NANO-CEMENT PROPERTIES AND MANFUCTURING

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In the Name of God
The Most Compassionate and the Most Merciful

بسم الله الرحمن الرحيم
وبسمه تعالى نستعين.....

DEDICATION

This research is dedicated to Engineering union of Kurdistan- Khanaqin Branch for their sacrifices and cooperation researching this study.

With Best Regards,

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Abstract

The main objective of this paper is to outline latest and promising research areas of nano cement and its components, furthermore, highlighting production technique and methodology of Nano-cement in Iraq.

Basic background information on nanotechnology research, state of the art on use of this technology in cement, opportunities and challenges are discussed.

However, Nanotechnology is one of the most active research areas that contains a number of disciplines including civil engineering and construction materials. Interest in nanotechnology concept for Portland cement composites is steadily growing. Currently, the most active research areas dealing with cement and concrete are: understanding of the hydration of cement particles and the use of nano-size ingredients such as alumina, silica particles and the effect of Nano materials of different cement types.

There are also a limited number of investigations dealing with the manufacture of nano-cement. If cement with nano-size particles can be manufactured and processed, it will open up a large number of opportunities in the fields of ceramics and other civil engineering applications.

This will elevate the status of Portland cement to a high-tech material in addition to its current status of the most widely used construction material. Very few inorganic cementing materials can match the capabilities of Portland cement in terms of cost and availability.

Introduction

As the world is growing rapidly specially in the construction industry, it is become necessary to develop smart and sustainable building materials, which will generate a minimum amount of climate-changing gases during its production.

It is estimated that a total of 4.3 billion tons of cement is produced annually worldwide with a rapid increase in demand, the production of such a huge amount of cement is associated with huge energy consumption, high cost, so it is necessary to develop alternative casings that are Cost-effective and more environmentally friendly, the introduction of a new technology for sustainable cement manufacturing methods could be an appropriate response to this necessity.

Today nanotechnology has advanced applications in the field of construction and building materials. But nanotechnology in cement on a commercial scale application remains limited with few results successfully converted into marketable products. The main progress has been done in the nanoscience of cementitious materials with an increase in the knowledge and understanding of basic phenomena in cement at the nanoscale (e.g., structure and mechanical properties of the main hydrate phases, origins of cement cohesion, cement hydration, interfaces in concrete, and mechanisms of degradation).

Recent strides in instrumentation for observation and measurement at the nanoscale are providing a wealth of new and unprecedented information about concrete and cement industry, some of which is confounding previous conventional thinking. The nanoscience and nano-engineering, sometimes called nano modification, of cement are terms that have come into common usage and describe two main avenues of application of nanotechnology in concrete and cement research.

Nanoscience deals with the measurement and characterization of the nano and micro scale structure of cement-based materials to better understand how this structure affects macro scale properties and performance through the use of advanced characterization techniques and atomistic or molecular level modeling. Nano-engineering encompasses the techniques of manipulation of the structure at the nanometer scale to develop multifunctional, cementitious composites with superior mechanical performance and durability potentially having a range of novel properties such as: self-sensing capabilities, self-cleaning, self-healing, high ductility, and self-control of cracks. Even though a huge and alluring potential of nanotechnology in civil engineering has been envisaged and enormous efforts throughout the world are being taken up to use nanotechnology in civil engineering applications, still few of grey areas need to be explored to make the technology more applicable.

Due to this, the present paper reviews the main developments in the field of nanotechnology and nanoscience research in cement, along with their implications and key findings. Further, the interest in nanotechnology concept for Portland cement composites is steadily growing. So, in this paper we discuss the most reported research work regarding application of nanotechnology in cement-based materials is either related to coating or enhancement of mechanical and electrical properties.

Some of the widely reported nanoparticles in cement concrete industries are **Titaniumdioxide (Ti02), Nanosilica (Si02), Alumina (A1203), Zr02, Carbon nanotube (CNT) nanoclay, etc**.

Currently, the most active research areas dealing with cement and concrete are; **understanding of the hydration of cement particles and the use of nano-size ingredients such as alumina and silica particles**.

In this paper we also discuss on general experimental methods like compressive stress, split tensile strength and Flexural strength that are carried out to determine strength of nanocement.

Further, we have discussed about the nanotechnology basic approaches such as top-down and bottom-up, Cement nanoparticles produced by top-down and bottom top nanotechnology concepts Nano cement manufacturing process in Iraq, waterproofing, acid resistive and self-healing qualities of nanocement.

Nano cement (Definition).

The definition of Nano cement can take the following simplified template (cement + nanomaterials (such as, Nano silica or carbon tube, etc.) = Nano cement. Nano cement is innovated to achieve the desire properties of cement.

However, we can find the Nano cement produced by another was such as mechanical activation of nuclear cement particles in the size range 2-3 μm by coating with 10 to 100 nm-thick membranes of modifier materials. More than 65% of mineral supplements such as sand, ash, slag, and tuff and polymer additives are used as modifier materials. The development of modern cement and concrete industry seeks for the improvement of the durability of the materials by the addition of required amount of nanoparticles, or nano-based structure of cement-based materials can be improved.

Frequently used nanoparticles are nano silica, nano clay, and carbon nanotubes. Improvement of durability of the materials is approached through alteration of the physicochemical properties of the binder.

In addition, usages of nano clay and carbon nanotubes can decrease the transport property, optimize microstructure, and decrease the volume instability of cement-based materials.

It has been reported that nano cement can be used to produce 500–800 brands of high-strength concretes and 1300–1500 brands of heavy-duty concretes. “US Patent on Method for producing nano-cement, and nano-cement” deals with the procedure developed to produce nano cement, which involves mechanochemical activation of dispersed grains of the Portland cement in the presence of a polymeric modifier.

They used at least 60% by wt. of sodium naphthalene sulfonate and mineral siliceous additive containing at least 30 wt.% SiO_2 and gypsum to form nano shells around cement grins. Capsules of 20–100 nm thickness are formed around Portland cement grains, which are made of sodium naphthalene sulfonate and structured by calcium cations. Subsequent to mechanochemical activation, the resultant material is ground to a specific surface area of 300–900 $m^2 \cdot kg^{-1}$.

