in sulfate exposure unless supplementary cementing materials are used with it. Thaumasite formation becomes the major form of sulfate attack at temperatures close to 5°C. This is a very important form of sulfate attack that is extremely sever in cements with high limestone content. Thaumasite formation and its effects have been confirmed and studies by many researchers such as Skaropoulou et al. (2009), Ramezanianpour and Hooton (2013), and Mirvalad and Nokken (2015). Mirvalad and Nokken (2015) also mentioned that due to the increase of limestone content, the active cementitious materials content was reduced which weakened the overall hydrated cement matrix and increased the impact of sulfate attack. Overall, the only way limestone cement can properly resist sulfate attack seems to be partially replacing it with SCMs. This replacement can reduce the total C_3A and calcium carbonate present for sulfate attack, improve C-S-H formation, and reduce calcium hydroxide due to the pozzolanic reactions.

2.6 Nanotechnology and Concrete

Nanoparticles by definition are the particles that have at least one dimension with the size in the range of 1 to 100 nm. The chemical composition of these particles along with their small size and extremely high surface area can potentially affect chemical reactions leading to C-S-H formation in cementitious environments. Therefore, studying nanoparticles and their effects seems crucial for concrete industry and can lead to improvements and development of innovative construction materials and methods.

Nanotechnology has been revolutionized ever since it first caught attention after the famous 1959 lecture by Richard Feynman, the American theoretical physicist, ‘‘There’s Plenty of Room at the Bottom” (Feynman-1960). In his lecture, he referred to nanoscale as “the bottom” emphasizing the potential for breakthroughs by conducting research in this field. The term “nanotechnology” has been widely used in various domains to describe anything related to an extremely small scale, but it is more specifically defined as “the understanding, control, and restructuring of matter on the order of nanometers (i.e., less than 100 nm) to create materials with fundamentally new properties and functions” (Sanchez and Sobolev-2010). There have been two main approaches in nanotechnology. The first approach is referred to as the “top-down” approach where the size of larger materials or structures are reduced to nanoscale without changing their original properties by any atomic-level control. The second approach is referred to as the “bottom-up" approach or molecular nanotechnology (Drexler et al.-1991) where materials are engineered and assembled from their atomic or molecular components. In concrete technology, grinding silica fume powder down to nano silica particles is an example of a top-down approach while making nona silica using methods like sol-gel process is considered a bottom-up approach.

Concrete is a multi-phase composite material made of amorphous phase, crystals, and bound water. The chemical and physical characteristics of concrete changes over time. Cement hydration that leads to C-S-H formation is an ongoing process that provides strength for concrete while other destructive chemical reactions occur that can result in the deterioration of concrete. The amorphous calcium silicate hydrate (C-S-H) gel is itself considered a nano-structured material with nano pores (Sobolev and Gutiérrez-2005). Sanchez and Sobolev (2010) stated that looking through a bottom-up view, "concrete at the nanoscale is a composite of molecular assemblages, surfaces (aggregates, fibers), and chemical bonds that interact through local chemical reactions, intermolecular forces, and intra-phase diffusion. Properties characterizing this scale are molecular structure; surface functional groups; and bond length, strength (energy), and density". Changes and processes that affect the propertied of concrete at nanoscale ultimately affect the properties and performance of concrete as a bulk material (Scrivener and Kirkpatrick-2008). Birgisson et al. (2010) specified the possible outcomes of incorporating nanotechnology in concrete to be development of better ultra-high performance concrete (UHPC), more sustainable and safer concrete, intelligent concrete, and novel concrete materials. Similarly, this research seeks developing a more durable and sustainable concrete by incorporating nano calcium carbonate particles in the cement paste.

2.7 Nanoparticles Used in Cement

The idea of using extremely fine materials such as nanoparticles in concrete has been around for decades. One of the first studies that used nanoparticles in cementitious mixtures was the work of Stein and Stevels (1964) where they incorporated extremely fine silica with very high surface area, similar to the currently existing nano-silica, to accelerate the hydration of C_3S. Their study signaled the potential of nanoparticles in modifying the properties of cement-based materials, but it did not attract many researchers until 2004 (Reches-2018). In recent years, the most common nanoparticles that have been used in cementitious mixtures are SiO_2, TiO_2, Al_2O_3, Fe_2O_3, carbon nanotube (CNT), and clays (Kumar et al.-2011 and Reches-2018) in order to effectively improve properties of fresh or hardened cement product. As discussed in Sections 2.3, 2.4, and 2.5, since fine limestone powder incorporation has shown promising effects on different properties of concrete, nano-sized limestone powder, i.e. calcium carbonate nanoparticles, have also been studied in recent years by several researchers.

Figure 2.7.1 compares the size and surface area of different constituents of concrete. Due to the sheer small size and high surface area, all nanoparticles (NPs) can contribute to cement matrix through both their nucleation effect and filler effect. In other words, they can provide the seeds for cement hydration reactions and fill the voids in the cement matrix to improve the packing density. This is why many researchers have used the nanoparticles as hydration accelerators. However, some types of nanoparticles can also directly participate in chemical reactions leading to C-S-H formation. Similar to nano-silica, Al_2O_3 and some clay nanoparticles have shown pozzolanic properties to form calcium silicate hydrates and calcium aluminate hydrates (e.g. Chang et al.-2007, Stefanidou-2017, El-Gamal-2018, and Reches-2018).

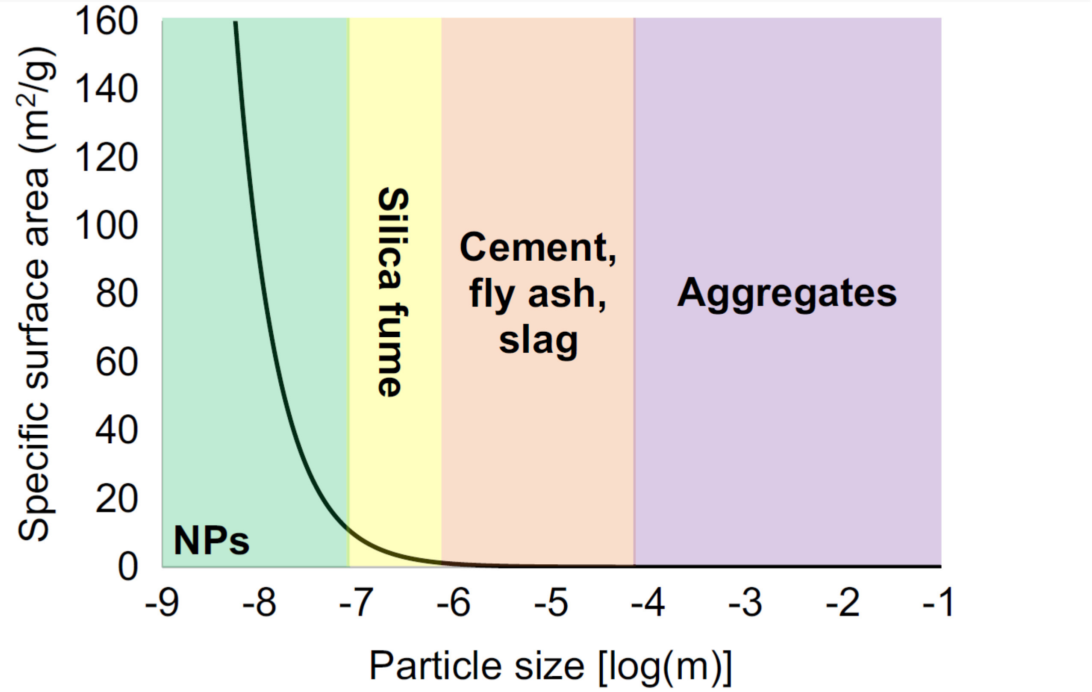

Figure 2.7.1: Comparing particle size and specific surface area of different constituents of OPC based products (Sobolev et al.-2006)

Overall, after several years of research on the effects of nanoparticles on cement-based products, the consensus seems to be that the major role of nanoparticles is their nucleation effect on hydration reactions. Moreover, some nanoparticles are still too expensive, and they may not be cost effective approaches for the concrete industry. While the price of nanoparticles is expected to decrease over time as their mass production expands, the concrete industry will be looking for cheaper nanoparticles that also have an efficient nucleation effect. This is why studies such as Reches (2018) suggested the use of nano-clays and nano-$CaCO_3$ that are generally less expensive than other commercially available nanoparticles in concrete industry. Another important factor in the use of nanoparticles in concrete is their content relative to cement. Proper dispersion of nanoparticles which prevents agglomeration can increase the efficiency and reduce the cost.

2.8 Effect of Nano Calcium Carbonate on Early Age Properties of Concrete

In Section 2.3, the four major effects of limestone powder in cementitious mixtures were discussed. Compared to micro limestone powder that can have a very wide range of particle sizes (tens to hundreds of microns), the narrow size range of NC particles (tens of nanometers) is specifically optimized to improve the hydration of cement through their nucleation effect. Due to their narrow size range, the NC particles can be very efficient in their nucleation effect. That is why even small NC contents of less than 5%, which is very common in the literature, can have a significant impact on the hydration reactions. Since the NC content is small with respect to cement, their dilution effect can be insignificant.

2.8.1 Workability and Bleeding

Similar to fine limestone powder, addition of NC can increase water demand and reduce bleeding and workability due to its very high surface area. This has been confirmed in many studies such as Li et al. (2015 & 2016), Supit and Shaikh (2014), and Wu et al. (2016). Li et al. (2016) replaced 1, 2, and 3% of the cementitious materials of their UHPC with NC and saw reduced flowability as a result of these additions (Figure 2.8.1). However, there have also been studies such as Camiletti et al.-2013 that reported better workability as a result of NC addition (Figure 2.8.2). It can be concluded that for a given type of NC with specific particle size, there may be an optimum NC content with regards to workability and bleeding (Yahia et al.-2005).

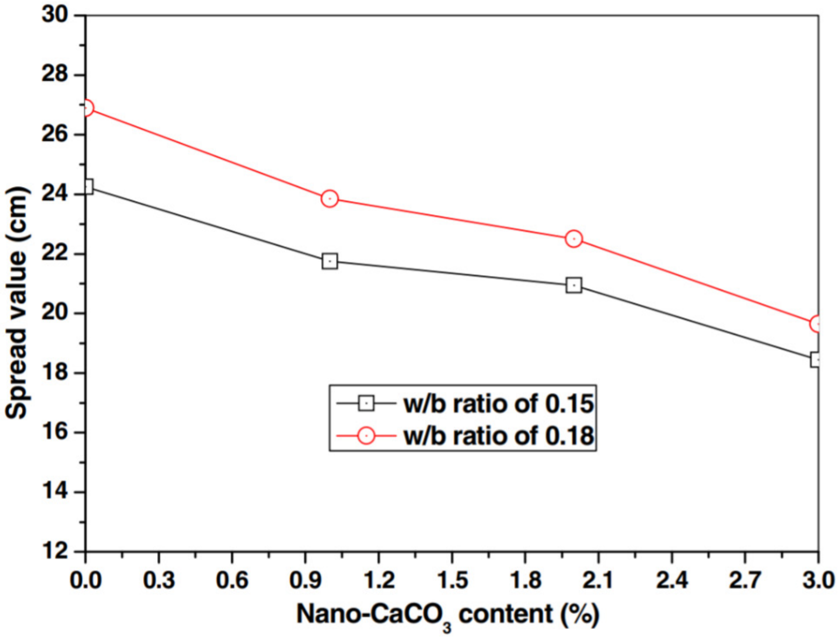

Figure 2.8.1: The effect of NC on flowability of UHPC (Li et al.-2016)

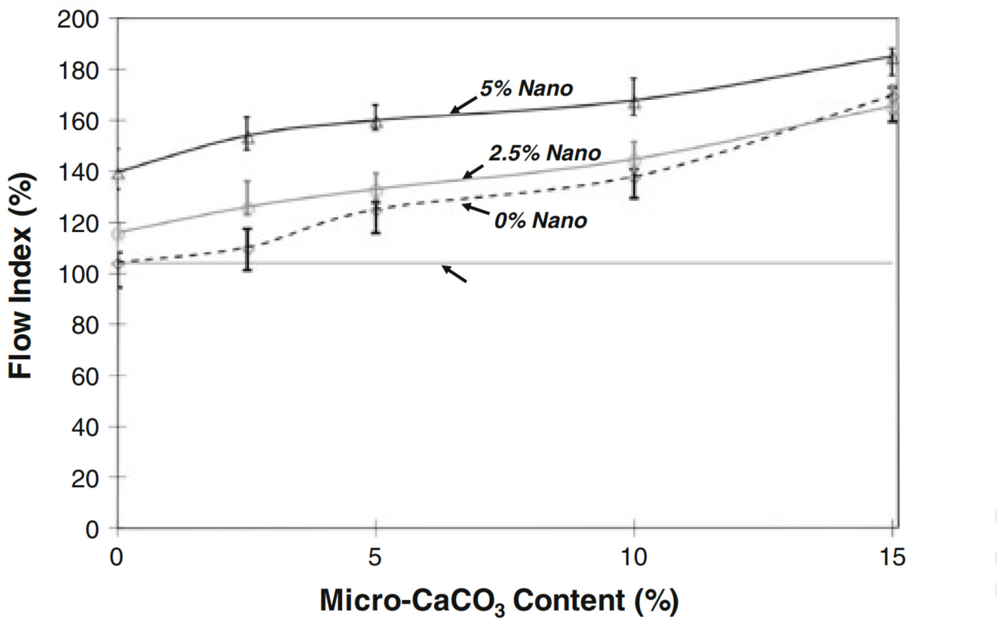

Figure 2.8.2: The effect of NC and regular limestone powder on flowability of UHPC (Camiletti et al.-2013)

2.8.2 Setting Time and Heat of Hydration

NC has been known to perform as an accelerator for cement hydration reactions due to its nucleation effect (e.g. Sato and Diallo-2010, Camiletti et al.-2012, Vance et al.-2013, and Wang et al.-2018). Therefore, many studies have used NC in mixtures with high volume of SCM that usually suffer from delayed hydration (Shaikh and Supit-2014, Supit and Shaikh-2014, Bentz et al.-2012, and Wang et al.-2014). Due to the extremely narrow and optimized range of particle size in NC, a group of other studies have used NC to improve rate and degree hydration in UHPC (e.g. Li et al.-2015 and Wu et al.-2016). Li et al. (2015) saw the acceleration effect of NC in their UHPC and reported that the peak of hydration occurred 1.3 hours earlier as a result of 2% replacement of cement with NC.

As mentioned in section 2.4.2, the dissolution of limestone particles, especially when they are extremely fine like in NC, can lead to the chemical reaction between carbonate ions and alumina to form carboaluminates which can result in a more pronounced second peak in the heat of hydration diagram. However, this chemical reaction is usually minor due the limited alumina content in cement, but may be increased if SCMs are used in cement or the cement has inherently higher alumina content than usual. The size of the second peak also depends on the amount NC present and can be insignificant at low NC contents. Sato and Beaudoin (2011) used limestone powder and NC as replacement to cement at very high contents of 10 and 20% and conducted isothermal calorimetry. Consequently, the second peak in their heat of hydration diagrams (Figure 2.8.3) were much more pronounced. As seen in Figure 2.8.3, comparing the effect of micro and nano limestone particles on heat of hydration, they found that the NC was much more effective. In addition to the rate of hydration of cement, the degree of hydration can also be improved by incorporating NC, and since heat of hydration is an indication of C-S-H formation, the setting time is expected to be shortened as well which has been seen in many studies. As an example, Wu et al. (2016) reported increased cumulative heat of hydration and decreased setting time in UHPC with increased NC addition.

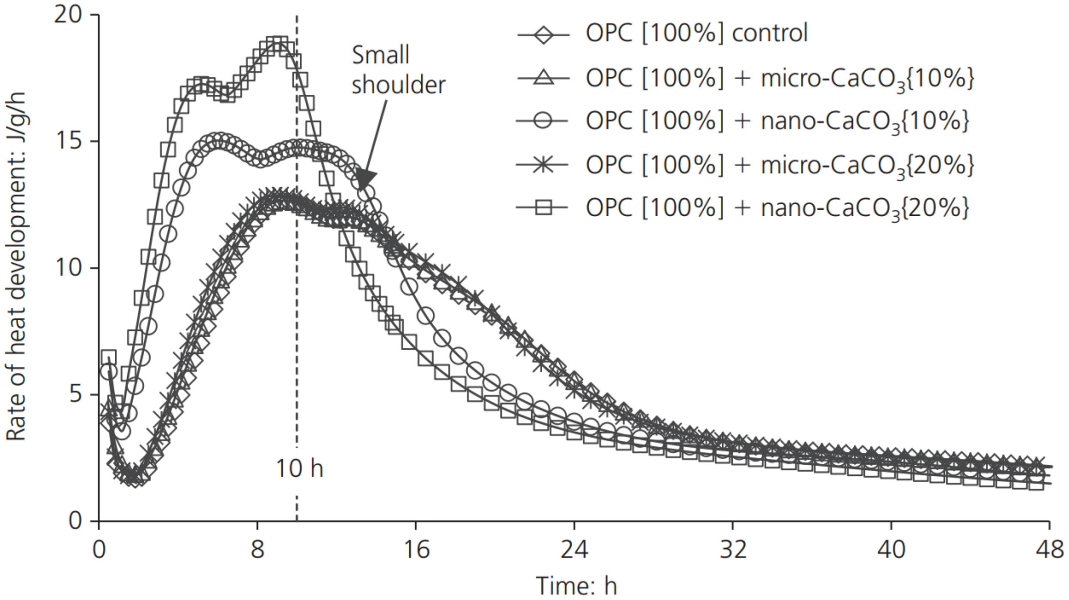

Figure 2.8.3: The effect of micro- and nano-CaCO3 incorporation on isothermal calorimetry of OPC for w/b of 0.5 (Sato and Beaudoin-2011)

2.9 Effect of Nano Calcium Carbonate on Mechanical and Durability Properties of Concrete

As discussed in Section 2.8, the approach of most of current literature with regards to NC has been to use it as a cement hydration accelerator which can be beneficial to early age properties of concrete. However, increased rate and degree of hydration in early ages can affect the cement matrix in such a way that mechanical and durability properties of concrete may also be improved. Many researchers have reported different extents of improvement of compressive strength and other mechanical properties as a result of NC addition. Sato and Beaudoin (2011) reported remarkable improvements in modulus of elasticity of samples that had NC additions. In a more recent study, Wu et al. (2016) used NC contents of 0, 1.6, 3.2, 4.8, and 6.4% by mass of cementitious materials. They found that when NC content was in the range of 1.6-4.8%, compressive and flexural strengths were improved 13-20% and 15-30%, respectively. However, when the NC content was increased to 6.4%, both strengths were reduced significantly suggesting that there can be an optimum NC content with regards to strength. Li et al. (2016) found noticeable increase in compressive strength and flexural strength of UHPC due to 1, 2, and 3% NC incorporations. Their results show that higher NC content led to higher strengths. Camiletti et al.-2012 used 2.5% and 5% of NC in their blended limestone mixtures for concrete. As a result of NC incorporation, the compressive strength of some of their samples were increased while that of some other ones were decreased. Supit and Shaikh (2014) measure the compressive strength of mortar samples with 1, 2, 3, and 4% NC content. They saw decreased compressive strength for 2, 3, and 4% NC contents and increased compressive strength for 1% NC content. They attributed the decreased compressive strengths to agglomeration of NC particles.

While there have been several studies on the effect of micro limestone powder on durability of concrete (discussed in Section 2.5), current literature lacks specific studies on the effect of NC on different durability measures. One rare example is the study done by Shaikh and Supit (2014). They investigated the effect of NC powder on mechanical and durability properties of high volume fly ash concrete. They investigated multiple durability measures and reported that mixtures with 1% NC addition exhibited improved compressive strength and lower permeability, porosity, volume of permeable voids, and absorption. Li et al. (2015) have also found NC particles to be effective in filling the pores and resulting in a denser matrix in ultra-high performance concrete which would potentially demonstrate better durability. The lack of research on durability of Portland cement and Portland limestone cement containing NC particles was one of the main incentives for this thesis.

2.10 Silica Fume's Action in Cement Paste

Silica fume is one of the most widely used SCMs which is a by-product of the silicon and ferrosilicon alloy production. It is an amorphous polymorph of silicon dioxide (silica) which is generally in the form ultra-fine powder consisting of spherical particles (less than 1 μm). Due to its extreme fineness and high silica content, it is a very reactive pozzolanic material. Silica fume can be beneficial to concrete through three different action mechanisms (Siddique-2011). First, because of the very small size of silica fume particles, they can refine the pore structure and lead to an overall denser cement paste matrix. Second, through the pozzolanic action, silica fume particles can react with the calcium hydroxide resulting from hydration of cement and form new C-S-H gel that can further densify the cement matrix. Third, silica fume reduces the thickness of interfacial transition zone (ITZ) between cement paste and aggregates and also decreases the degree of orientation of calcium hydroxide crystals in this layer. This leads to significant improvement of mechanical and durability of concrete.

2.11 Effect of Nano Silica on Early Age Properties of Concrete

Utilization of nano silica (NS) by researchers in cementitious products is more common than NC. In this research, NS is used as a comparative measure in order to evaluate the extent of effectiveness of NC particles in concrete. Therefore, the effect of NS on properties of concrete are briefly reviewed in Sections 2.11 and 2.12.

Most researchers have used NS as a very small (generally less than 5%) replacement of cement or addition (Aggarwal et al.-2015). In addition to the three action mechanisms of silica fume mentioned in Section 2.10, NS particles can also improve cement hydration thought their nucleation effect.

2.11.1 Workability and Bleeding

There seems to be a consensus among researchers on that fact that using NS significantly increases water demand and reduces bleeding due to its extremely high surface area. When studying cement paste samples, Senff et al. (2009 & 2010) saw significantly increased torque and yield stress in mixtures containing only 2.5% NS by weight. Rheology of cement pastes with various w/b ratios was investigated in the work of Berra et al. (2012) and Kawashima et al. (2012). They found that with the use of NS, in order to maintain a certain level of workability, more water should be added. They attributed the increase in water demand to the high surface area of NS. In order to improve workability without altering the w/b ratio, Berra et al. (2012) suggested the use of chemical admixture/superplasticizers or simply keeping certain amount of water to be added at a later stage. Also in order not to interfere with the reactivity of NS, they suggested delaying the addition of superplasticizers. Ltifi et al. (2011) stated that at a constant water content, increasing NS improves the packing density of particles resulting in reduced volume between the particles for free water. They concluded that this can increase the internal friction between the particles and reduce workability.

2.11.2 Setting Time and Heat of Hydration

The nucleation effect of NS can accelerate the hydration of cement and also the pozzolanic reactions both of which are exothermic chemical reactions leading to the formation of C-S-H gel. Generally, anything that accelerates hydration of cement and consequently formation of C-S-H can shorten both initial and final setting time. Senff et al. (2009) studied the effect of 0, 1, 1.5, 2, and 2.5% of NS content on cement paste and mortar. As a part of their investigation, they observed reductions in both initial and final setting time of mortar (Figure 2.11.1). At 2.5% NS content, the setting times were reduced by 50-60%. Moreover, Qing et al. (2007) and Ltifi et al. (2011) found that increasing NS content in their mixtures reduced the time between the initial and final setting.

Studies that show the increased rate and degree of hydration due to the use different form and contents of NS are quite common, and the effective nucleation of NS is well-known (e.g. Björnström et al.-2004, Qing et al.-2007, Senff et al.-2009, Thomas et al.-2009, Land and Stephan-2012, Kong et al.-2012, Torabian Isfahani et al.-2017, Rupasinghe et al.-2017).

Thomas et al. (2009) investigated the effect of 2, 4, and 10% of colloidal silica on the heat of hydration of C_3S. They saw that the peak of heat of hydration diagram was increased by 50-70% as a result of NS incorporation. The total heat of hydration in the first 24 hours was also increased. Land and Stephan (2012) synthesized silica particles with sizes of 7, 18, 86, and 295 nm to study the effect of silica particle size and surface area on the hydration of cement. At 1% NS content, the peak of heat of hydration was increased with the use of every silica particle size of their study, but the smaller particles were more effective (Figure 2.11.2). They concluded that the acceleration of cement hydration is correlated with the total surface area of the added particles which can be changed by changing the number and size of the particles. In other words, the surface area introduced to the system by the particles is the major contributing factor to the cement hydration. Rupasinghe et al. (2017) performed calorimetry on cement paste samples with NS contents of 0 to

12%. They concluded that the 8% NS content is the optimum amount, and lower and higher contents are not as effective.

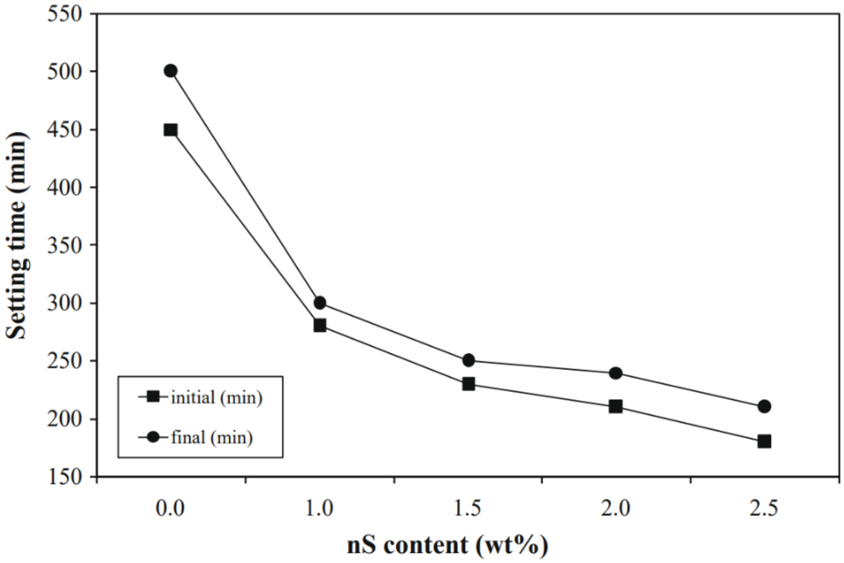

Figure 2.11.1: Effect of NS content on initial and final setting time of mortar (Senff et al.-2009)

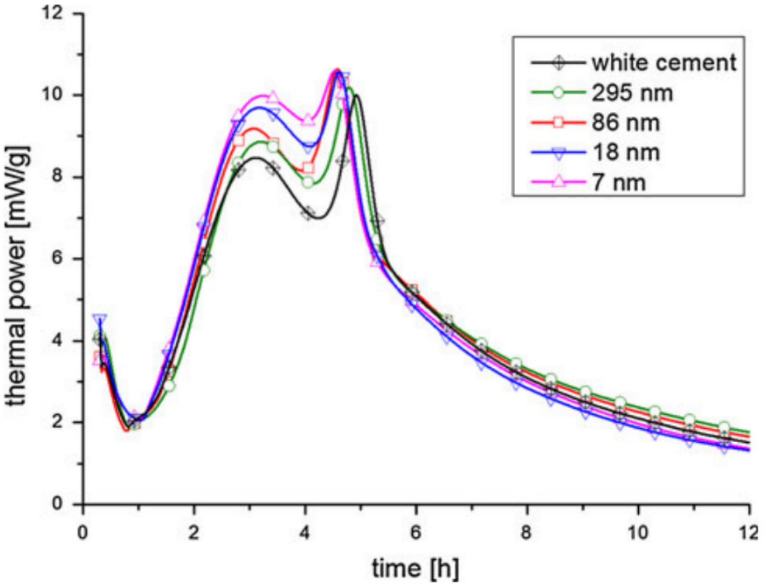

Figure 2.11.2: Effect of size of silica particles on the heat of hydration of cement using isothermal calorimetry (Land and Stephan-2012)

2.12 Effect of Nano Silica on Mechanical and Durability Properties of Concrete

There seems to be a general agreement in the literature on the fact that NS can improve compressive strength of cement paste, mortar, and concrete. The pozzloanic reactivity and the filler and nucleation effect along with ability of the NS to improve the ITZ can all contribute to a concrete with higher strength and better durability (Siddique-2011).

Jo et al. (2007) showed that 7-day compressive strength of mortar samples with 3-12% of NS (median particle size of 40 nm) addition were approximately twice that of samples with 5-15% of silica fume (median particle size of 0.1 μm) addition. Compressive strength was increased with higher contents of NS in their results. The 3-day compressive strength of high volume fly ash concrete was increased by 81% with 4% of NS in the work of Li et al. (2004). Givi et al. (2010) used up to 2% of NS in concrete and saw an increase in compressive, flexural, and split tensile strengths at all ages. The study of Sobolev et al. (2009) showed that even a small content of 0.25% of NS was enough to increase the 28-day compressive strength and flexural strength by 10% and 25% respectively. Shakhmenko et al. (2013) used 2% of NS that they synthesized by the sol-gel method into their cement paste samples and reported that the compressive strength was increased to more than three times. Ghafari et al. (2014) and Wu et al. (2016) also reported increased compressive strength due to the use of NS. There are several other studies that confirm the efficacy of NS in improving mechanical properties of cementitious products. However, some other studies have reported that increasing NS beyond certain contents may have negative impacts on compressive strength (e.g. Li et al.-2004 and Singh et al.-2013). This suggests that there can be an optimum content for NS, but since the NS particles used by different researchers are different in properties such as type, particle size distribution, and dispersion, there is yet no agreement on optimum NS content.

Generally, anything that decreases permeability of concrete can potentially improve its durability. Many researchers have reported improvements of different durability measures of concrete such as pore size distribution, resistance to chloride penetration, and sorptivity. Li (2004), Zhang and Li (2011), Zhang et al. (2012), and Jalal et al. (2012) reported reduced total and rate of water absorption. Moreover, Li (2004) and Zhang and Li (2011) found refined pore and lowered porosity even at early ages as a result of 4% NS addition. Some researchers such as Zhang et al. (2012) suggested that increasing NS content can improve their efficacy to enhance certain durability measures but did not discuss the possible optimum NS content. Resistance to chloride penetration was also increased due to incorporating NS in the works of Jalal et al. (2012), Zhang and Li (2011), and Zhang and Islam (2012).

