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INFLUENCE OF NANO-SILICA ON STRENGTH AND GAS PERMEABILITY OF CONCRETE

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ARAM SALIM ALI

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Supervisor

Assist. Prof. Dr. Nihat ATMACA

Co-Supervisor

Assoc. Prof. Dr. Mehmet İshak YÜCE

By

Aram Salim ALI

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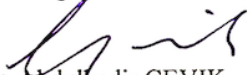
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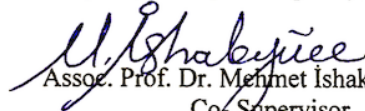
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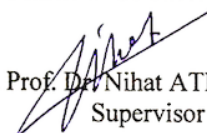Approval of the Graduate School of Natural and Applied Sciences.

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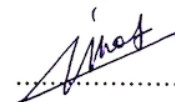Assoc. Prof. Dr. Mehmet İshak YUCE
Co-Supervisor

Assist. Prof. Dr. Nihat ATMACA
Supervisor

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Aram Salim ALI

ABSTRACT

**INFLUENCE OF NANO-SILICA ON STRENGTH AND GAS
PERMEABILITY OF CONCRETE**

ALI, Aram Salim
M.Sc. in Civil Engineering
Supervisor: Assist. Prof. Dr. Nihat ATMACA
Co-Supervisor: Assoc. Prof. Dr. Mehmet İshak YÜCE
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The study presented herein was carried out to investigate the Influence of Nano-Silica (nS) on Strength and Gas Permeability of Concrete. Three different series of concrete mixtures were designed with various water/binder (w/b) material ratios of 0.33, 0.45, and 0.55. The nS was used 0%, 1%, 3%, and 5% of the binder by weight in the mixes. Superplasticizer was used in varying amounts to adjust the workability. All groups of mixtures was incorporated binary cementitious blends of 0%, 1%, 3%, and 5% nS with each ratio of 0.33, 0.45 and 0.55 of w/b. Totally, twelve concrete mixtures were cast and tested for mechanical and durability related properties such as compressive strength, water sorptivity, and gas permeability. The tests were conducted at 28 days after casting. Test results demonstrated that using the nS

improved the strength and gas permeability properties of nS concretes. It was seen that the addition of nS enhanced the mechanical and durability properties of concrete depending on mainly nS content. The highest compressive strength observed at 3% of nS content as 66.7, 58.2 MPa with and without nS were obtained at first group, respectively.

Keywords: Nano-silica; Compressive strength; Gas permeability; Water Sorptivity.

ÖZET

NANO-SILICA'NIN BETONUN MUKAVEMETİ VE GAZ GEÇİRMEZLİĞİ ÜZERİNE ETKİLERİ

ALI, Aram Salim
Yüksek Lisans Tezi, İnşaat Mühendisliği Bölümü
Danışman: Yrd. Doç. Dr. Nihat ATMACA
Yardımcı Danışman: Doç. Dr. Mehmet İshak YÜCE
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Burada sunulan çalışmada, Nano-Silikanın (nS) betonun mukavemeti ve gaz geçirgenliği üzerindeki etkisi araştırılmıştır. Çeşitli su / bağlayıcı madde oranları (w/b) 0.33, 0.45 ve 0.55 ile üç farklı seramik beton karışımı tasarlanmıştır. nS, karışımlarda ağırlıkça % 0, %1, % 3 ve % 5 oranlarında bağlayıcı madde olarak kullanılmıştır. İşlenebilirliği uygun olarak ayarlayabilmek için farklı oranlarda Süperakışkanlaştırıcı kullanılmıştır. Tüm karışım grupları, 0.33, 0.45 ve 0.55 w/b oranları ile, % 0, % 1, % 3 ve % 5 nS oranlarında iki malzemeli çimentolu harmanları içermiştir. Toplam oniki beton karışımı hazırlanarak dökülmüş ve basınç dayanımı, su emme ve gaz geçirgenliği gibi mekanik ve dayanımla ilgili özellikleri test edilmiştir. Testler, dökümden sonraki 28. günde gerçekleştirilmiştir. Test sonuçları kullanılan nS oranlarının, beton numunelerin mukavemet ve gaz geçirgenlik özelliklerini geliştirdiğini göstermiştir. nS ilavesinin ağırlıklı olarak nS içeriğine bağlı olarak betonun mekanik ve dayanıklılık özelliklerini arttırdığı görülmüştür. % 3 oranında kullanılan nS ile maksimum basınç dayanımları 66.7, 58.2 MPa olarak birinci grup beton numunelerde gözlenmiştir.

Anahtar Kelimeler: Nano-silika; Basınç mukavemeti; Gaz geçirgenliği; Su Sorptivitesi.

To my parents

ACKNOWLEDGEMENT

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LIST OF SYMBOLS/ABBREVIATIONS

A	Cross-sectional area of the sample
ACI	American concrete institute
ASTM	American society for testing and materials
CC	Conventional concrete
CM	Cementitious material
CRM	Cement replacement material
D	Diameter of cylinder mold
E	Modulus of elasticity
EFNARC	European federation of national associations representing for concrete
FA	Fly Ash
GGBFS	Ground granulated blast furnace slag
HPC	High performance concrete
HRWRA	High range water reducing admixture xvi
K	Gas permeability coefficient
L	Height of sample
L	Length of cylinder mold
NCA	Natural coarse aggregate
NFA	Natural fine aggregate
NVC	Normal vibration concrete
P1	Inlet gas pressure
P2	Outlet gas pressure
PC	Portland cement
Q	Volume flow rate
RILEM	Recommendations for the testing and use of constructions material
NSBC	Nano-Silica Blended Concrete
nS	Nano-Silica

SP	Superplasticizer
SSD	Saturated surface dry
U	Length of beam
VMA	Viscosity modifying admixture
W	Depth of beam
W / b	Water to binder ratio
w/c	Water to cement ratio
η	Viscosity of oxygen
CCMs	Supplementary Cementing Materials
ASR	Alkali silica reactivity
SF	Silica fume

CHAPTER 1

INTRODUCTION

1.1 General

The new technological capabilities made it possible to explore and control new levels of existence which were never known before. Although the Nano-sized matter existed as early as the existence of earth, but it was not until early 20th century when the Nano-scale science started with the study of the molecular and atomic sized objects. However, the development of methods to control the materials on the Nano-scale level was not started until the last few decades (Porro, 2005).

Current global trends are shifting towards a more sustainable construction industry, which has generated new research needs to control and improve concrete performance. The main approach applied to produce sustainable concrete is to reduce consumption of Portland cement, while building more durable structures that have longer service life, yet require minimal maintenance. The reduction of Portland cement use may be achieved either by decreasing its content in concrete mixtures or through replacing cement with recycled materials, thus reducing the carbon footprint of concrete (Berndt, 2009). Furthermore, using other recycled materials (e.g. recycled concrete or aggregates) in mixtures is considered as one of the sustainable solutions for concrete (Domtoft et al., 2008).

Another significantly important aspect of concrete sustainability is extending concrete structures' service time while reducing maintenance cost. This is mainly depending on enhancing concrete serviceability, long-term durability and resistance to aggressive environmental attacks (Mehta, 2002). This aspect becomes especially critical in case of structure expected to have a long service life in harsh conditions including, but not limited to, highway pavements and bridges, dams and marine structures. In these cases improving durability of concrete may have a significant impact on the life cycle and maintenance plans for these structures. Concrete

pavements and dams demonstrated over the last century that adequately designed and maintained concrete can serve for several decades. As an example, the first concrete paved road in the United States constructed in Bellefontaine, Ohio is still in service. Although this 8 ft. strip of the street was built more than 120 years ago (in 1891), it is up till now opened for light vehicular traffic (Snell and Snell, 2002).

Nanotechnology was earlier described via Drexler et al., (1991) as (the control of the structure of matter based on molecule-by-molecule control of products and byproducts). Nanotechnology can be defined by the newest modern structural science and technology. Having major sector of potential marketing's and economic impact, one of the necessary reasons for researching in field of nanotechnology is increasingly on the rise. These studies aim at further developing the understanding of materials' behavior on the Nano-scale level, which can lead to the ability to improve the microstructures of these materials.

Nano-technology throughout the latest decennium has been expanding quickly through the many of fields of practical sciences, industry and engineering, mainly in the fields of medical, physical, chemical and fundamental material science. These latest evolution can be recognized by the fact of material's property and advanced may be considerably developed and organized into Nano-scale developments and structures (Sobolev et al., 2009). Nanotechnology is now being introduced into various applications and industrial sectors which lead to the need for further research and innovation. This includes biological molecular functionality, Nano-wires, magnetic random access memory and carbon Nano-tubes, etc. (Gopalakrishnan et al., 2011; Bergemannet al., 1999; Bartos, 2008). Several agencies in the United States of America are supporting nanotechnology research endeavors with more than a billion dollar per year (Balaguru and Chong, 2008). The ability to control the material properties at the Nano-level using nanotechnology may lead to the creation of new materials with unique characteristics and behavior. These developments are promising for breakthroughs in materials and construction industries.

Nano-SiO$_2$ particles designed for cement and concrete have been successfully used in limited applications over the last 20 years to develop both the strength and concrete's durability in order to address some of the aforementioned issues. The distinct advantages of concrete with integrated Nano-SiO$_2$ particles over standard Portland

cement concrete include: increased early age compressive strength development, larger modulus of elasticity, denser hydrated cement matrix (HCM) useful in more severe environments, and increased durability to alkali silica reaction. The distinctive aspects of the size and surface area of particle's Nano-SiO$_2$ result in densification of stable hydrates and decrease in unstable crystals within the hydrated cement matrix (HCM) of concrete. Unstable crystals have the potential to go through pozzolanic reaction when in the presence of free silica. Through pozzolanic reaction, unstable crystals convert to the denser and more stable hydrates, which effectively decrease the porosity of the HCM.

Fly ash (FA) is investigated by the best of one of the mostly used options that may mainly cement replacement of concrete industry due to its efficiency in reducing cost and its great availability. Also, FA as a side effect of coaly consuming is much extra environmentally likely compared to cement (Haque et al., 1984). Therefore, U.S. Green Building Council's (USGBC) considered by using FA with concrete is obtained better relationship development with Energy and Environmental Design (LEED) program. Besides FA is more economic and environmental supports, Class F fly ash can also perform better than ordinary Portland cement in cases where aggregates have potential alkali silica reactivity (ASR). Several studies indicated that fly ash may meaningfully decrease the growth in cement mortar caused by ASR (Alasali and Malhotra, 1991). This makes several agencies mandate the use of fly ash through its properties of concrete mixtures in a lowest percentage to eliminate or mitigate the effect of ASR (Malvar et al., 2002). The essential effect in fly ash concrete, especially which having Class F of fly ash, has been its slow amount of strength increment related with ordinary concrete (Carette et al., 1993 and Naik et al., 1998). Several studies were performed to identify different solutions for this problem (Naik and Ramme, 1989; Shi, 1998). Concrete with fly ash is not approved with a few advantages such as early strength is approved.

Unlike silica fume, Nano-SiO$_2$ is a manufactured material composed of silica particles having particle size smaller than 100 nm. Experimental results showed that the performance concrete including Nano-SiO$_2$ was generally better than that containing micro-silica in terms of mechanical properties and durability (Ghasemi et al., 2010). Furthermore, several studies showed that significant improvements of

performance of cement mortars and concrete occur by increasing Nano-SiO$_2$ (Li et al., 2004). It is initially assumed that such improvements in performance observed caused by increasing Nano-SiO$_2$ are assigned only by pozzolanic reaction and filler effects caused by the Nano-SiO$_2$. However, recent research showed that the effect of Nano-SiO$_2$ is not incomplete by this mechanism. The larger surface area of Nano-SiO$_2$ is improved by small particle sizes for the reaction so the smaller the particle sizes, the higher the rate of the early Cementitious and pozzolanic reaction (Belkowitz and Armentrout, 2009). Other evidence supporting this idea is that some nonreactive Nano-materials, which were mainly added for cosmetic purposes, lead to improvement in the reaction rate of the cementitious materials. For instance, experimental results (Lee et al., 2009) showed that adding Nano-titanium dioxide (TiO$_2$) accelerates the hydration of tricalcium silicate (C$_3$S) even though TiO$_2$ does not take part of neither the hydration nor pozzolanic reactions.

Nano-SiO$_2$ works on two forms, the first one is compacted dry grains and the second form is colloidal suspension. The dry grained Nano-SiO$_2$ depended on private production of procedure before mixing. The purpose of this procedure is to ensure dispersal of Nano-particles into the mixture through H$_2$O or watery admixtures also it may uniformly improve the cement matrix. This preparation, which is generally a mechanical dispersion process, may be associated with human exposure to Nano-particles, can be hazardous and has time limitation since agglomeration of particles can start directly after the mix is end. Furthermore, the colloidal Nano-SiO$_2$ that is produced as a function of electrochemically fixed in a dispersal solution is a function of the Nano-SiO$_2$ that is easier to use. Furthermore, adequate dispersion, provided electrochemically, prevents agglomeration of particles and maintains particle size at the Nano-level, thus ensuring the full benefit of Nano-SiO$_2$. This is supported by experimental results, which indicate this improved activities was obtained while colloidal Nano-SiO$_2$ was increased to mortar specimens compared by the dry grained of Nano-SiO$_2$ (Campillo et al., 2003). Accordingly, electrochemical dispersion is a more stable form of dispersion for Nano-particles compared to compacted dry grains where agglomeration can occur. Such better dispersion can lead to a more pronounced Nano-particle effect.