Nano cement improves the technical quality of the Portland cement, reduces cost of production due to the use of 70 wt.% mineral additives, 1.2–2 times reduction of the fuel cost, and 2-3 times reduction of emission of NO_x, SO_2, and CO_2 per ton of cement. Nano cement has very high performance; for instance, the deflection strength of nano cement-based concrete and ordinary Portland cement-based concrete at 2-day hardening are around 6.3–7.1 MPa and 2.9 MPa with corresponding compressive strengths of 49.3–54.7 MPa and 21.3 MPa, respectively. At 28-day hardening, deflection strength improves to 8.2–8.7 MPa and 6.4 Mpa, respectively, while compressive strength improves to 77.5–82.7 MPa and 54.4 MPa, respectively.

Nanotechnology approaches.

Usually, the nanotechnology encompasses two basic approaches such as top-down and bottom-up.

The top-down approach.

Is a method of nano-scale materials processing technique through which the larger structures are reduced in size to the nano-scale maintaining their original properties without controlling the atomic-levels?

On the other ways, in the top-down method, the composite materials are deconstructed from larger structures into their smaller composite parts without affecting their original behavior. In fact, the top-down approach starts from a bulk material that incorporates critical nano-scale details. In this approach, a material can be engineered by scaling down a complex entity into its component parts.

For example, of biomaterials processing technique, the small crystals from a bulk mineralized hard tissue can be created via acid-etching. Similarly, for the case of cementitious materials processing, comminution of the microscale cement particle to the ultrafine level (350w220 nm) can be done through grinding/milling.

Bottom-up approach, also termed as ‘‘molecular nanotechnology”.

Its named also ‘‘molecular manufacturing,” in which the materials are engineered from atoms or molecular components through a process of assembly or self-assembly. Fig. 2 represents a pictorial view of top-down and bottom-up approaches for nano-scale materials processing (collected from.

It is reported elsewhere that though the most contemporary technologies rely on the ‘‘top-down” approach; however, molecular nanotechnology (bottom-up approach) holds the great promise for breakthroughs in materials and manufacturing, electronics, medicine and healthcare, energy, biotechnology, information technology, and national security as well.

In fact, the hybridization and grafting of molecules can occur easily through the bottom-up approach that may allow for the direct manipulation of the fundamental structure of materials. Currently, the precise control of crystal growth at the nano-scale and the creation of natural structures of materials based on the bottom-up self-assembly mechanisms have inspired the scientists to control the materials properties by nano-engineering/nano modification.

To date, the advances in nano-engineered concrete are based on the nano modifications of concrete structures. The basic concept of nanomodification is the bottom-up engineering, starting with engineered modifications to the nano-scale structure/phase of cement concrete with an aim to improve the bulk properties of concrete.

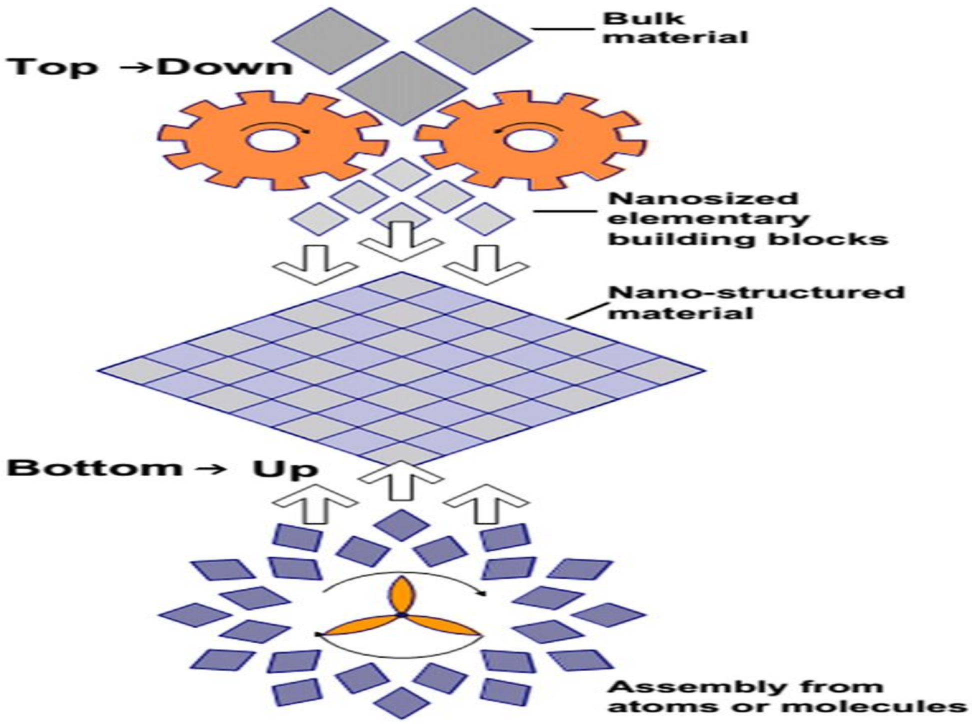

Figure 1schemactive view of top-down bottom-up nanotechnology approaches.

Nano-engineering of cementitious materials.

Nano-engineering is a quickly emerging field of science that attracts the attention of scientists toward the development of cementitious construction material with new functions and smart properties. As described in the earlier section, the nano-engineering of cementitious materials can be executed through two approaches such as top-down and bottom-up methods.

This section summarizes the impact of top-down and bottom-up nano-engineering approaches to control the properties and performances of the cementitious materials.

Nano-engineering of cementitious material by top-down & bottom-up method:

Cement nanoparticles produced by top-down nanotechnology concept.

The top-down nano-engineering of cementitious material is mainly based on the comminution of the micro-scale cement particle to the ultrafine level (**350w220 nm**) through physic mechanical crushing stated that the concrete containing <500 nm particle can be considered as a nano cement concrete.

It is reported elsewhere that the fine cement of the particle size 200e2 mm can be produced by the grinding of the cement using ball mill, vibration mill, Raymond mill, mixing mill or air-blow mill, stirred mill, and so forth It is also reported that the milling process increases the surface area of cement particles which in turn, exposes the higher surface area of cement for hydration reaction, as a result, the rate of hydration reaction can be increased.