2.13 Summary of Background and Gaps in the Literature

Global warming has become an ever-increasing concern in the past decades. The efforts to address this concern led to the 2016 Paris Agreement within the United Nations Framework Convention on Climate Change. The goal of this agreement, signed by 196 countries, is to substantially reduce the risks and impacts of climate change by keeping the increase in global average temperature to less than 2°C above the levels before the beginning of industrial revolution. This goal can only be achieved by extensively reducing the emission of greenhouse gases by all countries in different industries including the extremely high-emission concrete industry.

Introducing Portland-limestone cement (GUL), containing up to 15% limestone, by the Canadian standard in 2008 was a sign of growing interest in using this kind of cement and a step toward a greener concrete industry in Canada. While there have been certain types of cement allowed by the European standards containing up to 35% limestone for many years, the limestone content levels in Canadian standard has remained unchanged mainly to protect mechanical and durability properties of GUL. There have been countless efforts with great success by researchers to improve different properties of cement by using nanoparticles. Thus, there seems to be no doubt that aiming those efforts toward studies on PLC can result in improved performance which will eventually lead to adoption of higher limestone content levels by the Canadian standard. Studies with a clear goal of exploring the possibility of using higher limestone content appear to be lacking from the current literature.

Furthermore, while NC has been shown to be effective in accelerating cement hydration and improving certain performance measures of concrete, its influence on durability of cement and more specifically limestone cement is definitely missing from the existing literature. In addition, approach of most of the research conducted on NC have been to using it in UHPC or concretes with high levels of SCM. However, due to the relatively low cost of NC, research on its application in ordinary concrete may also be of great interest.

Limestone is one of the main ingredients of cement and is readily available to cement plants. Therefore, increasing the limestone content of cement at cement plants is a completely feasible practice that can also potentially reduce the grind cost as limestone is softer than clinker. The common practice in cement plants is to inter-grind limestone with clinker. This generally results in limestone particles in the range of tens of microns. Alternatively, micro limestone powder, in the same size range as it would exist after inter-grinding with clinker in cement plants, can be blended with cement to make limestone cement. Since this is an easier and more practical method in the lab at the university, it was adopted in this research.

Micro limestone powder was blended with general use Portland cement at 15% content level which represents the current limestone cement in Canada and at 20% and 25% for evaluating the contents beyond the 15% standard limit. High micro limestone contents were expected to negatively impact properties of concrete due to the lower overall hydrated products in the cement matrix. Most of literature show that small contents of NC (generally less than 5%) can lead to noticeable improvements in cement hydration and concrete properties. Therefore, the idea of using NC as an additive that can fully or partially compensate for lower overall quality of cement with high micro limestone content was evaluated. In other words, this research intends to demonstrate the efficacy of small additions of NC, in the range of a few percent, on mechanical and durability properties of cement with different levels of micro limestone content. This can potentially show the possibility of increasing micro limestone content of cement without compromising its properties which results in a greener cement with lower carbon footprint.

3. EXPERIMENTAL PROGRAM AND METHODS

As previously mentioned, the focus of this research is the durability properties of blended limestone cement containing calcium carbonate nanoparticles as an additive. Durability indicators such as bulk electrical conductivity, bulk electrical resistivity, rate of water absorption (sorptivity), volume of permeable voids, and expansion due to sulfate attack have been measured for mortar samples at different ages in order to compare and monitor their development over time. Moreover, isothermal calorimetry of cement paste and compressive strength of mortar cubes have been studied.

Colloidal Nano Silica (NS) is another type of nanoparticle commonly used in cementitious mixtures. In order to better understand the degree of efficacy and have a comparison between the performance of nano calcium carbonate and nano silica, all of the above-mentioned tests are also done on select mixtures containing nano silica as an additive.

3.1 Materials

In Canada, General Use cement (CSA A3000 Type: GU) contains up to 5% limestone, and General Use Portland Limestone cements (CSA A3000 Type: GUL) that are commercially available contain up to 15% limestone (the actual number is usually 12-13% (Hooton-2010), slightly lower than the 15% limit of CSA). In this research, Portland cement Type GU provided by Lafarge from the Saint-Constant plant in Quebec was used. This cement has 4.75% inter-ground limestone and its chemical composition and physical characteristics are presented in Table 3.1.

Limestone powder (calcium carbonate) was blended with GU cement in order to have an overall limestone contents of 5, 15, 20, and 25%. The limestone powder used was a dry white powder with a commercial name of Betocarb® HP provided by Omya, Perth, Ontario. Since limestone particles are softer than clinker, when they are inter-ground with clinker in cement plants, the final product contains limestone particles that are finer than cement particles. Therefore, Betocarb® HP limestone powder with slightly finer particles (Blaine fineness of 475 m^2/kg) was selected to better simulate an inter-ground limestone cement. This approach was selected rather than using commercially produced GUL cements in order to have consistent materials for all limestone replacement levels. However, it should be mentioned that blending limestone powder with GU does not provide an exact identical cement to the commercially available GUL which is inter-ground at cement plants. In commercial cements, the C_3A and sulfate content of GUL are optimized for better sulfate resistance and strength, and GUL is generally finer than GU cement.

Calcium carbonate nanoparticles (NC) are used in many industries and are commercially available. The one that was chosen for this study is in the form of a dry powder. It was purchased from SkySpring Nanomaterials Inc., Houston, Texas and has a particle size range of 15-40 nm. Also, colloidal nano silica (NS) in water (LUDOX® HS-40) was purchased from Sigma-Aldrich. It has 40% nano silica by mass with a median particle size of 12 nm.

Numerous researchers have used polycarboxylate water reducer admixtures as surfactants to stabilize NC particles (e.g. Camiletti et al.-2013a, Saraya and Rokbaa-2016, and Wu et al.-2016). In this study, a regular polycarboxylate high range water reducer admixture from Sika (ViscoCrete-2100) was chosen to stabilize NC particles in water after dispersion.

Table 3.1: Chemical composition and physical characteristics of the GU cement used in this research

Chemical Composition		**Potential Phase Composition**	
SiO_2 (%)	19.5	C_3S (%)	55
$Al2O_3$ (%)	4.8	C_2S (%)	15
Fe_2O_3 (%)	3.1	C_3A (%)	7
CaO (%)	61.6	C_4AF (%)	9
MgO (%)	2.9	**Physical Characteristics**	
SO_3 (%)	4	Fineness (Blaine) (m^2/kg)	398
Na_2O (%)	0.25	Retained on 325 mesh (%)	5.2
K_2O (%)	0.86		
Equivalent Alkalis (%)	0.82		
Loss on Ignition (%)	2.3		
Insoluble residue (%)	0.5		

3.2 Mixtures

Limestone cement in this research was prepared by blending limestone powder with GU cement. Since, the GU cement already has approximately 5% limestone content, additional limestone was blended with it to achieve the desired overall limestone contents of 15, 20, and 25% that are used for the cement paste and mortar mixtures. The 5% limestone content level consists only of the GU cement and is used as a reference, the 15% level represents the CSA limit set for GUL cement, and the 20% and 25% levels were intentionally chosen beyond the 15% to explore the possibility of exceeding the North American limit without compromising durability performance. In order to blend limestone powder and cement properly, the calculated proportions were measured and placed in a glass container. The cap was then closed tightly, and the container was shaken rigorously for three minutes to achieve a homogenous blend of limestone cement.

In this research, NC has been used as an additive to cementitious mixtures. NC has already been shown by many researchers to improve cement hydration reactions due to its nucleation or seeding action (e.g. Camiletti et al.-2012, Sato and Diallo-2010, Vance et al.-2013, and Wang et al.-2014). Therefore, it may be hypothesized that adding any amounts of NC will simply result in higher hydration degree in cement paste. However, this may not be completely true, and there have been conflicting results in the literature regarding the amount of NC that needs to be used in mixtures for increased hydration. Some studies have used amounts of up to 15% (e.g. Sato and Diallo-2010 up to 10% and Camiletti et al.-2012 up to 15%) of NC with respect to binding material, while some others such as Shaikh and Supit (2014) have found low percentages around 1% of NC to be the most effective. Also, mixing the NC with the rest of the materials has been done differently by researchers. Some researchers have dry-mixed NC powder in cement, some have used ultra-sonication in water before mixing, and others did not clearly provide the details of their mixing methods. Generally, NC particles can bond together and form larger particles that are no longer nano sized which significantly reduces their effectiveness. Any mixing procedure must ensure that these particles do not bond together, and as a result, dry-mixing the NC powder was not adopted in this research. One way to break this bond is to ultra-sonicate the particles in water and coat them with proper surfactants such as polycarboxylate high range water reducing admixtures to provide stability. In this research, in order to disperse the NC powder properly, the powder was added to the entire measured mixing water in a glass beaker. Polycarboxylate high range water reducer admixture (Sika ViscoCrete-2100) was also added to the water. The combination was then ultra-sonicated with a sonicator probe (Branson S-450 Digital Sonifier) for three minutes. As the sonication can generate heat, the beaker was kept in an ice bath during this process to keep its temperature at room temperature (23°C).

Since several standard methods use a 0.485 w/c ratio, this was selected as the basis for all of the mixtures in this research. Based on experience, adding more than 5% NC powder to this amount of water makes it so dense that ultra-sonication becomes impractical, and beyond 10% NC addition can result in a paste. Moreover, adding high percentage of NC powder can significantly alter the overall limestone content of the mixture which is not desired. Therefore, in this study, NC addition of less than 5% was intended from the beginning.

Table 3.2: Cement pasted proportions used to specify the favorable NC addition

Mixture ID	Micro Limestone Content (%)	Nano Calcium Carbonate (NC) Additive (%)
GU5-NC0	5	0
GU5-NC1	5	1
GU5-NC2	5	2
GU5-NC3	5	3
GU5-NC4	5	4
GU15-NC0	15	0
GU15-NC1	15	1
GU15-NC2	15	2
GU15-NC3	15	3
GU15-NC4	15	4
GU20-NC0	20	0
GU20-NC1	20	1
GU20-NC2	20	2
GU20-NC3	20	3
GU20-NC4	20	4
GU25-NC0	25	0
GU25-NC1	25	1
GU25-NC2	25	2
GU25-NC3	25	3
GU25-NC4	25	4

The first step in the experimental program of this research was to specify the favorable percentage for NC addition to the blended limestone cement mixtures. The favorable NC content was decided based on its effect on total 3-day heat of hydration of cement paste which can be a measure of progress of exothermic hydration reactions. Table 3.2 shows limestone and NC proportions used for this purpose. The first column of the Table 3.2 and 3.3 shows the mixture IDs where GU is the type of cement used for the blend followed by its micro limestone percentage content, and the two letters and the following number after the dash indicate the type of nanoparticles added to the mixture (NC for nano calcium carbonate and NS for nano silica) and the percentage addition respectively.

Figure 3.2.1 shows the total 3-day heat of hydration of all the mixtures of Table 3.2 resulting isothermal calorimetry of cement paste samples. This figure along with other calorimetry results are presented and discussed in details in Section 4.1.

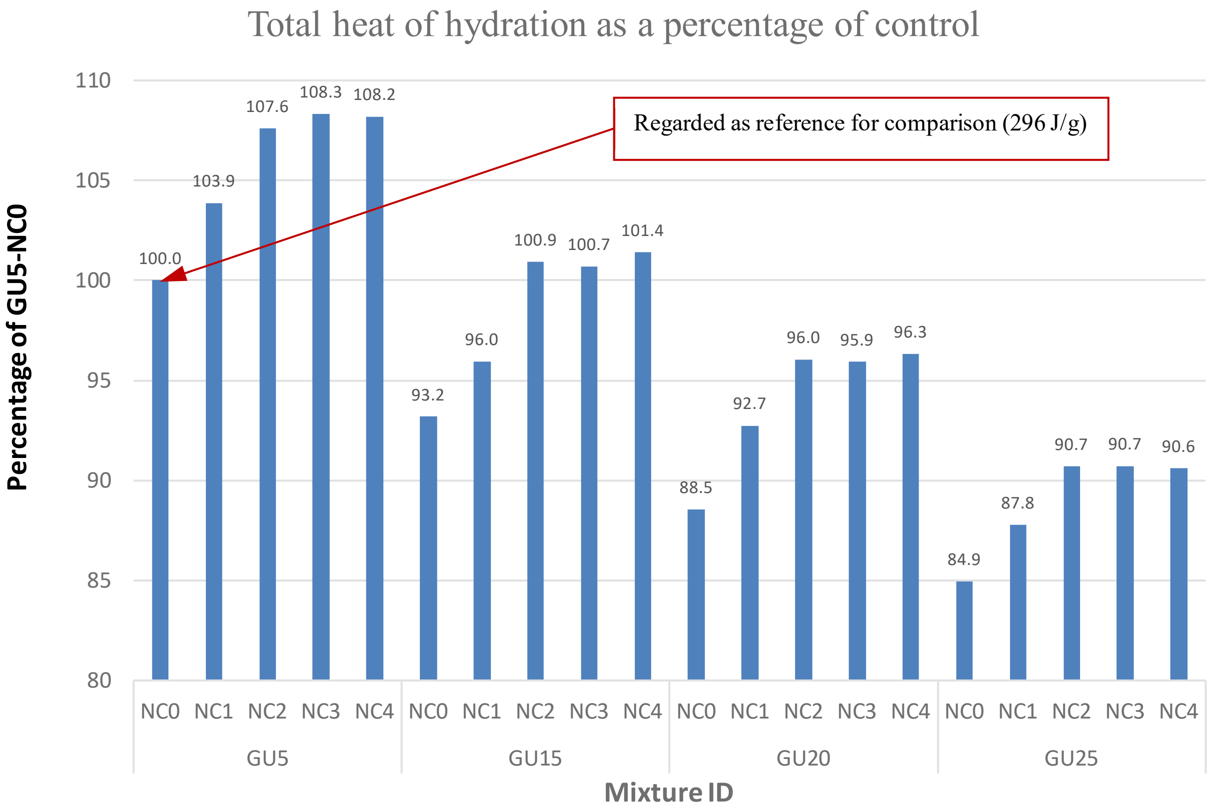

Figure 3.2.1: Total 3-day heat of hydration as a result of NC addition

The results showed that 2% NC addition had demonstrated the most favorable impact on heat of hydration in the first 3 days after mixing at the lowest addition level. Although, the heat of hydration was marginally higher at levels exceeding 2%, the small levels of improvement were not deemed as advantageous. Therefore, 2% NC was the only NC addition for the other experiments of this study. The main focus of this research is the durability properties of blended limestone cement containing NC. In order to compare the performance of NC with another commonly used nanoparticle, the same 2% addition level of nano silica has also been used for cement blends with 15%, 20%, and 25% limestone content levels. The cement, limestone, and additive proportions are listed in Table 3.3.

The NS used in this study is colloidal in water which can be simply added to cement blends along water without the risk of agglomeration, and there is no need for ultra-sonication.

Table 1.3: Clinker, limestone, NC, and NS proportions for the mixes

Mixture ID	Cement (%)	Limestone (%)	NC Additive (%)	NS Additive (%)
GU5-NC0	95	5	0	0
GU15-NC0	85	15	0	0
GU15-NC2	85	15	2	0
GU15-NS2	85	15	0	2
GU20-NC0	80	20	0	0
GU20-NC2	80	20	2	0
GU20-NS2	80	20	0	2
GU25-NC0	75	25	0	0
GU25-NC2	75	25	2	0
GU25-NS2	75	25	0	2

For mortars, the beaker containing water, water reducer, and nanoparticles was added along with cement and standard graded sand (conforming to ASTM C778) were placed into an electrical mixer. Depending on the required volume of mortar, more than one batch was needed for some tests to cast the specimens. In this study, all mortar samples were standard mortar made according to ASTM C305 and ASTM C109. Each mixture was proportioned as one part blended PLC and 2.75 parts standard graded sand at a constant water to cement ratio of 0.485 rather than a constant consistency.

3.3 Isothermal Calorimetry of Cement Paste

Hydration of cement is an exothermic reaction that produces Calcium Silicate Hydrate (or CSH) gel which is responsible for the strength development in cementitious mixtures. The heat evolution due to cement hydration can be studied through isothermal calorimetry. Isothermal calorimetry is a common test that provides information about the rate and degree of hydration of cement paste or mortar sample. In this procedure, the temperature of the sample is kept constant and the flow of heat between the sample and the machine's cell is measured. The isothermal calorimeter used in this research (Calmetrix I-Cal 2000 HPC) has two channels that can measure two samples simultaneously. The dry, blended cement was measured and placed in two plastic cups. Water, NC or colloidal NS additives, and the water reducer were measured and mixed separately in a glass beaker. In the case of NC, the mix of water, water reducer, and NC was ultra-sonicated to prevent the formation of agglomerates. The contents of the beaker were then added to the cement in the plastic cups and mixed with a wooden spatula for 2 minutes until a homogeneous paste was obtained as per manufacturer recommendations. The plastic cups were then capped and placed in the calorimeter. For each mixture listed in Table 3.2 and Table 3.3, two samples are tested for a period of three days at a fixed temperature of 23°C, and the average results are reported.

3.4 Compressive Strength of Mortar

Compressive strength is one of the most basic tests to evaluate strength development of mortar or concrete over time. Standard mortar from every mixture listed in Table 3.3 were cast and tested according to ASTM C305 and ASTM C109. Twenty-four hours after mixing, the cubes were demolded and stored in saturated limewater at 23°C for curing. Three cubes at the ages of 1, 3, 7, 28, and 91 days were removed from the limewater and tested using compressive strength machine (ADR Touch), and the average values are reported.

3.5 Volume of Permeable Voids of Mortar

Concrete is a porous solid material that can potentially host harmful liquids and gases. Permeability is one of the main transport modes of liquid and gases in concrete. Permeability can generally be defined as the property of concrete to allow the ingress of these substances due to an external pressure. The total volume of the pores, their size distribution, and their inter-connectivity can affect the permeability of concrete. Permeability is an important factor for water-retaining structures and elements such as tanks, canals, and pipes, but it is also a decisive factor in evaluating the durability of concrete. Smaller total volume of voids in general may result in a more durable concrete. These voids are potential hosts for liquids such as water which can bring in destructive ions or cause physical deteriorating actions such as freezing-thawing and wetting-drying cycles. The volume of these voids is usually measured as a percentage of total volume of concrete. As the cement hydration reactions progress, these voids continue to diminish due to the formation of more hydration products, and concrete becomes less porous.

In order to compare the volume of permeable voids between different mixtures and also monitor their changes over time, 50×50×50 mm cubes of standard mortar from every mixture listed in Table 3.3 were prepared according to ASTM C305. The cubes were demolded twenty-four hours after mixing and stored in saturated limewater at 23°C for curing. Three cubes at the ages of 3, 7, 28, and 91 days were removed from the limewater and tested according to the procedures described in ASTM C642. Saturated mass, oven-dry mass, and apparent mass while suspended in water were determined for each sample in order to calculate the total volume of permeable voids.

3.6 Rate of Water Absorption or Sorptivity of Mortar

Sorptivity is another main transport mode of water in concrete that can be defined as the ability of an unsaturated porous material to absorb liquids due to the capillary action. The absorbed liquids such as water can allow the ingress of destructive ions that chemically affect concrete or cause physical deterioration. Number, size, and interconnectivity of pores along with degree of saturation affect water sorptivity. High soprtivity can decrease the durability of concrete.

In this study, cylinders (100 mm in diameter and 50 mm in length) were made from standard mortar for every mixture listed in Table 3.3 and tested at each age of 28 and 91 days for their sorptivity according to ASTM C1585. The standard requires mass measurements of the pre-conditioned cylindrical samples exposed to non-pressurized water from one side over time so that initial and secondary sorptivity can be calculated. Two samples for each mixture were tested, and the average is reported.

3.7 Bulk Electrical Conductivity of Mortar

Destructive ions such as chloride and sulfate can penetrate into pore solution through the mode of diffusion. Diffusion is transport of substance through concrete due to concentration gradient. Concentration gradient causes a net flow of substance from regions of higher concentration to regions of lower concentration. Similar to permeability and absorption, diffusion depends on number, size, and interconnectivity of pores. To exclusively and solely evaluate the diffusion phenomenon, concrete must be fully saturated. Since resistance against the transport of destructive ions is an indication of durability, tests that evaluate electrical conductivity and resistivity are commonly conducted to provide a measure of diffusion and consequently durability. Bulk electrical conductivity of concrete is known to be directly related to chloride induced corrosion (Ghosh and Tran-2015).

In this study, bulk electrical conductivity is measured in accordance with ASTM C1760. The conditioning of the samples is the same as ASTM C1202 (which is very common for evaluating the resistance of concrete against chloride ion penetration), but the duration of the test is much shorter. The results of this test can provide a good comparative indication of susceptibility concrete to the penetration of destructive ions such as chloride. In this test, a fully saturated concrete cylinder is placed between two chambers containing sodium chloride solution connected to a constant external electrical potential for one minute and the electrical current passing through the sample is measure. Electrical conductivity can be calculated based on the electrical current passing, the voltage between the two cells, and the dimensions of the sample. The standard requires the samples to be 100 mm cylinders with a length of 100 to 200 mm, but due to the size limitation of available cells in the laboratory, the 50 mm length is chosen for the prepared samples.

Two cylinders (100 mm in diameter and 50 mm in length) were made from standard mortar for every mixture listed in Table 3. The samples were tested according to ASTM C1760 at 3, 7, 28, and 91 days of age, and their bulk electrical conductivity was determined, and the average is reported. It should be noted that higher conductivity indicates higher potential for penetration of ions and lower durability.

3.7 Bulk Electrical Resistivity of Mortar

Electrical resistivity is another important property of concrete that can predict its durability. Bulk electrical resistivity test is a non-destructive test that can be carried out on concrete samples in order to achieve a quick indication of their resistance to the penetration of destructive ions due to diffusion.

The test device that is used in this research is Proceq Resipod. It has two stainless steel plate electrodes that are electrically conductive. The sample is placed between the two plates and an DC voltage is applied to them. To ensure perfect contact, a flat layer of sponge which is soaked with tap water is placed between each plate and the sample. The device measures the current passing through the specimen and the voltage drop across the two plates and calculates the resistance of the specimen. Higher resistance can be interpreted as better durability for concrete samples.

In this study, three 50×50×50 mm standard mortar cubes are prepared from every mixture listed in Table 3.3 and tested at ages of 3, 7, 28, and 91 days. Currently, ASTM C1876 specifies the procedures for this test. Even though this test method was not yet adopted by ASTM when this experiment was being conducted, important measures where considered to provide reliable results. Bulk electrical resistivity highly depends on the moisture content and pore solution of concrete.

Therefore, to maintain similar conditions for all of the samples, the mortar cubes were all stored in saturated limewater after demolding and were fully saturated at the time of testing.

3.8 Expansion of Mortar in Sulfate Attack

The sulfate resistance of all PLC blends listed in Table 3.3 was studied according to CSA A3004-C8 (2018). There are two types of sulfate attacks; conventional sulfate attack also known as ettringite sulfate attack (ESA), and thaumasite sulfate attack (TSA) which is more severe at 3 to 7°C. The CSA A3004-C8 standard previously provided two procedures for studying sulfate attack; procedure A at 23°C where ESA is the predominant sulfate attack and procedure B at 3-7°C where TSA is the predominant sulfate attack. However, in the recent version of this standard, procedure B has been withdrawn. Even though, procedure B is no longer a standard requirement, it can still be performed as an effective durability test especially in regions with cold winters. Thus, expansion of mortar samples in both procedures have been studied in this research.

Standard mortar mixtures for every blend listed in Table 3.3 were made. The standard indicates that the w/c ratio has to be adjusted for different mixtures such that they reach the same level of flowability. Other researchers have used constant w/c in order to have better comparison between different mixtures and also to avoid trial mixings to reach the desired flow (e.g. Ramezanianpour and Hooton-2013 and Mirvalad and Nokken-2015). Therefore, a constant w/c ratio of 0.485 has been used for all mixtures of this study.

For each blend listed in Table 3.3, twelve 25×25×285 mm mortar prisms were cast (six for procedure A and six for procedure B) as well as twelve 50×50×50 mm mortar cubes that were used to specify the age at which the samples have reached 20 ± 1 MPa of strength. After casting, the molds were placed in containers that would ensure 100% humidity, and the containers were stored in an oven at 35 ± 3°C. After 23 ± 0.5 hours, the samples were demolded and stored in saturated limewater at 23°C for curing. At this point compressive strength of three mortar cubes were measured according to ASTM C109. The compressive strength was tested every twenty-four hours until the average measured value reached 20 ± 1 MPa.

For CSA A3004-C8 procedure A (23°C), once the specified compressive strength was achieved, the length of six mortar bars was measured using a digital comparator to 0.002 mm accuracy. This length was designated as the initial length of the bars. The bars were then placed in plastic containers containing sufficient sodium sulfate solution (4 ± 0.5 times the volume of mortar bars). The solution has a concentration of 50 g/L sodium sulfate in de-ionized water. Separators were used on the bottom of the containers to ensure proper contact of solution and the bars, and the containers were stored at 23°C.

For CSA A3004-C8 procedure B (3-7°C), once the specified compressive was achieved, six mortar bars were immersed in water containers at 5 ± 2°C. The water in the containers was already cooled to 5 ± 2°C for at least seven hours prior to the immersion of samples. At least seven hours after immersion, the length of the bars was measured with a digital comparator to 0.002 mm accuracy, and this length was designated as the initial length of the bars. Similar to procedure A, the bars were then placed in 50 g/L sodium sulfate solution, and the containers were stored in a refrigerator at 5 ± 2°C. It should be noted that the solution was precooled in the refrigerator to the same temperature for more than seven hours.

Using the same digital comparator, the length change of the bars were monitored at 1, 2, 3, 4, 8, 13, 15 weeks followed by 4, 6, 9, and 12 months or until the samples were deteriorated to the extent that they could not be measured. After each measurement, the old solution was replaced with new solution to make sure that the concentration of the sodium sulfate available for sulfate attack reactions remains constant.

4. RESULTS & DISCUSSIONS

In this chapter, the data obtained from each test method described in Chapter 3 is presented and discussed in separate sections. The results of each test provides valuable insight into the effect of nano calcium carbonate (NC) and nano silica (NS) addition on performance of blended limestone cement.

4.1 Isothermal Calorimetry of Cement Paste

In this section, the results of isothermal calorimetry of cement paste made from different mixtures at 23 °C are presented. Isothermal calorimetry is a common test that provides information about rate and degree of hydration of cement paste or mortar. The calorimeter machine used in this research (Calmetrix I-Cal 2000 HPC) has two channels, and as a result, it can measure two samples simultaneously. Two cement paste samples from each mixture were tested at the same time in the two channels of the machine and the average result is reported. The machine was set to log data points once every 30 seconds for the first hour after mixing when the heat fluctuation is significant and once every 1.0 minute after that for another 71 hours. Each cement paste sample was made of 50 g of total cement and limestone, 24.25 g of water (w/c of 0.485), and additives when required.

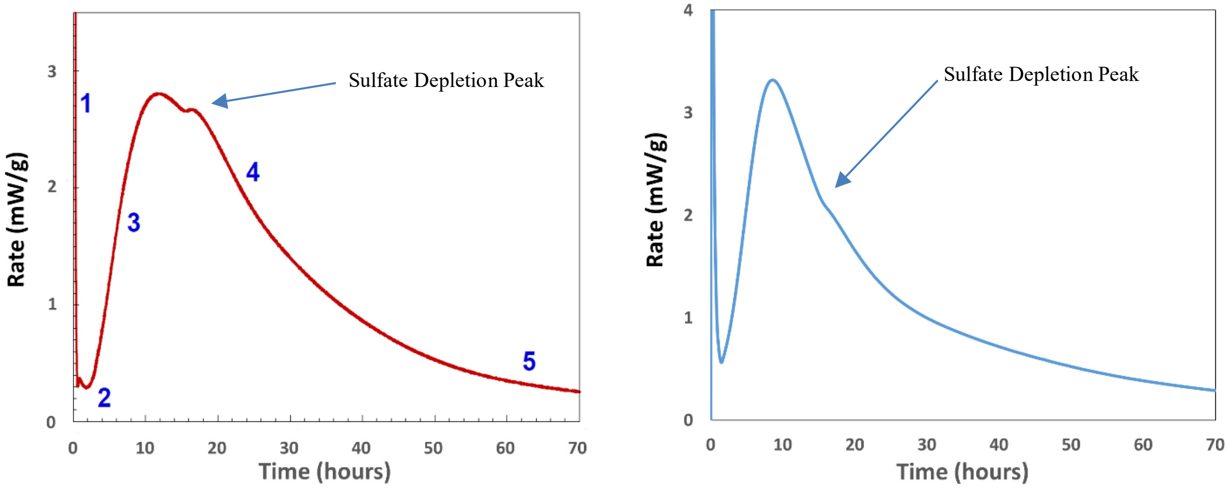

Figure 4.1.1: Rate of hydration of a typical Portland cement and its five different regions from Jennings et al. (2008) (left); rate of hydration of GU5 mixture of this research (right)

Figure 4.1.1 compares the rate of hydration of the GU5 cement paste mixture of this research (right image) with a typical Portland cement paste (left image). The vertical axis is the thermal power generated by cement hydration reactions and the horizontal axis is time. This diagram generally has five regions. The first region of the diagram, region 1, is called the initial period which occurs upon initial contact of cement particles and water right after mixing. At this stage, a burst of heat release is observed which is known to be the result of wetting of cement particles and rapid dissolution of a small amount of clinker phases and minerals such as CaO, calcium aluminates, and alkali sulfates. Even though the rate of heat evolution is very high in this region, the total released heat is not significant, and does not contribute to strength development. This region of high thermal power quickly ends and is followed by region 2 which is called the induction period. During the induction period that lasts for a few hours, production of calcium silicate hydrates (C-S-H gel) is relatively low, and the cement paste is in fluid/plastic state. Region 3 is the accelerating period during which the formation of C-S-H gel and calcium hydroxide from C_3S increases. These reactions occur and result in nucleation of hydration product near the surface of cement particles where the capillary water is available for reaction. The presence of nanoparticles such as NC and NS used in this study provide increased surface for the formation of hydration products and nucleation in this period and consequently increase the rate of hydration. As the surface of cement particles gets covered with layers of hydrated products, the rate of hydration gradually slows down (region 4, decelerating period). The slow rate of hydration (region 5, slow continued reaction period) continues for weeks, months, and years and may vary depending on the curing conditions. Hydration of C_2S is the major contributor to strength development during this time. There are usually two power peaks between region 3 and 4. The first peak which is more distinct and clear and occurs when the rate of hydration and exothermic reactions are the highest. This peak is often called silicate reaction peak. The second peak is usually less pronounced and depends on the chemical composition of the cement and is called the sulfate depletion peak. The second peak is often found in hydration of Portland cement and usually appears several hours after the first peak. Taylor (1997) suggested that this peak is related to the onset of secondary ettringite formation.