The need for durable concrete is being emphasized with the increased use of concrete as a major construction material in diverse marine and industrial environments. Concrete is normally selected for use in these conditions because designers believe it to be more durable titan competing materials. This accounts for the extensive use of concrete in severe exposure conditions where repairs are difficult to effect. As a result, producing a durable concrete has become a priority for the designer. In the past the mechanical properties of concrete, especially compressive strength, have been the dominant index in determining the overall behavior of concrete in service life. This approach is flawed because higher strength does not necessarily guarantee low permeability. Recently permeability has been recognized as the property that controls the durability of concrete. Permeability cannot be defined by a single test parameter as the external substances which may degrade the integrity of concrete vary with the service environment. For water-retaining concrete structures and concrete in submerged conditions, the permeability of the concrete to water is important while gas permeability is of little consequence. For concrete exposed to the atmosphere and periodically exposed to corrosive chemicals both liquid and gas permeability is important for the designers to consider if a durable structure is to be constructed. Since aggressive ions can travel through the water-filled pores in concrete due to concentration gradients, ion permeability becomes a key factor in evaluating the durability of the concrete under moist conditions. On the other hand, for concrete structures above ground which are partially or fully exposed to the atmosphere, low permeability to gas is important to prevent carbon dioxide gas in air from diffusing into the concrete.

Premature deterioration of concrete usually results from permeation of potentially harmful substances into the concrete in the service environment. Recently the most serious deterioration of concrete structures has resulted from corrosion of steel reinforcement embedded in the concrete. The corrosion process is initiated with the break-down of the covering oxide layer on the steel surface when corrosion-inducing substances like chloride salts and carbon dioxide penetrate of covering concrete and reach the surface of the reinforcing steel. Oxygen diffusion supports the corrosion activity in the presence of moisture in the concrete. It is essential, therefore, to prevent chlorides and other aggressive chemicals from contacting the steel so as to maintain favorable conditions under which the protective film retains its passive

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state. Now it becomes clear that with low permeable concrete a more durable concrete structure will result that can endure an aggressive environment over its service life. However, among other factors affecting permeability, cracks in concrete can have a pronounced influence. Cracks allow rapid movement of fluids and chemicals through the concrete, which leads to acceleration of the deterioration process. Therefore, to enhance the durability of the concrete in an aggressive environment it is necessary to minimize cracking and to make concrete as impermeable as possible.

1.2 Research Significance

Significant research has been achieved focused with influence of Nano technology to produce concrete. More recently, the Nano-SiO_2 has been used in the production of conventional concrete. Nano technology capabilities made it possible to explore and control new levels of existence which were never known before. During it's produced, regarding hydrated structure of cement with Nano scale pores. Some engineering concrete properties having Nano-SiO_2 have been investigated by researchers. However, the information about influence of Nano-SiO_2 on properties of concrete is still insufficient. The study related with effect of Nano-SiO_2 o_2 on the permeability behaviour of concrete is inadequate.

1.3 Outline of the Thesis

Chapter 1 gives the explanation about objective and aim of this study.

Chapter 2 presents a review of the literature and general background about gas permeability of Nano-SiO_2 concrete, applications and properties of Nano-SiO_2. The effect of Nano-SiO_2 on permeability behaviour of concrete is inadequate.

Chapter 3 includes the experimental program conducted throughout this study. Properties of cement, aggregates, mineral and chemical admixtures which used in this study as well as the tests on durability properties of Nano-SiO_2 blended concrete.

Chapter 4 provides the experimental results and discussion of the compressive strength, Sorptivity and gas permeability of Nano-SiO_2 blended concrete. Results, figures and evaluation are presented and discussed.

Chapter 5 contains conclusions of the tests.

CHAPTER 2

LITERATURE REVIEW

2.1 Nano-Silica history

In 1969, a patent was filed on an industrial production process for colloidal silica particles that measured in the mill-microns (nanometers), and had high silica purity and surface area (Iler and R., 1972). In 2004, the first industrial-scale use of Nano-SiO_2 in Cementitious composites was established. Brian Green of the US Army Corps of Engineers pioneered the use of Nano-SiO_2 to develop a rock-matching grout for military applications (Green and B. H., 2008). His work arose out of issues dealing with segregation of grouts comprised of heavyweight aggregates, specifically hematite. The Nano-SiO_2 dispersion was added to the heavyweight grout mixture as a viscosity-modifying agent. It increased the thickness of the grout mixture, ensuring the stable and universal suspension of the hematite aggregate while the grout was in a plastic state. The viscosity-modifying agent used was in the form of an ultra-fine amorphous colloidal silica, or Nano-SiO_2, with a particle distribution ranging between three and 100 nm. Green found which the Nano-SiO_2 not only enhanced the suspension of hematite, eliminating segregation, but also increased the density and strength of the grout (Green and B. H., 2008).

One of the first documented commercial uses of Nano-SiO_2 in concrete was in Gypsum, Colorado at the Eagle County Airfield during the construction of a training pad for the Air and Rescue Facility. At the Eagle County Regional Airport, high in the mountains of Colorado, twenty cubic yards of concrete was enhanced with Nano-SiO_2 as a means by increasing both the early strength of concrete and its durability against ASR (Belkowitz et al., 2014). The ready-mixed concrete provider (Lafarge North America) evaluated both the fresh and hardened properties of the Nano-SiO_2 enhanced concrete.

The performance of Nano-SiO$_2$ in increasing early strength development has been shown to come from the greater surface area of free silica (as compared to Class F FA) (Said et al., 2012). Similar to Class F FA, the free silica provided by the Nano-SiO$_2$ combines with calcium hydroxide (CH) in the hydrating cementitious matrix to create more calcium-silicate-hydrate (C-S-H), the backbone of concrete strength. Caused by the smaller size of the Nano-SiO$_2$ particles, there is a greater total surface area of free silica available for more immediate pozzolanic reaction and densification, thus increasing the early strength and durability of concrete (Nazari et al., 2011). Other possible means by which the Nano-SiO$_2$ size enhances the HCM are through pozzolanic reaction, nucleation of C-S-H, and accelerated dissolution of cement particles.

Since the (U.S.) Army Corps of Engineer's experience with Nano-SiO$_2$ in grout mixtures, the use of Nano-SiO$_2$ in cement components and concrete has ranged from 0.01- 10.9% replacement of OPC by weight (Belkowitz et al., 2014). Despite the ever-growing popularity of Nano-SiO$_2$ in cement composites and concrete, a deeper understanding on the impact of Nano-SiO$_2$ is needed in both the academic and construction arenas to give the industry confidence in this novel technology.

2.2 Compressive strength

Concrete compressive strength depends with some factors like water per cement content, strength of cement and Cementitious material, quality of concrete, and quality control while concrete produced.

Concrete compressive strength at different ages:

The Concrete compressive strength is development by age. Concrete strength at 28 days with various ages and differentiation of strength are shown in Table 2.1.

Table 2.1 Concrete compressive strength at different ages

Age	Strength per cent
1 day	16%
3 days	40%
7 days	65%
14 days	90%
28 days	99%

Zeidan, (2013) studied that compressive strength at different curing ages up to one year was estimated for six investigated mixtures. Concrete cylinders of 4 inches diameter and 8 inches height, prepared, molded and compacted according to ASTM C192, were used for evaluation of the compressive strengths. The cylinders were unmolded after 24 hours of mixing then cured in a curing room till the testing time. The compressive strength was estimated at ages of 3, 7, 28, 90 and 365 days, with the average of 3 cylinders at least for each age.

For the compressive strength testing, steel capping (according to ASTM C1231) was used for the evaluation of the early strengths up to 7 days for all the mixtures. For compressive strength testing at 28 days and beyond, capping was prepared for the cylinder of tests according by ASTM C617. The average strength of concrete at six mixtures with various curing ages is shown in Figure 2.1. Also, Table 2.2 shows the early age strength of concrete at six mixtures with 3 and 7 days as these values are not visually clear in Figure 2.1. For compressive strength testing, at least three cylinders were tested for mixture at the different testing ages.
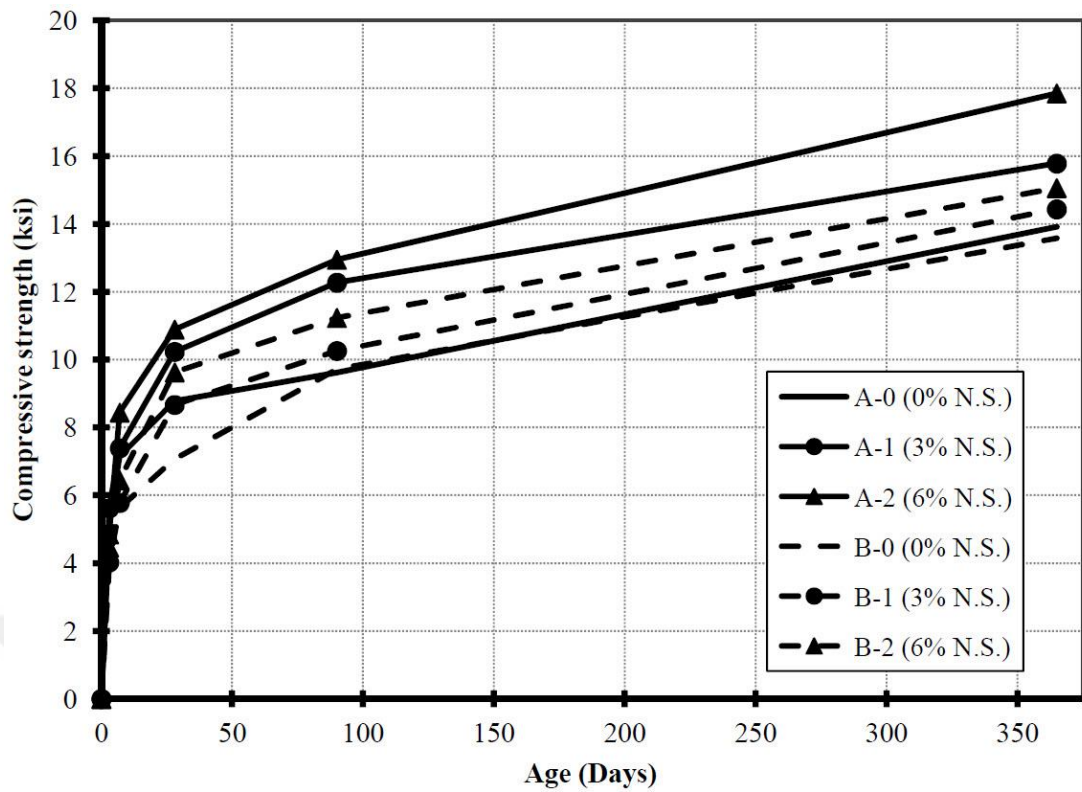
Figure 2.1 Compressive strength versus curing time

Table 2.2 concrete compressive strength at early age

Mixture	Compressive Strength (ksi)	
	3-days	7-days
A-0	5.25	7.14
A-1	5.61	7.39
A-2	4.85	8.44
B-0	3.97	5.63
B-1	4.02	5.78
B-2	4.47	6.45

The results generally show that compressive strength remarkably developed with increasing of Nano-SiO$_2$ in both of the mixtures groups. In Table 2.2, it can be observed that the rate of early age strength gain was improved for mixtures containing Nano-SiO$_2$ with or without FA. For Group A mixtures, the average (3 and

7 days) early age strength increased by about 18% with addition the amount of Nano-SiO_2 up to 6%. Comparably, for Group B mixtures incorporating Class F FA, the average increase at early age strength was about 14% with addition the dosage of Nano-SiO_2 up to 6%. This indicates that low early age strength of concrete including Class F FA may be improved by the increasing of colloidal Nano-SiO_2.

After 28 days at curing, the compressive strength of mixtures without FA (Group A) increased by 17% and 24% for 3% and 6% Nano-SiO_2 additions, respectively. For mixes with 30% FA (Group B), the 3% and 6% additions of Nano-SiO_2 increased the strength by 23% and 36%, respectively. The increasing of 3% and 6% of Nano-SiO_2 to mixes with 30% of FA (mixes B-1 and B-2, respectively) showed that the compressive strength of concrete corresponded or overdone the strength of their control concrete mix (A-0) before or at 28 days, while the mixes with FA and without Nano-SiO_2 (B-0) showed that the compressive strength of their control mix (A-0) at around 90 days. Strength after 28 days, the mixes with Nano-SiO_2 developed gaining higher strength.

The compressive strength results were systematically proved by exploration of modification (ANOVA), at an import level $\alpha = 0.05$. For instance, (ANOVA) for the results of compressive strength at 7 and 28 days indicated that by adding amount of Nano-SiO_2 from 0 to 6% had F values of 32.381 and 18.541, respectively that are higher than the parallel critical F value of 3.891. Montgomery (2001), was studied that the optimum value of an F-distribution density function mirrors that the tested changeable systematically involves that meaning of the results.