The faster rate of cement hydration reaction leads to developing the early strength gaining capability of cement concrete that in turn, reduces the time for the building construction.

On the other hand, the increased surface area of cement particle may lead to the agglomeration of the particles.

Therefore, a special arrangement is sought for its storage and packing, consequently, the ultimate cost of the ultrafine cement may increase.

A pilot scale dry grinding of cement by the open and closed circuit tube milling method using a vertical stirred mill. They stated that the prime reason for using stirred mills is their energetic efficiency in the production of submicron particles compared to other conventional grinding systems such as ball milling.

Results of this pilot-scale investigation revealed that a more finished and comparatively smaller size (average particle size 20e25 mm) of cement particle can be produced by open and closed circuit stirred milling method. reported the setting performances of ultrafine cement (<10 mm) produced by grinding.

They stated that the substantial increment of the specific surface area of cement is achieved due to the size reduction of cement particle that in turn, accelerates the cement setting and increases the early age strength gaining capability. However, it may cause the strength retrogression at the later age.

Additionally, the wet grinding method possessed the significant potential to produce ultrafine cement as stated by. They reported a new preparation technology for producing wet-ground fine cement (WFC). The maximum size of cement particles in the slurry is not bigger than 40 mm and the average size (50% by weight) is less than 10 mm after using wet-ground technology.

In fact, wet-grinding was first reported in Japan to prepare the slurry of fine cement (called WMC method). OPC was ground by a drum attrition mill to decrease the particle size in grouting fields. In this technology, the produced particle size depends on the milling time and thus, the longer milling time produces the finer cement particles. As the particle of cement becomes fine, therefore, there is a possibility of agglomeration. Hence, by avoiding package and storage designed especially for fine cement, WMC technology had been applied in many grouting projects.

Though the numerous research investigations were executed for producing ultrafine cement using top-down physic-mechanical grinding approach, however, very few investigations can able to produce nano-scale cement particles. Hence, with the aim to produce ultrafine (submicron) cement using the physic-mechanical crushing (top-down) method, bead milling technique was used by.

The following summarizes the effect of bead milling process (considered as top-down nanotechnology approach) to produce ultrafine cement of the particle size 220 nm from the ordinary Portland cement of 10e30 mm particles as a case study.

Nano-engineering of cementitious material by bottom-up method

Nano-engineering of cement concrete materials is a quickly growing field that usually refers to the modification of cement concrete composites at the nano-scale level with the help of bottom-up nanotechnology concept. In fact, the bottom-up nano-engineering can be done either by the direct modification of cementitious materials and hydrates using nano additives and/reinforcements or assembling the molecules at the nanometer scale of materials that in turn, finally develop a superior concrete by controlling the concrete properties, performance, and degradation processes and providing the material with new functions and smart properties.

Though the hybridization and grafting of molecules allow for the direct manipulation of the fundamental structure of cement phases that may lead to providing the superior properties and performances of concrete; however, these techniques are still difficult for the concrete science and engineering field.

The Nano-scale concrete engineering can take place in three locations, i.e., in the solid phases, in the liquid phase, and at interfaces, including liquid solid and solid-solid interfaces.

It is reported that the nano-engineering of cement-based materials possesses tremendous potential to control the properties of concrete, nonetheless, several challenges are still needed to be solved for realizing its full potential, including the proper dispersion of the nano-scale additives, scale-up of laboratory results and implementation on larger scale, and a lowering of the cost-benefit ratio.

The following some nano modification of cement-based materials using nano additives, nano-reinforcements, and nano-scale hydrate hybridization have been discussed, including a case study for the hydrothermal production of an alternative cementitious material (nano cement) with nano-scale particle size.

Nano cement manufacturing process in Iraq.

The production of Nano cement from sand & clinker is performed by mixing mineral supplement additions such as fly ash and slag or silica sand with crushed and grinded clinker or cement. Before processing into the mill which is shown in **Fig. 2**, the moisture content of the mixture must not exceed 3%.

This is achieved by making the mixture passing through a drying unit attached to the production unit. The mixture is grinded for 30 to 40 min in the mill. Finally, nano cement is produced as the output of chemical reaction of clinker particles with a modifier.

As shown in Fig. 2, the production process of nano cement begins with adding a tone of grinded Portland cement or clinker to a tone of materials comprising sand or silica sand and polymeric modifier such as sodium naphthalene (FDN – 05) in dry form (polymeric modifier of 0.6%–2.0% and silica sand additive).

Then, mineral supplements are added in a form of nuggets (300 mm in diameter) and gypsum of 5% to 6% moisture content (0.3%–6.0% gypsum rock). The output of the process is two tons of nano cement. Consequently, the cost of consumed fuel per a tone of cement is reduced considering the required cost for the additional grinding and energy.

Details of processing line to produce nano cement on the base of cement clinker processing are shown in Fig. 3. Raw materials except the modifier are weighted and mixed and processed to the Bin feeder. Then homogenizing and modifier addition take place before feeding the mixture into the Ball mill where grinding is performed to produce nano cement. The dust generated due to the process is cached and controlled by the fabric filter.