The first step in the experimental program of this research was to verify the efficacy of NC addition with isothermal calorimetry and also to specify the favorable percentage of NC addition for blended limestone cement mixtures. To accomplish this, the total 3-day heat of hydration of cement paste was measured. Figure 4.1.2 shows the results for total 3-day heat of hydration for all the cement paste mixtures listed in Table 3.2. For better comparison, GU5-NC0 (GU cement with 5% limestone content without NC addition) is regarded as a reference at 100% total 3-day heat of hydration, and the other mixtures are normalized accordingly.

The approach of this research has been to use NC as an additive that can potentially improve durability properties. As mentioned in Section 3.2, some researchers have used high percentages of NC in the past (10-15%), but based on more recent published studies and also experimenting in the lab, NC additions of less than 5% were expected to be most effective and practical from the beginning. Figure 4.1.2 shows that NC addition in general has considerably increased the heat of hydration. This can be attributed to the seeding action of NC particles that improves exothermic hydration reactions and C-S-H gel formation. This increase is between 3% to 4.5% for 1% NC addition and between 7% to 8.5% for 2% NC addition for all limestone content levels. However, the increase in hydration is not significantly improved once NC addition goes up to 3 and 4%. Therefore, the 2% NC addition has been selected as the most favorable addition amount and was used in the other experiments of this research.

As mentioned before, the main effect of NC particles in cement hydration is that they provide more surface area for the formation of CSH gel. Once water is mixed with cement, the space between cement particles is filled with water and the NC particles that are previously stabilized in water. The hydration products then start to form on the outer layer of cement particles and on the surface of NC particles that conduct a seeding action. The fact that 3 and 4% NC additions have did not perform significantly better than 2% may be due to two main reasons. First, it can be hypothesized that higher number NC particles in the space between the cement particles at 3 and 4% additions pack this space beyond its efficient state for hydration of cement particles. Secondly, since the water content is the same for all the mixtures, higher present NC particles in the mix may result in agglomeration that reduces the surface area and consequently effectiveness of NC particles.

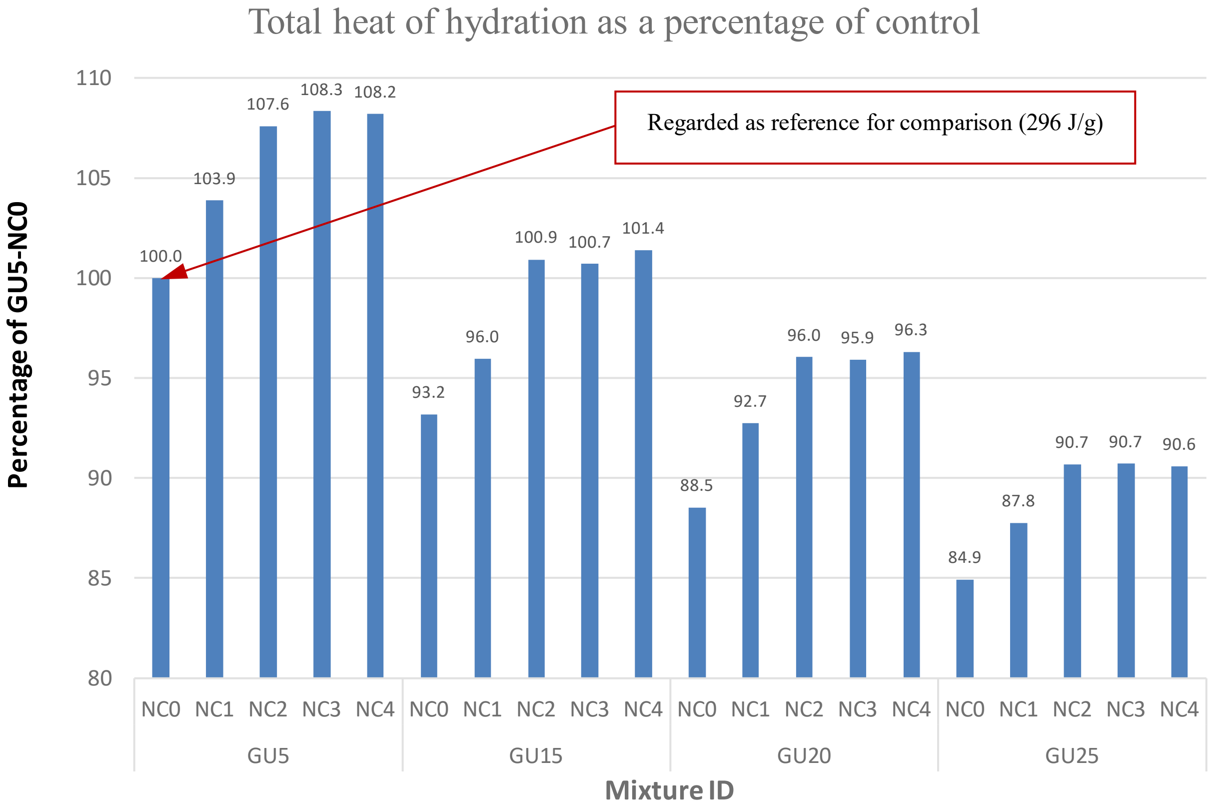

Figure 4.1.2: Total 3-day heat of hydration as a result of NC addition

This study intends to explore the possibility of increasing the limestone content level of cement beyond the current North American 15% limit without compromising its durability performance. Total heat of hydration is not a durability measure, but it is an indication of cement hydration progress which can significantly affect its durability. Investigating the results presented in Figure 4.1.2, it is also worth noticing that GU15-NC2 had a heat of hydration of slightly higher than GU5-NC0. This is especially interesting because it shows that 2% NC addition has been effective enough to compensate for the 10% less cementitious material in GU15-NC2 with respect to GU5-NC0. Similarly, GU20-NC2 and GU25-NC2 had higher heats of hydration than those of GU15-NC0 and GU20-NC0 respectively. This confirms that 2% NC addition has improved the cement hydration of the samples to the extent that they perform even better than samples with lower limestone contents.

As explained in Chapter 3, in order to reach a better understanding of the extent of efficacy of NC addition, colloidal nano silica (NS) particles that are commonly used in cementitious mixtures have also been incorporated in this study. To achieve better comparison, the same 2% addition level of nano silica (NS) has been used for cement blends with 15%, 20%, and 25% limestone content levels. The efficacy of NC and NS in cementitious mixtures arise from the sheer size of their particles. Both NC and NS particles are known to improve hydration through their seeding action and filler effect to some extent. However, NS can also further improve the performance of cementitious mixture through its pozzolanic reactions.

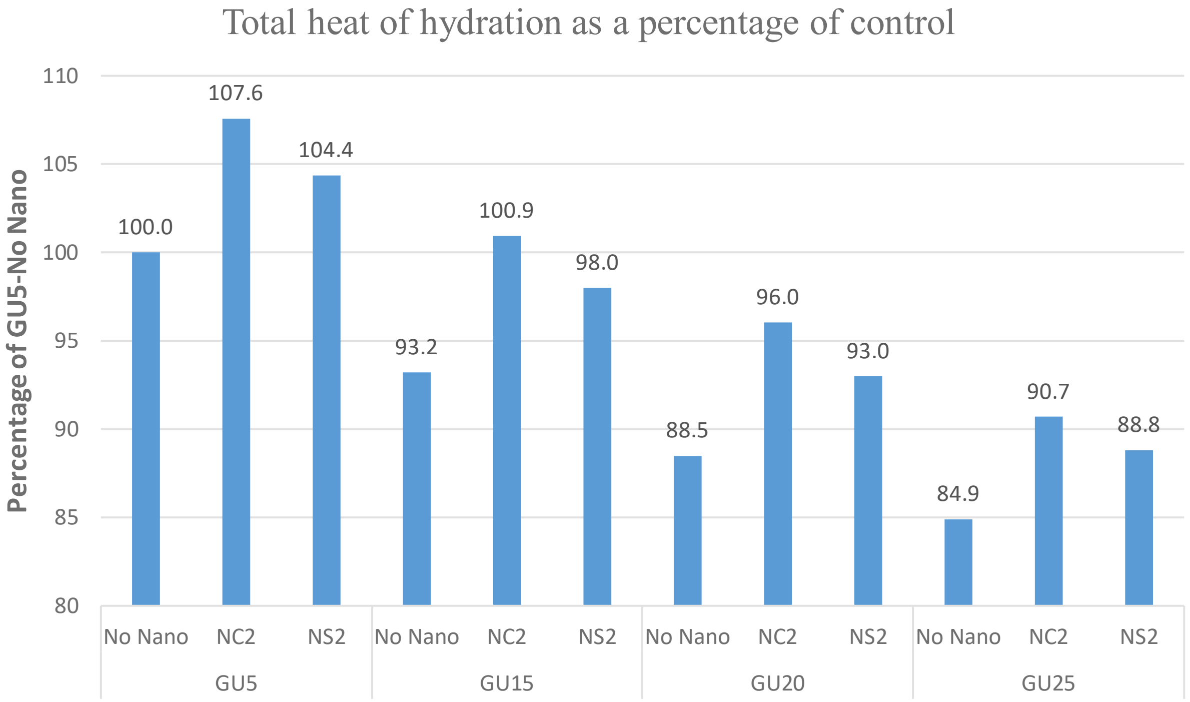

Figure 4.1.3: Total 3-day heat of hydration as a result of NC and NS addition

The total 3-day heat of hydration of the samples without the addition of nanoparticles, with 2% NC addition, and with 2% NS addition are demonstrated in Figure 4.1.3. The results clearly show that NS addition has increased the hydration of cement at every limestone content level. However, NC addition has been noticeably more effective in improving the heat of hydration, and this is consistent at every limestone content level. This is especially remarkable because NS particles are extremely reactive and are known to help the hydration process through their pozzolanic effect in addition to their nucleation and filler effect (e.g. Teichmann and Schmidt-2004 and Land and Stephan-2012) while the main effect of NC particles is their seeding action for hydration reactions. It can be concluded that at 2% percent, the seeding action of NC has been much more effective than NS. It is also worth mentioning that smaller nanoparticles are generally known to be more reactive. The median size of NC and NS particles of this study has been 25 nm and 12 nm, respectively. This shows that the NC particles have been more effective than NS particles even at a slightly larger size.

For the same amount of cement and water, more hydration products, which is a function of total 3-day heat of hydration, can generally result in a denser cement matrix and better overall strength and durability performance. Therefore, the total 3-day heat of hydration can be an effective initial evaluative measure. To further investigate the hydration process during the first three days after mixing, the rate of hydration as indicated by the power generated of all the cement paste mixtures listed in Table 3.3 are plotted and presented in Figure 4.1.4. This figure shows that the peak of hydration happens during the first 10 hours after mixing for all of the mixtures. The time of this peak is very similar for samples without nanoparticles and the ones with the 2% NC addition. However, this peak is slightly shifted to earlier hours in samples containing 2% NS additions.

The seeding action of nanoparticles that improves cement hydration is especially important for the region 3 of the hydration diagram (Figure 4.1.1) which is where the hydration starts to accelerate. Considering the hydration diagrams in Figure 4.1.4, the acceleration region of the diagram has higher slope in mixtures containing the nanoparticles. This is directly the result of seeding action of the nanoparticles.

Another important observation from Figure 4.1.4 is the difference in peaks power for different mixtures. In order to better compare the size of these peaks, they are included in Figure 4.1.5 normalized to GU5 mixture. According to this figure, it is clear that the peak value decreases as the limestone content increases. This is expected since with higher limestone content, there is less cement for hydration. Also, at every limestone content level, NC addition has increased the peaks more effectively than NS addition. The peaks in GU15-NC2 and GU20-NC2 are larger than GU5, and the peak of GU25-NC2 is almost the same size as that of GU5. Considering the lower cement contents in GU15-NC2, GU20-NC2, and GU25-NC2 compared to GU5, this shows that the rate of hydration has been improved significantly as a result of NC addition.

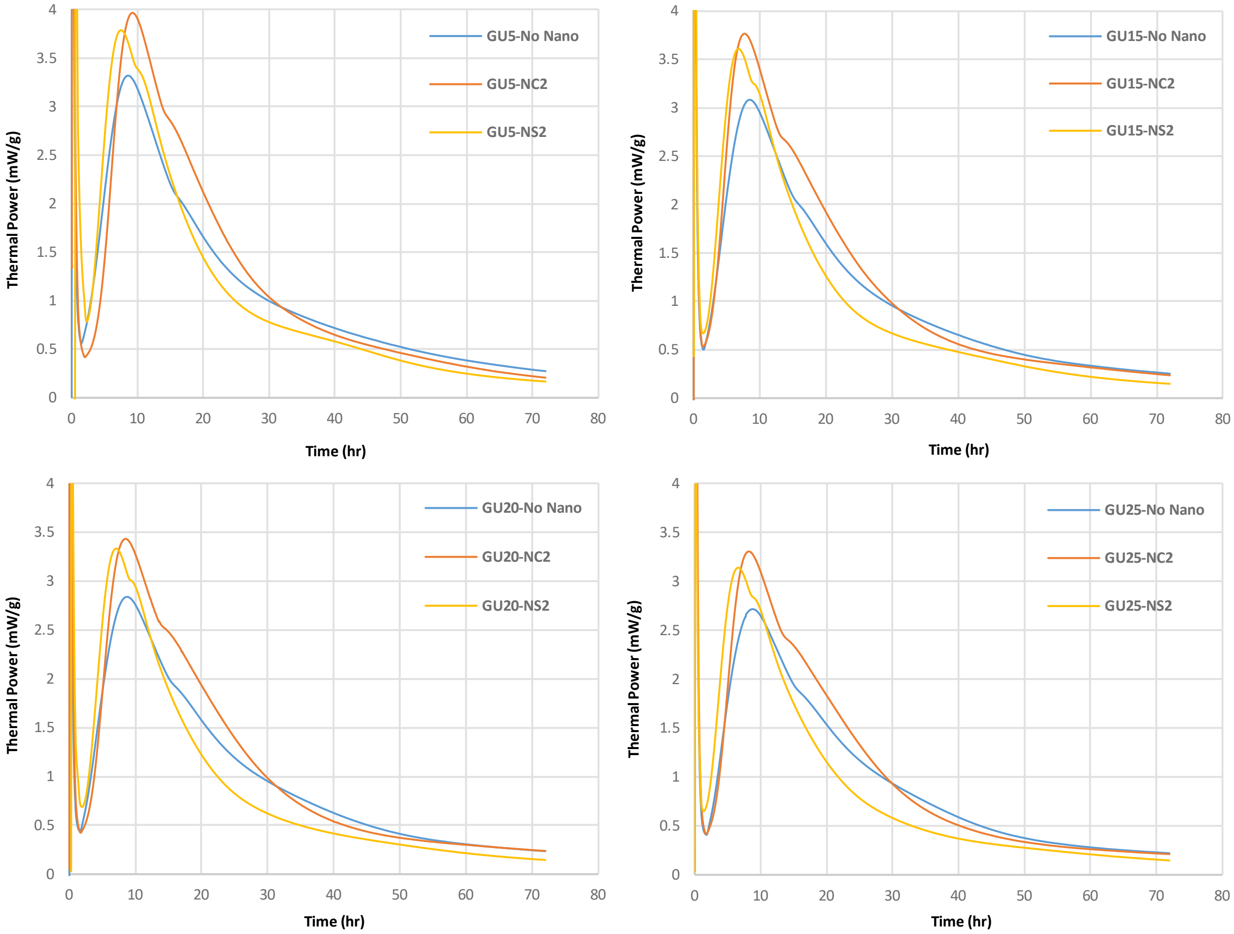

Figure 4.1.4: Rate of hydration in cement paste samples during the first 72 hours after mixing

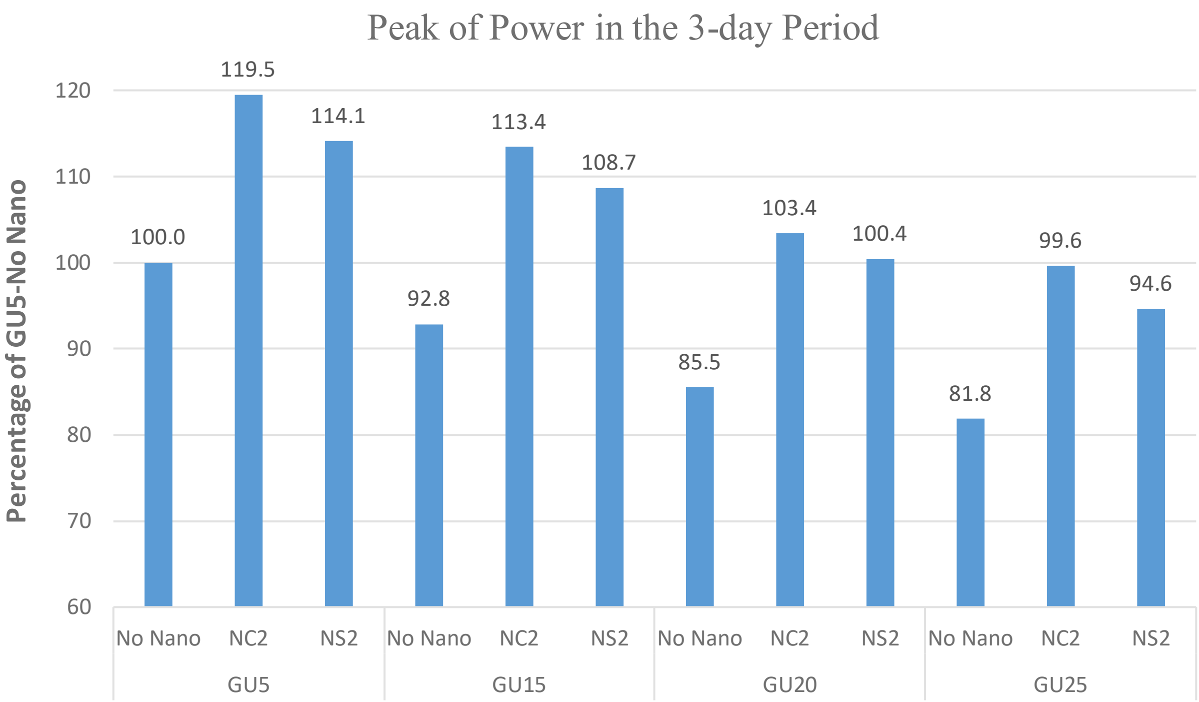

Figure 4.1.5: Peak of heat of hydration as a result of NC and NS addition

Figure 4.1.6 shows the cumulative heat of hydration of the same mixtures shown in Figure 4.1.4. The final values of curves after 72 hours is the basis for the comparison shown in Figure 4.1.3 and discussed previously. Figure 4.1.6 specifically shows that the cumulative generated heat for mixtures containing NC and NS remained higher than those of mixtures without nanoparticles for the entire 72-hour period. Moreover, the cumulative heat of mixtures with NS were higher than mixtures with NC from the first hours until around 30 hours after mixing. After this time, the cumulative heat of mixtures with NC surpassed the mixtures with NS at every limestone content level.

Overall, based on the calorimetry results presented in this section, it can be seen that increasing limestone content has a significantly negative impact on cement hydration. However, 2% NC addition has been very effective in compensating this negative impact to extents even better than 2% NS addition.

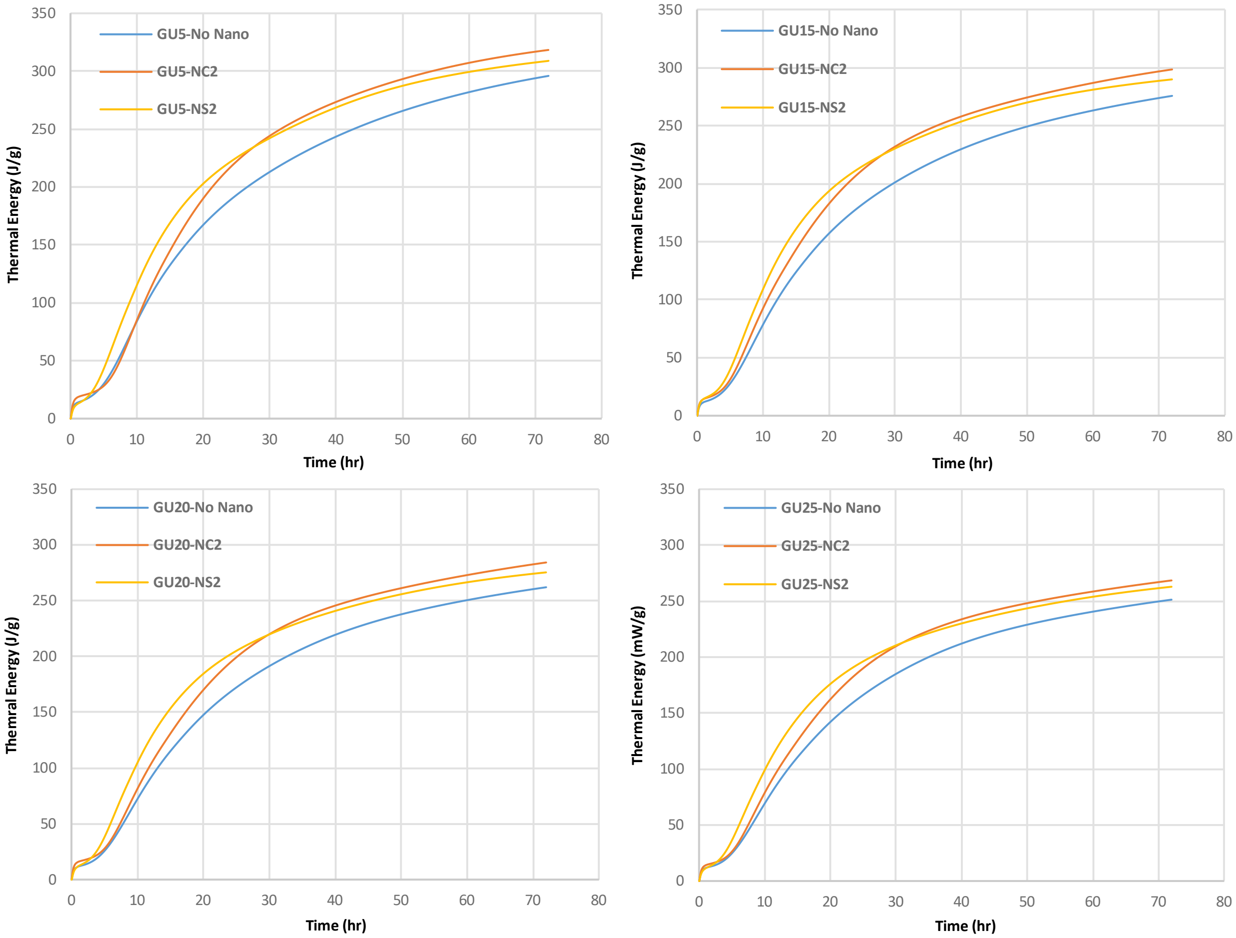

Figure 4.1.6: Cumulative heat of hydration of cement paste samples during the first 72 hours after mixing

4.2 Compressive Strength of Mortar

Compressive strength is a basic measure of mechanical properties of concrete. This research specifically focuses on investigating the changes in durability measures, but compressive strength results are also presented in order to have an idea of the effect of nanoparticles on mechanical properties of mortar samples.

Nano calcium carbonate (NC) and nano silica (NS) particles can improve the rate and degree of hydration especially in early ages. This is why most studies have used these particles when improved early age hydration is desired such as cases where high volume of supplementary cementing material is used (e.g. Sato and Beaudoin-2011, Supit and Shaikh-2014, and Steve and Faiz-2014). The results of Section 4.1 also confirm the effectiveness of NC and NS additions on improving the rate and degree of hydration during the first three days after mixing. While improved heat of hydration of cement paste is associated with increased C-S-H gel formation, and that can generally be a positive factor in the overall quality of concrete, it may not directly translate to higher compressive strength. For example, with the same amount of cement, a higher w/c ratio increases the heat of hydration, but decreases the compressive strength of the concrete by increasing the pore sizes and volume.

Several studies have generally reported increased compressive strengths with the incorporation of NS in the mixture. However, there is not an agreement on the optimum amount and size of NS particles and their level of efficacy on compressive strength. For example, Haruehansapong et al. (2014) reported very significant increase in compressive strength when they incorporated 3, 6, 9, and 12% NS replacements in their OPC mortar samples and found the 9% to be the most effective. They also saw better results with NS particles at 40 nm compared to 12 and 20 nm. Mukharjee and Barai (2014) saw an increase in compressive strength by replacing 3% of cement with NS in concrete made with recycled aggregates. The increase was much more significant in concrete made from natural aggregates. Shaikh et al. (2014) used 1, 2, 4, and 6% NS replacements in their OPC mortar samples. They found some increase in compressive strength at 1% NS replacement, highest increase at 2%, little increase at 4%, and some decrease at 6%. They also used 2% NS as fly ash replacement in mortar samples with high volume of fly ash. While they found a significant improvement in compressive strength at 28 days, they reported no improvement at 7 days.

There are fewer studies on the efficacy of NC compared to NS. Most of them reported some level of increase as a result of using NC in the mixture. Sun et al. (2020) used 1, 2, and 3% NC replacements in concrete samples incorporating different levels of fly ash. They found the 1% to the most effective in increasing compressive strength. In another study, Shaikh and Supit, (2014) tried 1, 2, 3, and 4% NC replacement in OPC mortar and high volume fly ash mortar samples and reported inconsistent results for improvements as a result of incorporating NC. They saw some increase in compressive strength of OPC mortar samples with 1% NC replacement, but compressive strength was reduced at higher NC replacement levels. They attributed this decrease in compressive strength to poor dispersion due to agglomeration. At 60% fly ash content with 1% NC replacement, they saw a significant increase in compressive strength of mortar samples and almost no increase in concrete samples. On the contrary, at 40% fly ash content with 1% NC replacement, the mortar samples had little improvement in compressive strength while concrete samples were significantly improved.

While there are studies that have reported increased compressive strength with NC and NS additions, there seems to be a lack of consistency and discussion on the effectiveness of these nanoparticles. The reason seems to be that the improvement in compressive strength is highly dependent on amount of nanoparticles used, mixing procedures, curing protocols, types of aggregates, and supplementary cementing materials used in the mixture.

In this research, from each mixture, three 50×50×50 mm mortar cubes were tested for their compressive strength at different ages and the averages are reported. The results are separated into early age (1-day, 3-day, and 7-day) results in Figure 4.2.1 and long term (28-day and 91-day) results in Figure 4.2.2 for better comparison. Considering these two figures, there is a clear increase in compressive strength of samples with NS addition with respect to the ones without nanoparticles. This increase is more pronounced at early ages in Figure 4.2.1 (approximately 26% on average) compared to the more mature ages in Figure 4.2.2 (approximately 9% on average). In other words, NS addition seems to be more effective in cases where there is a lack of early age strength development. It is also interesting to see that at early ages (as seen in Figure 4.2.1), NS addition has been so effective that the compressive strength of samples with 2% NS addition at 15% and 20% limestone content levels are comparable to the samples with only the GU cement (GU5).