Other researchers evaluated the performance of modified cement with pozzolanic materials regarding compressive strength at elevated temperatures. Yazici with other researchers illustrated that the deterioration of concrete which was exposed to elevated temperature was less affected in comparison with control mortars. They concluded that silica fume has an excellent fire resistance property up to 600° c. However at higher temperature it rapidly losses strength, develop more cracking and fragmented structure occurs. They attributed that to silica fume or Nano-SiO_2 since they are denser than FA and thus at elevated temperature the internal steam pressure will increase rapidly (Yazici, Sezer et al. 2012).

2.3 Permeability and capillary pores

Sugiyama (1994) studied the permeability of concrete is closely related to its microstructure. In particular, the permeability of hardened cement paste is closely related to capillary pores having through cement paste. The size, number, and continuity are important. The formation of capillary pores in cement paste originates from the hydration process which binds grains with mixing water. The cement hydration clinker with having of water produces very small fibrous crystals of calcium silicate hydrates and large prismatic crystals of calcium hydroxide which act as the chief cementitious materials. The individual particulate hydration products are tightly bonded to each other and to grains of anhydrous cement primarily by van der Waals bonds. With the progress of cement hydration the solid products of hydrated cement paste begin to fill up the empty space between aggregate particles as well as spaces formerly occupied by free water. Accordingly, as hydration progresses capillary pores are reduced since they are considered as the remnants of the originally water-filled spaces. The precipitation and development of the cement gel results in an increase in the gel pores. However, it is considered that the cement gels are relatively impermeable and hence gel pores present in the hydration products are not responsible for the permeability of the bulk paste. by regarding to the influence of pore structures on permeability Uchikawa stated that the permeability of hardened cement paste generally reduces with the progress of hydration, and the degree of this reduction of permeability has no direct relation to the amount of gel (hydrates produced) and is correlated with the sites where gel formation occurs (Uchikawa, 1986). Thus it is suggested that capillary voids (which are reduced with the hydration process) mainly contribute to permeability of the cement paste, and the permeability is decreased when the capillary pores are blocked by the precipitation or crystallization of cement gel in them. The amount of pores 100 nm or over in effective diameter is probably correlated with permeability. Assuming that 1 cm^3 of cement produces 2 cm^3 of hydration products, theoretical calculation indicates that no capillary pores would exist in cement paste with a water per cement content 0.32 after the cement had completely hydrated (Mehta, 1986). Thus, unused mixing water with respect to the completion of cement hydration will remain as free capillary water which will evaporate later leaving behind capillary pores. According to Powers (Powers & Brownyard, 1946), a gel pore is generally classified as a pore less than 10

nm in diameter while pores ranging from 10 nm to 10000 nm are regarded as capillary pores. Similarly as Neville pointed out (Neville, 1981), the interconnected capillary pores are mainly responsible for the permeability of the hardened cement paste. Mehta also supports the view suggesting that capillary voids larger than 50 nm in size are assumed to be detrimental to impermeability (Mehta, 1986).

2.4 Properties of materials

2.4.1 Cement

Cement is the main component of concrete, which is the binding materials that holds all concrete components together; moreover, concrete strength is directly related to cement paste strength. Cement plays a major role in concrete industry where it constitutes approximately 10% to 20% by weight of the concrete's total mass (Slag cement association, SCA). The American Society of Testing Materials (ASTM) identifies five types of Portland cement. These types are different from each other according to their content of C3A (tricalcium aluminate) and their fineness. As a result of these differences the early hydration and the resistance to sulfate attack will be affected. Table 2.3 illustrates the general features of each type. However, all types contain about 75% by weight calcium silicate minerals, and thus the properties of concretes made with all these types are quite similar. Thus all these types are known by the term "ordinary Portland cement", or OPC (The Science of Concrete, 2012).

Table 2.3 Classification of cements types (The Science of Concrete)

	Classification	Characteristics	Applications
Type I	General purpose	Fairly high C_3S content for good early strength development	General construction (most buildings, bridges, pavements, precast units, etc.)
Type II	Moderate sulfate resistance	Low C_3A content (<8%)	Structures exposed to soil or water containing sulfate ions
Type III	High early strength	Ground more finely, may have slightly more C_3S	Rapid construction, cold weather concreting
Type IV	Low heat of hydration (slow reacting)	Low content of C_3S (<50%) and C_3A	Massive structures such as dams. Now rare.
Type V	High sulfate resistance	Very low C_3A content (<5%)	Structures exposed to high levels of sulfate ions

Cement industry is facing great challenge to conserve energy and to minimize the depletion of our natural resources. Also the recent attention to climate change has led to concerns about (CO_2) emissions generated by the production of cement. Thus, the need to develop alternative sustainable cement with lower (CO_2) emission has affected research to acceptable variations of Portland cement to better meet the adding orders for sustainability in the sector of construction.

2.4.2 Cementitious materials

Sato (2006) studied FA, the most widely used SCM, was an after-effect of the burning of crushed coal in the electrical power generating plants. It contains silica, alumina, calcium and iron with minor constituents such as magnesium, sculpture, sodium, potassium and carbon. The typical ranges for the chemical burning of FA are given in Table 2.4. Two major classes of FA are specified by CSA A23.5 depending on their chemical compositions. Class F FA is the one with the low calcium content (less than 8 % (CaO) and is generally manufactured from combustion anthracite or bituminous coal. Class C FA is the one with the high calcium content (8 % to 20%)

and is generally produced from the burning of subbituminous coal and lignite. A replacement level for Class F FA is generally 15% to 25% and for Class C FA is generally 15% to 40% by mass of cementing material. Most of the FA particles are solid spheres, but they can also be hollow spheres or hollow spheres containing small spheres. An SEM image of the typical Class F FA particles is given in Figure 2.2. The particle size can vary from less than 1 pm to more than 100 pm. The BET surface area is typically in the range of 0.3 to 0.5 m^2/g, but some fly ashes can have surface area values as low as 0.2 m^2/g and as high as 0.7 m^2/g. The physical properties and chemical compositions of FA can vary widely depending on how it was processed. Therefore a careful quality control of FA is essential when it is to be used in the concrete mixes.

Table 2.4 Typical chemical composition of fly ash (wt %)

SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	C
35 ~ 52	15 ~ 23	5 ~ 20	6 ~ 30	1.0 ~ 2.0	0.8 ~ 4.1	0 ~ 5.8	0 ~ 2.0	0 ~ 5.0

IRC 2.0kV 8 0mm x5.00k SE(M) 5/10/2006   10.0um
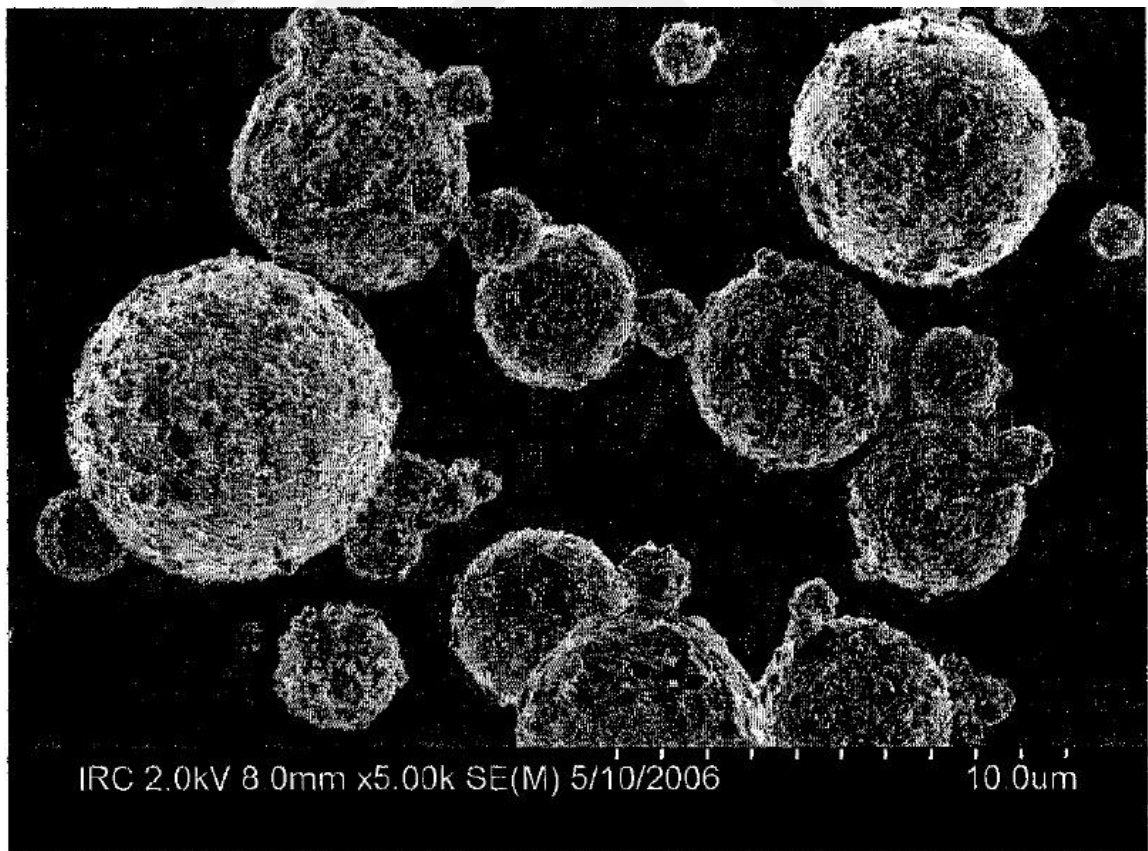
Figure 2.2 High resolution SEM image of the typical Class F fly ash particles

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2.4.3 Nano Silica

Nano-SiO_2 is a Silica dioxide Nano-particles (SiO_2) non-natural manufactured of porous and closely aspheric particles with great potential advantages (See Figure 2.3). The size of Nano-particles is considerably small, about one per thousand of the size of cement particle (Silica-Fume Association, 2012). Nano-SiO_2 is a crystal composition produced amply as sand, quartz, and several other minerals, it applied to produce different materials mainly with concrete and glass.
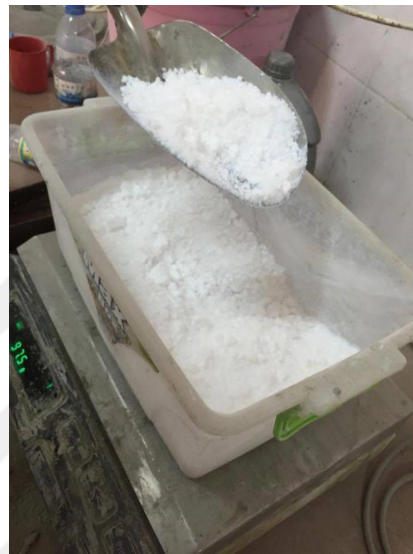
Figure 2.3 Images of Nano-Silica

According to Nano-SiO_2 composition particles, are distributed by two levels in particles: S-type Nano-SiO_2 (Spherical particles) and P-type Nano-SiO_2 (Porous particles). P-type Nano-SiO_2 has much greater surface area comparing with the other type of Nano-SiO_2 S-type (US Research Nano-materials, 2015), P-type Nano-SiO_2 surface area has a number of Nano-porous with the pore rate of 0.611ml/g, therefore, The particle size of Nano-SiO_2 ranges from 15-20 nm.

Most successful in this regard and one of the best candidates to be used as a substitute material for Portland cement is Nano-SiO_2. The main application of this novel material is in concrete industry. It is well known that using mineral replacement such as Silica-fume or Nano-SiO_2 will developed concrete strength and durability, because of more dense due to fine particles, larger surface area, and the high of SiO_2 content. While, Nano-SiO_2 is more chosen than SiO_2-fume because the particle size of Nano-SiO_2 is smaller than the size of SiO_2-fume with greater surface area and the effect of the fineness on improving the cement paste or mortar

properties and pore size will increase with the increasing of fineness, this will result in increasing the pozzolanic reaction.

2.4.4 Aggregate

Aggregates constitute approximately seventy five percent of a concrete mix. Aggregates are typically solid part of concrete and do not interact chemically in the concrete mix. It is important for aggregates to be free of organic impurities.

The aggregates are classified according to the size as:

Figure 2.4 Photographic view of Natural Coarse aggregate

2.4.4.1 Coarse aggregate

Gravel or crushed stone is the main coarse aggregate in construction practice. The strength of aggregate directly affects the final strength and durability of concrete. Weight of coarse aggregate defines the concrete weight classification as normal weight concrete, heavy weight concrete, or light weight concrete. Light weight aggregates are artificially made, processed aggregates. Heavy weight aggregates are special type of aggregates which are used for special applications such as in nuclear plants for protective purposes. Coarse aggregate should have at least the same strength as the cement paste to be suitable for high strength concrete (Nawy and Edward, 2009).

2.4.4.2 Fine aggregate

The most common fine aggregate is sand in the US standard sieve sizes between No. 4 and No. 100. The fine aggregate is used as filler in the concrete mixture. In special cases fine steel shot or crushed iron ore are used for radiation protection purposes. Fineness modulus of sand is the cumulative percentage of sieving from pan No. 4 to pan No. 100 divided by 100. Concrete high strength with fineness modulus in range of 2.5 to 3.2 exhibits better workability. Higher values of fineness modulus increase workability.

