

A REVIEW ON MICROSTRUCTURAL CHARACTERISTICS OF NANO-SILICA BASED HIGH STRENGTH CONCRETE

Suhail Ahmad Ahanger

Department of Civil Engineering, Islamic University of Science and Technology, Awantipora

Abstract:

The development of new and efficient admixtures in the field of concrete technology has made possible the concept of high strength concrete. The incorporation of the small sized particles in the conventional concrete has made the process of formation of high strength concrete easier and flawless. Concrete strengths much higher than 55 MPa are gaining acceptance in the modern construction industry. The Nano sized particles upon incorporation in the concrete effects the microstructure of concrete remarkably. The paper reviews the various microstructural characteristics of high strength concrete that differentiates it from the conventional concrete or normal concrete. Various remarkable effects on the hydration products are discussed which are due to the addition of Nano sized particle in the concrete.

Key words: *High strength concrete; Nano sized particle; Microstructure of Concrete; Hydration products.*

INTRODUCTION:

In the present age, great emphasis is laid on sustainable development and strategies which help encourage sustainable design and production methodologies. Similar trends need to be followed in the concrete/ cement industry. Concrete is undoubtedly one of the most commonly used materials in construction industry and consumes almost the total cement production of the world. Although it has revolutionized the construction industry in ways more than one but still its development in a sustainable way is the need of an hour.

The one problem associated with the large consumption of cement is that the production of cement results in increasing carbon dioxide emissions and as a consequence the Green House Effect. In 2016 the total global carbon dioxide emission from fossil fuel and industry amounts to 36.2 Giga tonnes(downtoearth.org.in), which was 62% more than 1990 mark, while as production of cement results in carbon dioxide emissions of the order of 900 kg for every ton of cement produced.

The increasing carbon dioxide levels (due to cement production) in the atmosphere undermines the positive credits of the concrete industry and mainly civil engineering. The gradual development of concrete technology has promoted the use of cement replacement. Different materials are incorporated in the conventional concrete to make the process of cement replacement easier and flawless. The introduction of cement replacements not only decreases the demand of cement but also we are able to develop high strength concrete. The finer structure of these materials help in filling the voids of the concrete and thus we are able to get the concrete with maximum density or in other words, the high strength concrete.

Nano materials (Nano-Silica) are extremely small sized particles (10^{-9} m). Due to their extreme small size they highly effect the properties of concrete at ultra-fine level. The small size of the particle also represents greater surface area. Since the rate of hydration of the concrete is proportional to the surface area of the cement or binding materials, therefore the rate of hydration enhances and hence more hydration products are formed, thus forms high strength concrete. In order to achieve the desired results only a small percentage of cement can be replaced. The presence of Nano-Silica in concrete mix results in increase in compressive, tensile and flexural strength. Nano-Silica mixed cement can generate Nano crystals of C-S-H (Calcium Silicate Hydrate) gel after hydration. These Nano crystals get deposited in micro pores of the cement concrete. Due to this the permeability and strength of the concrete is highly improved

Nano-Silica:

Nano Silica (SiO_2) has the features of small particle size, narrow particle size distribution, porous, large surface area. The particle size of Nano silica used in the concrete industry generally comes in the range of 10-25 nm. The BET (Brunauer, Emmett and Teller) surface area of the Nano silica particles used in the concrete study is mostly $200 \text{ m}^2/\text{g}$. The specific gravity of the Nano –Silica particles is 2.2 g/cm^3 . Table 1 shows the general properties of Nano-Silica used in most of the concrete studies.

Table 1: Properties of Nano-Silica

B.E.T Surface area	200 m ² /g
pH (4% aqueous slurry)	3.7-4.3
Bulk Density	3.0lb/ft ³ (Max.)
Loss on Heating	< 1.5 % Max.
Specific Gravity	2.2 g/cm ³
Refractive Index	1.46
X-Ray form	Amorphous
Assay(% SiO ₂)	>99.8

Figure 1 shows the specimen of Nano-Silica in powder form which is used for developing high strength concrete. The Nano – Silica in powder form is made into slurry by mixing the powdered Nano-Silica with water in mixer of very high RPM.