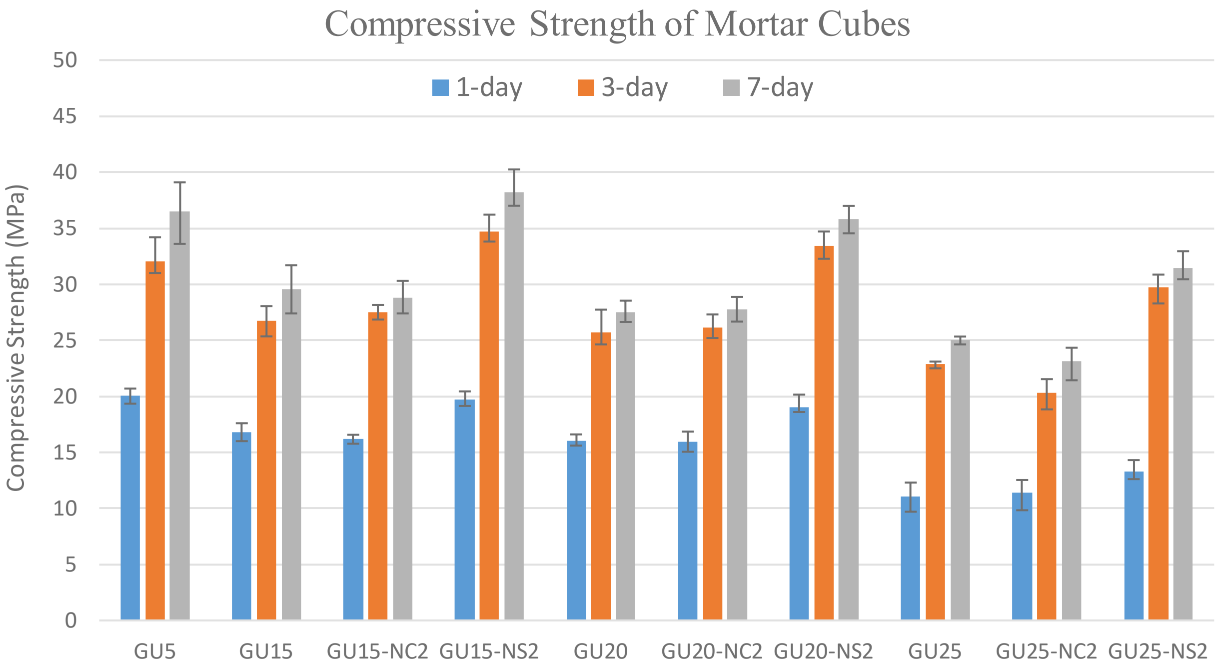

Figure 4.2.1: Early age compressive strength of mortar cubes with NC and NS additions

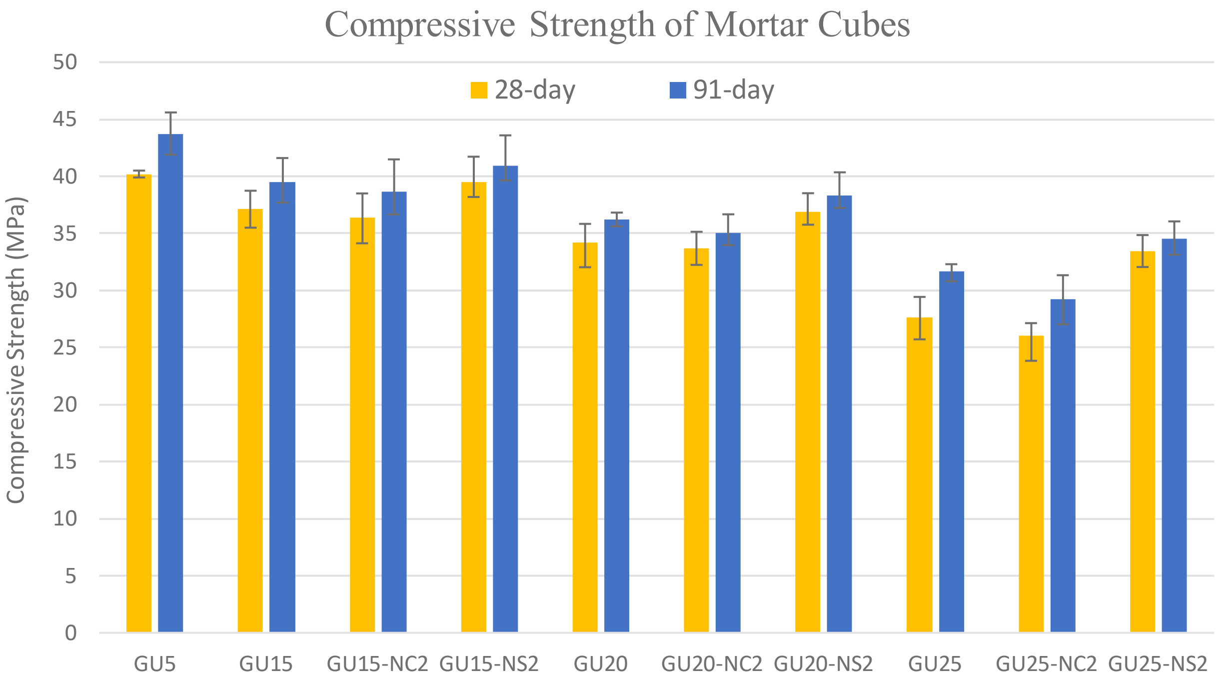

Figure 4.2.2: Long term compressive strength of mortar cubes with NC and NS additions

Section 4.1 showed that early age heat of hydration of cement paste was better improved by 2% NC addition as opposed to 2% NS. As a result, an improvement of compressive strength may also be expected in samples containing NC comparing to samples containing NS. However, the results show otherwise. Both Figures 4.2.1 and 4.2.2 show that NC addition does not have a significant effect on compressive strength of the samples at both early ages and long term. As discussed earlier, while there are other studies which have reported improved compressive strength due to NC addition (Supit and Shaikh-2014 and Wang et al.-2014), none of them used cements with high levels of limestone content. It can be hypothesized that even though the overall hydration is improved due to NC addition, the high levels of limestone content in the cement have decreased the structural quality of hydrated cement matrix to the point that the compressive strength could not be improved by NC addition.

Generally, mechanical properties of concrete including its compressive strength and modulus of elasticity depend on mechanical properties of bulk hydrated cement matrix, aggregates, and more importantly the Interlayer Transition Zone (ITZ). The ITZ is where the surface of aggregates meets the cement matrix, and is the weakest constituent of concrete which significantly affect its mechanical properties. The ITZ is mostly studied around large aggregates in concrete. However, there have been studies such as San Nicolas and Provis (2015) and Maghsoodi (2018) that showed the importance of the ITZ around fine aggregates and specifically studied this zone in mortar.

Under an increasing compressive force, the ITZ tends to develop micro-cracks early on which is mainly responsible for the nonlinear pre-peak behavior of concrete. Scrivener and Nemati (1996) proved that the properties of ITZ is affected by the size and packing of cement particles. Since incorporating nanoparticles can affect the packing of cement particles, it may also affect the ITZ. Capillary pores are also known to be larger in ITZ and some micro-cracks are present even before concrete is subjected to external loading. Since ITZ has significantly lower stiffness compared to bulk cement paste and the aggregates, it may also be a cause of stress concentration in concrete.

Moreover, presence of calcium hydroxide (CH) crystals that are highly soluble and cleavable in the ITZ increases the porosity of this zone and can negatively impact its mechanical performance. Calcium hydroxide, along with the C-S-H gel is a product of cement hydration, and high concentration of it may be a sign of progressive hydration reactions. Therefore, while more hydration reactions as a result of NC addition can improve the mechanical properties of cement matrix, it may have a negative effect on the ITZ and consequently compressive strength of mortar. However, some of the CH resulted from cement hydration is consumed due to the pozzolanic action of NS addition which may reduce the presence of CH crystals in the ITZ and improve the overall compressive strength of this zone. This could be another reason for lower compressive strength in mortar cubes containing NC compared to the ones containing NS which is shown in Figures 4.2.1 and 4.2.2.

It is also worth mentioning that since NC is considered as an additive in this study, the overall cement content in samples with NC are slightly lower than the samples without it at the same limestone content level. For example, at 15% micro limestone content, cement (clinker) is 85%. When 2% NC is added, the overall cement content becomes 85/(100+2) = 83.33%. This could also have a small negative impact on the compressive strength of the samples with NC addition.

Compressive strength of Portland limestone cement mixtures is usually expected to be lower than ordinary Portland cement which is one of the reasons cement plants grind limestone cements finer so that possible lack of hydration and strength can be compensated. In many cases, limestone cement with very high limestone content (more than the 15% allowed in North America) is not even used in structural elements due to its lower strength. The results of this section show that even though NC addition has not increased compressive strength of the samples, it has not decreased it either. After all, the main goal of this study has been to improve durability of limestone cement with the aid of NC addition. Therefore, based on the results of this section, it can be concluded that NC addition to limestone cement with the purpose of improving its durability is not expected to negatively impact strength.

4.3 Volume of Permeable Voids of Mortar

In this research 50×50×50 mm standard mortar cubes were cast for each mixture. At ages of 3, 7, 28, and 91 days, three cubes were tested according to ASTM C642 and the average values for volume of voids are presented. After weighing the samples, they were dried in an oven at 110°C. Their mass was determined at every 24 h until they had reached a stable mass (less than 0.5% difference between two successive measurements). They were then immersed in water at room temperate, and their mass was measured after every 24 h until a stable mass was achieved. Then, they were boiled in a steel pot covered with tap water for 5 hours to remove any air from the voids, and their saturated mass after boiling was determined. Their immersed apparent mass was then measured while suspended in water tank.

As explained in Section 3.5, the total volume of the pores, their size distribution, and inter-connectivity can affect the permeability of concrete. Since the same mix design and cast procedures were conducted in this research, lower total volume of permeable voids can mostly translate to higher durability of concrete. Lower volume of the voids is generally associated with lower potential for hosting liquids and destructive ions that can physically and chemically damage concrete. It should be noted that drying the samples at 110°C may affect the chemical phases present and consequently alter the pore structure.

Volume of permeable voids (VPV) has been rarely analyzed in the existing literature to evaluate durability improvements due to NC and NS incorporations. In one study, Supit and Shaikh (2015) reported some reductions in VPV as a result of 2% and 4% NS replacement in OPC concrete and high volume fly ash concrete. However, in another study Shaikh and Supit (2014) saw very significant decrease in VPV in the same mixtures due to 1% cement and fly ash replacement with NC.

Figures 4.3.1 includes all of the results of all of the mixtures and the subsequent figures of this section include partial results for better comparison. Figure 4.3.1 shows a clear downward trend for the VPV of all of the mixtures as the samples age. This was expected since the samples were curing in saturated limewater at 23°C, and formation of new hydration products gradually fill up the voids in mortar over time as a result of the ongoing hydration process.

Increasing limestone content of cement is expected to decrease performance of concrete due to lower cement content for hydration. This can be seen in Figure 4.3.2 which compares the mixtures that do not contain nanoparticles. As the limestone content is increased from 5% to 25%, the VPV has also increased. This increase seems to be more at earlier ages, and relatively fades at more mature ages. Since higher VPV can negatively impact durability, this is a limiting factor for acceptable limestone content in cement.

Figures 4.3.3 and 4.3.4 compare the effect of NC and NS additions on the VPV of the samples. It can be observed from the two figures that while both types of nanoparticles have reduced the VPV in mortar samples, NC has been more effective compared to NS (4-8% reduction as opposed to 1-3% reduction) at every limestone content level. Even though these improvements which are presumably the consequence of promoted cement hydration and filler effect of nanoparticles, may seem small, they can be significant in their effect on overall durability of concrete. The other important observation from the two figures is that as a result of NC addition, VPV of the 2% NC mortar samples at 20% and 25% limestone content levels (GU20-NC2 and GU25-NC2) are reduced to smaller and more favorable values than that of samples at 15% limestone content without nanoparticles (GU15). In other words, detrimental effect of increasing limestone content beyond the 15% standard limit was compensated adequately with the 2% NC addition which is in line with the objectives of this research.

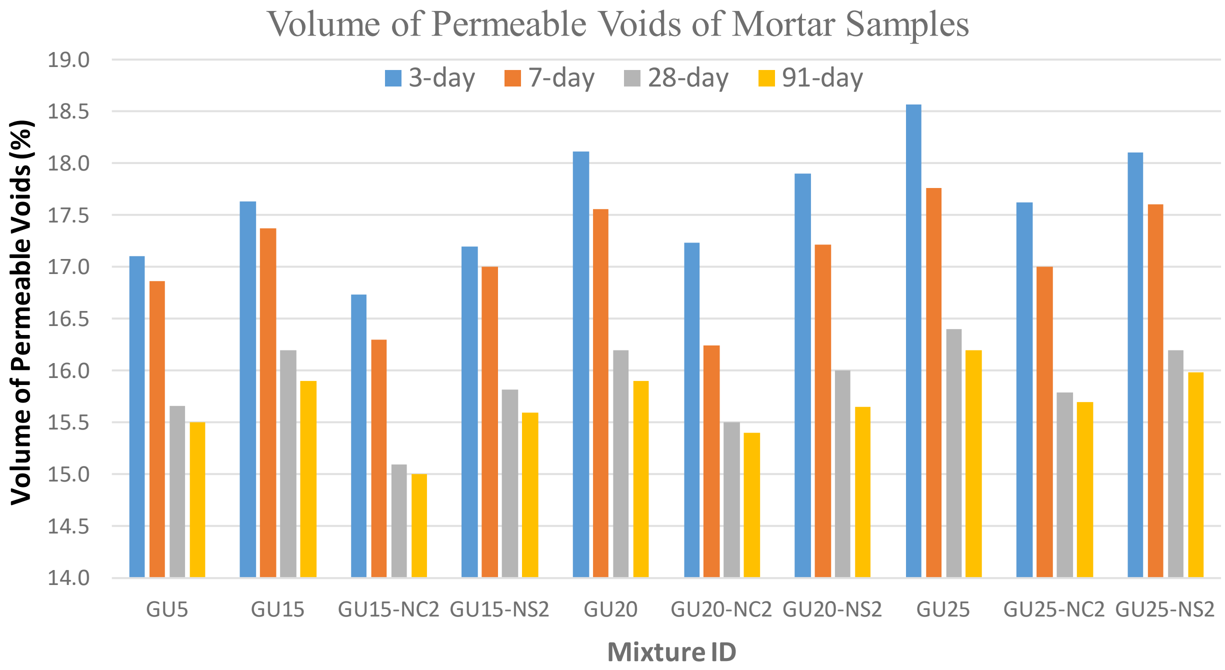

Figure 4.3.1: Changes of volume of permeable voids of mortar samples over time

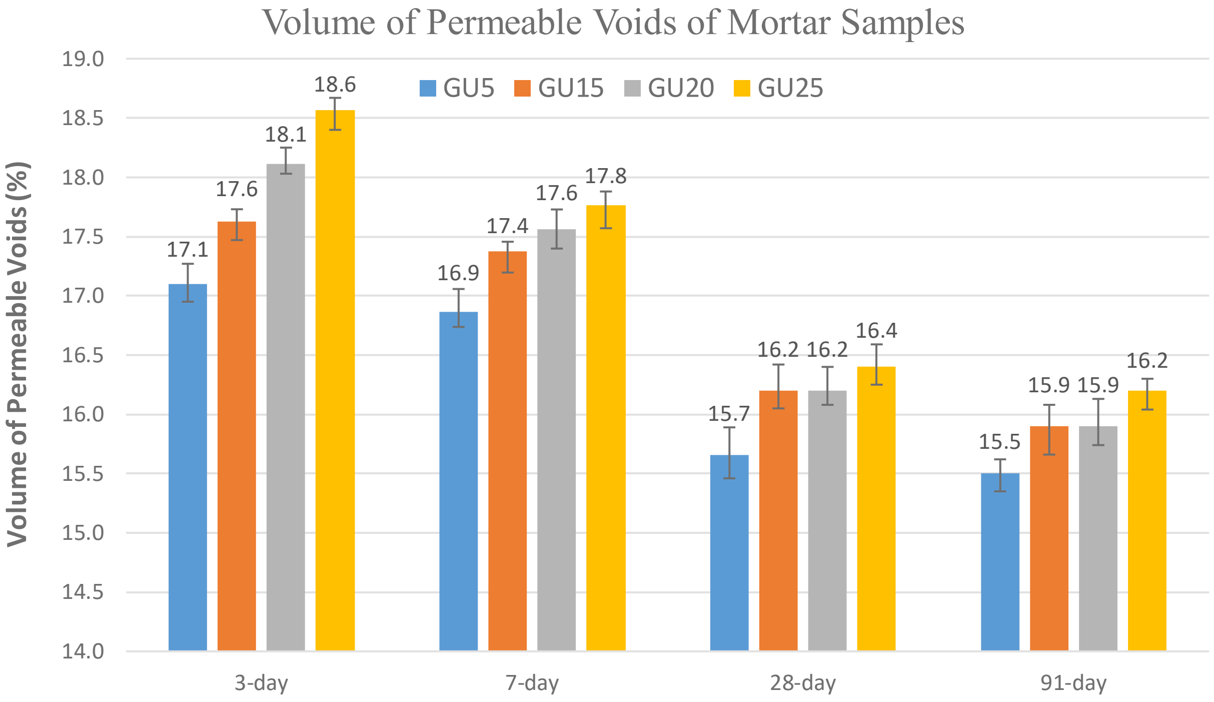

Figure 4.3.2: Changes of volume of permeable voids of control mortar samples with increasing limestone content

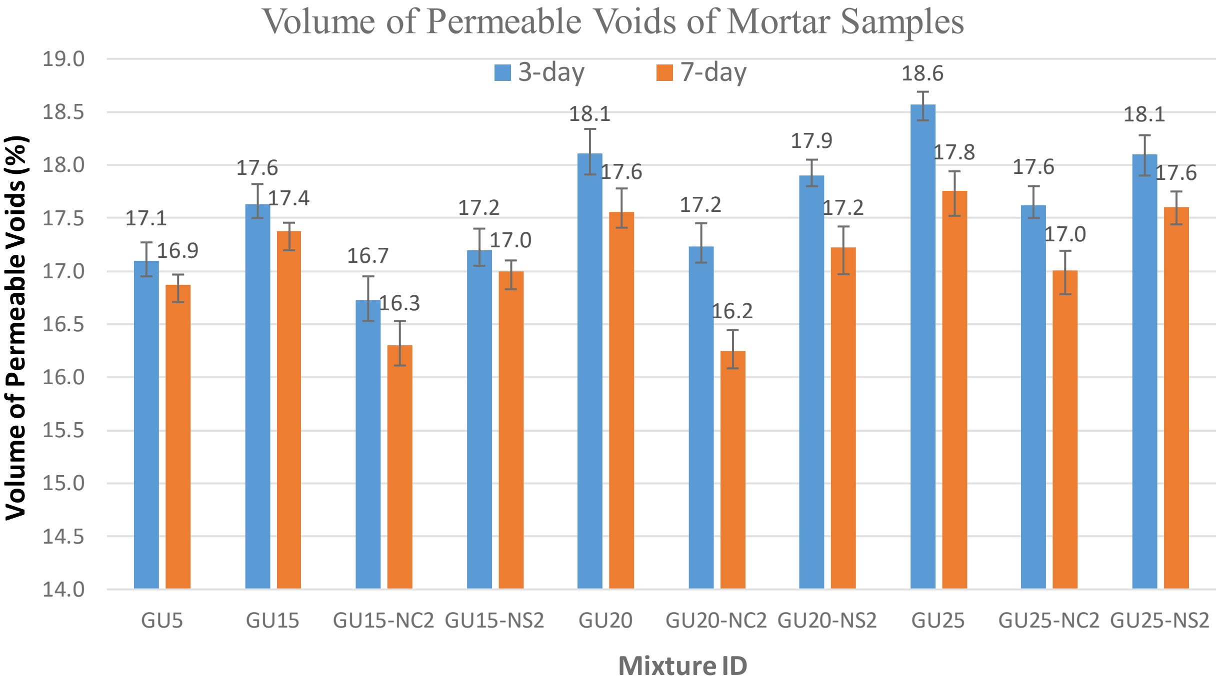

Figure 4.3.3: Volume of permeable voids of mortar samples at 3 and 7 days of age

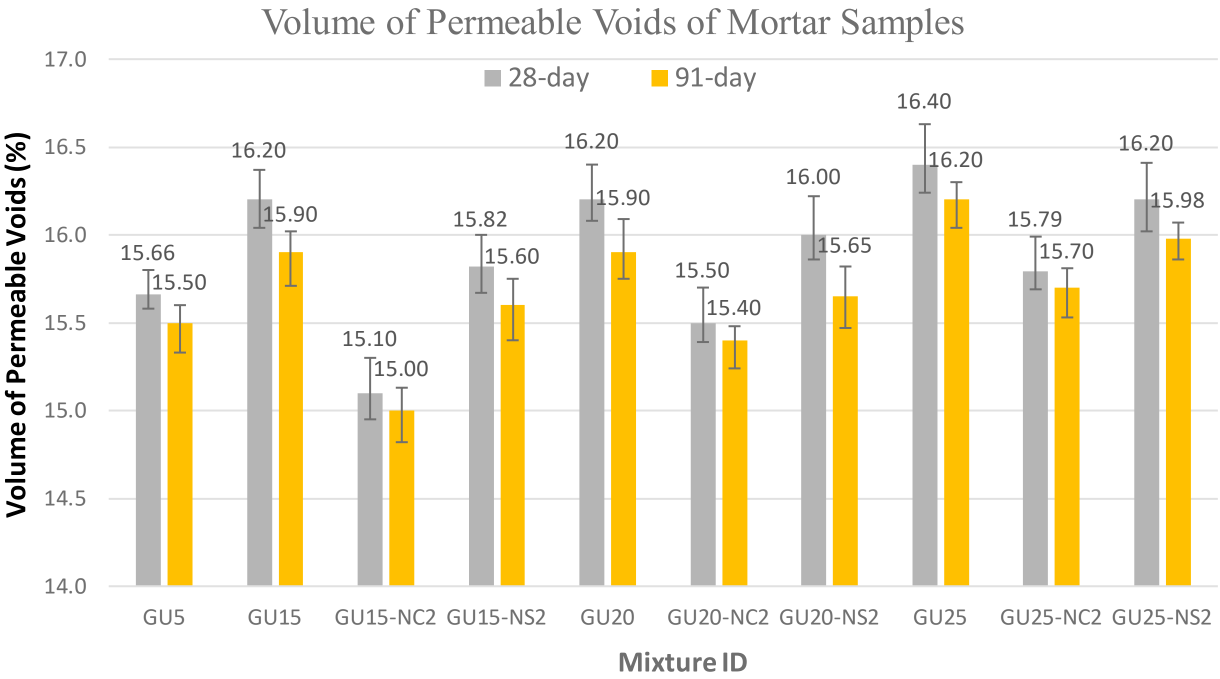

Figure 4.3.4: Volume of permeable voids of mortar samples at 28 and 91 days of age

4.4 Rate of Water Absorption or Sorptivity of Mortar

Rate of water absorption or sorptivity is an indication of how fast liquids can penetrate through the mass of concrete due to the capillary action. These liquids may contain destructive ions which can cause chemical damage to concrete or simply cause physical damage as a result of freeze-thaw action or crystallization of salts. Therefore, lower sorptivity can be interpreted as better durability.

In this study, mortar cylinders (100 mm in diameter and 50 mm in length) were cast for every mixture listed in Table 3.3, and two samples at each age of 28 and 91 days were tested for their sorptivity according to ASTM C1585 and the average results are reported. According to ASTM C1585, the samples are sealed from the top and the circular circumference, and only the bottom of samples is slightly submerged in water (2 ± 1 mm) to ensure proper contact between water and the sample's bottom surface while minimizing the effect of water pressure on the penetration of water into the sample. The mass of the samples is measured over time and the depth of penetration of water is calculated in millimeters accordingly. This depth is called absorption (I, mm) which is usually plotted against square root of time ($sec^{0.5}$). The depth of absorption is indicative of how deep water and possibly destructive ions can penetrate into concrete over time and potentially cause deterioration.

As an example, Figure 4.4.1 includes the absorption values calculated for GU15 mixture. There are 11 mass measurements in the first 6 hours after the samples have been in contact with water, and after that the measurements are done at around every 24 hours. The slope of the line that best fits the data points in the first 6 hours is called initial sorptivity ($mm/s^{0.5}$), and the slope of the lines that best fits the rest of data points is called secondary sorptivity. As the time passes, the rate of absorption which happens through the capillary action slows down. This is why the absorption results are plotted against square root of time for achieving a linear behavior and also the initial sorptivity is always greater than secondary sorptivity.

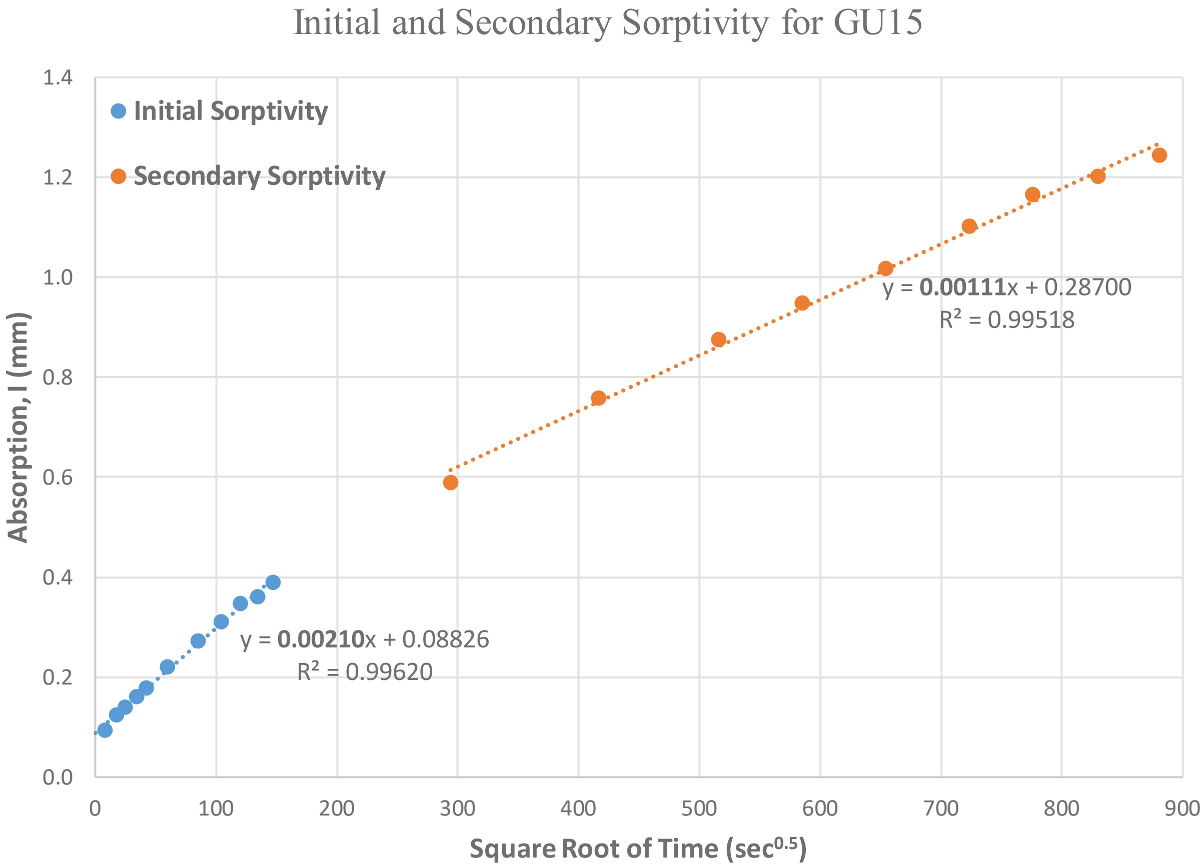

Figure 4.4.1: An example for Initial and secondary sorptivity calculations

Figures 4.4.2 to 4.4.7 include the graphs required to calculate the initial sorptivity at 28 days and 91 days for all the mixtures listed in Tables 3.3. The measurements were done during the first 6 hours after the samples became in contact with water. For each graph, two samples were tested, and the average is presented. The slope of fitted line to each set of data points is the initial sorptivity for that mixture. ASTM C1585 indicates that if the correlation coefficient is less than 0.98, the relationship cannot be deemed linear, and the initial sorptivity cannot be determined. The correlation coefficient in all of the graphs of these figures is greater than 0.98. It can be seen in Figures 4.4.2 to 4.4.7 that at every limestone content level, the slope of line for mixtures containing the nanoparticles is clearly smaller indicating that they have lower sorptivity and consequently better durability. Also, the slope is smaller for mixtures containing NC compared to mixtures containing NS suggesting that at 2% addition, NC has been more effective than NS.

Figures 4.4.8 to 4.4.13 include the graphs required to calculate the secondary sorptivity at 28 days and 91 days for all the mixtures listed in Tables 3.3. The same samples that were used to calculate initial sorptivity were monitored for another 8 days after their initial contact with water, and measurements were done in order to calculate secondary sorptivity. The slope of the fitted line to each set of data points is the secondary sorptivity. The correlation coefficient in all cases is greater than 0.98, and therefore the linear relationship can be accepted according to ASTM C1585. The trend that was discussed for the graphs of initial sorptivity can be seen for secondary sorptivity as well. At each limestone content level, the slope of the line for mixtures containing nanoparticles is smaller than that of the mixture without nanoparticles indicating lower sorptivity and better durability as a result of nanoparticles additions. Also, it can be seen in all the figures that the 2% NC addition was more effective than the 2% NS addition in reducing the sorptivity of the mixtures.

Figures 4.4.14 and 4.4.15 summarize and combine the results of Figures 4.4.2 to 4.4.13 in order to have a better overall view of the effect of nanoparticles on sorptivity of the samples. As mentioned earlier, lower sorptivity can translate to better durability. Considering Figures 4.4.14 and 4.4.15, there is clear improvements in mixtures containing the nanoparticles. These improvements are more pronounced as a result of NC addition as opposed to NS addition. The effect of NC on sorptivity has rarely been studied in the existing literature. Shaikh and Supit (2014) studied the initial sorptivity of the Portland cement concrete and high volume fly ash concrete samples with and without 1 and 2% NC replacement. They saw a decrease in initial sorptivity as a result of incorporating NC and reported that 1% NC replacement was more effective than the 2% replacement in their study. In another study, Supit and Shaikh (2015) replaced binding materials in OPC and high volume fly ash concrete with 2 and 4% NS and evaluated some durability measures. Their results showed that there was a clear decrease in sorptivity of concrete samples that contained NS.