2.4.5 Water

Water has two major roles in the concrete mix: starting chemical reaction and lubricating the paste for a better workability. Water should be free of any chemicals or organics particles in order to reach the highest required concrete properties. The amount of water should always be in balance with cementitious material, mainly for chemical purposes. If water cement ratio is too low, proper chemical reaction will not happen. Furthermore, if water per cement ratio is too high, the chemical reaction products create problems such as uneven honeycombed concrete finish. Water cement ratio in high strength concrete should be low for strength purposes. This is achieved by using certain chemical admixtures. In this research, high range water reducer (HRWR) admixtures were used to decrease the amount of water without a Chemical reaction of cement with having of water is called hydration.

The amount of water in concrete has an important part in hydration and curing and is one of the variables in this research. Water also shows an important role in decreasing the concrete durability because of its ability to transfer harmful chemicals into concrete thereby causing various forms of deterioration effecting the required chemical reaction in the concrete paste.

2.4.6 Superplasticizer

Superplasticizer is a linear polymer including sulfonic acid groups connected to the polymer backbone at liner intervals. The main reasons for using Superplasticizer is (a) to produce a flow-able concrete to be used in heavily reinforced structures to avoid consolidating vibration and (b) to produce a high compressive strength concrete with a low water per cement ratio of 0.3 to 0.4. High range water reducers

are made from organic sulfonates and are termed Superplasticizer in view of their considerable ability to facilitate reducing the water content in concrete. Superplasticizer generally is increase the slump of concrete and, for most types of cement, improves the workability of concrete. Superplasticizer reduces the amount of required water by 12-40% without influencing the workability of high compressive strength concrete.

2.5 Pozzolanic reaction

Pozzolanic reaction is the reaction of the additives with some by-products produced from cement hydration. In their nature some of these materials such as FA, doesn't have any pozzolanic properties, while silica fume and Nano-SiO_2 has a low pozzolanic property while react with the C-H (non-natural of the reacting of cement and water) and developing C-S-H as a main product and calcium hydroxide as non-natural.

2.6 Cement Hydration

Portland cement (PC) is a commonly used as binder in concrete construction. Anhydrate cement consist of four main types of minerals which they belite (C_2S), alite (C_3S), aluminate (C_3A) and a ferrite (C_4AF). The developed of Portland cement strength is related to (alite) and (belite). Alite (C_3S), is answerable for short term strength development (days to months) when C_2S shows the long term strength development (~years). Cement hydration affected by different parameters such as fineness of particles, curing method, surrounding temperatures, etc. Any change in each of these conditions may yield different products or different proportion of each product. In the presence of water, cement reacts and produce cementitious materials (hydration products) this reaction generates heat (exothermic). Soon after adding water to cement, some of the clinker sulphates and gypsum dissolve forming an alkaline, sulfate-rich, solution. Then after mixing, the (C_3A) phase will start, which is the most reactive mineral of cement constituting compounds. This phase yields an aluminate-rich gel, which last for few minutes then react with the sulfate in solution to form small crystals of ettringite and release of heat. After this phase, the alite and belite in the cement start to react and formulates calcium silicate hydrate and calcium hydroxide. During this reaction, the anhydrous particles become smaller and concrete

strengths increase. Also (C_3A) hydration continues, as anhydrate crystals become in touch or accessible to water. In a mixture having Portland cement only, most of the strength gains within about a month. However when cement partly-replaced by other materials, such as Nano-SiO_2, strength growth continue for several months or even year. But when adding fly ash, the strength growth may gain more slowly and for longer time. The slow development in strength commonly because a layer of iron hydroxide gel forms and working as a barrier as coating the ferrite and thus preventing further reaction (Understanding cement, 2005).

2.7 Applications of Nano-Silica

Nano-SiO_2 has been produced since the early 1950s but has only been used in concrete for the last two decades. Despite the early availability of nS to the concrete and construction industry, little has been used on commercial job-sites. Early on during the commercial application of nS in the concrete industry, misuse and lack of understanding of the importance of particle size and surface area when dealing with these Nano-scale pozzolanic materials resulted in concrete failures. Unfortunately, these early failures hindered the use of nS in U.S. markets and resulted in a less than favorable foundation for future use.

Although nS is used at a much lower quantity than standard pozzolanic materials such as Class F FA and silica fume, it offers several distinct advantages over standard pozzolanic materials when used in cement composites and concrete: 1) early strength development, 2) increased cement efficiency 3) concrete densification, and 4) increased resistance to chemical degradation. Nano-SiO_2 dispersions, like standard pozzolanic materials, are characterized by their particle size (measured by diameters), particle distribution, silica purity, and percent replacement of cementitious material. Subsequently, the main hydrate of both pozzolanic materials (nS and Class F FA) yield a C-S-H similar to that produced from the cementitious reaction of di-calcium silicate (C_2S)(Taylor, 1997).

While Nano-SiO_2 dispersions offer particular benefits over standard pozzolanic materials, when using these particles in cement composites and concrete in laboratory and commercial applications, the distinct properties of nS require attention. Particularly, nS dispersions are extremely prone to agglomerating from

poor dispersion and over-saturation based on the size, surface area of the particle used, and the proportion of ordinary Portland cement (OPC) replacement.

Nano-silica's in concrete experience pozzolanic reaction, a microstructural enhancement that increases the density of the hydrated cement matrix (HCM), as a result, increases the strength and durability of concrete. Furthermore, the use of nS provides an excessive amount of free silica breaching the pessimism for alkali-silica reactive (ASR) gel polymerization and expansion (a form a concrete chemical degradation). Ultimately, Nano-SiO_2 brings a much greater amount of free silica content than standard pozzolanic materials to enhance the microstructure and macroscopic properties of the concrete.

2.8 Influence of Nano-Silica on hydration process

Björnström and other researchers have studied the accelerated effect of introducing (5 nm) Nano-SiO_2 on the hydration process of C_3S pastes. Their study includes: phase dissolution of C_3S, silica polymerization, calcium– silicate–hydrate (C–S–H) gel formation and bulk properties of the hardening paste. They have proven that the accelerated effect were very clear when the concentration of colloidal silica CS increased from 1% up to 5%. However, 1% of replacing seems to have remarkable effects. The DR-FTIR was used in their study to monitor all the phases (Björnström, Martinelli et al., 2004).

Regarding the early age properties and tensile strength of concrete which consider an important requirement for the design of precast and pre stressed concrete, Saker has proven that the inclusion of pozolanic materials in the binder can show a remarkable effect on tensile strength development (Saker, 2013). However, it was shown that replacing a significant amount of cement by such materials can decrease the compressive and tensile strength as well as water permeability but increase modulus of elasticity (Arezoumandi and Volz, 2013). Other researchers show that using additives such as water reducing or plasticizing admixture with Nano-SiO_2 decreases the aglomeration and directly impacts kinetics of hydration, resulting in powerful dispersing capability, without significantly impacting sitting behavior, so it will lead to improvement in workability as well as durability and concrete strength through increase the formation of silicate calcium hydrate (Cheuny, Jeknavoria et al., 2011).

Jonbi and others studied the use of Nano-SiO$_2$ for improving compressive strength and durability. They replaced cement with Nano-SiO$_2$ by weight of 3%, 5%, 10%, and 15%, along with superplasticizer. Their result indicates the best improvement in compressive strength was with 5% Nano-SiO$_2$ at 28 days. Also, there was a small decline in compressive strength with 10% nS, while there was a big decrease of compressive strength with 15% nS compared to the reference compressive 0% nS (Jonbi, 2012). Collepardi and other researchers studied the effect of Nano-sized mineral and Superplasticizer increases on performance of self-compacted concrete (concrete that can fill the formwork and make a full compaction under its own weight) (SCC). Their conclusion were that the increase in compressive strength of Self-CC with introducing of amorphous colloidal silica is due to the high content (>99%) of amorphous silica and the decrease size of its spherical particles (1-50 nm), and established that super plasticizers can save the initial slump for at least 1.0 hour without any retarding the early strength of concrete and also decrease drying shrinkage (Collepardi et al., 2004).

Soblev, Flores and others studied polycarboxylic mixed with nS to develop flowability and strength of "SCC". Their results indicated a growth in compressive strength in the concretes modified with Nano particles. The effective dispersion of Nano particles is important in order to obtain better performance of composite materials (Soblev et al., 2010).

Daniel and Belkowitz concluded that as the size of Nano-SiO$_2$ decreases the reduction in CH will increase and the possibility of a change in C-S-H will increase which mean develop in compressive strength, and they demonstrated the hydration process and the progression of pozzolanic reaction in the presence of Nano-SiO$_2$ in cement mortar as a formula (Daniel and Belkowitz, 2010).

Stage 1 $C_3A + 6H \rightarrow C_3AH_6$ (2.1)

Stage 2, 3, & 4 $2(C_3S) + 6(H_2O) \rightarrow C_3S_2H_3 + 3(Ca (OH)_2)$ (2.2)

Stage 4, 5 $2(C_2S) + 4(H_2O) \rightarrow C_3S_2H_3 + Ca (OH)_2$ (2.3)

Pozzolanic Reaction $S + Ca(OH)_2 \rightarrow C_3S_2H_3 + Ca(OH)_2$ (2.4)
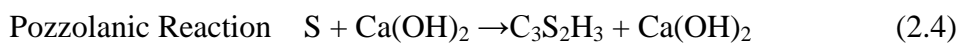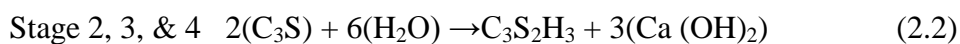
2.9 Optimal percentage of Nano-Silica

Zaki and Ragab (2009) was tested by using 0%, 0.5%, 0.7%, and 1% of Nano-SiO$_2$ in concrete sideways with 20% of silica fume in all mixtures. They estimated after test resulting that the optimum percentage of Nano-SiO$_2$ was 0.5% by weight as a cementitious material (Zaki and Ragab 2000). Jonbi investigates the use of Nano-SiO$_2$ for improving concrete compressive strength and durability. He used percentages of Nano-SiO$_2$ by weight of cement replacement of 3%, 5%, 10%, and 15%, along with Superplasticizer. His results indicate that the optimum development of 28 days compressive strength was with 5% Nano-SiO$_2$ (Jonbi 2003).

2.10 Effect of Nano-silica on setting time of concretes

Zeidan (2013) studied the impact of Nano-SiO$_2$ on the setting time of concrete and mortars, Vicat needle testing was performed according to ASTM C191. Pastes were prepared by mixing 650 grams of cementitious materials with 260 grams of water (w/c=0.40) and mixed as specified in the ASTM standard. Unlike concrete mixtures, no water reducing admixtures were used for any of the pastes as most types of admixtures may affect setting times. The cementitious materials used were selected to represent the same proportions of the concrete mixtures tested during this study (see Table 2.5). The paste was molded in the standard molds and kept in a moisture closet with temperature of $20 \pm 2°C$ and comparative humidity not less than 90%. The penetration of the standard Vicat needle (1 mm in diameter) was recorded every 15 minutes and the molds were kept in the moisture closet between readings. The initial setting time is discussed as the time when the needle penetration is equal to 25 mm. This value was determined via interpolation between the two closest readings to 25 mm. On the other hand, final setting time was determined as the time when no penetration could be visually observed. Table 2.5 shows the tested pastes along with the measured initial and final setting times. Also, Figures 2.5 and 2.6 show the measured penetration depths during the testing period for the pastes without fly ash (corresponding to Group A mixtures) and for the pastes incorporating 30% FA (corresponding to Group B mixtures), respectively.