Figure 1: Sample Specimen of Nano-Silica

MICROSTRUCTURE OF CONCRETE:

Concrete is a typical multiscale material, therefore its structure cannot be approached at a single level of scale, but requires examinations over wide ranges of scales and magnifications. According to Diamond (1993) [1], the structure of concrete can be examined at five levels: visual, petrographic, intermediate scanning electron microscopy, (SEM), high magnification SEM and at Nano meter level. Figure 2 shows the images of concrete at different levels. The visual examination of concrete is done with the help of unaided eye and reveals details of course aggregate and voids in the concrete specimen. The petrographic examinations done with the help of optical microscope and reveals fine aggregates, air voids and some paste details. The intermediate Scanning Electron microscopy (SEM) is done with the help of backscatter scanning electron microscope and reveals arrangement of juxtaposition of cement paste particles, sand and capillary voids. The high magnification SEM reveals details of internal structure of individual cement particles. The Nano structure of the concrete specimen reveals very minute details of Calcium Silicate Hydrates (C-S-H).

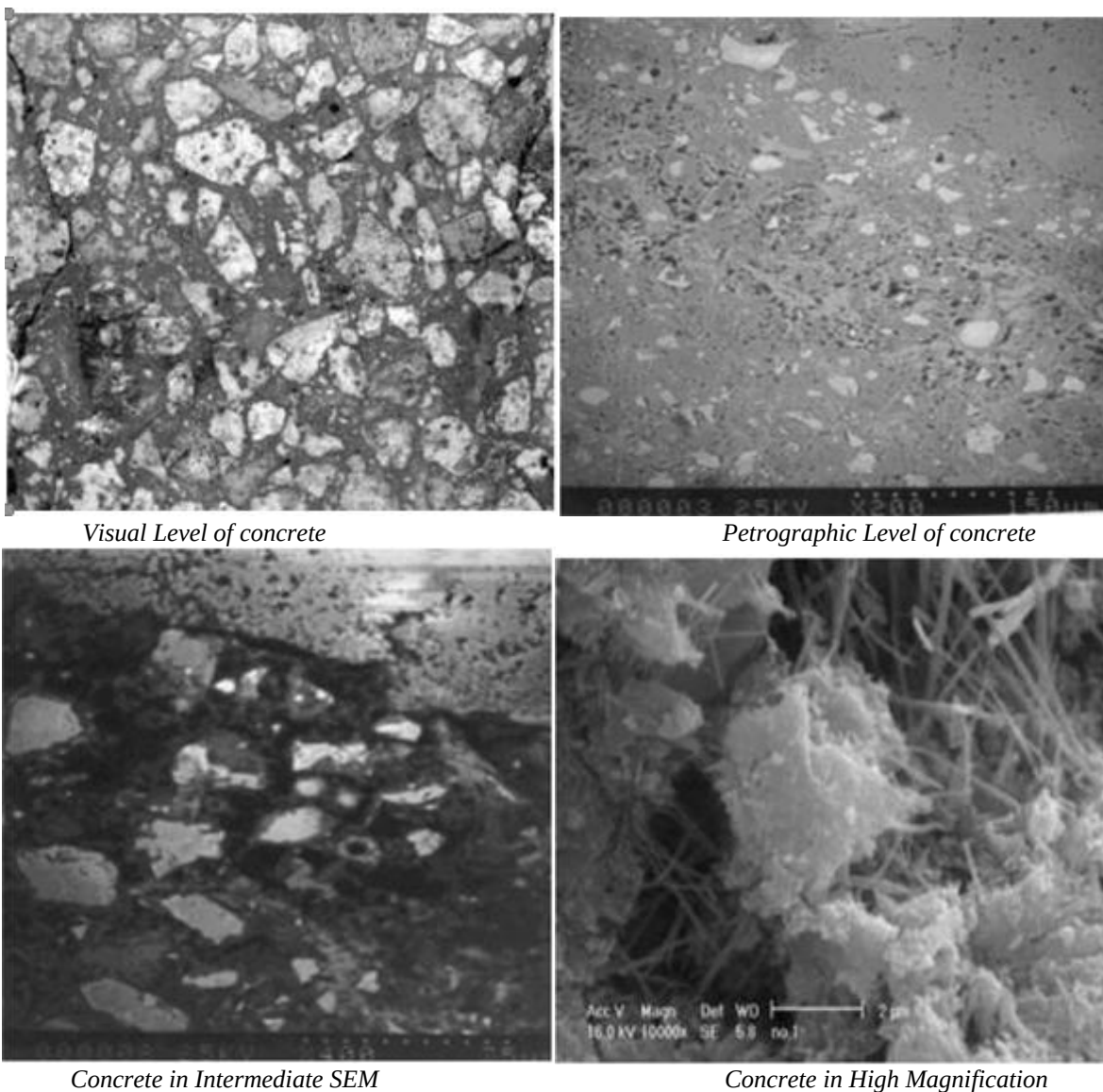
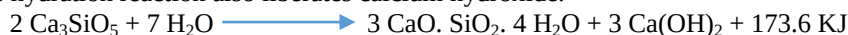