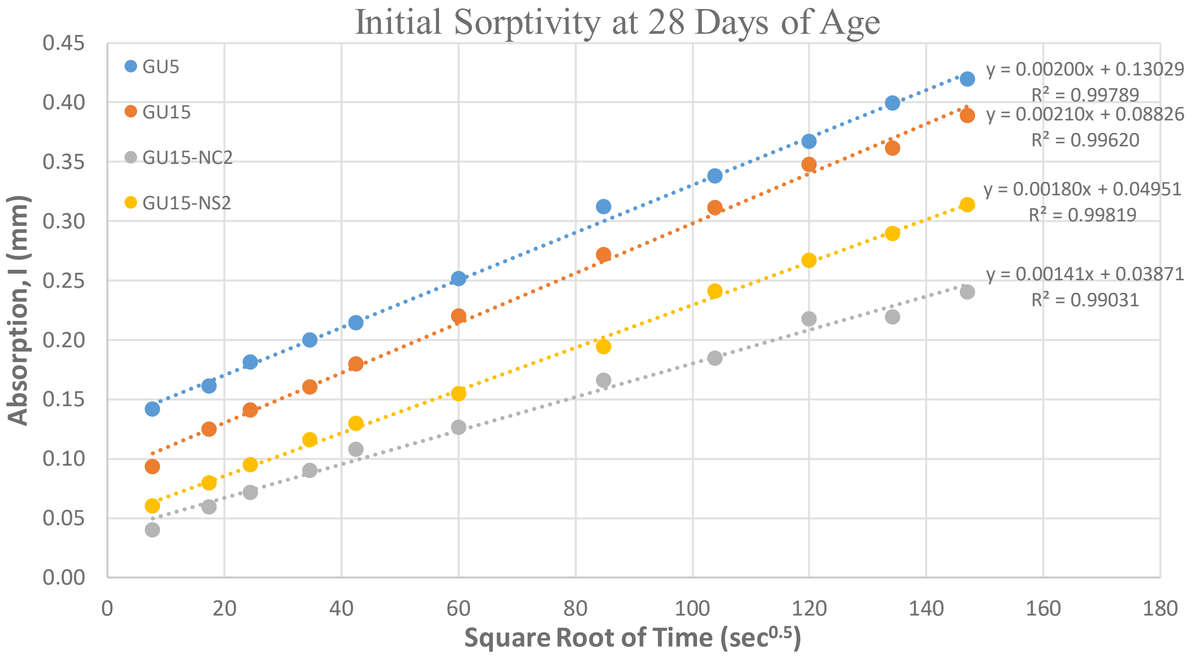

Figure 4.4.2: Initial sorptivity graphs for GU5, GU15, GU15-NC2, and GU15-NS2 mixtures at 28 days of age

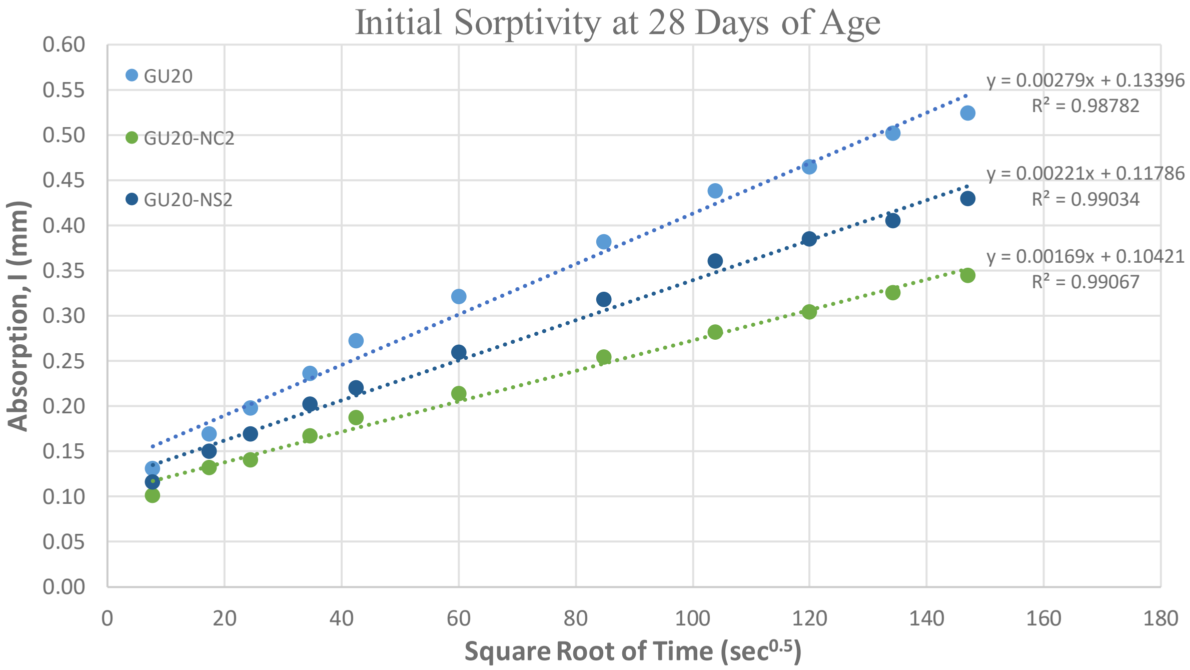

Figure 4.4.3: Initial sorptivity graphs for GU20, GU20-NC2, and GU20-NS2 mixtures at 28 days of age

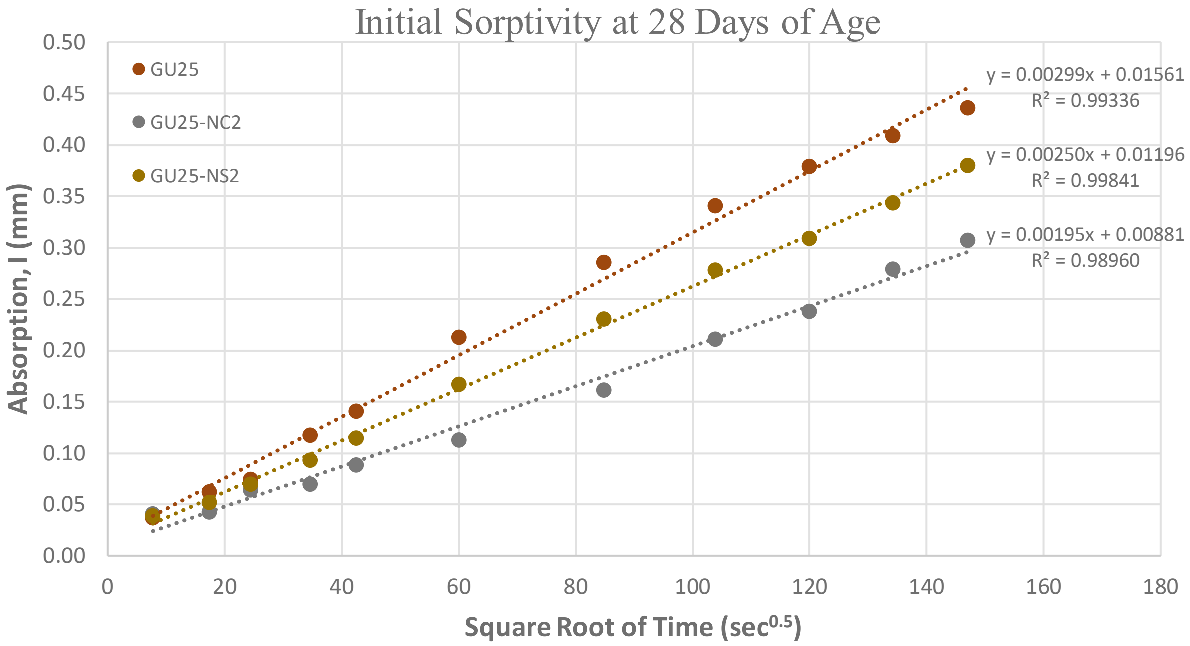

Figure 4.4.4: Initial sorptivity graphs for GU25, GU25-NC2, and GU25-NS2 mixtures at 28 days of age

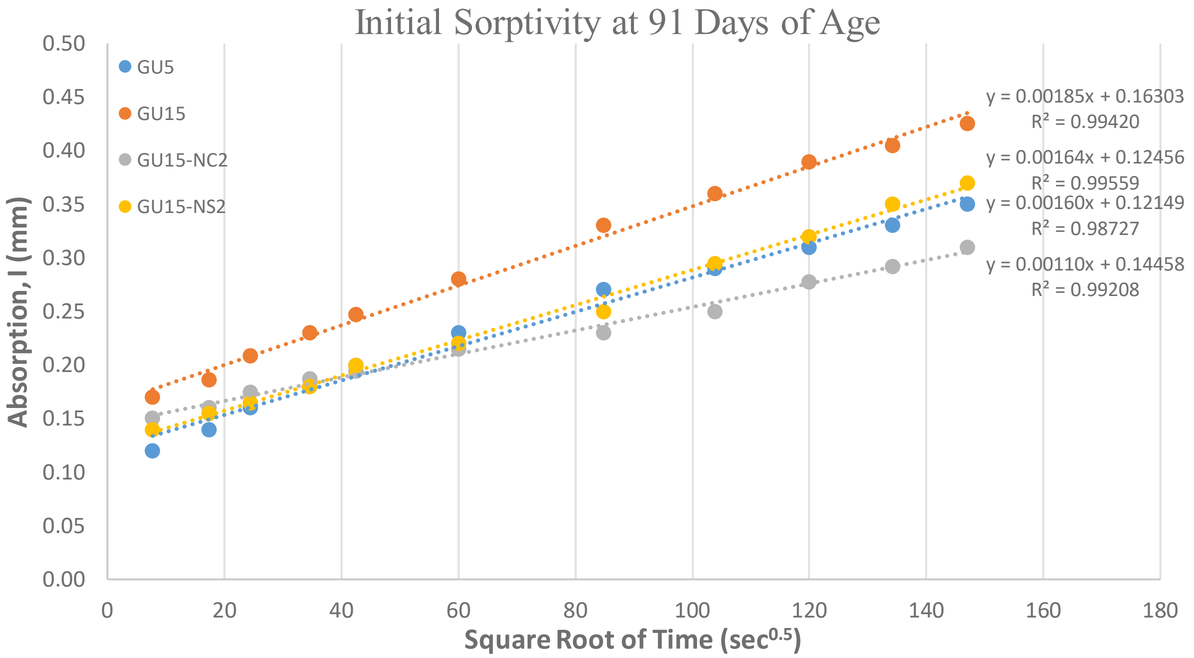

Figure 4.4.5: Initial sorptivity graphs for GU5, GU15, GU15-NC2, and GU15-NS2 mixtures at 91 days of age

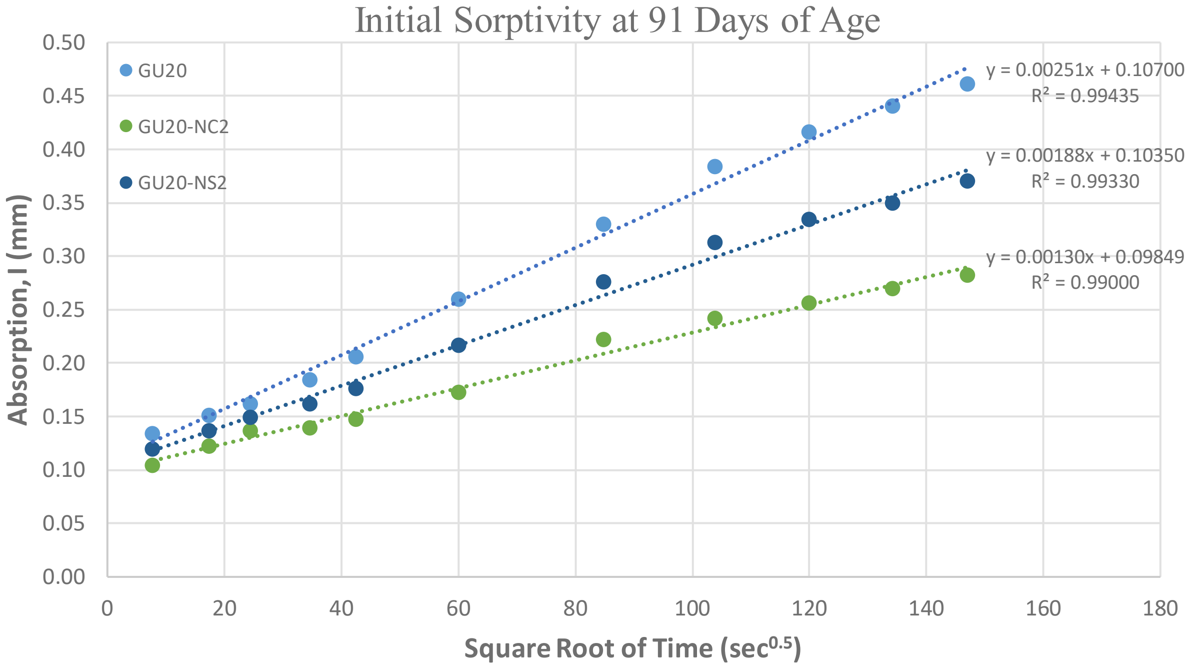

Figure 4.4.6: Initial sorptivity graphs for GU20, GU20-NC2, and GU20-NS2 mixtures at 91 days of age

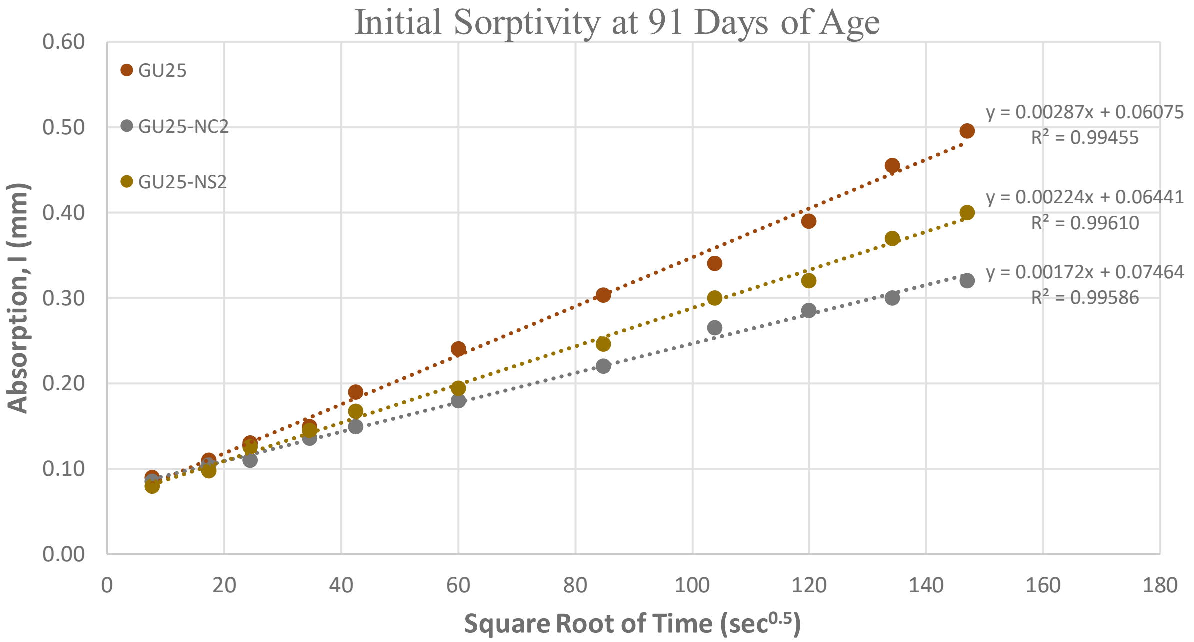

Figure 4.4.7: Initial sorptivity graphs for GU25, GU25-NC2, and GU25-NS2 mixtures at 91 days of age

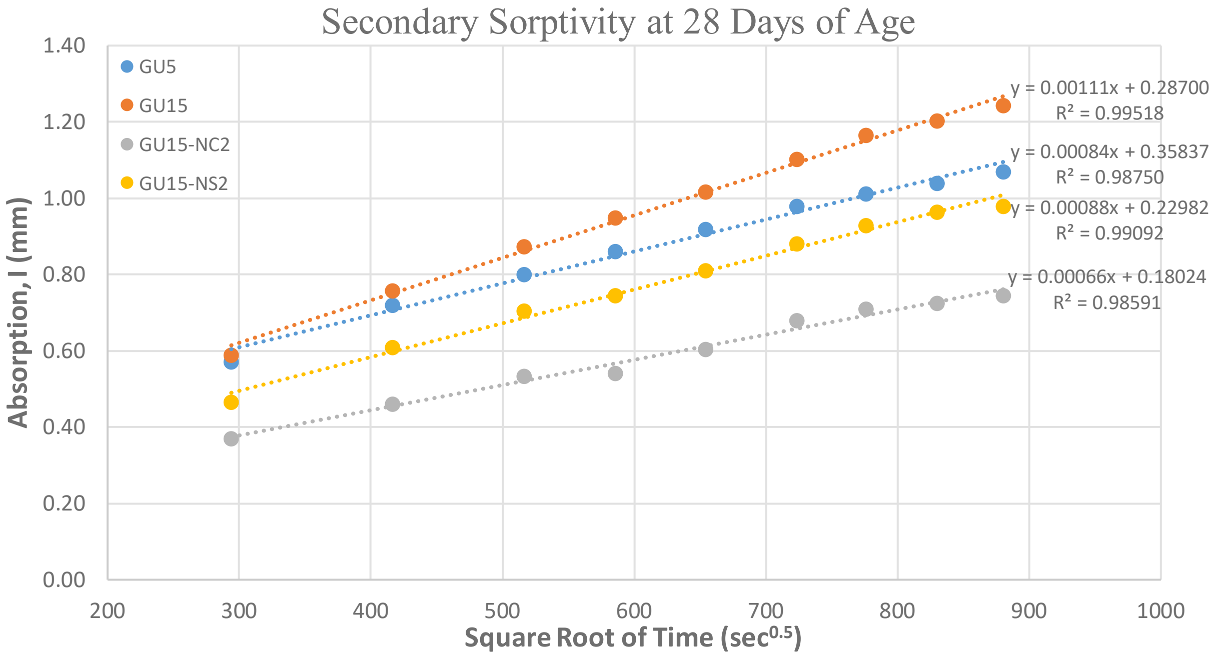

Figure 4.4.8: Secondary sorptivity graphs for GU5, GU15, GU15-NC2, and GU15-NS2 mixtures at 28 days of age

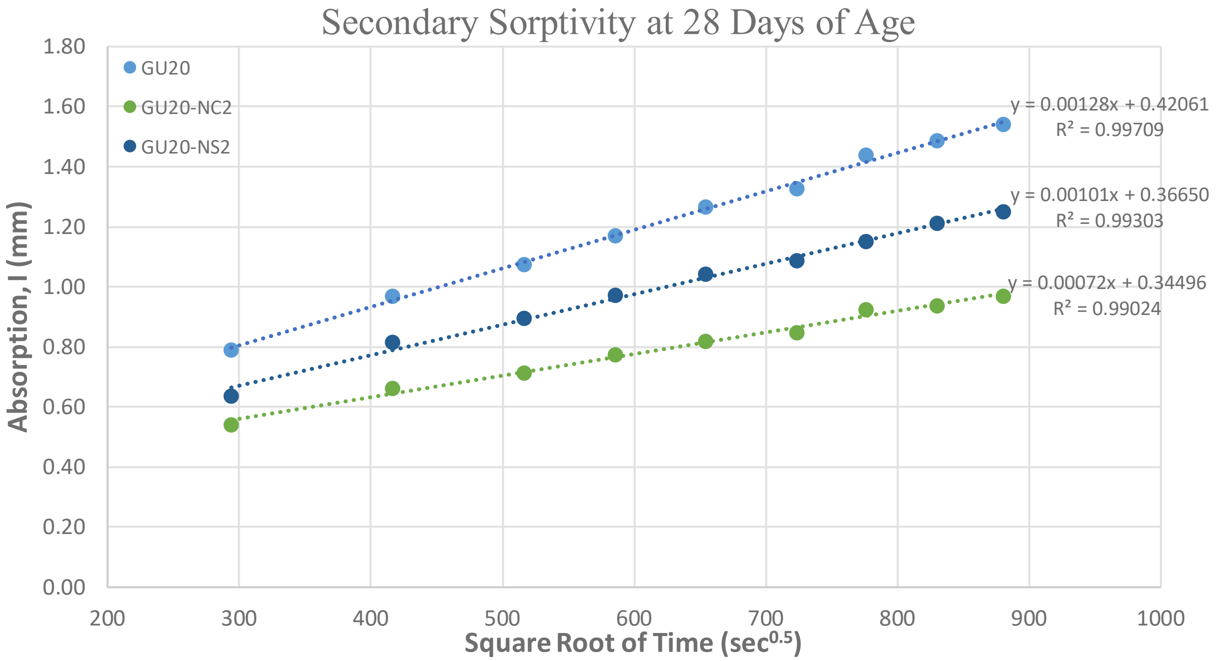

Figure 4.4.9: Secondary sorptivity graphs for GU20, GU20-NC2, and GU20-NS2 mixtures at 28 days of age

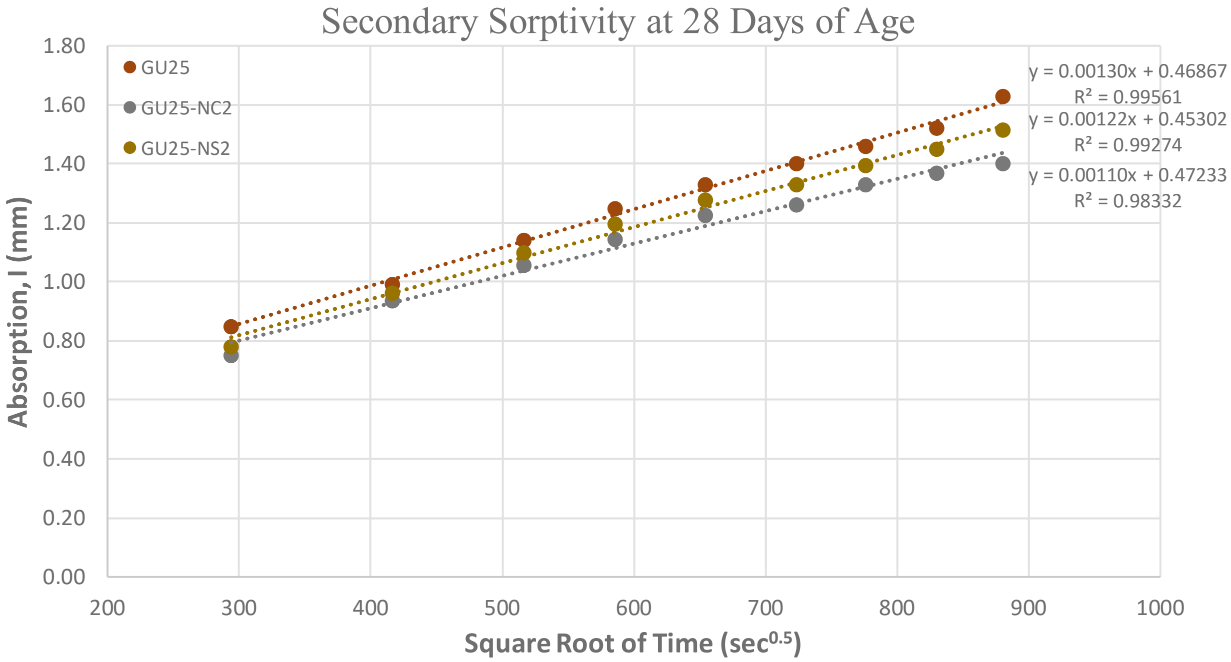

Figure 4.4.10: Secondary sorptivity graphs for GU25, GU25-NC2, and GU25-NS2 mixtures at 28 days of age

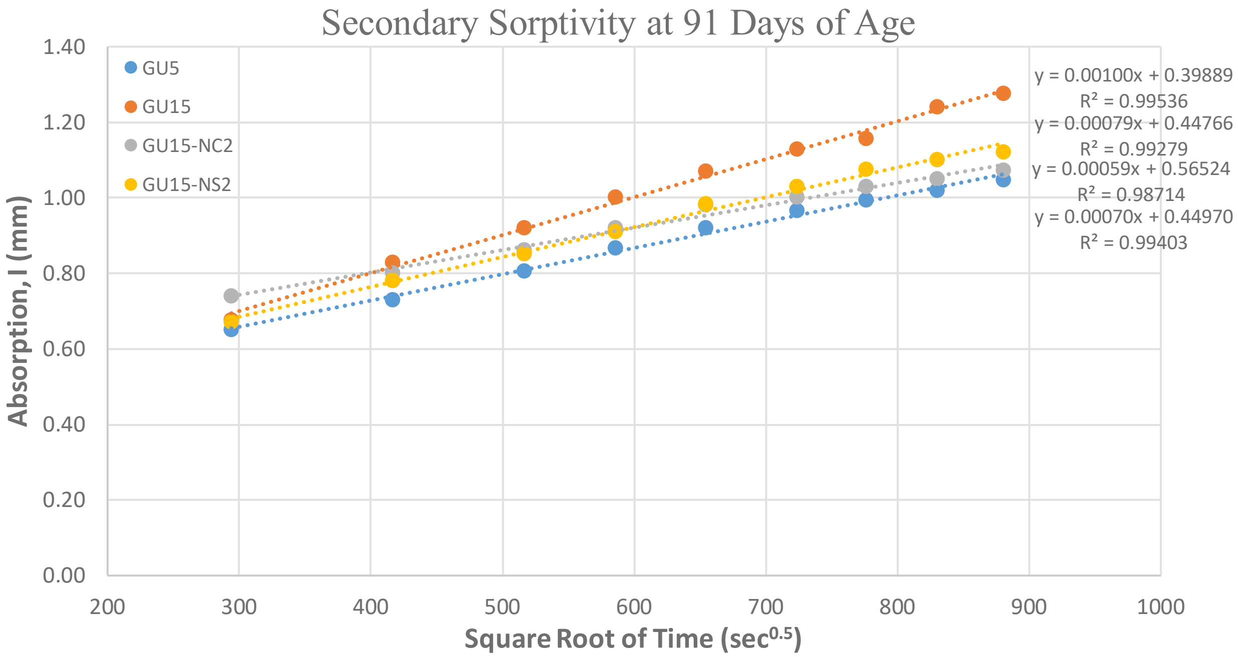

Figure 4.4.11: Secondary sorptivity graphs for GU5, GU15, GU15-NC2, and GU15-NS2 mixtures at 91 days of age

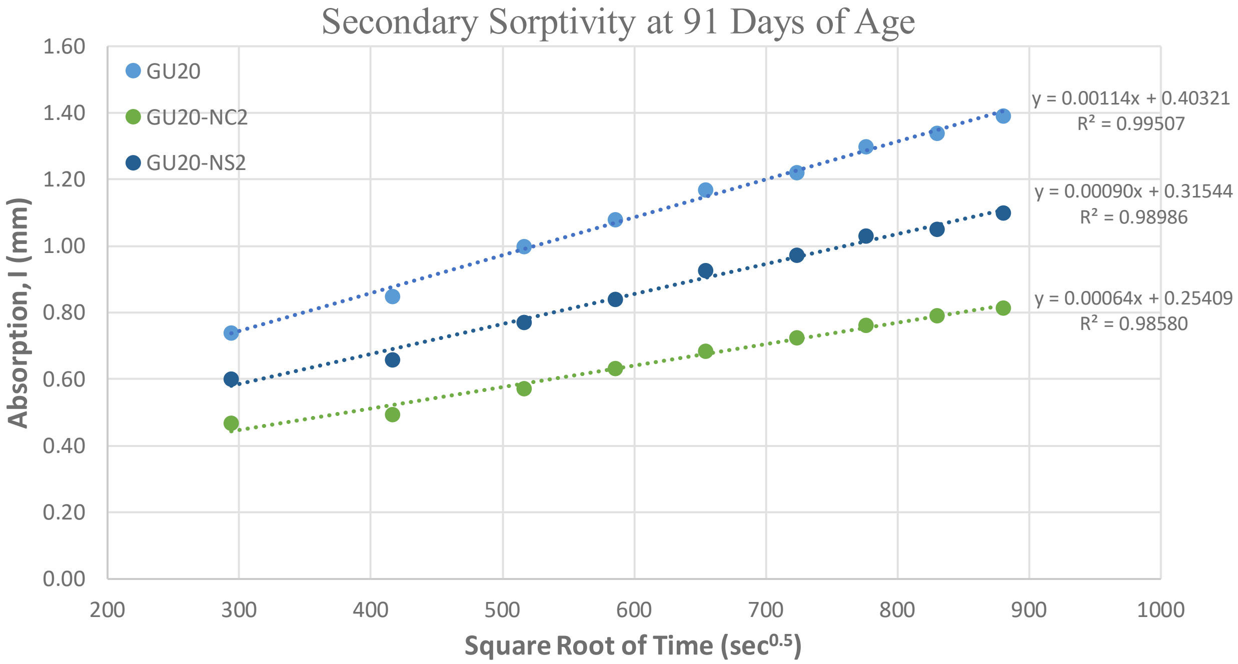

Figure 4.4.12: Secondary sorptivity graphs for GU20, GU20-NC2, and GU20-NS2 mixtures at 91 days of age