Table 2.5 Summary of Vicat needle testing results

Cementitious Materials Proportions	Corresponding Concrete Mixture	Initial Setting Time (min)	Final Setting Time (min)
Cement only	A-0	190	245
Cement +3%Nano-Silica	A-1	192	246
Cement +6%Nano-Silica	A-2	145	222
70%Cement+30%Fly Ash	B-0	300	396
70%Cement+30%Fly Ash+3% Nano-Silca	B-1	258	307
70%Cement+30%Fly Ash+6% Nano-Silca	B-2	244	285

Generally, the results of Vicat needle testing indicate that using nS has an impact on shortening of both of the initial and final setting times. For mixtures without FA (Group A), adding 6% nS reduced the initial setting time by around 25%, while the final setting time was reduced by around 10%. However, 3% of added nS did not have a considerable effect on setting times in this case. The influence of Nano-SiO_2 could be more readily observed in case of mixtures incorporating FA (Group B). Class F fly ash may generally extend the setting time of cement paste due to the slow hydration process. However, adding 6% of Nano-SiO_2 to the FA concrete reduced the initial and final setting time by around 25%, while this reduction was around 20% in case of adding 3% of Nano-SiO_2.
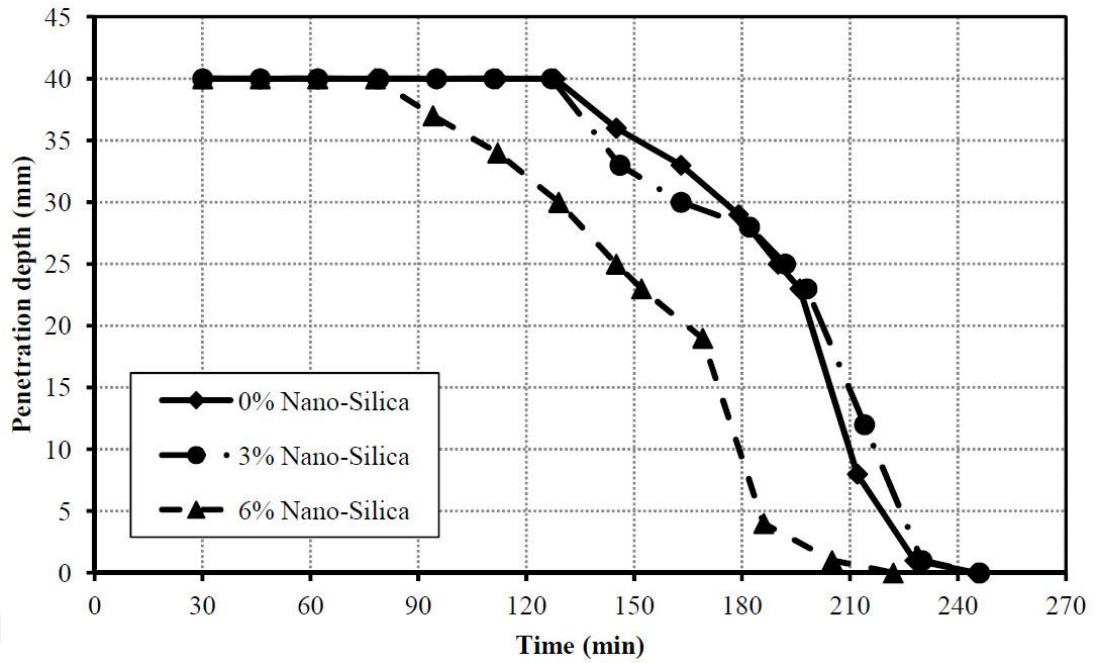
Figure 2.5 Vicat needle penetration depths for pastes without fly ash.
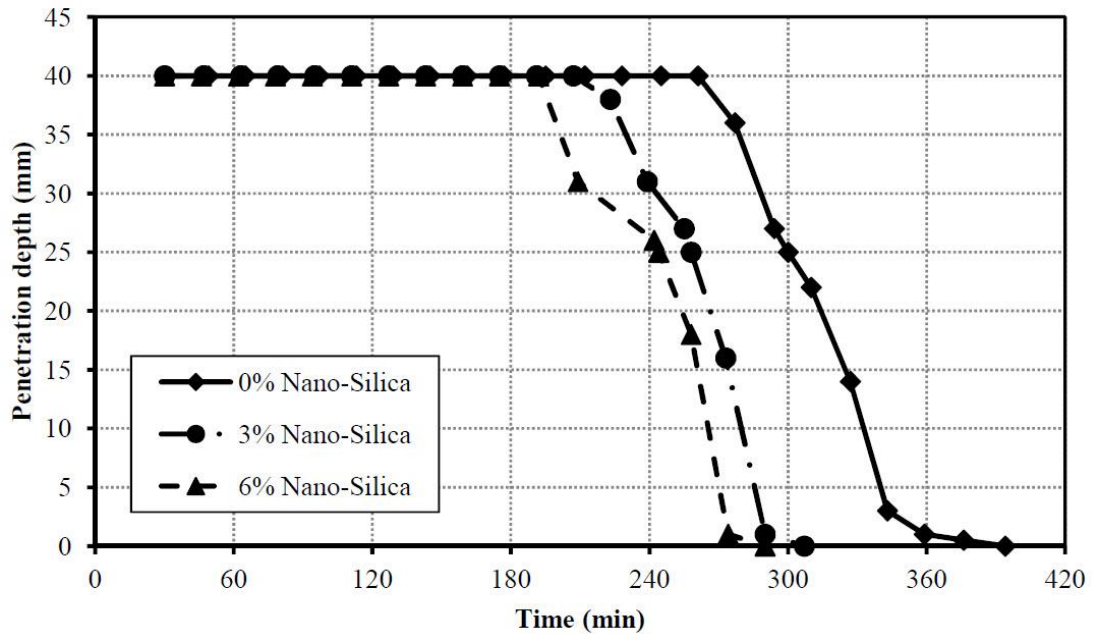
Figure 2.6 Vicat needle penetration depths for pastes including 30% fly ash

The impact of Nano-SiO$_2$ on the fresh properties of concrete was generally significant especially on the workability level in terms of slump values and setting times. This effect was expected due to the very small particle size of Nano-SiO$_2$ having significantly larger surface area compared to other concrete components. The large surface area increases the adsorbed water on the surface which impacts the fresh properties of concrete. However, these observations are inconclusive to project

an impact of nS on hardened concrete properties. Generally, any fine particles added to concrete, mortar or paste mixtures can impact the workability and sitting time in a similar way. The next sections and chapters of this study discuss the evidence of the influence of nS on hardened concrete performance and cement reactivity.

The previously presented results indicate that the fresh properties of concrete including Nano-SiO_2 may be a controlling factor for mixture design and proportioning for some application. This is attributed to the significant impact of Nano-SiO_2 on workability and setting time of concrete.

2.11 Effect of drying procedure on gas permeability measurements

The development of gas permeability of concrete was studied by Kameche et al. (2014), two various drying temperatures (60 ˚C and 80 ˚C) with specimens of 15 cm in diameter as shown in Figure 2.7. So, compared the test results of gas permeability by changing average pressure proved between concrete specimens dried 24 hours at 60 ˚C and concrete specimens dried 48 hours at 80 ˚C, it was indicated that the measurement of apparent permeability was affected by drying procedures, based on the values of the essential permeability. A difference that was obtained between the essential permeability estimated by specimens dried 24 h at 60 ˚C and those dried 48 h at 80 ˚C are shown in Figure 2.3. Higher permeability was observed with concrete specimens that were dried at 80 ˚C, compared to those dried at 60 ˚C, the greater variation in permeability was observed by lower degree of saturation, values. It was demonstrated that the higher temperature 80 ˚C seems to be most probably lead to modification the micro-structural of concrete and thus the permeability of the concrete will be increased.
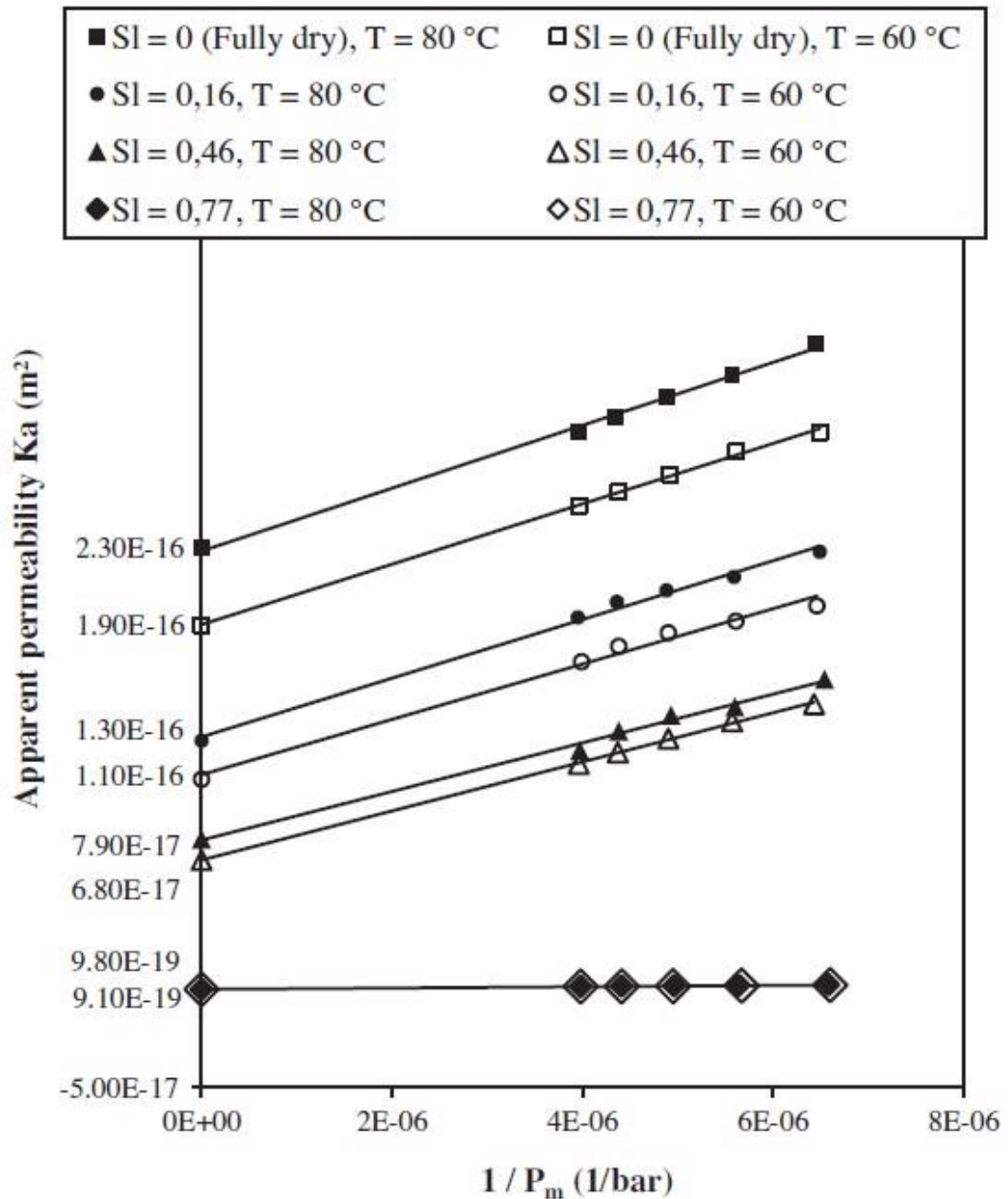
Figure 2.7 Concrete gas permeability coefficient when dried after (24 h at 60 ˚C) and (48 h at 80 ˚C)

2.12 Influence of Nano-silica particle size's on compressive strength

Cement of mortar's compressive strength was done by Kameche et al. (2004), three groups of cement mortar were prepared, the first group was OPC without Nano-SiO$_2$, the second group was cement mortar with silica fume, and the third cement mortar with Nano-SiO$_2$, the results of compressive strength of cement mortar at 7 days are showed in Table 2.6. According to their results, the higher compressive strength of cement mortar was observed with Nano-SiO$_2$ compared to cement mortar with OPC,

and systematically developed by increases amount of Nano-SiO$_2$. By adding 6% of nS and 0.65 of w/b ratio, the compressive strengths of cement mortars about 1.25, 1.52 and 1.65 times increased respectively, with Nano-SiO$_2$ particle sizes of 12, 20 and 40 nm, in comparison to cement mortar with OPC. However, by 9% replacement Nano-SiO$_2$ content caused better strength improvement that estimated strength of cement mortar by 1.322, 1.671 and 1.743 times compared to controlled mortar, respectively.

In spite of the cement mortar made up of SF, cement mortar which was replaced by 6% and 9% of Silica-fume, the compressive strength slimly increased by 1.031 and 1.060 times respectively. In the case of lower compressive strength improvement which is compared between the cement mortar with Silica-fume and cement mortar with Nano-SiO$_2$ could be clarified within the fact that Silica-fume has less SiO$_2$ content, that produce lower pozzolanic in comparing with the NS. In addition, the particle size of Silica-fume is greater than nS (Li et al., 2006; Senff et al 2009) consequently; it will give lower packing activity than that of nS. Beside of, the small particle size of Nano-SiO$_2$ could be easy filling the voids of cement paste, therefor the strength of cement mortar will greater than the cement with Silica-fume.

The different particle sizes of nS and strengths of cement mortar which is compared to the cement mortar without nS and with Silica-fume, at 7 days are shown in Figure 2.8. The compressive strength has its own effect on nS particle size by varying the Nano-SiO$_2$ content was also presented. The greater compressive strength was completely gained for all Nano-SiO$_2$ contents when the largest particle size of nS was increased to the mixes. Therefore, the compressive strength of cement mortar was straightly affected by nS particles. Greater strength of Cement mortar was obtained with Nano-SiO$_2$ particle size of 40 nm compared with cement mortars with Nano-SiO$_2$ 12 and 20 nm of particle sizes. The results were obtained showed that very small particle of Nano-SiO$_2$ (12 nm and 20 nm) are not agreeable to the saving ability. Despite the particles of nS fills the voids of cement paste, which will probably, covered the surface area of cement particles, due to the reduction of the hydration activity of cement paste. At this time, the development of strength is lesser in effect with respect to pozzolanic reaction and packing ability. Also, another suitable purpose is that agglomeration and poor dispersion behaviors can be produced with Nano-SiO$_2$ particle of 12 and 20 nm. This behavior (agglomeration

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and low dispersal of 10 and 15 nm-Silica) were also claimed in the study Chaichana et al. (2007).Which was proved nS for LLDPE/SiO2 Nano-composite materials. In addition, Sanchez and Sobolev, 2010; Singh et al. (2013) reported that the most important issue for all nanoparticle applications is the effective of dispersion of nS into cement mortar.

The highest mortar strength was obtained when (40 nm) particle size of Nano-SiO$_2$ were used with cement mortar. The acceptable purpose while the particle size is medium, furthermore its acceptable size that is very affective and beneficial in relations of pozzolanic reaction, particle uniform dispersion, and packing ability.