Figure 2: Concrete Images at different Magnification Levels.

CALCIUM SILICATE HYDRATE (C-S-H):

The Calcium Silicate Hydrate also known as C-S-H is the main product of hydration of Portland cement. The C-S-H is the main strength contributing component of concrete. The Calcium Silicate Hydrate product is formed when the Tri-calcium silicate (C_3S) or Di-calcium silicate (C_2S) present in the Portland cement reacts with water. This exothermic reaction also known as hydration reaction also liberates calcium hydroxide.



The internal structure of the Calcium Silicate Hydrate varies from poorly crystalline to amorphous. The C-S-H occupies about 50-60% of the solid volume of hydrated cement paste. The strength in C-S-H is mostly due to the ionic/covalent bonds (almost 65%) and due to van der Waals bonding (35%). The outer product or early C-S-H is formed during early hydration and is formed away from the cement particle surface. The early C-S-H has higher porosity and contains higher level of impurities. On the other hand, the inner C-S-H forms during later hydration and grows inwards and outwards from the C-S-H barrier. The inner C-S-H takes the shape of cement grains and has less porosity and high density. The inner C-S-H consists of lesser impurities and is more resistant to physical change in drying. The Calcium Silicate Hydrate forms a continuous layer that holds together the cement particles into a cohesive whole. The difference between the C-S-H and other hydration products is that the other hydration products are discrete and do not form continuous connections and hence contribute very less in the strength of concrete.

The microstructure of calcium silicate hydrate (C-S-H) when viewed in the scanning electron microscope apparently shows two different types of morphologies. One of them is less dense (more porous) and occupies the space that was originally water filled, while the other appears denser and is found in those areas originally occupied by cement particles.

INTERFACIAL TRANSITION ZONE (ITZ):

The interfacial transition zone is about 50 μm thick and plays a central role in the permeability, stiffness and strength of cementitious particles containing aggregate due to its lower density and strength compared to bulk cement paste. The ITZ suffers cracks due to its weakness leading to quasi –brittle nature of concrete. The ITZ is a region with a higher water cement ratio (w/c) and hence has higher porosity than the bulk paste. The ITZ region comprises of large crystals of calcium hydroxide due to its large pore size. The ITZ becomes the weakest region of the concrete and thus the strength of the concrete is determined by the strength of the ITZ region. With the increase in the total amount of large aggregates the total volume of ITZ increases and strength is observed to decrease. The large volume of the ITZ also affects the permeability of the concrete because permeability is directly related to the porosity of the concrete.

CALCIUM HYDROXIDE Ca(OH)_2 :

The calcium hydroxide is one of the byproduct of hydration reaction of Portland cement. The calcium hydroxide forms a crystal with wide range of shapes and sizes depending primarily on availability of space for its development. There is very slight contribution of calcium hydroxide to the strength of the concrete. The solubility of calcium hydroxide is very high and thus weakens the durability aspects of the concrete.

LITERATURE REVIEW:

Juliana Calabria-Holley, Kevin Paine, Styliani Papatzani (2014) [2] experimentally investigated the effects of Nano-Silica on the Calcium Silicate Hydrates in Portland cement-fly ash system. The study found the increase in the pozzolanic action with the addition of Nano-Silica as cement replacement. The results from the study suggest that the addition of Nano-Silica in Portland cement-fly ash system modifies the calcium silicate hydrate network leading to more complex arrangement of microstructure which is rich in silicon. The study also found decrease in calcium silicium ratio (C/S) with the addition of Nano-Silica, which can be accounted to the seeding effect of Nano-Silica in the formation of calcium silicate hydrate network or by the calcium hydroxide donating calcium atoms to form the calcium silicate hydrate gel, which in turn is derived from pozzolanic reaction.