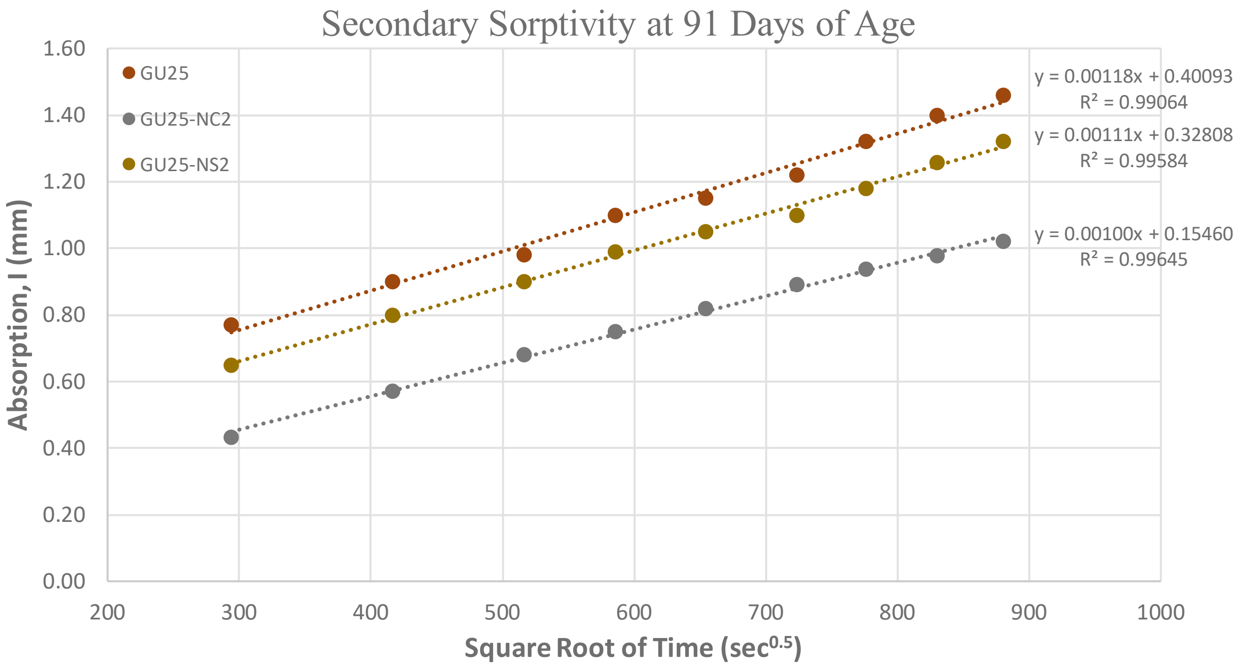

Figure 4.4.13: Secondary sorptivity graphs for GU25, GU25-NC2, and GU25-NS2 mixtures at 91 days of age

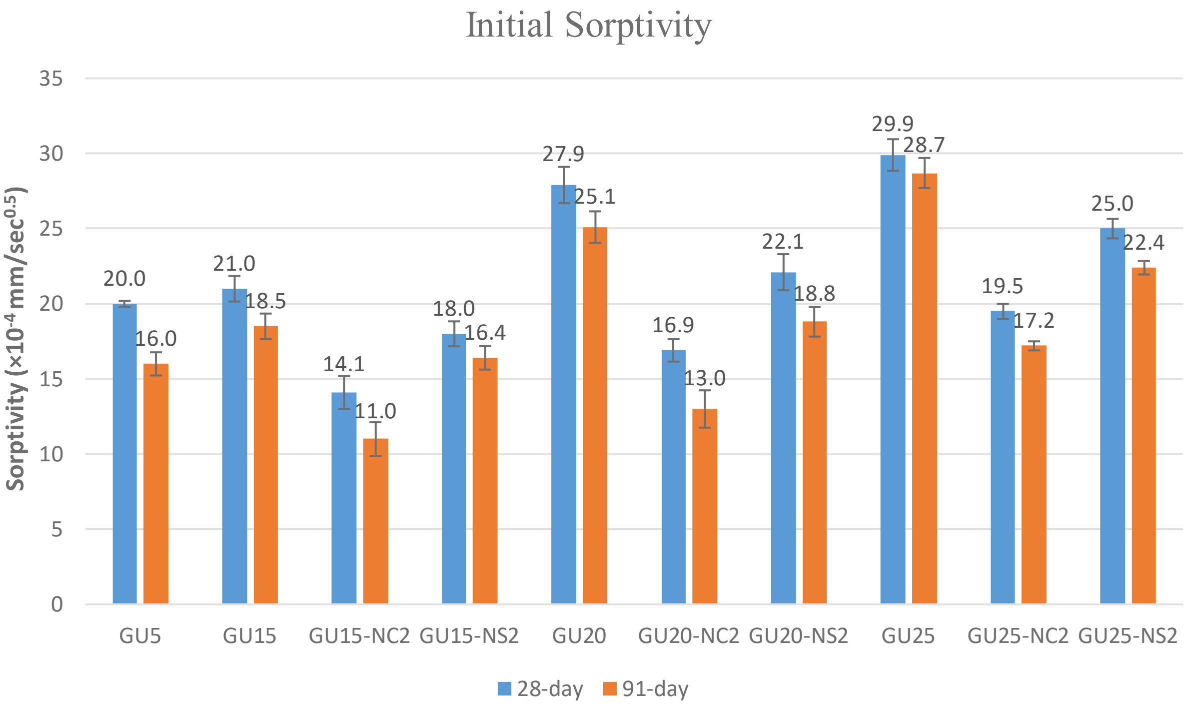

Figure 4.4.14: Initial sorptivity results at 28 days and 91 days of age

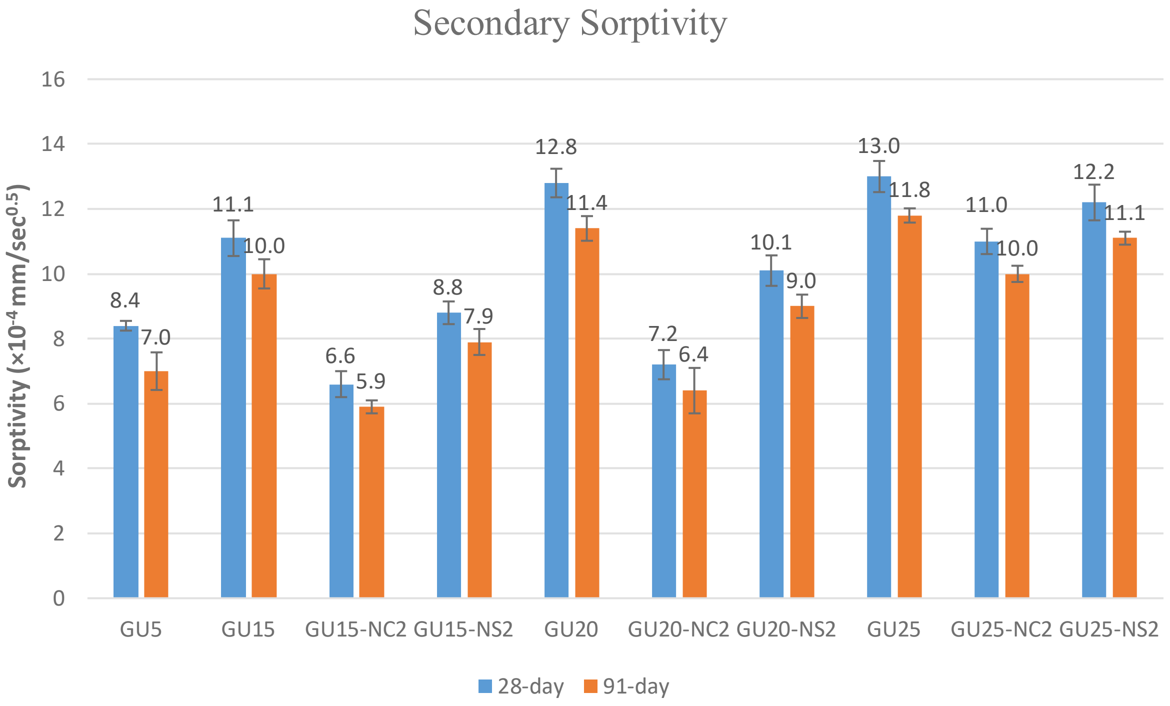

Figure 4.4.15: Secondary sorptivity results at 28 days and 91 days of age

Sorptivity is directly related to durability for above ground structures that are exposed to unpressurized water. Figure 4.4.14 includes all the results for initial sorptivity of the samples. Initial sorptivity, which is the rate of water absorption in the first six hours of contact with water, can be especially important characteristic in cases where concrete is in contact with water through hours-long cycles of wetting and drying. It can be seen that there is a clear decrease in the sorptivity of each mixture between 28 days to 91 days. This is expected as the samples are kept in curing condition (saturated limewater at 23°C) and the ongoing hydration process fills up the pores with new C-S-H gel resulting in a less porous and permeable mortar. Initial sorptivity represents the penetration of water into the interconnected network of gel and capillary pores through capillary suction (Qiao et al.-2019). Gel and capillary pores (10^{-3} to 1 μm) fill up faster than the much larger air voids (10 to 10^3 μm) which will require several days to fill. This is why the slope of the curve in Figure 4.4.1 is larger in the initial hours of the test. Higher initial sorptivity means that destructive solutions can penetrate faster into the gel and capillary pores and consequently reduce durability. Figure 4.4.14 also indicates that increasing the limestone content from 5% to 25% (GU5, GU15, GU20, and GU25) increases the initial sorptivity. This increase is slight from GU5 to GU15, but it becomes more pronounced when limestone content goes up to 20 and 25%. However, adding the 2% NC has a very positive effect on samples at every limestone content level. This effect is so significant that all of the samples containing NC have outperformed GU15 which has the standard limestone content and even GU5 (with the exception of GU25-NC2 at 91 days). Figure 4.4.14 also shows that while 2% NS addition has not been as effective as 2% NC addition, it has been very effective in decreasing initial sorptivity of the samples at every limestone content level.

Figure 4.4.15 includes all the results for secondary sorptivity of the samples. Secondary sorptivity is especially important when concrete is in continuous contact with water for several days. Once water filled the gel and capillary pores during the first several hours (initial sorptivity), it starts to penetrate into the much larger and disconnected pores and air voids. Samples with higher volume of voids have more space and consequently absorb more water over time (Helmuth-1961). This process which is the secondary sorptivity occurs at a slower rate compared to initial sorptivity due to the diffusion of air and overpressure in the air voids (Fagerlund-1993). The air voids can potentially provide the space for the expanding freezing water to prevent damage during freeze-thaw cycles. Damage caused by freeze-thaw cycles depends on the degree of saturation with respect to the critical degree of saturation below which freeze-thaw cycles do not cause deterioration (Maclnnis and Becaudoin-1968 and Fagerlund-1973). Durability of concrete under freeze-thaw cycles mainly depends on the time required to reach critical degree of saturation from the completion of initial sorptivity (filling of gel and capillary pores). In other words, given a similar volume of the voids, samples with higher secondary sorptivity can reach the critical degree of saturation faster and be more susceptible to freeze-thaw deterioration.

Similar to Figure 4.1.14, Figure 4.1.15 indicates that all of the samples show reduced sorptivity from 28 days to 91 days as a result of ongoing hydration process. Also, in mixture that do not contain nanoparticles, higher limestone content has obviously resulted in higher secondary sorptvity (GU5, GU15, GU20, and GU25). Comparing Figures 4.4.14 and 4.4.15, it can be seen that higher limestone contents have been more damaging to secondary sorptivity that initial sorptivity. The results of Figure 4.4.15 also show that while both NC and NS addition have had a positive effect in decreasing secondary sorptivity at every limestone content level, NC has been more effective than NS. It is also worth-noticing that with the help of NC addition, GU15-NC2 and GU20-NC2 have outperformed GU15 and even GU5, and GU25-NC2 has had the same performance as GU15.

4.5 Bulk Electrical Conductivity of Mortar

Bulk electrical conductivity of concrete was done in accordance with ASTM C1760. In this test, the current passing through the cylindrical sample exposed to 3.0% sodium chloride solution from the two ends is measured at 1 min ± 5 sec. The preparation, procedure, and basis of this test are similar to ASTM C1202, commonly known as Rapid Chloride Penetration Test (RCPT), which requires measuring the total charge passed over a 6-hour period while a constant voltage (60 V) is applied to the two ends of the sample. Over the 6-hour testing period of RCPT, the temperature of the sample and solution may increase due to the passing current. This increase in temperature is more significant if the concrete's conductivity is higher which generally happens in concretes with high permeability. Since electrical conductivity is sensitive to temperature, heating will lead to a higher overall measured passing charge. Therefore, some researchers (e.g. Julio-Betancourt and Hooton-2004) have recommended ASTM C1760 which is conducted over one minute and its results are not affected by changes in temperature.

Using the passing current, applied voltage, length, and diameter of the samples, electrical conductivity σ is calculated based on equation 4.5.1 (ASTM C1760):

$$\sigma = K\frac{I_1}{V}\frac{L}{D^2} \qquad \text{Equation 4.5.1}$$

where:

σ = bulk electrical conductivity, mS/m

I_1 = current at 1 min, mA

V = applied voltage, V

L = average length of specimen, mm

D = average diameter of specimen, mm

K = conversion factor = 1273.2

The SI unit for electrical conductivity is siemens/meter where a siemens has units of Ω^{-1}. The conductivity of concrete is governed by the chemical composition of the pore solution and overall pore structure (Krieg -2007). If concrete has a higher conductivity, it can be more susceptible to penetration of destructive ions such as chloride, and it can generally have a lower durability.

In this study, bulk electrical conductivity of two cylindrical mortar samples of each mixture listed in Table 3.3 were measured at 3, 7, 28, and 91 days and the averages are reported. Figure 4.5.1 includes the results at ages of 3 and 7 days, and Figure 4.5.2 includes the results at more mature ages of 28 and 91 days. Both figures show that conductivity has decreased consistently as the samples aged from 3 days to 91 days. In fact, on average the conductivity of the samples has decreased 52% from 3 days to 91 days of age. This was expected since the samples had been curing in saturated limewater at 23°C, and with the ongoing hydration process, the samples become less porous and conductive. Moreover, it can be seen that both NC and NS additions have been effective in reducing conductivity at every limestone content level. Similarly, Shaikh and Supit (2014 and 2015) performed RCPT and reported reduced charge passed through their regular and high volume fly ash concrete samples which contained 1 and 2% NC replacements and 2 and 4% NS replacements. In another study, Adak et al. (2014) also saw reduced charge passed through their fly ash based geopolymer concrete as a result of 6% NS addition. According to Figures 4.5.1 and 4.5.2, for each limestone content level, the 2% NC additions have on average decreased the conductivity by 17% while this decrease has been 11% as a result of 2% NS additions. Therefore, it can be concluded that at 2% the NC addition has been more effective than NS for deceasing conductivity.

Figures 4.5.1 and 4.5.2 indicate that the increase of limestone content level from 5% to 25% has clearly increased the conductivity. At all ages, this increase has been on average around 26%. This can be attributed to the lower overall hydrated products that results in a more porous and conductive mortar. Both figures show that the conductivity of GU15-NC2 is lower than GU5 while having 10% less cementitious material. Also, GU20-NC2 and GU25-NC2 have outperformed GU15. In other words, mixtures that have limestone contents of more than 15% (the standard limit for limestone content) were significantly improved using the 2% NC addition to perform better than the mixture which is currently allowed by the standard.

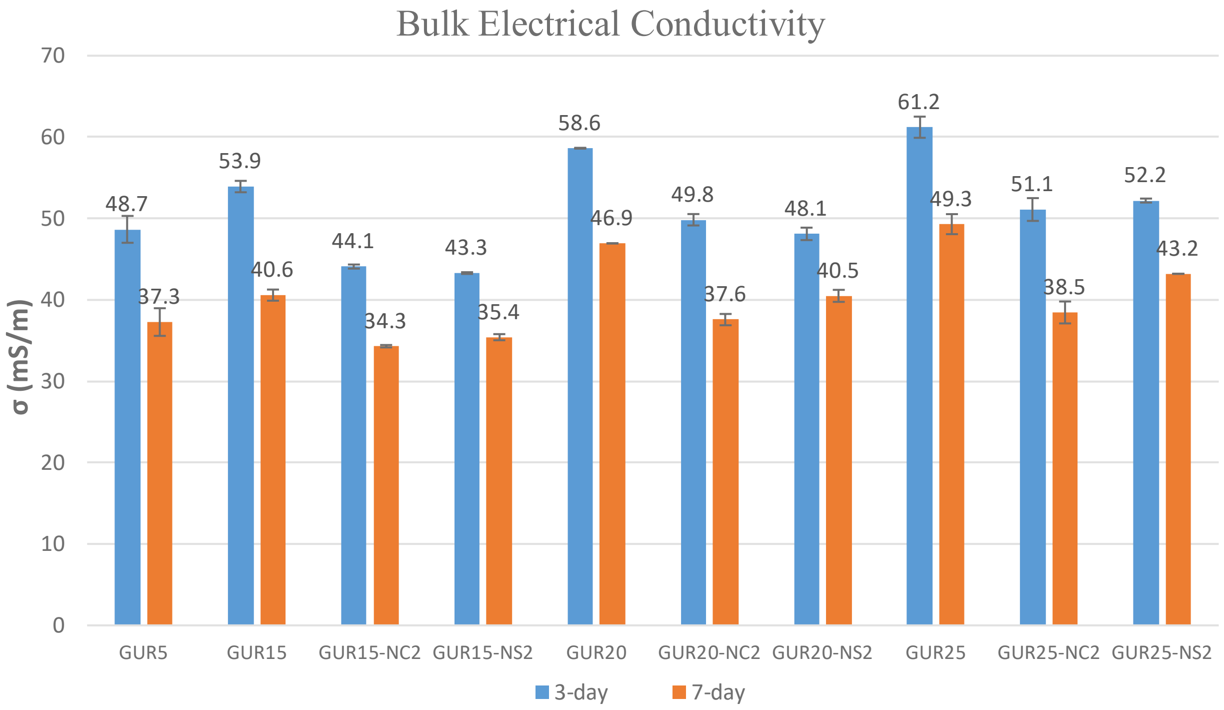

Figure 4.5.1: Bulk electrical conductivity of mortar samples at 3 and 7 days of age

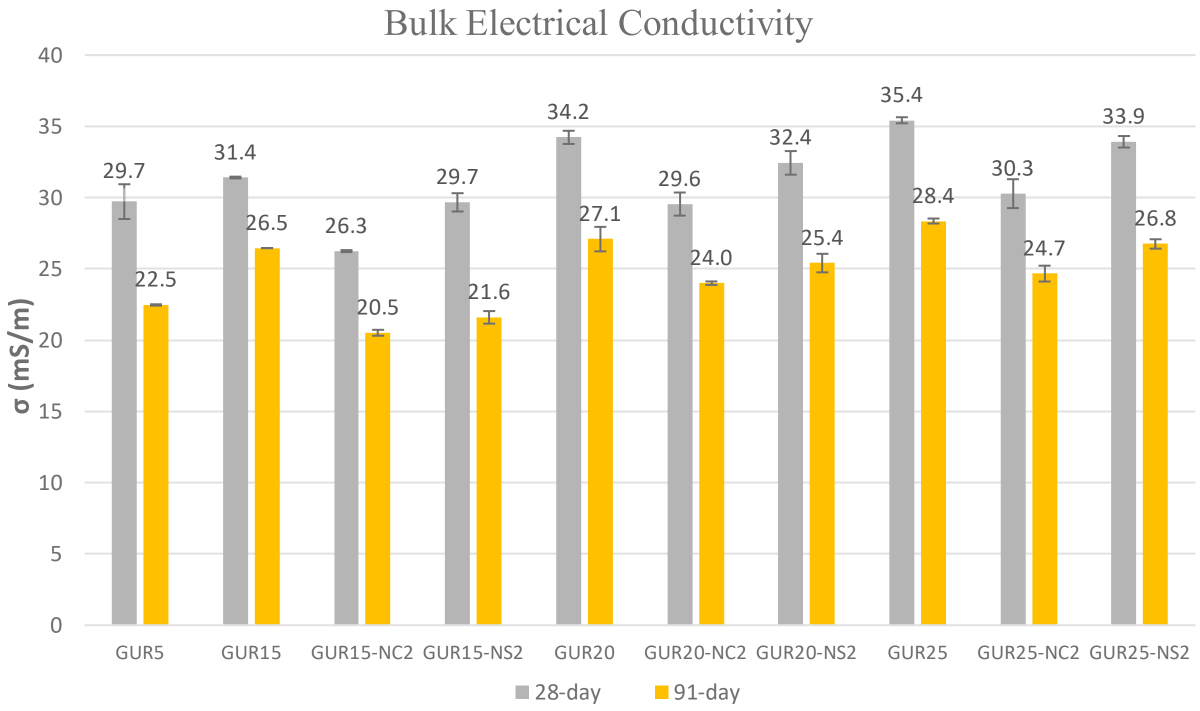

Figure 4.5.2: Bulk electrical conductivity of mortar samples at 28 and 91 days of age

4.6 Bulk Electrical Resistivity of Mortar

Bulk electrical resistivity test is a simple non-destructive test that can provide information about durability of concrete. This test involves placing the flat surfaces of the samples between the two steel plates of the machine that measures resistivity. Resistivity can be an indication of the resistance of concrete to penetration of destructive ions and damage due to chemical deterioration. Hence, higher resistivity can simply be interpreted as potential for higher durability.

As mentioned in Section 3.7, in this study, three 50×50×50 mm standard mortar cubes are prepared from every mixture listed in Table 3.3 and tested in two different directions at ages of 3, 7, 28, and 91 days, and the average values of their electrical resistivity are reported. Bulk electrical resistivity can be highly affected by changes in sample's moisture content and pore solution. At the time of performing this test in this study, there was no available standard procedure for measuring bulk electrical resistivity. Therefore, to maintain similar conditions for all of the samples, the mortar cubes were all stored in saturated limewater at 23°C after demolding and were fully saturated at the time of testing. Recently ASTM C1876 has been published and describes the standard procedure required for this test.

To increase precision, three cubes from each mixture were tested at each age, and resistivity of each cube was measured in two different directions. For better comparison, the results are presented in two separate figures; Figure 4.6.1 for early ages of 3 and 7 days and Figure 4.6.2 for more mature ages of 28 and 91 days.

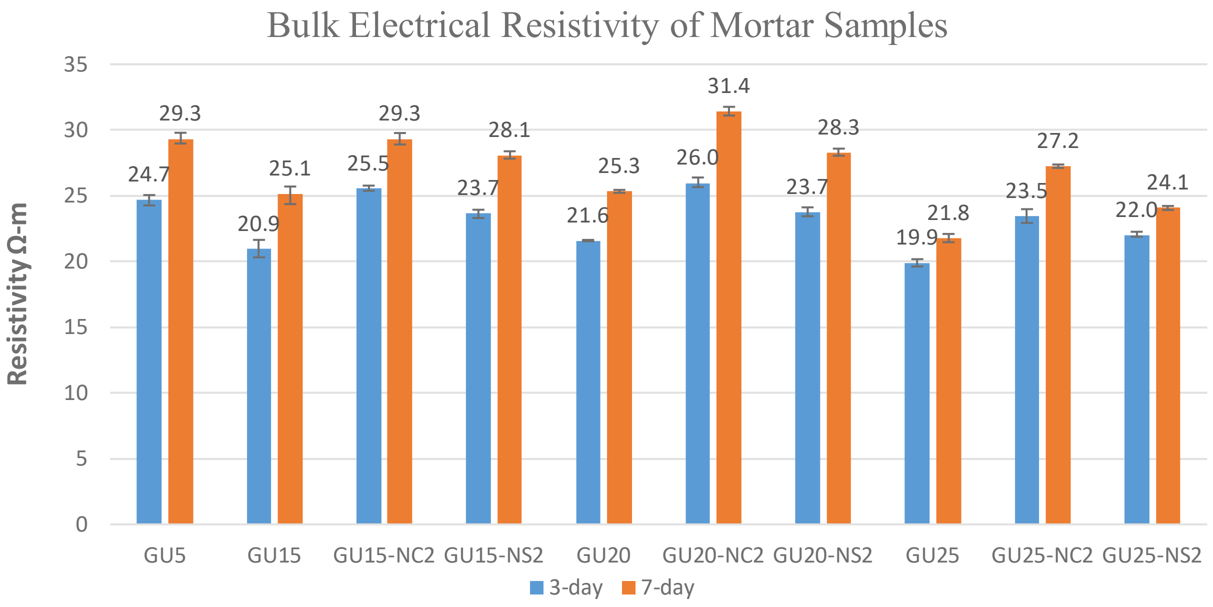

Figure 4.6.1: Bulk electrical resistivity of mortar samples at 3 and 7 days of age

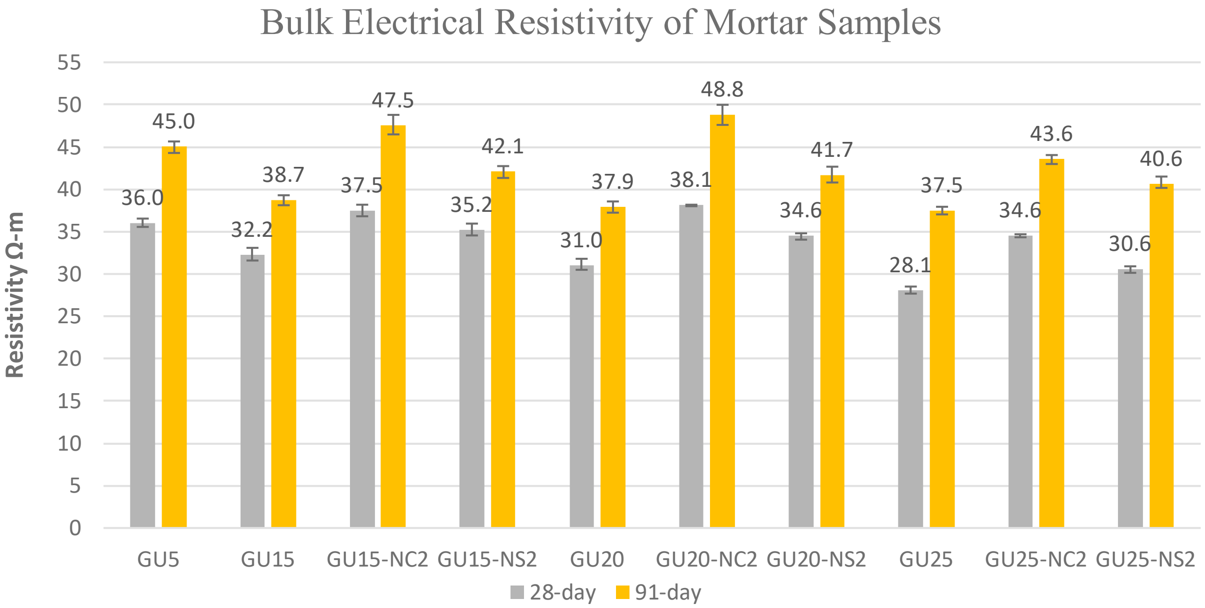

Figure 4.6.2: Bulk electrical resistivity of mortar samples at 28 and 91 days of age

Electrical conductivity and electrical resistivity are similar by nature and are essentially related to pore solution and pore structure of concrete. Some researchers have even tried to develop models to correlate the results of electrical resistivity and electrical conductivity (e.g. Ramezanianpour et al.-2011). Size of the pores and their interconnectivity are important aspects of microstructure that can severely affect resistivity. When concrete has a denser microstructure with smaller and less interconnected pores, it can have a higher resistance and lower conductivity and consequently better durability.

Pozzolanic reactions due to incorporating supplementary cementitious materials such as silica fume in concrete are well-known for reducing permeability by providing a denser microstructure which results in a more durable concrete. As mentioned before, NS particles can perform a seeding action for cement hydration, act as filler in cement matrix, and also improve cement hydration through pozzolanic action. Therefore, an increase in resistivity of mortar samples when NS is added could be expected. Jalal et al. (2012) compared the effect of 2% NS and 10% silica fume replacement of cement in self consolidating concrete on resistivity. Their results showed that overall 2% NS replacement was even more effective in increasing the resistivity than 10% silica fume replacement.

A quick glance at Figures 4.6.1 and 4.6.2 show that resistivity of all mixtures increased over time. This increase was approximately 83% on average from 3 days to 91 days of age. This is clearly the result of ongoing cement hydration that reduces the capillary pores and consequently increases resistivity. Section 4.1 discussed how the replacement of cement with limestone has reduced overall cement hydration due to lower amounts of cementitious material. However, it is also known that limestone powder can act as a filler and help to reduce permeability, and as a result, it may increase resistivity. The figures indicate that the resistivity of GU5 is on average 16% higher than GU15 at all ages which is substantial. This can be caused by lower cement content of GU15 with respect to GU5. The resistivity of GU15 and GU20 are very close, and GU25 is slightly lower at 3, 7, and 28 days, but at 91 days the difference between their resistivity is negligible. It can be concluded that increasing limestone content beyond 15% has not had a significant negative effect on the resistivity even without the addition of nanoparticles especially at later ages.

Addition of both NC and NS have increased resistivity of the mortar samples significantly for all mixtures and at all ages. This increase with respect to the same mixtures without the nanoparticles has on average been 21% for NC addition and 10% for NS addition which implies higher effectiveness of 2% NC with respect to 2% NS addition. Mixtures GU15-NC2, GU20-NC2, and GU25-NC2 showed higher resistivity compared to GU15 at all ages; 19, 23, and 10% respectively. Interestingly, GU15-NC2 and GU20-NC2 even outperformed GU5 which has a much lower limestone content. In other words, based on the results of this study, increasing the limestone content in cement beyond the 15% standard limit did not have a negative effect on resistivity, and with the help of NC addition, the mixtures with even 20% and 25% limestone content significantly outperformed the 15% limestone content level.

4.7 Correlation of Bulk Electrical Resistivity and Bulk Electrical Conductivity

Electrical resistivity (ρ) is a fundamental property of material for quantifying how strongly it resists an electric current. Electrical conductivity (σ) is the reciprocal of electrical resistivity and quantifies how strongly a material conducts electric current and is by definition the inverse of electrical resistivity.