Figure 2 Nano cement factory machinery in Iraq-Kufa;a

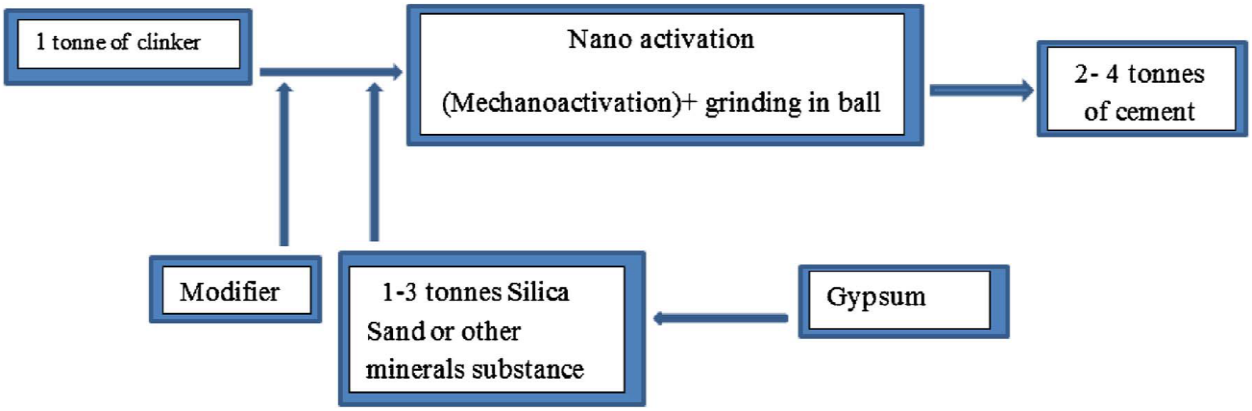

Figure 3 Production of Nano cement processing in Iraq-Kufa'a

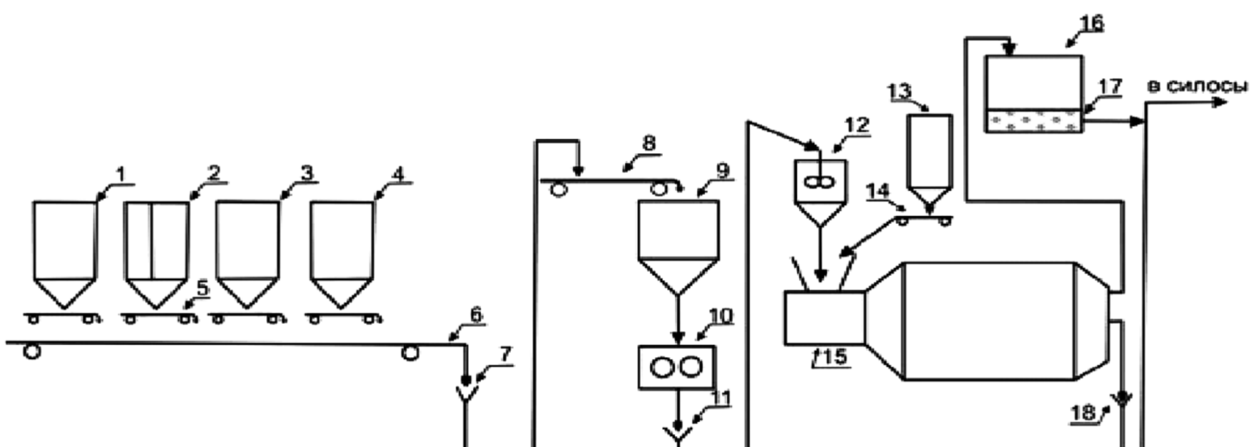

Figure 4 Production of Nano cement machinery stages in Iraq-Kufa'a

Advantages of producing Nano cement in Iraq.

The following advantages can be achieved by producing and using nano cement:

• Increase of cement production without building a new plant.

• Utilization of local raw materials such as silica sand, damped wastes slag or fly ash in new production and usage of semi-finished clinker as raw material.

• Because of increased fineness of cement, concretes develop super high strength, high resistance to water, sulfate, chloride and acids. This enables construction of complexes civil engineering and architectural members such as thin membranes, supporting columns, beams, large-span structures, tubing, concrete frames and bridge structures. The effect of nano cement improves the impermeability of concrete that will eventually increase of service life of structures.

• Possible reduction in the ratio of reinforcement by 30–50% due to the use of strong and super strong concretes.

• Achieving compressive strength of 60–70 MPa within 24 h and 70% of 28-day strength of concrete within 72 h. Thus, the economic benefit can be achieved through reduction of form release time and significant reduction of overall construction time of the project.

The proposed project of Nano-cement factory in Iraq AlKufa'a.

In this project, the use of nanotechnology is proposed to produce nano cement through establishing a new line of production. within Alkufa Cement factory in Iraq.

This choice was made because the raw materials for manufacturing nano cement are available in the vicinity of the factory. The other necessary resources such as land, water, electricity etc. are also available for the establishment of the extended production line. Alkufa Cement factory is a part of the Southern Cement State Company which was established in 1977. The head office of the company laid in Al-Najaf Governorate, about 7 km from the city of Kufa.

The company owns several plants in the Southern region of Iraq. Each plant has four production lines with annual capacity of 1781000 t of cement. The factory produces ordinary Portland cement which conforms with the Iraqi Specifications No. 5/1984 as well as the requirements of the Ministry of Industry and Minerals.

In August 2010, the factory was awarded Certificate of Quality by the Ministry of Planning and Development cooperation central agency for standardization and quality control.

Raw **materials and cost** used to produce Nano cement in Iraq.

Different Supplementary materials can be used to produce nano cement depending on what is available in the region of production.

For instance, sand is used in deserted countries while fly ash and furnace slag are used in industrial areas where industrial salvage is available. Iraq is a country which is rich in silica sand that usually exists in a form of white rock containing a high ratio of silica (up to 99% SiO_2).

In this study, therefore, silica sand is used as a Supplementary material. Ardima sand quarry is selected as a site to supply the raw material because it has sand of a high level of silica and it is the nearest location to Alkufa Cement factory (about 100 km). The clinker will be supplied from Alkufa Cement factory. Tables 1 and 2 present the properties of Ardima province sand and Alkufa's cement.

They conform with specified properties of nano cement raw materials as described by Ikhlef . The modifier, sodium naphthalene sulfonate (FDN–05) with density varying from 0.78 to 0.88 gm/cm3 will be imported from Russia. This type of modifier has been used for producing nano cement e.g. Abu Dhabi National Cement Factory. The gypsum with minerals will be brought from the markets of Najaf.

Table below shows the quantities and costs of raw materials used to produce a tone of Nano cement including transportation cost. Based on cost of materials in Iraqi market at the time of this study, the total cost of raw materials will be US$ 58.75 per ton.