Table 2.6 Compressive strength at various cement mortars of 7 days

Compressive strength of different cement mortars at age of 7 days.

Mixture	Compressive strength (MPa)			
	3%	6%	9%	12%
OPC	19.16	–	–	–
NS 12 nm	22.11	24.07	25.29	24.48
NS 20 nm	26.05	29.06	32.09	30.13
NS 40 nm	29.14	31.52	33.35	32.54
SF	19.27	19.69	20.24	19.64

Thus, the strength enhancement develops with all changes. Cement mortar with 100 nm of Silica-fume, the strength enhancement is lesser compared by mortar with Nano-SiO$_2$. The factor of this enhancement at strength is by larger of Silica-fume particle sizes, and due to its lower amount of silicon in Silica-fume compared with nS particles. Silica-fume is lesser effective in pozzolanic reaction and saving ability compared with Nano-SiO$_2$ particles.
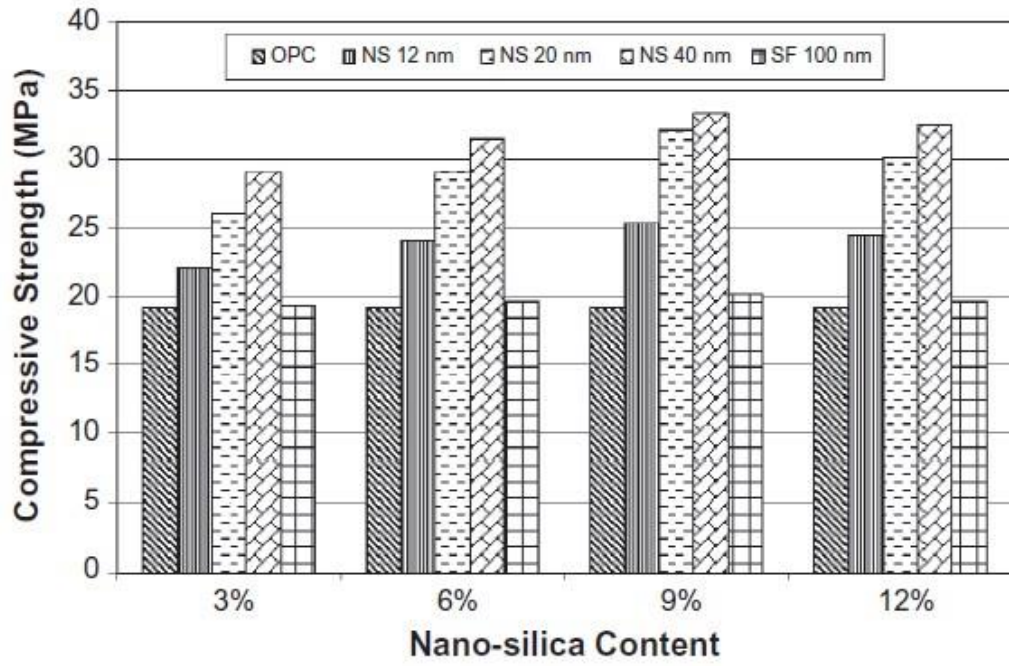
Figure 2.8 Compressive strength of cement mortar with OPC, cement with Silica-fume and different particle sizes of Nano-SiO$_2$ at 7 days

CHAPTER 3

EXPERIMENTAL PROGRAM

3.1 Materials

3.1.1 Cement and Fly ash

In this current study, Ordinary Portland cement CEM I 42.5R was used for producing all concrete mixtures. Type F FA, gave from Çatalağzı, Turkish Zonguldak, and was used like a secondary binder material by 20% of substitution level by weight of cement in mixing Nano-SiO_2 blended concrete. Chemical compound and Physical properties of cement and FA are given in Table 3.1.

3.1.2 Nano Silica

Nano-SiO_2 is highly pozzolanic material. It contains very fine particles approximately 1000 times smaller than the cement particles. Nano-SiO_2 used in the present study was manufactured by AEROSIL (domestic USA-CHEMTREC), (domestic Canada – CANUTEC). Properties of nS is given in Table 3.1

Figure 3.1 Photographic view of Nano-Silica

Table 3.1 Chemical compound and physical properties of Portland cement, FA and nS

Constituent (%)	Cement	FA	nS
CaO	62.12	4.24	_
SiO_2	19.69	56.2	99.8
Al_2O_3	5.16	20.17	_
Fe_2O_3	2.88	6.69	_
MgO	1.17	1.92	_
SO_3	2.63	0.49	_
K_2O	0.88	1.89	_
Na_2O	0.17	0.58	_
Cl	0.0093	_	_
Loss on ignition	2.99	1.78	_
Insoluble residue	0.16	379	_
Free CaO	1.91	_	_
Specific surface (m^2/kg)	394[a]	379	150000[b]
Specific gravity	3.15	2.25	2.2

3.1.3 Aggregates

Natural fine (NFA) and Crushed Limestone coarse aggregates (NCA) were used together to produce NSBC. For natural fine aggregate, a natural river sands with a maximum size of 4 mm was used. For Coarse aggregate, a Crushed Limestone coarse aggregate with a maximum size of (4-16) mm were used.

The particle size distribution and physical properties of natural aggregates are shown in Table 3.2.

Table 3.2 Sieve analysis and physical properties of natural aggregates

Sieve size (mm)	Fine aggregate	Coarse aggregate
31.5	-	100
16	-	100
8	-	7
4	87.7	0
2	61.74	-
1	41.24	-
0.5	24.4	-
0.25	9.4	
0.125	2.81	-
pan	0	-
SG	2.7	2.67

(a)   (b)
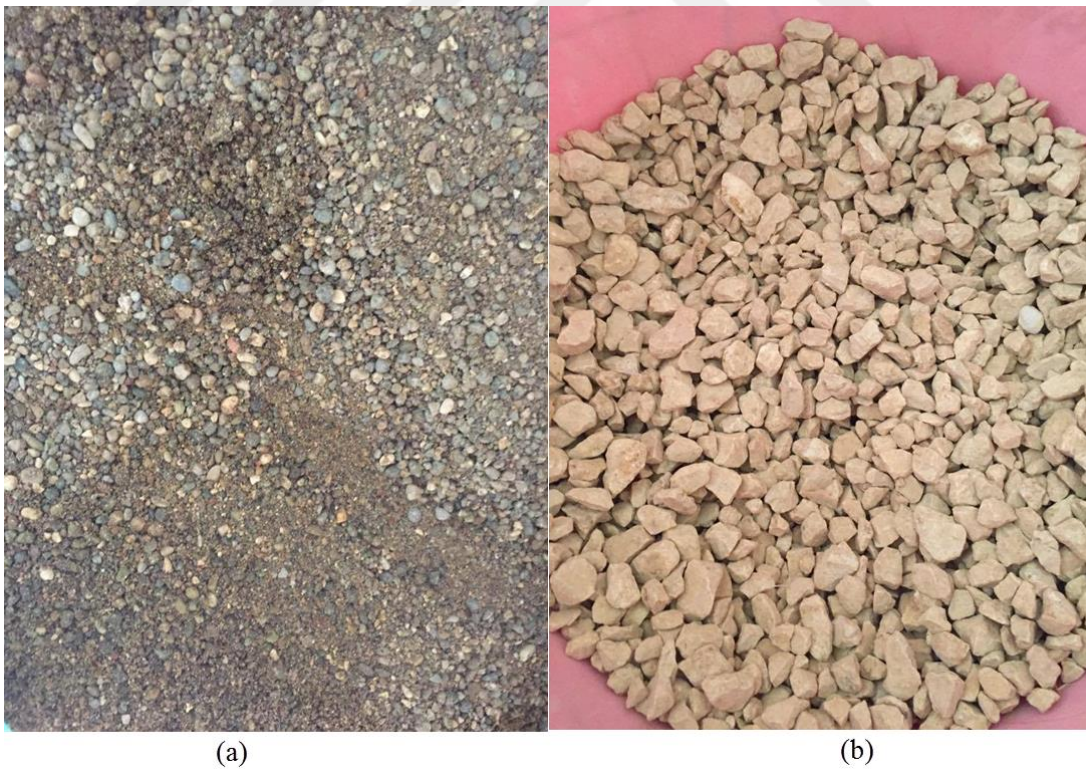
Figure 3.2 (a) Photographic view of Fine aggregate (b) Photographic view of Coarse aggregate

3.1.4 Superplasticizer

Even though well known as high range water reducing (HRWR) admixtures, it is a chemical admixture required where well-divided particle suspension is important. Often pointed to as super-plasticizers, help in increasing the workability of concrete without additional amount of water.

3.2 Gas Permeability concrete Mix Properties

The mixture proportioning consisted of twelve concrete mixes which divided by three groups as shown in Table 3.3 and Figure 3.3; three different groups of concrete mixtures were designed with various w/b material ratio of 0.33, 0.45, and 0.55. The nS was used about 0%, 1%, 3%, and 5% of the binder by weight in the mixes. To produce good workability used small amount of Superplasticizer. All groups of mixtures was incorporated binary cementitious blends of 0%, 1%, 3%, and 5% nS with each w/b of 0.33, 0.45 and 0.55. Adequate mixing is needed to attain desired performance of concrete and homogeneity.

Figure 3.3 Photographic view of Mixing of concrete

Table 3.3 Concrete mix proportions in kg/m^3

Mix ID	w/b	Binder Kg	Cement Kg	Water Kg	FA Kg	nS %	nS Kg	Superplasticizer Kg	Fine agg. Kg	Coarse agg. Kg
Mix 1	0.33	380	323.0	125.4	57.0	0	0.0	5.7	876.5	1059.4
Mix 2	0.33	380	319.2	125.4	57.0	1	3.8	6.7	874.8	1057.3
Mix 3	0.33	380	311.6	125.4	57.0	3	11.4	7.6	872.4	1054.5
Mix 4	0.33	380	304.0	125.4	57.0	5	19.0	8.6	870.1	1051.6
Mix 5	0.45	325	276.3	146.3	48.8	0	0.0	3.3	876.4	1059.3
Mix 6	0.45	325	273.0	146.3	48.8	1	3.3	4.1	875.0	1057.5
Mix 7	0.45	325	266.5	146.3	48.8	3	9.8	4.9	873.0	1055.1
Mix 8	0.45	325	260.0	146.3	48.8	5	16.3	5.7	871.0	1052.7
Mix 9	0.55	300	255.0	165.0	45.0	0	0.0	2.3	865.0	1045.5
Mix 10	0.55	300	252.0	165.0	45.0	1	3.0	3.0	863.7	1043.9
Mix 11	0.55	300	246.0	165.0	45.0	3	9.0	3.8	861.8	1041.6
Mix 12	0.55	300	240.0	165.0	45.0	5	15.0	4.5	860.0	1039.4

3.3 Concrete mixing and casting

To obtain the good concrete mixing production needs good mixing procedure and duration of mixing before casting. For this purpose, mixing procedure and timing procedure was discussed by Khayat et al., (2000). Thus in the current study, was trailed in demand to gain the same homogeneity and uniformity in all Mixes. About this mixing procedure, the fine and coarse aggregates were mixed in a power-driven rotating pan mixer and continued to gain mix homogeneously for about 30 seconds as shown in figure 3.4. After that nearby %50 of mixing water was added into the mixer and it was continued to proceed the mixing for one minute. The fine and corase aggregates with water, were left for 1 minute to the purpose of absorption of the water. Also, the powder materials cement, FA and Nano-SiO_2 were added together to the moistened aggregate mixture for about mixing another minute. After that Superplasticizer with lasting water was added to the mixture, the concrete was mixed for about 3 min and then left to break for about 2 min. At the end of the porocedure, the concrete was mixed for additional 2 min to complete the procedure. Test obtained concrete were cast for each type of mixture as shown in figures 3.4-3.9, by using small amount of Superplasticizer.

After the mixing procedure had completed, fresh concrete mixtures were tested for workability. The compressive strength, water Sorptivity, and gas permeability of Nano-SiO_2 blended concrete (NSBC) were also determined in the hardened state. All of the specimens were cast with compaction.

Figure 3.4 Mixing of fine and coarse aggregate

Specimens were cast from each mixture consisting of the following:

➢ Three 150 mm cubes for the compressive strength evaluation at 28 days.
➢ Two 150x300 mm cylinder for gas permeability test at 28 days.
➢ Four 100x200 mm cylinders for Water Sorptivity at 28 days.