The RCPT procedure was originally proposed by Whiting (1981) and has been adopted by ASTM C1202 and AASHTO T 227. It provides an indication of concrete's resistance to chloride penetration, but what it actually quantifies is electrical conductivity through the measurement of charge passed over a 6-hour period. Flow of electric current in concrete is essentially the result of ionic movement which can be increased by an increase in temperature. The importance of maintaining a constant temperature for RCPT relies on this fact. Depending on the conductivity of the concrete sample, the 6-hour length of RCPT can be associated with increased temperature which affects the results. In fact, a temperature change of 1°C can result in a 3% change in electrical resistivity of concrete (Elkey and Sellevold-1995). Moreover, the rather long 6-hour period of the test results in an increase in the ionic concentration of the pore solution of concrete by chloride penetration that may also affect the results. Therefore, the otherwise perfect inverse relationship between electrical conductivity and electrical resistivity cannot be expected from the results obtained through RCPT (Layssi et al.-2015). Procedures provided by ASTM C1760 do not suffer from the two mentioned shortcomings. Ramezanianpour et al. (2011) correlated their RCPT results with the results of surface resistivity test done by the four-point (Wenner probe) technique. The correlation function they used was in the form of $x^{1.028}$.

In this study, bulk electrical conductivity was obtained according to ASTM C1760 (results are presented in Figures 4.5.1 and 4.5.2). In this test, the cylindrical mortar samples that are fully saturated are placed between two chambers that contain 3.0% sodium chloride solution while a constant voltage is applied to the chambers. Bulk electrical resistivity was done on 50×50×50 mm cube mortar samples that were fully saturated in limewater (results are presented in Figures 4.6.1 and 4.6.2). A correlation based on an inverse function between the all the results is presented in Figure 4.7.1.

Even though there are differences between the size and shape of the samples and procedures for the two tests, there is a good correlation with an acceptable coefficient of determination (R^2) of 0.93893 between the results. Since the bulk electrical resistivity is a much easier and faster test, the results suggest that it can be a proper alternative for either RCPT or bulk electrical conductivity.

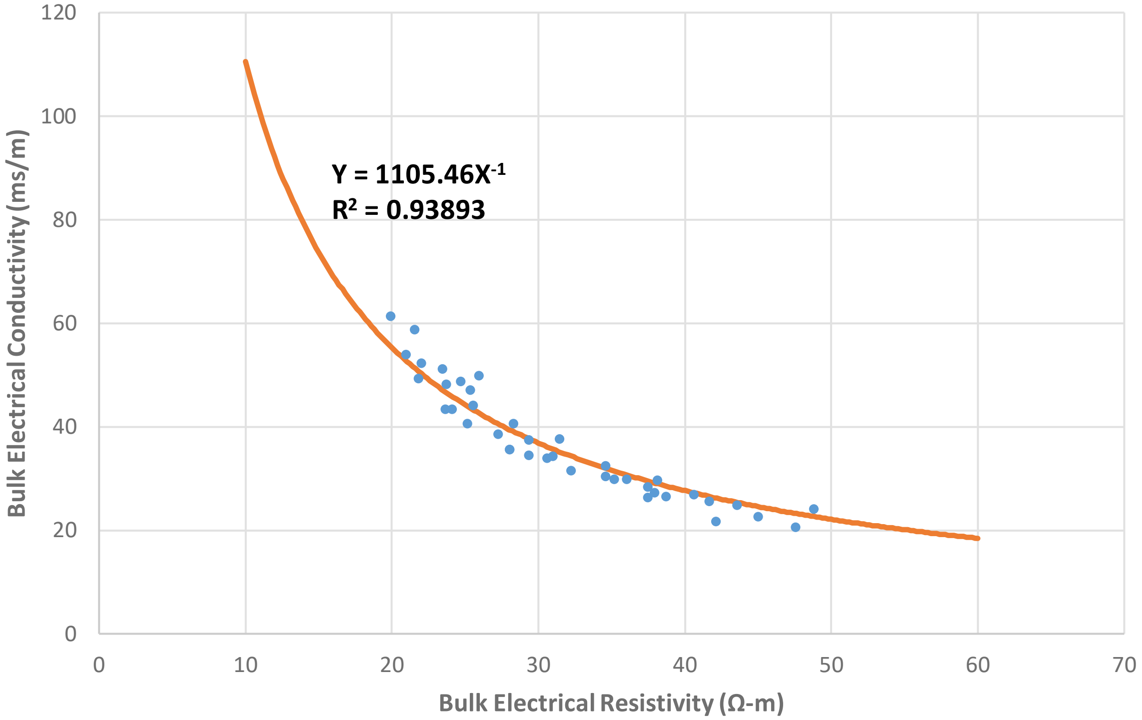

Figure 4.7.1: Correlation between bulk electrical resistivity and bulk electrical conductivity

4.8 Expansion of Mortar Bars Due to Sulfate Attack

In this section, the results of CSA A3004-C8 (similar to ASTM C1012) expansion test are presented. The test has been performed at 23°C where ettringite sulfate attack (ESA) is the predominant sulfate attack and at 5°C where thaumasite sulfate attack is the predominant sulfate attack. In this section, the sulfate attack at 23°C and the sulfate attack at 5°C have been referred to as Room Temperature Sulfate Attack (RTSA) and Low Temperature Sulfate Attack (LTSA) respectively. Even though the low temperature sulfate attack expansion test is not a requirement in the latest CSA 3000-18, it has still been used in this study as a durability measure.

According to CSA 3000-18, Portland limestone cement should not be used in sulfate exposures unless it is tested and used with sufficient proportions of supplementary cementing material (SCM). Therefore, none of the 15, 20, and 25% limestone addition levels of this study is allowed by CSA 3000-18 to be used alone in sulfate exposures even with the addition of the nanoparticles. The pozzolanic effect of SCMs such as slag, fly ash, silica fume, and metakaolin on durability of concrete is well documented. Many researchers have also examined sulfate resistance of different binary and ternary blend of cement or limestone cement with SCMs. Ramezanianpour and Hooton (2013) found that partially replacing Portland limestone cement with 50% slag made it sulfate resistant even at 5°C. Mirvalad and Nokken (2015) tested numerous binary and ternary blends of Portland limestone cement and different types of SCMs in sulfate attack at both 5°C and

23°C. They concluded that increasing the SCM content in their PLC blends resulted in improved sulfate resistance. Among their mixtures, they reported that the ternary blends of PLC, slag, and fly ash were the most resistant to sulfate attack.

As mentioned before, the conventional sulfate attack (ESA) happens when sulfate ions that penetrate into concrete react with calcium hydroxide to form gypsum. Gypsum will then react with C_3A and form ettringite. Gypsum and especially ettringite are larger in volume than the reactants, and their formation can cause cracks and deformations in concrete. The other type of sulfate attack (TSA) happens when sulfate ions in the presence of carbonate ions and water react with the C-S-H gel and form thaumasite which is non-cohesive and results in disintegration of cement paste and concrete. A very important source of carbonate ions is calcium carbonate (limestone) in cement.

Partial replacement of cement with pozzolanic materials can significantly improve sulfate resistance of concrete through three mechanisms. First, since the concrete becomes denser and less permeable, the penetration of sulfate ions is essentially reduced for both ESA and TSA. Second, a portion of calcium hydroxide generated as a result of cement hydration is consumed through the pozzolanic reactions. This reduces the amount of available calcium hydroxide for ESA reactions. Third, since cement is partially replaced with the supplementary cementing materials, there is less C_3A present for ESA and also less calcium carbonate for TSA. Out of these three mechanisms, only the first one can increase the sulfate resistance of concrete as a result of NC addition. The NC particles can reduce permeability of concrete that hinders the ingression of destructive ions such as sulfate ions. Moreover, the 15, 20, and 25% limestone content levels significantly increase the susceptibility of mortar samples to sulfate attack. Therefore, high sulfate resistance may not be expected from the proposed mixtures of this research.

Moreover, it is worth emphasizing that the limestone cement used in this study is a blend of GU cement and limestone powder. In practice, GUL has 12-13% limestone content in Canadian cement plants (Hooton et al.-2010). Even at 15% limestone content, GU15 blend used in this research is not exactly identical to a GUL which is inter-ground at the cement plant. Compared to GU cement, the C_3A and sulfate content of GUL are specifically optimized, and it is generally ground more to ensure sufficient level of sulfate resistance and early-age strength. In other words, a GUL cement is expected to be more sulfate resistant than all of the blended limestone cements of this study. The blended limestone cements used in this study are only selected in order to evaluate the effect of NC and NS addition.

According to CSA A3004-C8, twelve 25×25×285 mm mortar prisms were cast and placed in 50 g/L sodium sulfate solution. Six of them were stored at 23°C for Procedure A (RTSA) and the other six at 5°C for Procedure B (LTSA). The lengths of the mortar bars were measured periodically according to CSA A3004-C8 at 1, 2, 3, 4, 8, 13, 15, 17, 26, 39, and 52 weeks. Table 4.8.1 includes the requirements of CSA A3001-13. As mentioned before, in the most recent version of the standard (CSA A3001-18), Procedure A has remained intact, but Procedure B has been removed. The averages of the six length measurements for each mixture at 3, 6, and 12 months are listed in Table 4.8.2.

Table 4.8.1: The CSA A3001-13 expansion limitations for mortar samples studied according to the CSA A3004-C8 sulfate attack procedures

	MSb and MSLb*	HSb and HSLb*	Reference
Maximum expansion at 6 months (%)	0.10	0.05§	CSA A3004-C8 Procedure A
Maximum expansion at 18 months (%)	0.10**	0.10**	CSA A3004-C8 Procedure B

*MSb stands for moderate sulfate resistant blended hydraulic cement
HSb stands for high sulfate resistant blended hydraulic cement
MSLb stands for moderate sulfate resistant blended Portland limestone cement
HSLb stands for high sulfate resistant blended Portland limestone cement
**If the increase in expansion between 12 and 18 months exceeds 0.03%, the sulfate expansion at 24 months shall not exceed 0.10% in order for the cement to be deemed to have passed the sulfate resistance requirement.
§ If the expansion is greater than 0.05% at 6 months but less than 0.10% at 1 year, the cement shall be considered to have passed.

Table 4.8.2: Expansion of CSA A3004-A and CSA A3004-B mortar bars for both room temperature and low temperature sulfate attack tests

	Average Expansion (%)					
	Room Temperature Sulfate Attack			**Low Temperature Sulfate Attack**		
	3 months	**6 months**	**12 months**	**3 months**	**6 months**	**12 months**
GU5	0.021	0.071	0.182	0.030	0.074	Failed
GU15	0.033	0.115	0.367	0.034	0.302	Failed
GU15-NC2	0.028	0.084	0.278	0.021	0.053	Failed
GU15-NS2	0.031	0.102	0.327	0.032	0.220	Failed
GU20	0.038	0.152	0.476	0.025	0.666	Failed
GU20-NC2	0.027	0.092	0.311	0.021	0.430	Failed
GU20-NS2	0.032	0.124	0.412	0.024	0.612	Failed
GU25	0.039	0.192	0.570	0.024	0.793	Failed
GU25-NC2	0.028	0.110	0.412	0.022	0.560	Failed
GU25-NS2	0.032	0.149	0.506	0.026	0.727	Failed

4.8.1 Room Temperature Sulfate Attack (RTSA)

According to Table 4.8.1, the average expansion of the mortar bars at 6 months should not exceed 0.10% in order to consider that mixture moderate sulfate resistant. In order to categorize a mixture as high sulfate resistant, the average expansion of the mortar bars should not exceed 0.05% at 6 months or if the expansion is greater than 0.05% at 6 months, it should still be less than 0.10% at 1 year. For better visual comparison, the 6-month and 12-month average expansions of mortar samples at 23°C are also shown in Figure 4.8.1 and 4.8.2. Considering Figure 4.8.1, none of the mixtures can be categorized as high sulfate resistant. Mixture GU5 which has only the GU cement and no additional limestone powder has an expansion of 0.071% at 6 months and can be considered moderate sulfate resistant. It is clear that with limestone contents of 15, 20, and 25% (GU15, GU20, and GU25) the expansions have increased beyond the moderate sulfate resistance level. Both figures also show that 2% NC and 2% NS additions have decreased the expansions of the mortar bars. This is presumably because the NC and NS additions have reduced the permeability of the mortar samples that hinders the sulfate ions penetration and consequently the expansions resulting from the sulfate attack chemical reactions. The improvements in the expansions have been more significant in NC additions as opposed to NS (on average 36% versus 17% at 6 months and 30% versus 12% at 12 months) at every limestone content level which shows that at 2% addition of nanoparticles, NC has been more effective than NS.

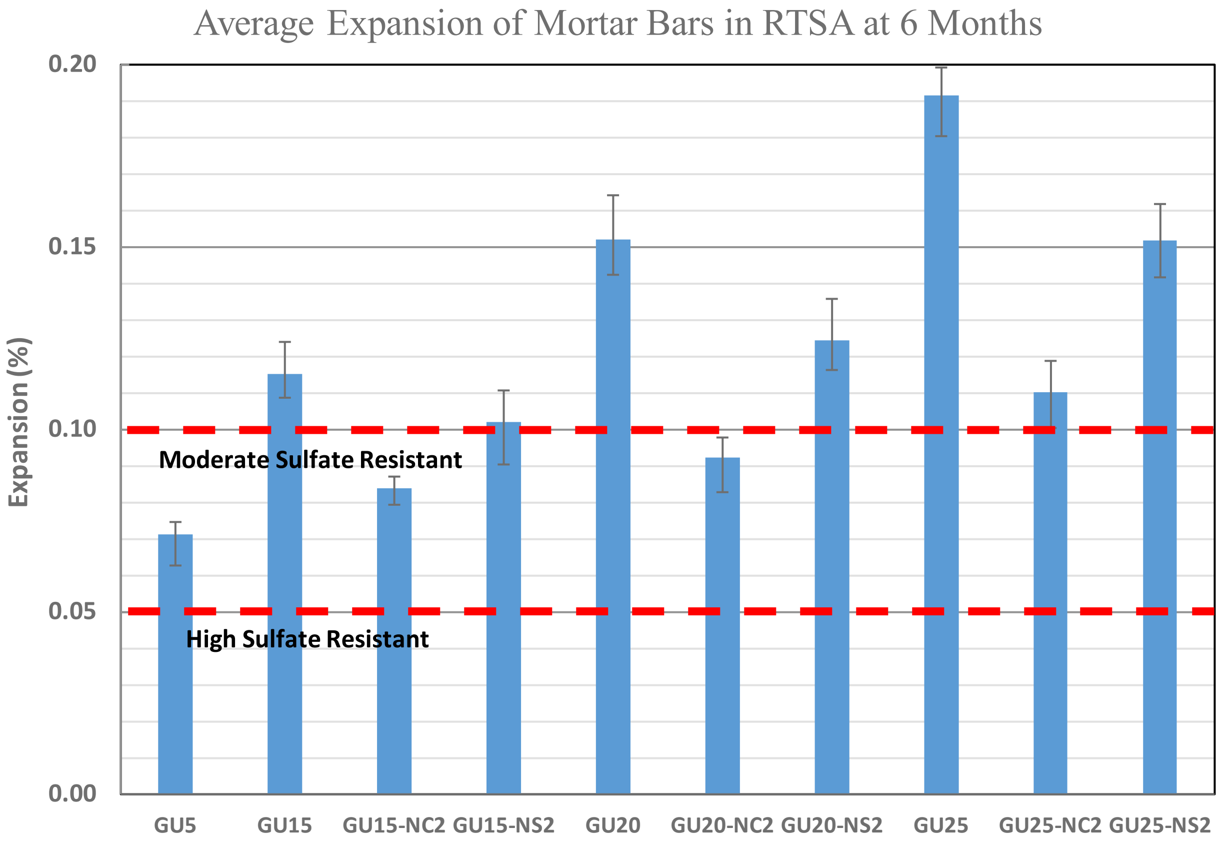

Figure 4.8.1: Average 6-month expansion of mortar bars in RTSA with respect to CSA A3001-18 limitations

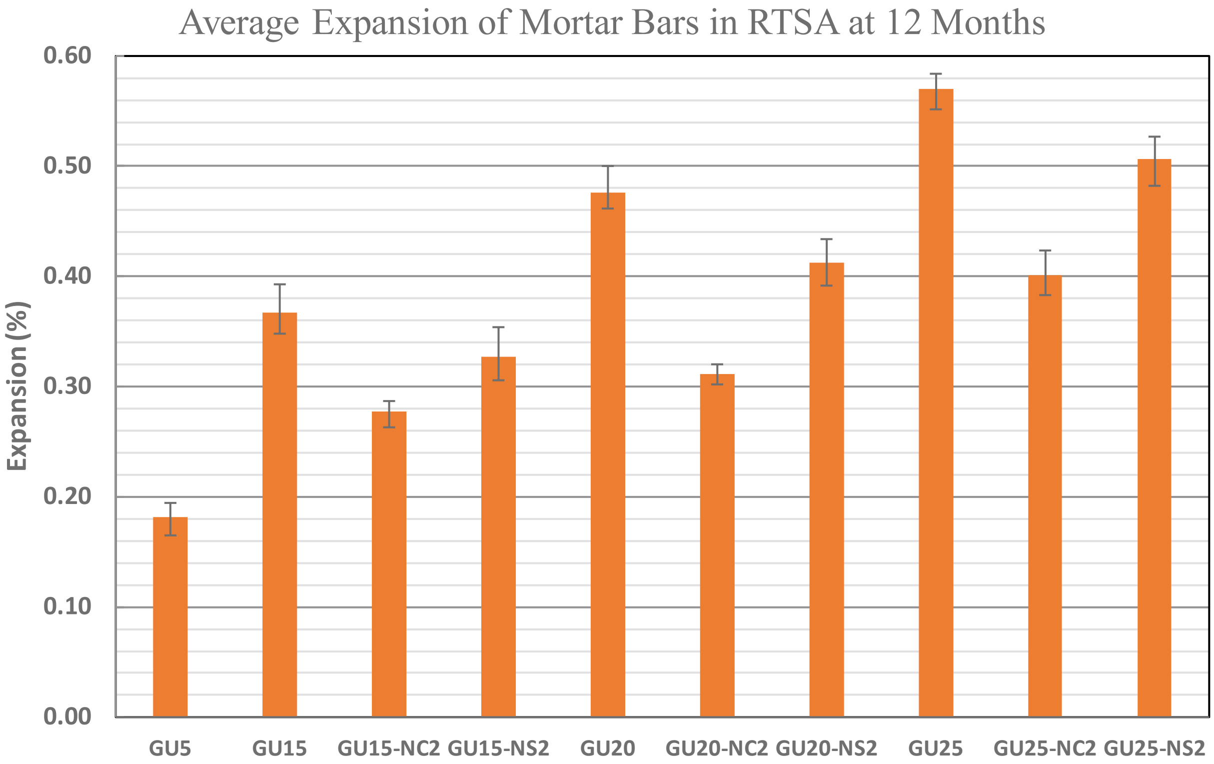

Figure 4.8.2: Average 12-month expansion of mortar bars in RTSA

A very interesting observation from Figure 4.8.1 is that although GU15 and GU20 have expansions greater than the limit for moderate sulfate resistance, with the addition of NC, the expansions of GU15-NC2 and GU20-NC2 have been reduced to 0.084% and 0.092% respectively (less than the 0.10% limit for moderate sulfate resistance). Therefore, GU15-NC2 and GU20-NC2 can be categorized as moderate sulfate resistant. This is especially important for GU20-NC2 which has a limestone content beyond the 15% limit of the standard. Even though GU25-NC2 and all of the mixtures containing NS have shown reduced expansions compared to their nanoparticle-free counterparts, none of them can be categorized as moderate sulfate resistant except for GU15-NS2 which may be marginally accepted at 0.102% of expansion. Also, GU20-NC2 and GU25-NC2 have performed better than GU15 at 6 months only because of their improved durability due to NC addition.

The CSA A3001-13 limitations for mortar samples stored at 23°C are only for expansions at 6 months. However, the samples were measured periodically and monitored for up to a year, and the 12-month expansion are included in Figure 4.8.2. Also, detailed expansion evolutions are presented in Figure 4.8.3. The 12-month expansion results shown in Figure 4.8.2 follow almost the same trend as Figure 4.8.1. Mixture GU5 which has only the GU cement has had the lowest expansion. As the limestone content is increase from GU5 to GU15, GU20, and GU25, the expansion has also increased. Similarly, the 2% NC and NS additions have been effective in decreasing the expansion of the mortar bars, and NC has been more effective than NS in all cases. As mentioned, the 6-month expansion of GU20-NC2 and GU25-NC2 have been lower than GU15 even though they have 5 and 10% more limestone content respectively. At 12 months, GU20-NC2 still has shown around 15% less expansion than GU15 while GU25-NC2 has slightly surpassed the expansion of GU15. There may be two explanations for this discrepancy between the 6-month and 12 month expansions. First, due to the high limestone content of GU25-NC2, the sulfate attack chemical reactions may have increased over time to the extent that the limited permeability due to NC addition could not sufficiently reduce the expansions. Second, at 12 months, all samples have been experiencing relatively large expansions, and the expansion for GU25-NC2 is around 0.4%. The large expansion may cause some curvature in some mortar bars which can over time result in errors in length measurements.

Figure 4.8.3 presents the detailed average expansion evolutions over the 12-month period for all mixtures. The expansions of all mixtures have stayed in relatively the same range over the first 13 weeks. However, after 13 weeks, the increase in expansions have accelerated. As the time passes from 13 to 52 weeks, the differences in the expansions of the mixtures becomes more and more noticeable. As explained earlier, none of the mixtures of this study can be considered high sulfate resistant, and only three mixtures (GU5, GU15-NC2, and GU20-NC2) can be categorized as moderate sulfate resistant. Therefore, an accelerated expansion increase can be expected from all samples especially after 13 weeks.

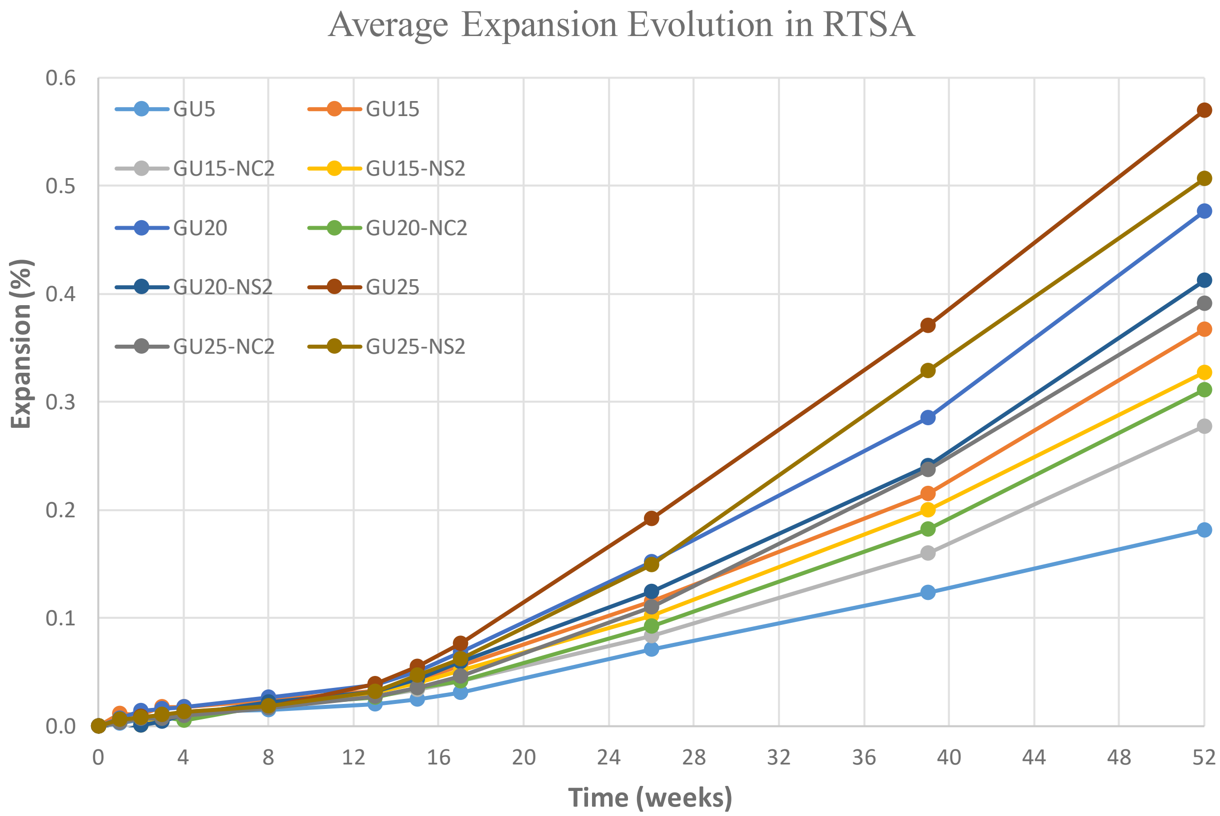

Figure 4.8.3: Expansion of CSA A3004-C8 mortar bars in RTSA over the 1-year test period

4.8.2 Low Temperature Sulfate Attack (LTSA)

Thaumasite sulfate attack is a severe form of deterioration of concrete which is the predominant form of sulfate attach at low temperatures (3-7°C). In TSA, the hardened C-S-H mainly responsible for the strength of concrete reacts with sulfate ions in the presence of carbonate ions and water to form thaumasite which is non-cohesive. This causes both severe expansion and deterioration in concrete. Mixtures with excessive carbonate ions, such as the ones used in this study with high limestone content, are extremely susceptible to TSA.

According to CSA A3001-13 limitations for mortar samples listed in Table 4.8.1, the expansion of mortar samples should not exceed 0.10% at 18 months in order for the mixture to be considered sulfate resistant. The deteriorations of the samples were so drastic that except for mixture GU5, none of the samples were measurable beyond 26 weeks (6 months). The last measurement for GU5 mortar bars was possible at 39 weeks. The average expansion evolutions of the mortar bars of all the mixtures are presented in Figure 4.8.5.

Figure 4.8.4 shows the average expansion for all the mixtures at 6 months. Except for GU5 and GU15-NC2, the expansions are considerably larger than those of the samples in 23°C at the same age of the test. Mixtures GU5 and GU15-NC2 have had the smallest expansions and may be considered most resistant to LTSA compared to the other mixtures. As the limestone content increases from GU5 to GU15, GU20, and GU25, the susceptibility of the samples to LTSA increases, and this is clearly reflected in their increasing expansions. At every limestone content level, the samples with the additional NC and NS have had smaller expansions which confirms the effectiveness of these particles in improving durability. In other words, the permeability of the samples that contained nanoparticles was reduced, and consequently the penetration of sulfate ions for sulfate attack were delayed. Also, the expansions of samples with NC additions have been smaller than those with NS at every limestone content level. Similar to the previous durability measures presented in this chapter, this shows that at 2%, NC addition has been more effective than NS.

Considering the expansion evolutions in Figure 4.8.5, the mortar bar expansion of all the mixtures have increased in almost the same manner up to 13 to 15 weeks. For GU5 and GU15-NC2, almost the same rate of expansion continues up to 26 weeks. However, the expansion rate for the other mixtures have extremely accelerated from 13 to 26 weeks when the last length measurement was able to be taken. Even though GU15-NC2 has slightly smaller expansions than GU5 up to 26 weeks which may be the result of the NC addition, the samples did not survive until 39 weeks while GU5 mortar bars were still measurable at 39 weeks. Overall, it can be concluded that none of the mixtures of this study has an acceptable resistance to LTSA.