H. Paiva, A.S. Silva, A. Velosa (2017) [3] studied microstructure and hardened state properties on pozzolan containing concrete and found that the microstructure and hardened state properties of the concrete are dependent on the pozzolanic reactivity of the concrete reflected in calcium hydroxide consumption, development of porosity and final compressive strength. Moreover it was found that the use of water reducing agent for enhancement of workability helps in improvement of both microstructure and the hardened state features like porosity.

Gustavo Braz de Abreu, Suellen Mota Marques Costa, Adriana Guerra Gumieri, Fabricio Carlos Franca², Claudio Silva (2017) [4] studied the mechanical properties and microstructure of high performance concrete containing stabilized Nano-Silica and found substantial increase in the secant modulus of elasticity of concrete made with stabilized nano-silica. The analysis by SEM showed effective improvements in the microstructure of the concrete with the addition of stabilized Nano-Silica. The study also revealed use of stabilized Nano Silica reduced the cement consumption in the production of concrete. The study also revealed much dispersion and homogenization of material during the concrete mixing by the use of stabilized Nano-Silica.

Hui Li, Hui-gang Xiao, Jie Yuan, Jinping Ou (2003) [5] studied the microstructure of cement with Nano particles and found that the addition of Nano silica enhanced both the compressive and flexural strength of the concrete. The SEM observations also revealed that the nano particles acted as the activators to promote hydration and makes the microstructure of concrete uniformly dispersed. The study also revealed the decrease in the big crystals of calcium hydroxide on addition of nano particles in the concrete. The decrease in the calcium hydroxide content is attributed to the pozzolanic reaction of the concrete wherein the calcium hydroxide is converted into strength giving calcium silicate hydrate. The study also revealed the texture of the concrete as more compact and dense on the addition of nano particles.

Nikolajs Toropovs, Diana Bajare, Genadijs Sahmenko, Linda Krage, Aleksandrs Korjajkins (2014) [6] studied the formation of microstructure in the high strength concrete containing micro and nano silica. The study revealed that the use of micro silica and Nano silica resulted in the increase of compressive strength by 28% comparing 28 days and 180 days old samples. The study also revealed that the porosity decreased from 3.9 % to 1.7 % by the use of micro silica and Nano silica during long term hardening. The study also revealed that 28 day sample of concrete containing microsilica and Nano silica still contains unreacted round shaped Nano silica and Micro silica particles having round shapes. The Micro silica and Nano silica particles do not form agglomerated, rather are uniformly distributed.

Liguo Wang, Dapeng Zheng, Shupeng Zhang, Hongzhi Cui, Dongxu Li (2016) [7] studied the effects of Nano-Silica on the hydration and microstructure of Portland cement. The study revealed the effect of Nano-Silica with an average diameter of 20 nm on the mechanical properties, hydration and pore structure of cement based materials. The study revealed that the reaction of Nano-Silica started within 01 h and formed C-S-H gel. The study revealed an obvious change in the microstructure of the concrete with increase in age on addition of Nano silica. Many needle-like and bar like crystals emerged at the surface of early ages. The flocculated material becomes denser with the increase in the curing age of concrete. The Nano Silica promoted hydration heat of cement paste. The hydration heat of second exothermic peak which occurred after 2.5 h earlier was increased 0.002 W/g on 3% dosage of Nano silica and 0.003W/g on 4% dosage of Nano silica. The calcium

hydroxide content decreased by 0.27% ,0.82%,2.24%, and 3.95% at one day, three day, seven day and 28 days respectively. The compressive strength of Nano silica based concrete increased by 33.2 % ,29.1 % , and 18.5 % at three days, seven days and 28 days respectively on addition of 3% Nano silica. When the dosage was increased to 5% ,the three day strength increased by 44.9 % , seven day strength increased by 29.7% and 28 day strength increased by 10.6%.