Table 1 Cost of Raw materials for 1 tone of Nao Cement

No.	Type	Quantity	Cost US$/unit	Total Cost(US$)
1	Clinker	750	0.065	48.75
2	Sand Silica	250	0.04	10
3	Gypsum and mold fiber	26.5	0.0003	0.00495
Total cost				58.75

Table 2 Properties of Alkufa Portland cement

Parameters	**Range**
Lime saturation coefficient	0.9–1.0
Magnesium oxide (MgO)%	1.5–2.5
SO3 Content%	2.2–2.6
Loss on ignition%	2.5–3.5
Insoluble residue%	0.5–1.2
Fineness (m2/kg)	325–340
Initial setting time (min)	125–180
Final setting time (hr)	3–3.7
(mm) Le-Chatelier soundness	0–2

Feasibility of producing nano cement in a traditional cement factory in Iraq.

It is estimated that a total of 4.3 billion tons of cement is produced worldwide annually with a rapid increase in demand. The production of such a huge quantity of cement is associated with enormous energy consumption, significant cost and greenhouse gas emissions to the environment.

It is therefore necessary to develop alternative binders which are cost effective and more environment friendly. Introducing a new technology to cement manufacturing methods that are consistent with the principles of sustainability can be a proper response to this necessity.

Using nanotechnology for producing nano cement may be considered as a potential approach in this regard. This technology of manufacturing can be achieved by increasing the specific surface area of cement by producing cement particles of nano scale i.e. the particle of size less than 100 nano meter. Increasing the surface area increases the chemical reactivity and nucleation effect, thus improving strength and durability of concrete with less quantity of cement.

The grains of Nano cement are covered by solid shells in the process of grinding (mechanical activation). The shell is a capsule with thickness of several tens of nanometers of modified polymer compound, which imparts a radically new quality to Portland cement and concretes. Nanotechnology can help to overcome major environmental challenges by reducing CO2 emissions and produce cement of better quality. With the use of this technology, the amount of carbon dioxide emitted from cement factories is reduced significantly through reduction of the quantities of produced cement. The technology has also been used for producing cement of better properties as a result of incorporating various nanomaterials such as Silicon Dioxide nanoparticles (SiO_2), nano-$CaCO_3$, Carbon nanotubes composite fibers, and Aluminum Oxide nanoparticles (Al_2O_3).

The nanomaterials are mainly used to enhance various mechanical properties of the cementations materials: crack resistance, corrosion resistance, tensile strength and compressive strength.

Since 2001, an increased number of researches have been conducted indicating that nanotechnology is a potential alternative to the traditional cement production methods [25–29]. Thus, there is a technical possibility of adopting nanotechnology in cement production.

However, in addition to the ongoing scientific research, it is also necessary to study the economic aspects of this alternative in order to evaluate its cost effectiveness. This paper presents a study evaluating the suitability of introducing nanotechnology through the establishment of nano cement production line within a traditional cement factory. The economic feasibility of establishing a production line of nano cement within the Alkufa cement factory of Iraq, using the silica sand, has been studied.

The results of this study confirms that the establishment of nano cement production line within existing cement factory is feasible.

The new product can reduce the unit price of cement by US$25 and improve the quality of the cement.

The calculated NPV, IRR and BEP indicate that the proposed project is feasible with the advantage of low risk. Considering the project is sensitive to the inflation rate, increasing the cash flow by 1% will lead to rise in IRR to reach 28.5% or more.

Hence, the project is economically feasible. As the expected IRR is 26.8%, there will be encouragement for the establishment of the project. It was also determined that from calculation of the breakeven point, the factory can make a profit if the sale rate is at least 250,000 t per year. The payback period is between 1 and 3 years. In addition, the current demand for cement gives a strong indication that all of the produced quantity will be sold. In order for the project to be profitable, the proposed production line should sell an amount of nano cement larger than 800000–900000 t. This means that the production line starts to make profit, approximately, when its production reaches 17.3% of the planned productivity within 1–3 years. The use of nanotechnology can increase the annual volume of cement production without construction of new cement plants.

Types of Cement Nanoparticles used to produce Nano cement;

Nano cement made with Portland cement in which particle sizes ranging from a few nanometers to a maximum of about 100 micrometers and in Nano ingredients with at least one dimension of nano meter size. The various constituents of Nano cement are as shown in Figure.3 So the particle size has to be reduced in order to obtain nano-portland cement. Further, if these nano-cement particles are processed with nanotubes and reactive nano-size silica particles, then strong, tough, more flexible, cement can be developed with enhanced properties. However, there are different types of Nano cement according to the production methods (cement + nanoparticles) and properties such as:

- Carbon Nano-tube.
- Nano-silica: Nano-Sio2
- Nano-Alumina: Nano-Al2o3.
- Nano-Iron: Nano-Fe2o3.
- Nano-Montmorillonite.
- Zinc Nano-oxide.
- Copolymer nanoparticles.

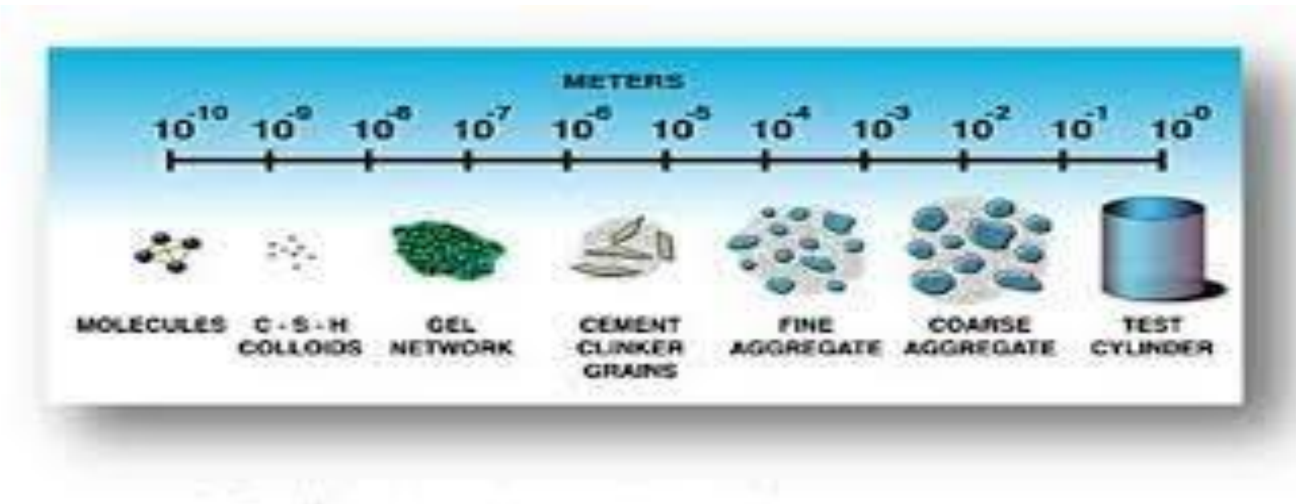

Figure 5 Particle sizes

However, in this paper we will discusses the latest researches about nanoparticles in cement concrete industries are based on Titaniumdioxide (Ti02), Nanosilica (Si02), Alumina (A1203), Zr02, Carbon nanotube (CNT) and nanoclay.