Figure 3.5 Adding Cementitious material to fine and coarse aggregate mix

Figure 3.6 Cementitious materials with fine and coarse aggregate before mixing

Figure 3.7 Photographic view of specimens at curing time
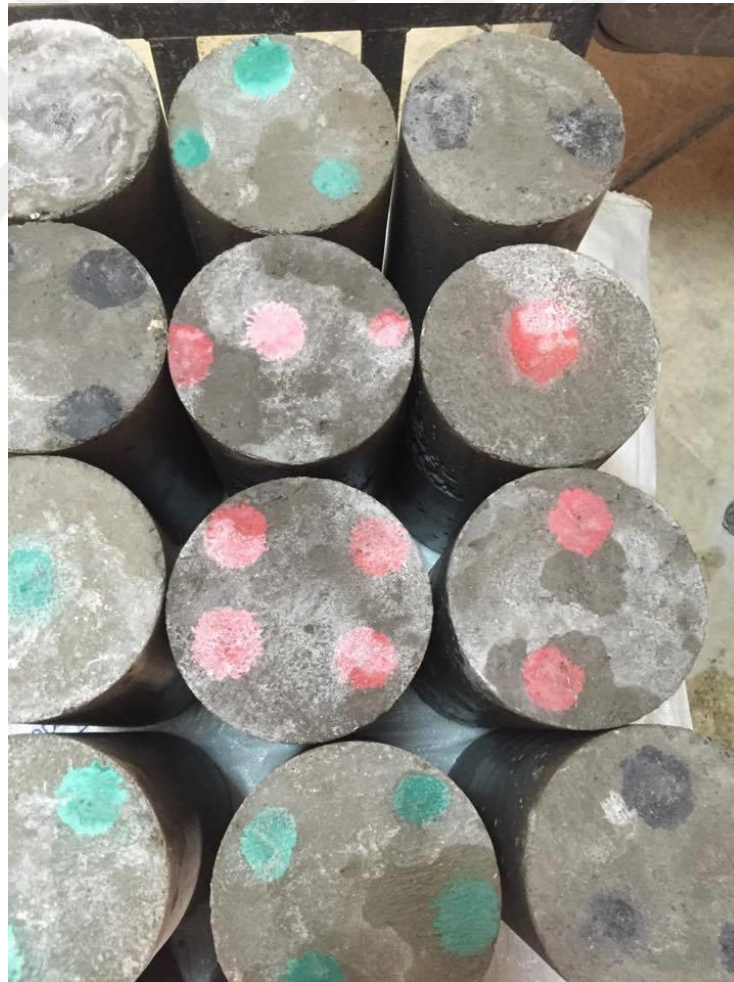
Figure 3.8 Photographic view of specimens after curing

Figure 3.9 Photographic view of specimens before cutting

The workability of concrete was evaluated using slump test. In this study, all mixes were tested for just gain workability. In case of standard mix, the slump was 75 mm but in case of mixes with 1% Nano-SiO_2 the slump was 70 mm, in case of 3% Nano-SiO_2 the slump was 62 mm and in case of 5% Nano-SiO_2 slump was 50 mm. However mixes with 1% and 3% Nano-SiO_2 of the weight of cement held good for workability as required for concreting but mix with 5% Nano-SiO_2 did not achieve required workability which means it becomes very difficult to use it for construction purposes.

3.4 Test methods

3.4.1 Compressive strength test

For compressive strength measurement of Nano-SiO_2 blended concrete (NSBC), cubical specimens of 150 mm were tested with respect to ASTM C 39 (2012) by means of 3000 kN capacity testing machine. The test was showed on three samples from each NSBC mix at 28 days as shown in figure 3.10. The compressive strength was measured   by averaging the results from the three tested specimens at age of testing.

Figure 3.10 Photographic view of compressive strength at testing time

3.4.2 Water Sorptivity

The Sorptivity estimates the rate at which water in drawn through the pores of concrete. In current study, four test samples taking a dimension of Ø100x65 mm cut from Ø100x200 mm cylinders were employed. The samples dried in oven at 100±5oC till gotten the stable weight, and then kept in closed container to cool in ambient temperature. After wards, the one side of the specimens coated by silicone, the Sorptivity test was conducted by placing the samples on glass rods in at ray such

as which their lowest surface upto a height of (3mm) is contacted with water. This process was measured to permit allowed water disposition through the lowest surface. Generally the surface area of water in the closed glass had better more than 10 times compared to cross-sectional area of the specimens (Razak et al., 2004). The samples were shifted from the closed glass to gain weighting at several minutes for about 64 minute to calculating mass at different times. The absorbed water volume was determined by distributing the mass obtained by the minimal surface area of the sample and by the water density. Then, the square root of time versus these values was plotted and the Sorptivity index of concretes was 42 calculated by the slope of the line of the best fit. Test setup was given in Figures 3.11-3.14. For each mixture, four specimens were tested for 28 days, and the average of them was stated, consecutively, at various times such as, 0, 1, 4, 9, 16, 25, 36, 49 and 64 min.

Figure 3.11 Photographic view of water sorptivity specimens after rying

44

Figure 3.12 Photographic view of water Sorptivity specimens after coating by silicone

Figure 3.13 Photographic view of water Sorptivity specimens at weighting time

Figure 3.14 Photographic view of water Sorptivity specimens at testing time

3.4.3 Gas Permeability

A RILEM TC 116 (1999) procedure, the CEMBUREAU method was used for measuring the gas permeability coefficients of concretes. The gas permeability was determined on 50 mm height and 150 mm diameter cylinder specimens cut from the midpoint section of Ø150x300 mm cylinders. When the curing period of 28 days were ended, the samples dried at $50\pm5oC$ in oven to making certain each sample weight change was smaller than 1%. Then, the samples were saved in a closed container before testing. At 28 days, two specimens were discussed and the average of the samples was estimated. The procedure of the testing method are shown in Figures 3.15-3.19. The steps of the gas permeability test are as follows;

1. Measure the diameter of the test specimen in 4 positions (two perpendicular diameters in both top and bottom faces) with a precision of 0.1 mm. The diameter D is the mean value of the four readings. The thickness L of the test specimen is determined in four positions equally distributed along the perimeter.

2. Place the test specimen in the cell and assemble the apparatus.

3. Build up a minimum lateral pressure of 7 bar (0.70 MPa) on the rubber tube.

4. Select 3 pressure stages: start with 1.5 bar (0.15 MPa) and increase to 2.0 (0.20 MPa) and then 3.0 bar (0.30 MPa) absolute gas pressure. Correct the input pressure of gas if necessary within 10 minutes.

5. Wait for 30 seconds before measuring the first flow.

6. Measure the flow at each pressure stage until it becomes constant, as follows:

a. Moisten the capillary of the soap bubble flow meter 1 minute before creating the bubble for measurement.

b. Always start the time measurement when the bubble is at the lowest marking of the calibrated tube.

c. Select the measuring volume by choosing the appropriate soap bubble flow meter such that the time reading is more than 20 seconds.

d. Take provisional readings of the flow rate. If the difference between successive readings within 5 to 15 minutes is less than 3%, take at least 2 readings in quick succession and determine the flow rate. Qi:

V/ti (m^3/s) for the given pressure stage. If this condition is not reached within 3 hours (no constant flow is attained, e.g. very low-permeability concretes), take the previous value of the flow rate.

7. Increase the pressure to the next pressure level and repeat the procedure with steps (6a) through (6d). Ensure that there are no leaks during the tests: the coefficient K should decrease when the pressure increases. If this is not the case, check the test setup for possible leaks and repeat the measurements.

$$k = \frac{2P2QL\eta}{A(P1^2 - P2^2)} \qquad\qquad (3.1)$$

Where,
K: Coefficient of Gas permeability (m^2)
P1: Inlet gas pressure (N/ m^2)
P2: Outlet gas pressure (N/ m^2)
A: Cross-section area of the sample (m^2)
L: Height of the sample (m)
η: Viscosity of oxygen (2.02x10-5Nsn/ m^2)
Q: Rate of flow of air bubble (m^3/sn)

Figure 3.15 Photographic view of gas permeability specimen after drying

Figure 3.16 Photographic view of gas permeability specimen in the cell

Figure 3.17 Photographic view of gas permeability specimen at testing time

Figure 3.18 Photographic view of gas permeability at testing time

Figure 3.19 Photographic view of gas permeability test

CHAPTER 4

TEST RESULTS AND DISCUSSIONS

4.1 Compressive Strength

The 28 days compressive strength versus the replacement level of Nano-SiO_2 for Blended Concrete are given in Figure 4.1. The results showed that a systematical Increase in compressive strength with the decrease in w/b content for the concretes without Nano-SiO_2, and compressive strength increased by increasing the amount of Nano-SiO_2. The concretes without nS had compressive strength increasing from 37.3 to 58.2 MPa at 28 days, with decreasing w/b content from 0.55 to 0.33. The compressive strength without nS was 58.2, 49.1and 37.3 MPa at 0.33, 0.45 and 0.55 w/b content, respectively. the maximum compressive strength without nS was 58.2 MPa at 0.33 w/b Content, while the lowest compressive strength were observed for concrete at 0.55 w/b content as 37.3 MPa. At first group the compressive strength was 58.2, 62.3, 66.7 and 61.6 MPa at 0%, 1%, 3%, and 5% of nS, respectively. At second group the compressive strength was 49.1, 51.4, 54.4 and 49.3 MPa at 0%, 1%, 3%, and 5% of nS, respectively. At third group the compressive strength was 37.3, 40.2, 44.1 and 40.1 MPa at 0%, 1%, 3%, and 5% of nS, respectively. At first group with increasing Nano-SiO_2 from 1% to 3% by total binder weight the improvement in compressive strength was as high as 10.7%, and 14.6%, correspondingly. Furthermore, with any 1% addition of Nano-SiO_2 at 28 days, the average increments of compressive strength were 2.7 MPa for the second and 3.4 MPa for the third groups. The results demonstrated that Nano-SiO_2 blended concretes with compressive strength of higher than 60 MPa may be produced by using a Nano-SiO_2 content of as high as 3% replacement level by total binder weight, it was observed that there was about 14.6% increment in compressive strength when 3% of the total binder weight was replaced by nS. When nS added to the mix improves the bond between the cement paste and the aggregate

Particles as well as increasing the density of the cement paste. Therefore, in this study all mixes at first group showed that the compressive strength more than 60 MPa at 28 days, it can be named as a high compressive strength Concrete.
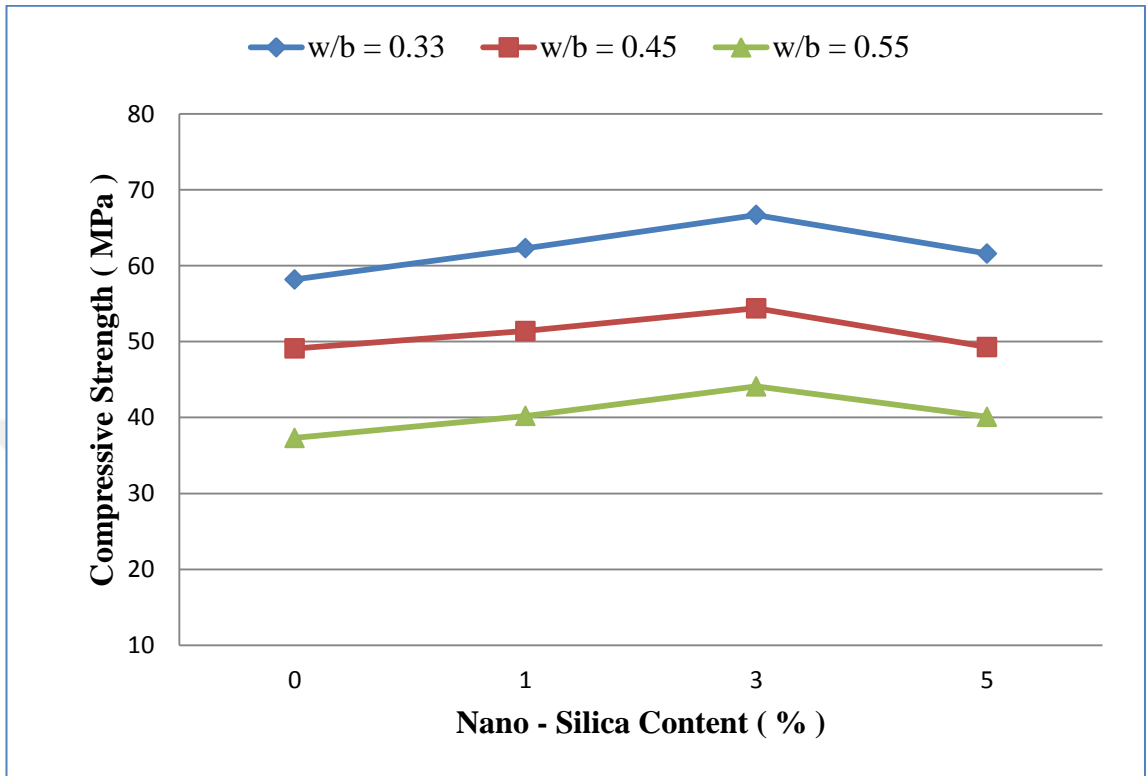

Figure 4.1 Variations in the compressive strength of concrete with and without Nano-silica at 28 days