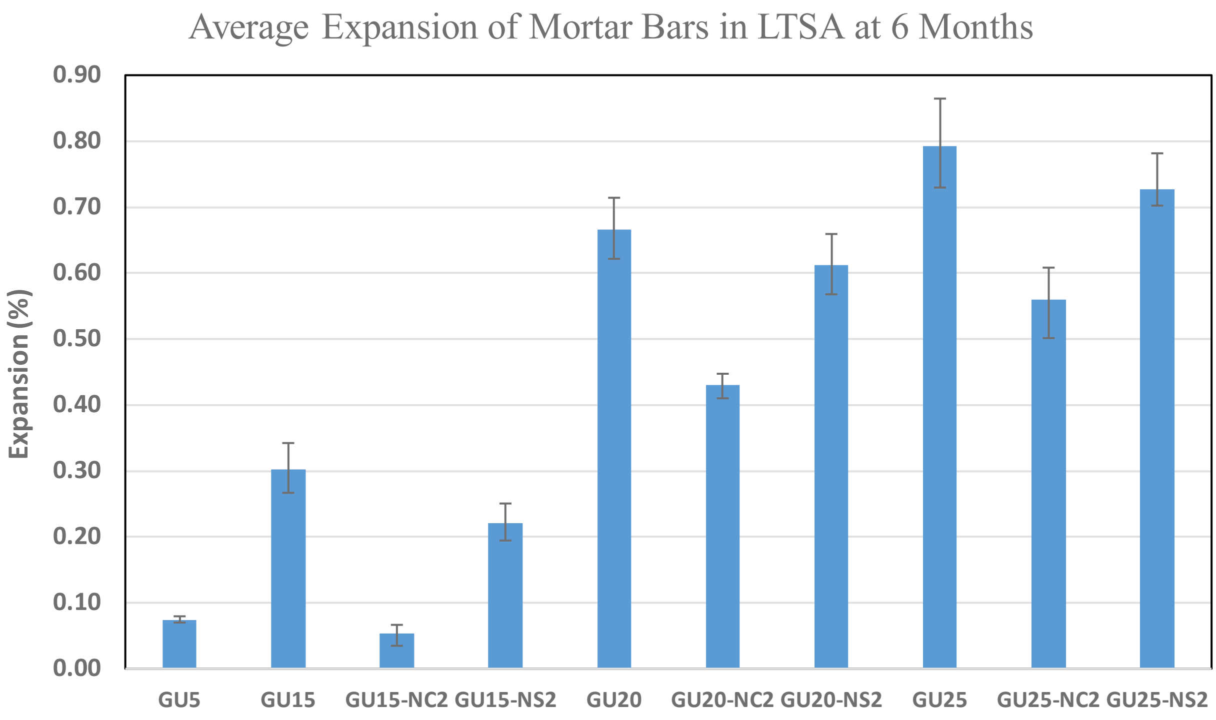

Figure 4.8.4: Average 6-month expansion of mortar bars LTSA

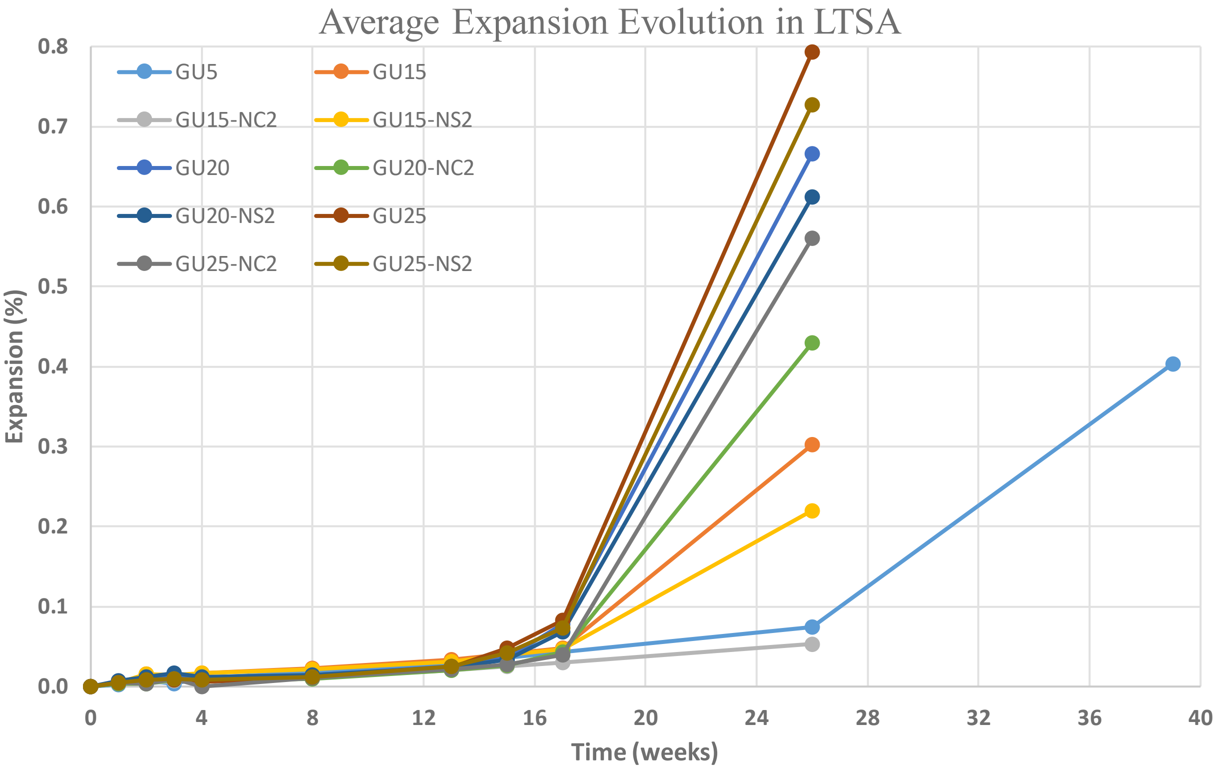

Figure 4.8.5: Expansion of CSA A3004-C8 mortar bars in LTSA over the 39-week test period

4.9 Overall Improvement of Durability

In the previous sections of this chapter, the results of several tests for all the mixtures of Table 3.3 were presented and discussed separately. Different measures of durability were examined through tests for volume of permeable voids, sorptivity, bulk electrical conductivity and resistivity, and sulfate attack. Each one of these tests has its own limitations, and they cannot be separately considered as fully decisive durability measures. However, when all the results are combined, a better overall picture of the effect of the NC and NS on durability can be achieved.

One of the main objectives of this study has been to explore the possibility of increasing the limestone content of cement beyond the 15% limit of Canadian standard without compromising the durability performance with the help of NC addition. Results of Section 4.2 for compressive strength showed that increasing micro limestone content had a negative impact on the compressive strength of the samples, and NC addition did not increase the compressive strength. Depending on the application, high compressive strength may not always be the most important requirement for concrete. However, if needed, this reduction in compressive strength could be potentially prevented by the extra grinding of cement which is commonly practiced at cement plants for GUL cement. On the other hand, NC addition showed to be significantly effective for improving almost all of the durability measures considered in this study. Mixture GU15 represents the current PLC allowed by the Canadian standard, and mixtures GU20-NC2 and GU25-NC2 represent attempts to make PLC blends with higher limestone contents improved with 2% NC additions. In this research, all of the PLCs were made by blending cement and limestone powder. However, they could alternatively be inter-ground at cement plants. Given that the grinding and chemical composition of GUL cement are usually optimized at cement plants, blending the same limestone content with GU cement does not result in a completely accurate representation of GUL cement. However, since the grinding and chemical composition of GUL are optimized, even better performance is expected from it, and the decision to use blended limestone cement in this study has been a conservative one. To better compare the three aforementioned PLC blends, GU15 is regarded as the reference, and improvements of the durability measures of GU20-NC2 and GU25-NC2 with respect to GU15 are presented in Table 4.9.1.

The improvements in Table 4.9.1 are color-coded for comparison. Green color shows increased durability, and red color shows decreased durability. Also, darker colors are indications of larger increase or decrease in durability. The results clearly show that except for sulfate attack at 5°C, all of the other durability measures of GU20-NC2 and GU25-NC2 were significantly improved with respect to GU15 as a result of 2% NC addition which is quite encouraging, considering their 5% and 10% lower cement content, respectively. These improvements are much more noticeable in GU20-NC2 because of its higher cement content compared to GU25-NC2. While the standard does not allow using limestone cement in sulfate exposures, the results still show improved performance against sulfate attack at 23°C due to NC addition. These improvements are especially important because while GU15 did not pass as moderate sulfate resistant according to the CSA A3001-18 limit, GU20-NC2 could be categorized as moderate sulfate resistant. In fact, GU20-NC2 was the only mixture with micro limestone content of higher than 15% that could be categorized as moderate sulfate resistant all with the help of the 2% NC addition. As discussed previously, thaumasite sulfate attack is extremely severe especially at high limestone contents. Therefore, the resistance against sulfate attack at 5°C was highly reduced at higher limestone contents and could not be compensated by NC addition. It is worth emphasizing that the 5°C sulfate attack test has been removed from the Canadian standard as it is unreasonably severe and not related to field performance, and limestone cement is not to be used in sulfate exposures without the SCMs. The fact that blends of cement at 20% and 25% limestone content (GU20-NC2 and GU25-NC2) have demonstrated even better durability than the blend with 15% limestone content (GU15) is promising. This shows that it is possible to increase the limestone content and maintain the durability with the addition of NC.

Table 4.9.1: Improvements in durability measures of GU20-NC2 and GU25-NC2 with respect to GU15

	Improvement with Respect to GU15						
Mixture	**28-day Volume of Permeable Voids**	**28-day Initial Sorptivity**	**28-day Secondary Sorptivity**	**28-day Conductivity**	**28-day Resistivity**	**6-month Sulfate Resistance at 23°C**	**6-month Sulfate Resistance at 5°C**
GU20-NC2	**+4.3%**	**+19.5%**	**+35.1%**	**+5.9%**	**+18.2%**	**+19.7%**	**-42.1%**
GU25-NC2	**+2.5%**	**+7.1%**	**+0.9%**	**+3.6%**	**+7.1%**	**+4.3%**	**-85.4%**

Since GU20-NC2 was the only mixture with micro limestone content of higher than 15% that could be categorized as moderate sulfate resistant, it is compared separately in Table 4.9.2 with GU5 and G15 which represent the current standard general use cement and limestone cement, respectively. This table shows that compressive strength of GU20-NC2 was about 9% lower than GU15. Also, the expansion of GU20-NC2 due to sulfate attack at 5°C was higher than GU15. However, the results of all of the other tests for GU20-NC2 were better than GU15, and in some cases, they were even better than GU5. This emphasizes that the improvement in the performance of GU20-NC2 as a result of the 2% NC addition is significant.

Table 4.9.2: Summary of test results for mixture GU5, GU15, and GU20-NC2

Mixture	28-day Compressive Strength (MPa)	28-day Volume of Permeable Voids (%)	28-day Initial Sorptivity (units)	28-day Secondary Sorptivity	28-day Conductivity (mS/m)	28-day Resistivity (Ω-m)	6-month Sulfate Attack Expansion at 23°C (%)	6-month Sulfate Attack Expansion at 5°C (%)
GU5	**40.2**	**15.7**	**20.0**	**8.4**	**29.7**	**36.0**	**0.071**	**0.074**
GU15	**37.2**	**16.2**	**21.0**	**11.1**	**31.4**	**32.2**	**0.115**	**0.302**
GU20-NC2	**33.7**	**15.5**	**16.9**	**7.2**	**29.6**	**38.1**	**0.092**	**0.430**

Another important observation from the results of this study is the consistency. For the samples of all mixtures, a clear improvement of durability measures was witnessed as the samples aged. Moreover, almost in all cases, reduced durability was seen as the micro limestone content was increased. With regards to the efficacy of nanoparticles, 2% NC was more effective than 2% NS in all tests except for compressive strength. Overall, the acceptable level of consistency of the results provides confidence in the main message that this research carries which is the potential of NC particles for improving durability.

Additionally, all of the 10 mixtures listed in Table 3.3 are ranked based on their performance in each of the durability tests and are given a score from 1 to 10; higher scores indicating better performance. This can provide us with an overview of the durability performance of the mixtures. The results are listed in Table 4.9.3 and also shown in Figure 4.9.1 for better comparison.

Durability of concrete highly depends on its application and exposure, and the results of each durability test presented in this chapter cannot be easily compared with other durability tests. For example, a certain concrete mixture can be durable in normal conditions, but be extremely susceptible to deterioration when used in sulfate exposures. Also, a scoring system merely based on ranking the mixtures without considering the quantitative measures of performance that each test provides cannot be taken as a comprehensive approach for comparison. Therefore, the scoring system in this section is simply used to provide an overview and comparative summary of all the durability test results presented in Chapter 4.

Considering Figure 4.9.1, it is clear that increasing limestone content from 5 to 15, 20, and 25% (GU5, GU15, GU20, and GU25) has drastically reduced the durability score of some mixtures. This is one of the reasons the current standard limits the limestone content level to 15%. However, the results of this research have shown that NC addition can significantly improve durability measures of mortar samples. This is reflected in the higher scores of mixtures containing NC compared to their nanoparticle-free counterparts. It can also be seen that NS additions have increased the durability score of the mixtures but not as effectively as NC. The most important observation from Figure 4.9.1 is that GU15-NC2, GU20-NC2, and even GU25-NC2 have higher scores than GU15. This has been achieved with only the 2% NC addition. Mixtures GU15-NC2 and GU20-NC2 have even higher scores than GU5 which is the general use cement with only 5% limestone content.

Table 4.9.3: Durability score of the mixtures of this study

Mixture	**Durability Score** **28-day Volume of Permeable Voids**	**28-day Initial Sorptivity**	**28-day Secondary Sorptivity**	**28-day Conductivity**	**28-day Resistivity**	**6-month Sulfate Resistance at 23°C**	**6-month Sulfate Resistance at 5°C**	**Overall Durability Score**
GU5	8	6	8	7	8	9	10	**56**
GU15	4	5	4	5	4	7	5	**34**
GU15-NC2	10	10	10	10	9	10	9	**68**
GU15-NS2	6	8	7	8	7	8	7	**51**
GU20	3	2	2	2	3	3	2	**17**
GU20-NC2	9	9	9	9	10	6	8	**60**
GU20-NS2	5	4	6	4	6	4	4	**33**
GU25	1	1	1	1	1	1	1	**7**
GU25-NC2	7	7	5	6	5	5	6	**41**
GU25-NS2	2	3	3	3	2	2	3	**18**

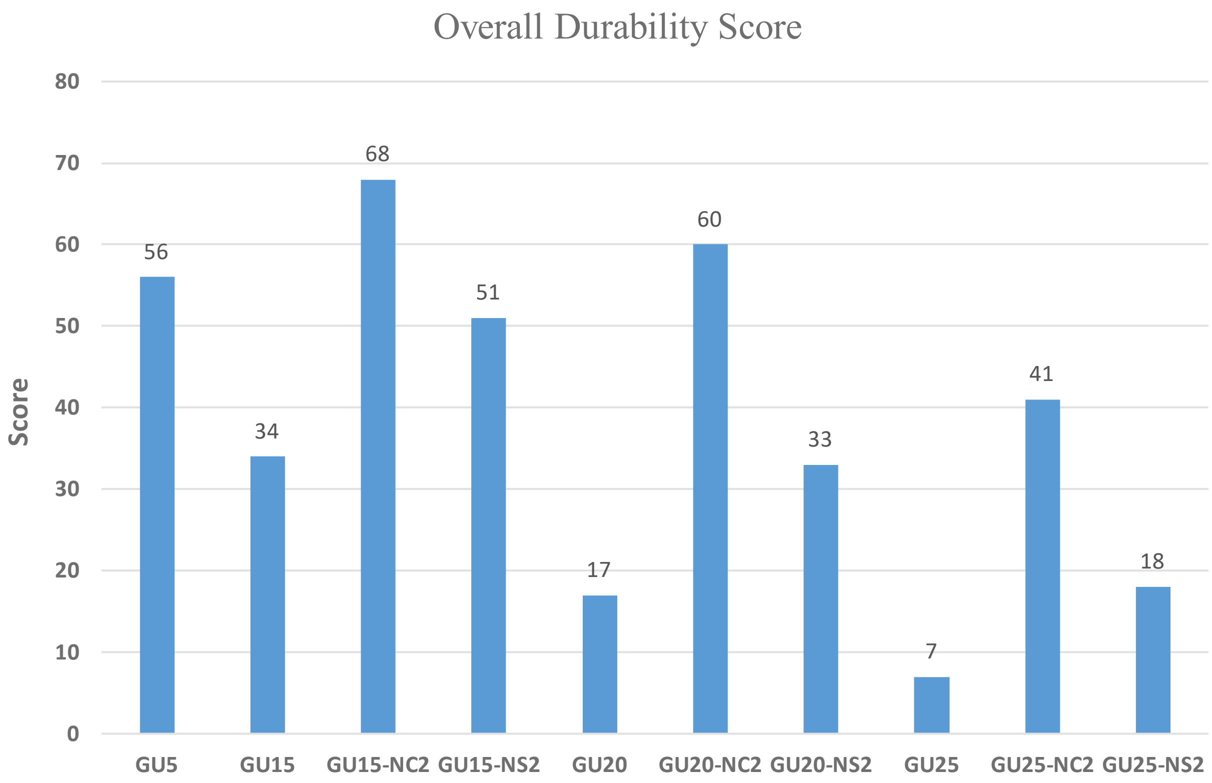

Figure 4.9.1: Overall durability score of all the mixtures listed in Table 3.3

4.10 Limitations of Research

While this study presents very promising results for the addition of NC in order to increase limestone content of cement, it is important to understand certain limitations of the results of this research and the general application of NC in concrete jobs. In this section, these limitations are briefly discussed.

4.10.1 Size of Nano Calcium Carbonate Particles

The NC particles used in this study have a size range of 15-40 nm as specified by the manufacturer. In order to have an idea of the size distribution of the particles, particle size analysis using Dynamic Light Scattering (DLS) method was performed, and the result is presented in Figure 4.10.1. The figure shows that in fact around 90% of the particles are in the 15-40 nm range. As discussed in previous sections, the effectiveness of NC depends on the sheer size of its particles. Particle size analysis is a missing segment of most of current literature on the application of NC in cement. Nanoparticle is a general term used to refer to particles that are usually in the range of 1-100 nm. However, the distribution of NC particles in this range may have an impact on their efficacy and their seeding action for hydration reactions. The focus of this study was to verify and quantify the effect of NC particle on durability of mortar samples. The results presented in this thesis may depend on the specific particle size distribution of NC presented in Figure 4.10.1, and further studies on the effect of size distribution of nanoparticles seem to be needed for future applications. Similarly, NS particles used in this study had median particle size of 12 nm, and consequently the results presented only represent the specific particle size for NS.

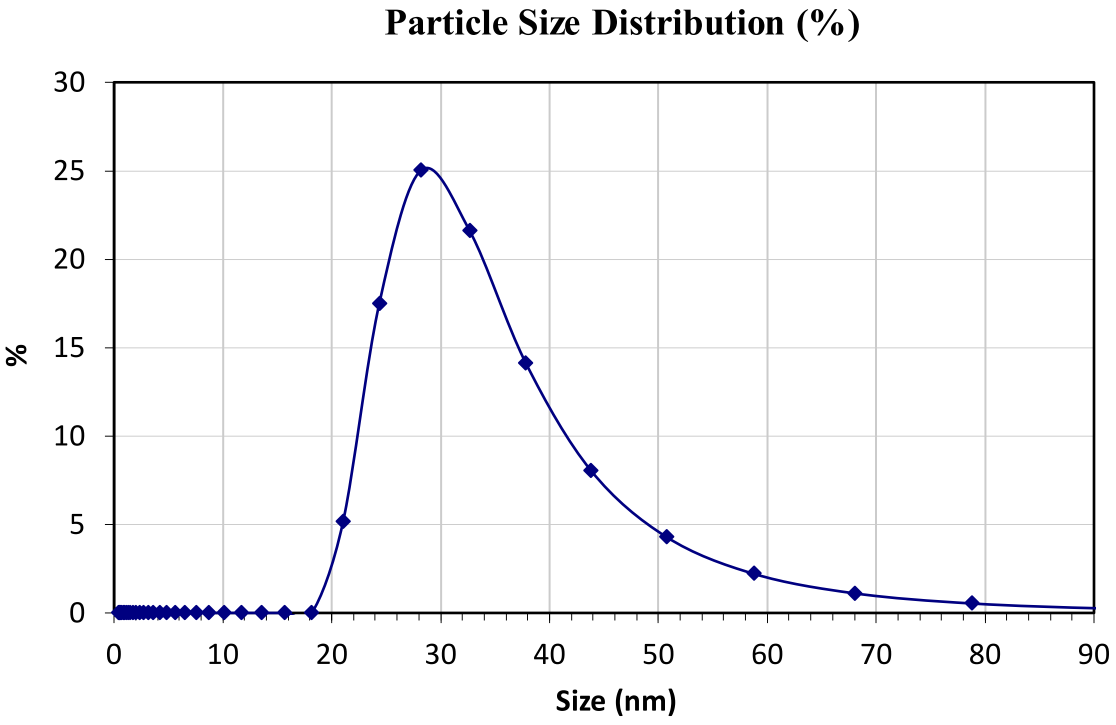

Figure 4.10.1: Particle size distribution of NC particles using DLS method

4.10.2 Size of Blended Limestone Particles

In cement plants, limestone is proportioned and inter-ground with clinker to make Portland limestone cement. While the standard limit for limestone content in PLC is 15%, most of the PLC produced in Canada contains 12-13% limestone (Hooton-2010). However, the GU15 blend used in this study to represent the limestone cement on the market in Canada has exactly 15% limestone which is slightly higher than the commonly used limestone content of 12-13%.

In addition, since limestone has a lower hardness compared to clinker, limestone particles become smaller than cement as a result of inter-grinding. To achieve different levels of limestone content in this study, the limestone powder was proportioned and blended with GU cement. Therefore, in order to better simulate an inter-ground PLC, a limestone powder with slightly finer particles than cement particle was used. Also, compared to GU cement, the C_3A and sulfate content of GUL are specifically optimized, and this type of cement is generally ground to a higher degree to ensure sufficient level of sulfate resistance and early-age strength, while the cement used in this study was simply GU cement blended with limestone powder. However, the justification for this research to use GU rather than GUL as the base cement was to investigate 15, 20 and 25% micro limestone on a comparative basis and blending was selected as the most appropriate method to achieve this goal. Therefore, the performance of limestone cement of this study cannot be deemed completely identical to GUL.

4.10.3 Dispersion of Nano Calcium Carbonate in Water

The efficacy of calcium carbonate nanoparticles on cement hydration arises from their sheer small size and can be significantly reduced due to agglomeration. In this study, ultra-sonication along with a polycarboxylate based high-range water reducing admixture as a surfactant has been used in order to reduce and prevent agglomeration. More in depth studying of dispersion of NC particles in water was beyond the scope of this study. However, it should be mentioned that any improvement in proper dispersion and stabilizing of NC in water can affect the results. Also, ultra-sonication as used in this study which is only possible in lab-scaled studies may lack feasibility for on-site applications. Different dispersion methods such as shear mixing in addition to long-lasting stabilization of the NC particles in water can facilitate the application of NC in the industrial scale.

5. CONCLUSIONS, CONTRIBUTIONS, AND RECOMMENDATIONS

In this chapter, the main conclusions of the study are summarized, the contributions are laid out, and the recommendations for future studies are presented.

5.1 Conclusions

1- Since the cement hydration is an exothermic reaction, heat of hydration evolution can be an indication of cement reactivity. Micro limestone content mainly acts as a filler and does not affect the hydration reactivity of cement. In contrast, NC content can increase the hydration reactivity of cement through nucleation. Increasing micro limestone content from 5 to 15, 20 and 25% resulted in lower intensity of heat of hydration evolution and lower total 3-day heat of hydration of cement paste. This was observed in the isothermal calorimetry diagrams. On the other hand, addition of any amounts of NC from 1% to 4% increased both the intensity and quantity of heat of hydration mainly due to the nucleation effect of nanoparticles. Among 1, 2, 3, and 4% NC additions, the 2% was found to be the most favorable amount. As a result of 2% NC addition, blended limestone cement with 20% and 25% micro limestone content released 3% more and 2.7% less heat than the one with 15% limestone content while containing 5% and 10% less cement content respectively.

2- Both NC and NS were found to be effective in increasing the total 3-day heat of hydration and also the peaks of hydration in the isothermal calorimetry diagram. At 2% addition, NC resulted in 7-8.5% increase in the total 3-day heat of hydration at every limestone content level while this increase was 4.4-5.1% for samples with NS additions indicating higher effectiveness of NC compared to NS at 2%. Moreover, the 2% NC and 2% NS addition on average resulted in 21% and 16% higher peaks of hydration in the isothermal calorimetry diagram at every limestone content level, respectively. The time of this peak was not significantly changed due to NC additions, but it was slightly shifted towards earlier hours in the samples with NS additions suggesting that NS is a more effective hydration accelerator than NC.

3- Increasing micro limestone contents resulted in a decrease in compressive strength of mortar cubes. Other studies have conflicting results on the effect of NC on compressive strength. While the 2% NC addition increased the heat of hydration of cement paste, its effect on compressive strength of mortar cubes was negligible. On the contrary, there was a clear increase in compressive strength of samples with the 2% NS addition. This increase was more pronounced at early ages compared to the more mature ages. In other words, NS addition seems to be more effective in cases where there is a lack of early age strength development.

4- Increasing micro limestone content led to a higher volume of permeable voids in all mixtures. This effect was more noticeable in earlier ages and faded at more mature ages. Also, the 2% NC and 2% NS additions resulted in 4-8% and 1-3% reduction of the total VPV at every limestone content level, respectively. As a result of 2% NC addition, VPV of the mortar samples at 20% and 25% limestone content levels (GU20-NC2 and GU25-NC2) are reduced to smaller and more favorable values than that of samples at 15% limestone content without nanoparticles (GU15). The mere lower VPV does not guaranty better durability and size distribution and interconnectivity of voids should also be considered, but given the identical mix design and mixing procedures, lower VPV can be considered a positive factor for durability.

5- Increasing micro limestone content generally increased the initial sorptivity for all samples. This increase is not large from 5% to 15% limestone content, but it becomes significant when limestone content goes up to 20% and 25%. Higher micro limestone content also resulted in higher secondary sorptivity. On the other hand, the 2% NC addition was remarkably effective in decreasing both initial and secondary sorptivity at every limestone content level. The 2% NS addition was also effective in reducing the sorptivity in all cases, but it was not as effective as NC.

6- Bulk electrical conductivity generally increased as the micro limestone content was increased most probably due to the lower overall content of hydration products that results in a more porous and conductive mortar. In contrast, both NC and NS additions were clearly effective in reducing the electrical conductivity of the samples. At each limestone content level, the 2% NC additions on average decreased the conductivity by 17% while this decrease was 11% as a result of 2% NS additions.

7- Increasing micro limestone content beyond 15% did not have a significant negative effect on the electrical resistivity even without the addition of nanoparticles especially at later ages. Addition of 2% NC and 2% NS increased electrical resistivity of the mortar samples significantly for all mixtures and at all ages. This increase on average was 21% for NC addition and 10% for NS addition which implies higher effectiveness of NC with respect to NS addition at 2%.

8- There was a good correlation with an acceptable coefficient of determination (R^2) of 0.939 between the results of bulk electrical resistivity and bulk electrical conductivity. Since the bulk electrical resistivity is a much easier and faster test to perform, the results suggest that it can be a proper alternative for either RCPT or bulk electrical conductivity.

9- All mortar bars of all of the mixtures showed continuous expansion while immersed in the sodium sulfate solution at 23°C and 5°C. This was due to the formation of gypsum, ettringite, and thaumasite. Continuous visual inspection and measuring of expansions of the mortar bars showed that TSA was significantly more aggressive than ESA. In fact, none of the mixtures survived until 12 months past their immersion in the sulfate solution at 5°C, and they cannot be considered resistant to TSA. This is due to the extremely high susceptibility of cement with high limestone content to TSA.

10- Increasing the micro limestone content resulted in higher expansions at 23°C at 6 and 12 months. This is presumably because higher limestone content is associated with lower content of cementitious materials that can lead to higher permeability and consequently higher susceptibility to sulfate attack.

11- The 2% NC and 2% NS additions led to reduced expansion of mortar bars at 23°C and 5°C at 6 and 12 months. The reduced expansions can be attributed to the fact that the NC and NS additions reduced the permeability of the mortar samples that hinders the sulfate ions penetration and consequently the expansions resulted from the sulfate attack chemical reactions.

12- Combining the results of different durability measures that were used in this study, it is clear that increasing limestone content from 5 to 15, 20, and 25% (GU5, GU15, GU20, and

GU25) drastically reduced the durability score of the mixtures which is one of the reasons the standard limits the limestone content level to 15%.

13- The 2% NC and 2% NS additions were clearly effective to improve the durability scores at every limestone content level. However, at 2%, NC was more effective than NS.

5.2 CONTRIBUTIONS

The followings are the main contributions of the present research:

1- The limestone content of GUL which was first introduced in the Canadian standard (CSA A3001) in 2008 is limited to 15%. The results of the present research have shown that there is potential to use NC as an additive in order to safely increase the limestone content of GUL beyond 15% without compromising its durability properties.

2- Compared to GU, GUL cement is usually ground to finer particles in cement plants in order to increase its reactivity and compensate for its lower cement content. The NC additions, whose effectiveness is proved in the results of the present research, may be taken as an alternative to the extra grinding that is usually required for GUL cement and consequently reduce carbon and energy footprints.

3- CSA A3001 already has requirements for using SCMs along with PC and PLC. The results of the present research along with many others in the past decade can establish new horizons for the standard to devise new provisions for using nanoparticles, especially NC particles, along with cement.

4- The effect of NC particles in particular on durability of concrete has rarely been studied in the existing literature. The present research provides a valuable perspective on the possibilities of using NC as an additive to improve durability of concrete.

5.3 RECOMMENDATIONS FOR FUTURE WORK

The following are some important subjects that seem to require extensive research in order to be able to confidently and widely use NC in concrete.

1- There is a wide range for the content of NC used by different researchers in the existing literature, and there is no consensus on the optimum content of NC. One of the main reasons for this wide range is the different particle size distribution of the NC that have been used in different studies. Quite interestingly, discussing this important piece of information has usually been ignored by researchers. The main reason for the effectiveness of nanoparticles such as NC is the sheer small size of them. Therefore, studying the effect of NC's particle size distribution on cement hydration and microstructure while considering the size distribution of cement particles as an influencing factor can be an important step forward in this field.

2- Another important and often neglected reason for the wide range for the content of NC used by different researcher is the agglomeration of the NC particle. If the nanoparticles are not properly dispersed and stabilized, their effectiveness will significantly suffer. In the present research the NC particles were dispersed by ultra-sonication and stabilized by polycarboxylate based high range water-reducing admixture as a surfactant. From a practical standpoint, performing this process on the site could be difficult. Thus, developing methods to properly disperse and stabilize NC particles which could remain stable without agglomeration and sedimentation for extended periods of time can be extremely valuable.

3- Limestone particles have four different action mechanisms in cementitious environments which are discussed in Chapter 2. The nucleation effect of NC is its major action that can improve cement hydration reactions. However, even small contents of NC can have some level of filler, dilution, and chemical effect in cement paste. Calcium hydroxide is a by-product of C-S-H gel formation, and when SCMs are not used, its content can be a good indication of cement hydration reactions. Also, the changes in the calcium carbonate content can be an indication of NC's chemical effect. Therefore, alongside isothermal calorimetry of cement paste, chemical analysis of cement paste when NC is incorporated can be of great interest. This can be done by monitoring and measuring the calcium hydroxide and calcium carbonate contents in cement paste using methods such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

4- Several durability measures were studies in the present research in order to evaluate the effectiveness of NC particles in the cement paste. However, further investigations of pore size distribution and microstructure of cement paste, which can highly affect the durability of concrete, using methods such as mercury intrusion porosimetry (MIP) and scanning electron microscope (SEM) imaging seem to be required.

5- The focus of this research was on the behavior of cement paste and mortar samples. Further investigations seem to be needed on concrete samples in order to verify the efficacy of NC additions.

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