Nano-silica Di Oxide.

Current research activity in concrete using nano cement and nano silica includes:

(i) Characterization of cement hydration.

(ii) Influence of the addition of nano-size silica to concrete.

(iii) Synthesis of cement using nano particles and coatings (applied to protect concrete).

In order to utilize these unique advantages, many researchers have attempted to improve the behaviors of cementitious matrix by incorporating nano silica. Especially the Nano silica in concrete or mortar will increase the density, reduces porosity, and improves the bond between cement matrix and aggregates with higher compressive and flexural strength. The compressive strength evaluation of cement mortar with nano silica fume was discussed for different w/c ratio. From the experimental results it is confirmed that the compressive strength of mortars with nano Silica were higher than those of mortars containing silica fume at 7 and 28 days. Figure 4 shows how the mineral additive takes in the cement constituent and nano-Si02. It was proved from the earlier studies by Qing et.al that the enhancement of strength mainly depends on nS addition rather than addition of silica fume. Also, it was found that the nS behaves not only as a filler to improve the microstructure, but also as an activator to promote pozzolanic reactions and super-plasticizer plays an important role during mixing cement with nano particles.

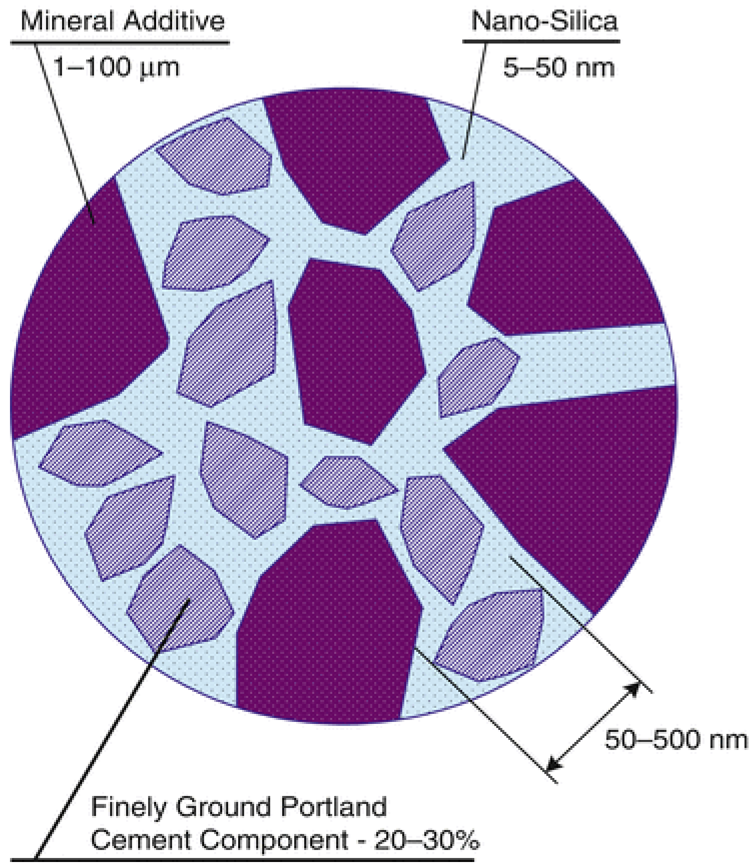

Figure 6 Macroscopic pictures drawing showing the Nano silica effect to fill he caps in concrete

One of the researchers studied and proved the effect of silica nano particles on the reduction of calcium leaching rate of cement paste and it was concluded that addition of nS can control the C-S-H degradation due to calcium leaching and can increase the overall strength of cement-based materials at every stage.

Nano Silica was mostly used in making Self Compacting Concrete and High-Performance Concrete. Normally those two concretes can be named as eco-concrete.

The Eco-concretes are mixtures where cement is replaced by waste materials mainly sludge ash, incinerated sludge ash, fly ash or other supplementary waste materials. The main problem in these types of eco-concrete is segregation. By adding nS in the corresponding mixtures and accelerates setting time and compressive strength of concrete. Nano silica is used for the preparation of rock-matching grouting, gypsum particle board, additives in tile, workability increaser, anti bleeder etc. demonstrated the effect of addition of nS in high volume fly ash concrete and the results are compared with control concrete.

Nano Titanium Di Oxide;

Researchers conducted the studies on the compressive-, split tensile- and flexural, strength, and workability and setting time of concrete by partial replacement of cement with nano-phase Ti02 particles.

Similar to investigations on nano Si02 in cementations matrix, many researchers have discussed the possible methodologies and observed advantages by using nano Ti02 in cement matrix specially to achieve high compressive- and flexural- strength. Jayapalan investigated the effect of chemically Ti02 nanoparticles on early-age hydration of cement and the effects of different percentage rates of added Ti02 to Portland cement on early-age behavior were examined.

Nano Aluminum Di Oxide

The role of Nano A1203 in increasing the mechanical properties of cement has been carried out by few researchers.

The optimized level of usage of nano particles to attain the ultimate strength was reported. The effect of curing medium on microstructure together with physical, mechanical and thermal properties of concrete containing A1203 nano particles was explored by Nazari and Riahia . Further, Campillo et al emphasized the potential of nano materials for activation of the initial strength of behte cements.

In this study two types of A1203 based nano materials such as an agglomerated dry alumina (ADA) with an average grain size ranging from 0.1 \xm (100 nm) to 1 |im and colloidal alumina (CA) composed of 50 nm alumina nanoparticles dispersed in water was used for the activation of early strength of be lite cements.