R. Yu , P. Spiesz, H.J.H. Brouwers (2014) [8] studied the effect of nano silica on the hydration and microstructure development of ultra high performance concrete with a low binder amount .The study revealed that by utilizing the nano silica (3.74% by the mass of binder amount) the highest mechanical properties of concrete is achieved .The study revealed that using the modified Andreasen and Andreasen particle packing model ,a homogenous and dense skelton of ultra high performance concrete can be obtained with low binder amount (440 kg /m³).The study revealed under SEM that the samples without nano silica showed considerable amount of calcium hydroxide and has still large space available to grow in the concrete.The SEM analysis of samples with nano silica (4%) shows very dense structure with only a few air pores present.The SEM analysis also found fine C-S-H gel which develops due to the pozzolanic reaction of nano silica with calcium hydroxide .The SEM study of samples with 5% nano silica shows dense hydration products with a large number of pores .The presence of large number of pores is attributed to the fact that the increase in the nano silica percentage increases the viscosity of cementitious mixtures ,wherein large amount of air is entrapped thus increasing the porosity of hardened concrete.

R. Palla ,S. R. Karade, G. Mishra, U. Sharma , L.P. singh (2017) [9] studied high strength sustainable concrete using nano particles .The experimental study involved the effect of silica nano particles in high volume flyash cement paste , mortar and concrete .The silica nano particles content used was (0.5% -3%) by thr weight of binder .The experimental study revealed that the addition of silica nano particles accelerated the hydration process and dormant period was shortened by 4 h with 2 % nano silica particles as compared to the control. The SEM analysis of control specimen revealed that the hydration products were hardly formed and the fine aggregates particles were distributed all over the surface .The study also revealed that the cement grains in the control specimen was covered with very thin layer of fibrous network which possibly might be calcium silicate hydrate network.The SEM analysis of specimens with addition of 2% silica nano particles showed the large number of calcium silicate hydrate clusters .It was also revealed that the surface of cement grains were covered with hydration products ,thus conforming the nucleation effect of silica nano particles .The control specimen at 3 days and 7 days showed porous structure under SEM .Calcium silicate hydrate gel was present in separated colloids .

Gengying Li (2003) [10] experimentally studied the properties of high volume fly ash concrete incorporating nano silica .The study revealed the increase in the pozzolanic reactivity of fly ash concrete on the addition of small volumes of nano silica .The study revealed that the addition of Nano silica increased both short term and long term strength .The addition of flyash results in higher porosity at short curing time ,while as nano silica which acts as accelerating additive helps in development of more compact structures even at short curing temperatures.

Tao Ji (2005) [11] experimentally studied the water permeability and microstructure of concrete incorporating nano silica.The study compared the microstructure of normal concrete and concrete with nano silica at 28 days .The microstructure was studied with ESEM(environmental scanning electron microscope) .The normal concrete under ESEM shows fly ash particles being available in the binding paste matrix.The Nano silica sample shows the large concentration of hydration products particularly calcium silicate hydrate and very small amount or no fly ash was found in the sample.This shows that the pozzolanic reaction of flyash with nano silica is very quick as compared to normal concrete.The study revealed the large crystals of calcium hydroxide present in the normal concrete , and considerable decrease in the calcium hydroxide content on the addition of nano silica in the concrete.The nano silica particles absorb the calcium hydroxide crystals and thus reduces the size and amount of calcium hydroxide in the concrete making inter transition zone (ITZ) of aggregates and binding paste matrix denser.

Ye Qing , Zhang Zenan , Kong Deyu, Chen Rongshen (2005) [12] studied influence of Nano silica addition on properties of hardened cement paste as compared with silica fume .The study involved the use of amorphous Nano silica and micro silica for comparing the effects on the hardened concrete. The experimental study revealed that the pozzolanic reaction of Nano silica is much faster than micro silica. The Nano silica makes cement paste thicker and thus enhances the hydration mechanism. The compressive strength of concrete increases with the addition of Nano silica as compared to the addition of micro silica. The pozzolanic activity of Nano silica is much greater than that of silica fume. The Nano silica consumes crystals of calcium hydroxide much greater than that of silica fume.