Figure 4.2 Photographic view of compressive strength of concrete test at 28 days

4.2. Water Sorptivity

The water Sorptivity of concrete is influenced by many of factors containing concrete mixture proportions, the use of supplementary cementitious materials and chemical admixtures, the physical characteristics and composition of the cementitious materials and of the aggregates, the air entrained content, the duration and type of curing, the age or degree of hydration, the presence of micro cracks, and the presence of surface treatments for instance sealers or form oil, and placement method including compaction and finishing. The 28 days Water Sorptivity versus the replacement level of Nano-SiO_2 for Blended Concrete are given in Figure 4.3. The results showed that a systematical decrease in Sorptivity coefficients with the decrease in W/b content for the concretes without Nano-SiO_2, and on the other hand Sorptivity coefficient decreased by increasing the amount of Nano-SiO_2. The concretes without Nano-SiO_2 had Sorptivity coefficient decreasing from 0.1155 mm/$min^{0.5}$ to 0.0542 mm/$min^{0.5}$ at 28 days, with decreasing w/b content from 0.55 to 0.33. The Sorptivity coefficient without nS was 0.0542, 0.0821and 0.1155 mm/$min^{0.5}$ at 0.33, 0.45, and 0.55 w/b content, respectively. the minimum Sorptivity coefficient without nS was 0.0542 mm/$min^{0.5}$ at 0.33 w/b Content, while the highest Sorptivity coefficient were observed for concrete at 0.55 w/b content as 0.1155 mm/$min^{0.5}$. At first group the Sorptivity coefficient was 0.0542, 0.0473, 0.0347 and 0.0379 mm/$min^{0.5}$ at 0%, 1%, 3%, and 5% of nS, respectively. At second group the Sorptivity coefficient was 0.0821, 0.0746, 0.0609 and 0.0627 mm/$min^{0.5}$ at 0%, 1%, 3%, and 5% of nS, respectively. At third group the Sorptivity coefficient was 0.1155, 0.1021, 0.0876 and 0.0876 mm/$min^{0.5}$ at 0%, 1%, 3%, and 5% of Nano-SiO_2, respectively. At first group with increasing nS from 1% to 3% by total binder weight the improvement in Sorptivity coefficient was as low as 11.6%, and 15.6 %, correspondingly. Furthermore, with any 1% addition of nS at 28 days, the average reduction of Sorptivity coefficient were 10% for the second and 11.3% for the third groups. It was observed that there was about 15.6% reduction in Sorptivity coefficient when 3% of the total binder weight was replaced by Nano-SiO_2.
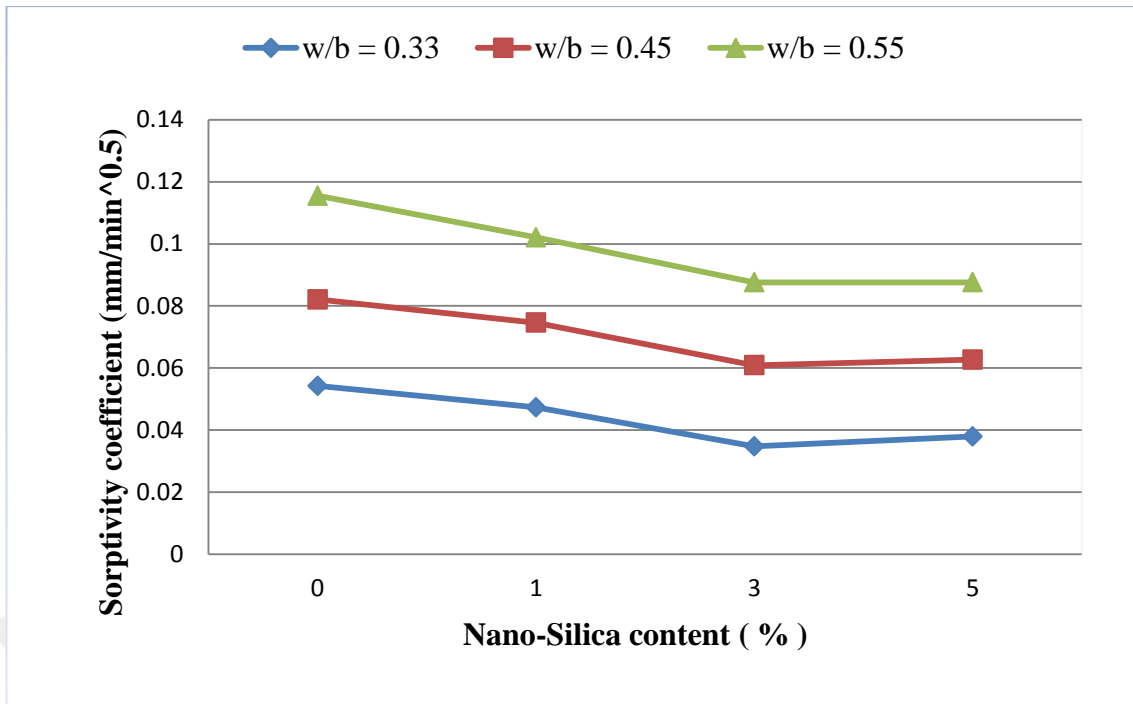
Figure 4.3 Variations in the water Sorptivity coefficient of concrete with and without Nano-silica at 28 days

Figure 4.4 Photographic view of water Sorptivity of concrete at 28 days

4.3. Gas Permeability

The 28 days gas permeability versus the replacement level of Nano-SiO$_2$ for Blended Concrete is given in Figure 4.5. The results showed that a systematical decrease in gas permeability coefficients with the decrease in W/b content for the concretes without Nano-SiO$_2$, and on the other hand gas permeability coefficient decreased by increasing the amount of Nano-SiO$_2$. The concretes without nS had gas permeability coefficient decreasing from 5.92 x 10^{-16} (m²) to 3.3 x 10^{-16} (m²) at 28 days, with decreasing w/b content from 0.55 to 0.33. The gas permeability coefficient without nS was 3.3 x 10^{-16}, 4.77 x 10^{-16} and 5.92 x 10^{-16} (m²) at 0.33, 0.45, and 0.55 w/b content, respectively. The minimum gas permeability coefficient without nS was 3.3 x 10^{-16} (m²) at 0.33 w/b content, while the highest gas permeability coefficient were observed for concrete at 0.55 w/b content as 5.92 x 10^{-16} (m²). At first group the gas permeability coefficient was 3.3, 2.71, 2.21 and 2.32 (x 10^{-16} m²) at 0%, 1%, 3%, and 5% of Nano-silica, respectively. At second group the gas permeability coefficient was 4.77, 4, 3.51 and 3.38 (x 10^{-16} m²) at 0%, 1%, 3%, and 5% of nS, respectively. At third group the gas permeability coefficient was 5.92, 5.11, 4.38 and 4.21 m(x 10^{-16} m²) at 0%, 1%, 3%, and 5% of nS, respectively. At first group with increasing nS from 1% to 3% by total binder weight the improvement in gas permeability coefficient was as low as 12.2%, and 14.9 %, correspondingly. Furthermore, with any 1% addition of Nano-SiO$_2$ at 28 days, the average reduction of gas permeability coefficient were 11.9% for the second and 11.6% for the third groups. It was observed that there was about 14.9% reduction in gas permeability coefficient when 3% of the total binder weight was replaced by Nano-SiO$_2$.
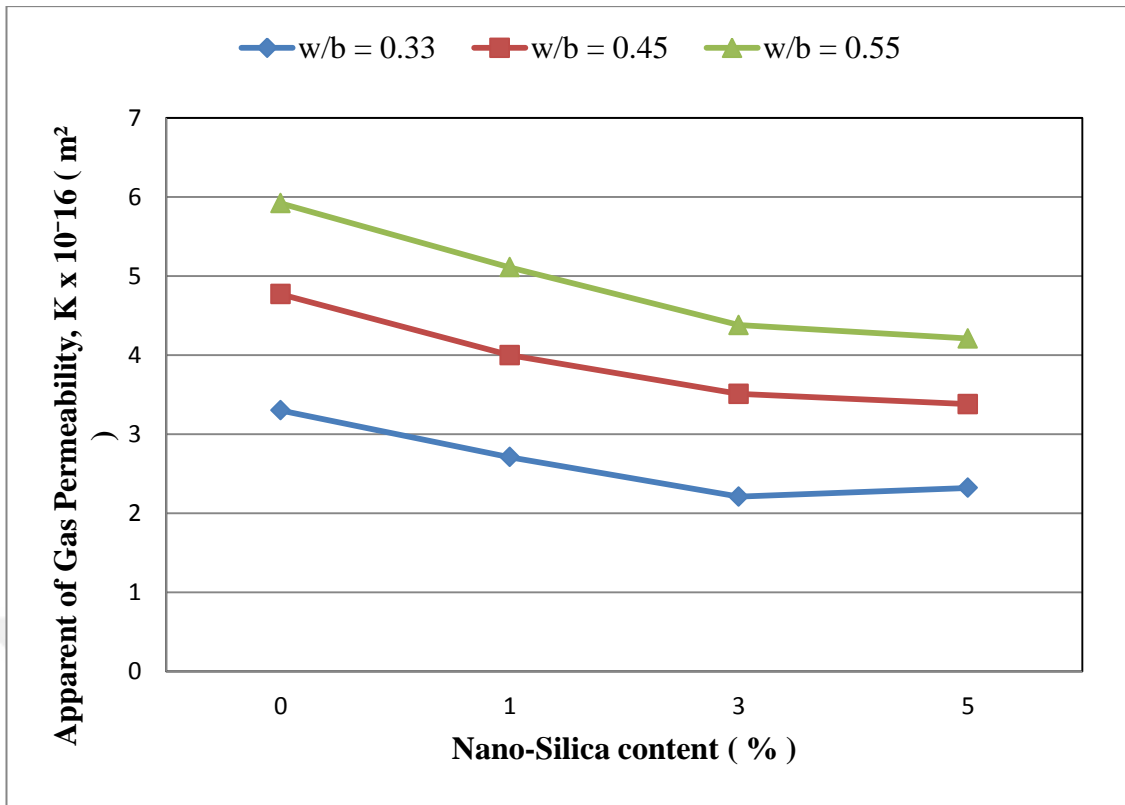
Figure 4.5 Variations in the gas permeability coefficient of concrete with and without Nano-silica at 28 days

Figure 4.6 Photographic view of gas permeability at 28 days

CHAPTER 5

CONCLUSIONS

Based on the results presented in current study, the following conclusions can be drawn:

1. The results showed that a systematical Increase in compressive strength with the decrease in w/b content for the concretes without nS, and compressive strength increased by increasing the amount nS.

2. The highest compressive strength observed at 3% of Nano-SiO$_2$ content as 66.7 MPa, for the concrete, while the highest compressive strengths without Nano-SiO$_2$ were obtained at first group as 58.2 MPa.

3. The minimum gas permeability coefficients observed at 3% of nS content as 2.21 x 10^{-16} m², for the concrete, while the minimum gas permeability coefficients without nS were obtained at first group as 3.30 x 10^{-16} m².

4. The minimum water sorptivity coefficients observed at 3% of nS content as 0.0347 mm/min$^{0.5}$, for the concrete, while the minimum gas permeability coefficients without nS were obtained at first group as 0.0542 mm/min$^{0.5}$.

5. It is proved that the gas permeability coefficients were decreased by increasing nS content. Combination of mineral additives is efficient in the reduction of gas permeability. Combining of the blends in ternary system enhanced the quality of nS blended concrete, due to its pozzolanic activity and void filling ability of nS.

6. It was shown that the compressive strength of blended concrete increased with using Nano-SiO$_2$ up to 1%. Increasing 1% and 3% Nano-SiO$_2$ enhanced the compressive strength by 10.7% and 14.6% for the first group, 10.5% and 10.8% for the second group, and 10.8% and 11.8% for the third group and respectively, compared to the controlled mixtures.

7. The gas permeability showed that a systematical decrease in gas permeability coefficients with the decrease in w/b content for the concretes without nS

and on the other hand gas permeability coefficient decreased by increasing the amount of Nano-SiO_2.

8. The Sorptivity showed that a systematical decrease in Sorptivity coefficients with the decrease in w/b content for the concretes without Nano-SiO_2, and on the other hand Sorptivity coefficient decreased by increasing the amount of Nano-SiO_2. With the addition of Nano-SiO_2 the improving percentage of gas permeability coefficient and water Sorptivity of concrete reaches approximate rate of about 14.6% and 15.6%, respectively, with respect to the control mixes.

9. Nano-SiO_2 have remarkable improvement on the compressive strength of blended concrete at 28 days, due to the reaction of Nano materials with calcium hydroxide $Ca(OH)_2$ crystals, which are arrayed in the interfacial zone (ITZ) between hardened cement paste and aggregates, and produce CS- H gel and the filling action of Nano particles which cause more densified micro structure.

10. The optimum percentage for replacement of cement with Nano-SiO_2 which was 3%, and additional percentage may reflect negatively on the compressive strength of concrete, water sorptivity coefficients and gas permeability coefficients, due to agglomeration of Nano-SiO_2, also to achieve economical mix since increasing the cost of mix without major effect on the mechanical properties is noticed.

11. Nano-SiO_2 reduces the workability of concrete.

12. 3 % replacement of cement by Nano-SiO_2 reduces gas permeability coefficient of concrete compared to the reference concrete.

13. 3 % replacement of cement by nS reduces 14.6 % of gas permeability coefficient of concrete compared to the reference concrete.

14. 3 % replacement of cement by nS reduces 15.6 % of water Sorptivity coefficient of concrete compared to the reference concrete.

15. The workability of concrete was evaluated using slump test. In case of standard mix, the slump was 75 mm but in case of mixes with 1% nS the slump was 70 mm, in case of 3% nS the slump was 62 mm and in case of 5% nS slump was 50 mm. However mixes with 1% and 3% nS of the weight of cement held good for workability as required for concreting but mix with 5% nS did not achieve required workability which means it becomes very difficult to use it for construction purposes.

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