The study concluded that an addition of nano particles notably increases the early strength (7 days) and the nano particle can be used as an agent for activating hydraulic properties of belite cement thereby changes in microstructure causes improved mechanical property.

The effect of Nano A1203 on elastic modulus and compressive strength of the cement composites was brought out by Li et al . The role of nano particles as a fine aggregate was confirmed through SEM and EDS study stating that the nano A1203 fill the ITZ of cement- sand and some capillary in the matrix and hence the elastic modulus and compressive strength of mortars were increased. But, no significant improvement in compressive strength was noticed due to insufficient filling of pores in the cement matrix under experiment condition.

Nano Zirconium Di Oxide

Researchers investigated the possibility of increasing split tensile strength of self-compacting concrete (SCC) by adding Zr02 nano particles.

The results showed that inclusion of Zr02 up to 4 wt% was able to increase the split tensile strength of SCC due to the formation of more hydrated products in presence of Zr02 nano particles and improvement in pore structure. Further, Nazari et al investigated the compressive strength and workability of concrete by partial replacement of cement with nano-phase Zr02 particles.

Further it was observed that the addition of nano-Zr02 particles decreased the fluidity and increased the water demand for normal consistency. Therefore, the use of super-plasticizers was insisted while adding Zr02 nano particles. A significant improvement in compressive strength was achieved. Same researchers studied the split tensile- and flexural- strength together with the setting time of concrete by partial replacement of cement with nano- Zr02 particles.

Nano Ferrous Oxide

Researchers conducted studies on the compressive strength and workability of concrete by partial replacement of cement with nano-phase Fe2O3 particles and results were compared with control specimen. A significant achievement in high compressive strength has been obtained and also decrease in workability has been seen in presence of nano particle blended concrete.

Earlier investigations suggest that inclusion of nano-phase Fe2O3 particles in cement improves the properties hke spht tensile- and flexural-strength together with the setting time of cement.

A delay in setting time was observed in nano particles blended concrete. The optimized level of usage of nano particles to attain the ultimate strength was reported. Mechanical properties such as compressive- and flexural- strengths of cement mortar containing nano particles such as nS and Nano Fe2O3 (hybrid incorporation) were studied and their impressive results (improvement in both compressive and tensile strength) were reported by Li et.al and the smart behaviors of nano Fe2O3 in self-stress sensing was also observed which can lead to a paradigm shift in techniques for health monitoring of structures.

Carbon Nano-Tube.

Carbon Nano-materials, especially Carbon Nanotubes (CNT) and Carbon Nanofibers (CNF), are two of the most prospective advanced materials for application in cement-based products for the construction industry, due to their excellent material properties. As a test, two mechanical properties, 28-day compressive strength and flexural strength, of CNT and CNF cement composites were investigated herein.

The flow value of fresh mortar composites and Scanning Electron Microscope (SEM) images of hardened mortar samples were also explored. Composites with 0.1% and 0.2% of CNT and CNF and water/cement ratios of 0.35 to 0.5 were utilized, together with appropriate sonication techniques, based on the results from a previous study. Both CNT and CNF composites demonstrated significant increase in compressive strengths, as compared to plain mortar control samples (maximum 154% for CNT and 217% for CNF samples).

The flexural strengths were also enhanced, although not at the same level as compressive strengths (maximum 53% for CNT and 50% for CNF samples). Water/cement ratios in the range of 0.35-0.4 were found to produce the higher strengths, together with a 0.1% dosage rate for the CNT/CNF. Statistical analysis of the test results showed the significance of the enhanced strengths.

It seemed that the CNT was better dispersed in the cement matrix than the CNF, because a correlation between the flow test results and the compressive strengths was detected for the CNT samples. SEM (Scanning Electron Microscope) images showed fair to good dispersion of CNT/CNF in the hardened samples.

Nano clays.

Nano clay raw material is montmorillonite; a 2-to-l layered smectite clay mineral with a platey structure.
The Naturally occurring montmorillonite is hydrophilic. Through clay surface modification, montmorillonite can be made organophilic and, therefore, compatible with conventional organic polymers. Nanoplate fillers can be natural or synthetic clays, as well as phosphates of transition metals.

The most widely used reinforcement is clay due to its natural abundance and its very high form factor. The Clay-based nanocomposites generate an overall improvement in physical performances. The most widely used ones are the phyllosilicates (smectites).

They have a shell-shaped crystalline structure with nanometric thickness. Clays are classified according to their crystalline structures and also to the quantity and position of the ions within the elementary mesh. The elementary or primitive mesh is the simplest atomic geometric pattern, which is enough for duplicating the crystalline network, by repeating itself indefinitely in the three directions.

The most common usage concerns organ modified Montmorillonite (MMT), a natural phyllosilicate extracted from Bentonite. Raw formula of Montmorillonites (Na, Co) 0, 3(AZ, Mg) 2Si4O10 {OH) 2, nH20.

Applications of Nano-Engineered Cementitious Composites

The Nano-engineered cementitious composites have great potential in practical applications for infrastructures such as oil well, high-rise buildings, large-span bridges, tunnels, high-speed railways, offshore structures, dams, and nuclear power plants. At present, they still stay at the research stage and only countable applications have been put into practice. Therefore, there should be some profound investigations focused on the application of Nano-engineered cementitious composites.

Better understanding the properties/performances of the Nano-engineered cementitious composites and their members/structures is a fundamental approach to explore their potential applications. Furthermore, even at very low rates of addition, current prices of some Nano-engineered composition materials (e.g., Nano-cement, carbon nanotubes, and carbon nanofibers) are high enough that the production of significant structures is cost prohibitive. For some types of Nano-engineered composition materials adopted in previous researches (e.g., graphene), even with large reductions in their prices, the resulted Nano-engineered cementitious composites are most likely to be used in niche application. Some novel retrofits of Nano-engineered cementitious composites should be developed based on their superior performances and the actual demands. For example, the Nano-engineered cementitious composites can be developed into important structural elements or used in key positions of significant engineering infrastructures.

Effects of Nano Particles on some Cement Types and Performances:

1- EFFECT OF NANO-SILICA ADDITIONS IN, BLENDED CEMENTS OVER ORDINARY CEMENT FOR, BOTH SHORT & LONG TERMS.