Jeng-Ywan Shih , Ta-Peng Chang , Tien –Chin Hsiao (2006) [13] experimentally studied the effects of Nano silica on characterization of Portland cement composite .The experimental results showed that when 0.60% of nano silica is added to Portland cement composite ,the specimen has an optimum compressive strength, in which increase in compressive strength is about 43.8%.The sample of Portland cement with nano silica addition reveals in MIP techniques that the pore volume increases and the fractal dimension of microstructure decreases in the regions where pore size is smaller than 10 nm .However the results are opposite in the regions where the pore size is larger than 10 nm.

SUMMARY:

The incorporation of Nano particles like Nano Silica and Micro Silica in the ordinary concrete results in the manifold increase in the compressive strength of concrete .The nano particles act as nucleation sites where pozzolanic reaction with

calcium hydroxide occurs ,resulting in development of more strength giving calcium silicate hydrates .The addition of nano particles helps in decreasing the quantity of unwanted calcium hydroxide through the pozzolanic reaction .Due to very small sizes of Nano particles and very large surface area ,they promote very quick and efficient hydration reactions at their surfaces . The addition of nano silica helps in the development of dispersed microstructure.The microstructure of the concrete becomes denser and compact on addition of nano particles like nano silica .The SEM analysis of the concrete specimen shows remarkable decrease in the calcium hydroxide crystals and other flocculated crystals .The SEM analysis of the concrete specimens showed that the nano particles not only acted as fillers ,but also as an activator to promote hydration .The addition of Nano silica also results in substantial increase in the early age strength of the concrete .

REFERENCES:

- [1] Sidney Diamond and Diamond Bonen(1993), “ Microstructure of Hardened Cement Paste –A new interpretation” . Journal of American Ceramic Society.
- [2] Juliana Calabria-Holley, Kevin Paine, Styliani Papatzi (2014) “ Effects of nano-silica on the calcium silicate hydrates in Portland cement –fly ash systems” ,Advances in Cement Research.
- [3] H. Paiva, A.S. Silva , A. Velosa (2017), “ Microstructure and hardened state properties on pozzolan-containing concrete”,Construction and building materials .
- [4] Gustavo Braz de Abreu, Suellen Mota Marques Costa, Adriana Guerra Gumieri, Fabricio Carlos Franca2 , Claudio Silva (2017) , “Mechanical properties and microstructure of high performance concrete containing stabilized Nano-Silica” , REVISTA MATERIA V.22 N.02.
- [5] Hui Li , Hui-gang Xiao, Jie Yuan, Jinping Ou (2003), “ Microstructure of cement mortar with Nano particles” Composites Part B: Engineering ,ELSEVIER.
- [6] Nikolajs Toropovs , Diana Bajare , Genadijs Sahmenko , Linda Krage , Aleksandrs Korjajkins (2014), “ The Formation of Microstructure in High Strength Concrete Containing Micro and Nanosilica” , Key Engineering Materials Vol 604 (2014) pp 83-86.
- [7] Ligu Wang, Dapeng Zheng, Shupeng Zhang, Hongzhi Cui, Dongxu Li (2016), “ Effects of Nano-Silica on the hydration and microstructure of Portland cement” . Nanomaterials 2016, 6, 241; doi:10.3390/nano6120241
- [8] R. Yu , P. Spiesz, H.J.H. Brouwers (2014) , “ Effect of nano silica on the hydration and microstructure development of ultra high performance concrete with a low binder amount”.Construction and Building materials ,ELSEVIER.
- [9] R. Palla ,S. R. Karade, G. Mishra, U. Sharma , L.P. singh (2017), “ High strength sustainable concrete using nano particles” . Construction and Building Materials ,Volume 138 ,Pages 1-548.
- [10] Gengying Li (2003), “ Properties of high -volume fly ash concrete incorporating nano silica”.Cement and Concrete Research .
- [11] Tao Ji (2005) , “ Water permeability and microstructure of concrete incorporating Nano silica’.Cement and Concrete Research.
- [12] Ye Qing , Zhang Zenan , Kong Deyu, Chen Rongshen (2005), “Influence of Nano silica addition on properties of hardened cement paste as compared with silica fume” .Construction and Building Materials.
- [13] Jeng-Ywan Shih , Ta-Peng Chang , Tien –Chin Hsiao (2006), “ Effects of Nano silica on characterization of Portland cement composite”.Construction and Building Materials.