The Nano additions improve the performance for all types of cements and the optimizations for Nano materials are nS=0.75%, for OPC, 1% for PPC & 0.5% for PSC. In the long term strength, some contradictions were noticed for which the reasons are not clear.

For long term it is noticed that with slightly increasing the % of Nano materials above that of the optimized one, yielded maximum strength gain.

Also it may be pointed out that the presence of Fly ash prohibits these abnormalities & certain consistencies in optimization results of PPC with nS additions, was observed. Further research on micro structural studies is necessary for characterization of Nano materials.

2- EFFECT OF NANO-CEMENT ON THE HYDRATION AND MICROSTRUCTURE OF PROTLAND CEMENT

(1) The reaction between nano-SiO2 and Ca(OH)2 started within 1 h, and the reaction rate was faster in the three-day period, and the C–S–H gel was formed. Nanomaterials 2016, 6, 241 14 of 15

(2) When the content of nano-SiO2 was 3%, the compressive strength increased by 33.2%, 29.1%, and 18.5% at three days, seven days, and 28 days, respectively. The compressive strength increased by 44.9%, 29.7%, and 10.6% at 3 days, 7 days, and 28 days, respectively, when the dosage of nano-SiO2 was 5%. Nano-SiO2 had the most obvious effect on compressive strength at 3 days, followed by 7 days and 28 days. Taking this into account, 3% was the best dosage of nano-SiO2.

(3) Nano-SiO2 promoted the hydration heat of cement paste. The effect was obvious when the dosages of nano-SiO2 were 3% and 5%, and the heat release rate of hydration heat of the second exothermic peak was increased 0.002 W/g, 0.003 W/g respectively. The second exothermic peak appeared approximately 2.5 h earlier. The cumulative heat release of the paste increased with the adding of nano-SiO2.

(4) The content of Ca(OH)2 of cement paste with 3% nano-SiO2 was decreased by 0.27%, 0.82%, 2.24%, and 3.95% at one day, three days, seven days, and 28 days, respectively. The Ca(OH)2 diffraction peak intensity increased by 32.24% and 13.07%, but the tricalcium silicate (C3S) and dicalcium silicate (C2S) diffraction peak intensity increased by 31.40% and 3.24% at three days and 28 days, respectively. The addition of nano-SiO2 promoted the formation of C–S–H gel, and the promotion effect mainly occurred in three days.

(5) The total porosity of cement paste decreased 2.21%, 5.51%, 2.95%, and 5.4% at one day, three days, seven days, and 28 day, respectively, when the dosage of nano-SiO2 was 3%.

Nano-SiO2 optimized the pore structure of cement paste, and much-detrimental pores and detrimental pores decreased while less harmful pores and innocuous pores increased.

3- NANO-SLICA SOL-GEL AND CARBON NANTUBE COUPLING EFFECT ON THE PREFORMANCE OF CEMENT-BAESD MATERIALS.

In this study, damping properties were first investigated to study the influence of NS on the interactive behaviors between MWCNTs and cement matrix. Addition of NS to MWCNT-reinforced cement composite is proposed as an effective way to improve the interactive behaviors in the interface. The effect of NS on MWCNT dispersion in aqueous suspension was characterized using UV-Visible spectroscopy. Hydration heat and morphology were also investigated to demonstrate the nucleation effect and interface of MWCNTs. Damping properties were evaluated with a DMA test to demonstrate the energy dissipation capacity of MWCNT/cement composite. The following conclusions were drawn:

(a) For MWCNT dispersion in NS gel, the optimal dosage of MWCNTs in this study is 0.02% by

weight of cement;

(b) Addition of NS does not affect the dispersion of MWCNTs in aqueous suspension;

(c) NS absorbs on the surface of MWCNTs and promotes the formation of hydration products on the surface of MWCNTs;

(d) NS improves the interfacial adhesion between MWCNTs and cement matrix, leading to higher loss modulus and improved energy dissipation ability. The property enhancements in the MW0.24-NG sample were 48% and 66% higher than in the MW0.24-W and MW0-W samples, respectively.

4- EFFECT OF NANO-SIO2, NANO-TIO2 ADDTION ON FUILD LOSS IN OIL-WELL CEMENT SLURRY.

A number of tests were successfully conducted to examine the helpfulness of NS, NT and NA nanoparticles and their combined effects on fluid loss in oil-well cement. Based on the investigational outcome, the following are our conclusions;

1. Designing of conventional cement slurries without any additional filtration control agent causes much water to be lost from the set-cement, thereby affecting
other characteristics of the slurry such as viscosity, thickening time and compressive strength.

2. Additional of NS, NT and NA nanoparticles control the out-flow of fluid from the slurry, and its performance varies with temperature and the nanoparticles dosages. The ratio of 3% NS reduced the filtration loss more significantly compared to other single nanoparticles. However, excessive amount of NS decreases the slurry fluidity.

3. By comparison regarding the combined of effect of nanoparticles, the binary combination mixtures containing NST demonstrated the superlative results likened to other binary groups followed by ternary combination of NSTA samples. The highest rate of the blended cement to trap its liquid phase was found at a dosage of 4% nanoparticles. This indicates that the efficiency of the oil-well cement slurry containing nanoparticles to retain water depends intensely on the concentration of the nanoparticles.

4. In summary, by relating all the examined samples containing nanoparticles, NS provided the best performance in controlling fluid loss. The optimal ratio of NS in the blended cement system was 3%.

Nano cement Test Methods.

To test the hardness of the cement, the following simple tests have been conducted are given below, which include:

(a)Test for Compressive strength.

(b) Test for Split tensile strength.

(c) Test for Flexural strength.

Based on the experimental studies presented in the paper, it was concluded that the Compressive and tensile strength of the cement mortars with Nano clay is higher than that of the plain cement mortar with the same w/b ratio. Further, the enhancement of compressive strength was about 300% at 1% NC Nano clay replacement and is about 290% at 2% NC for seven-day testing. While for 28 days testing it was 310% for 1% NC and 200% for 2% NC.

Figure 7 Batch of cub Specimens casted

Compressive Strength

Concrete cubical molds of size 15 cm x 15cm x 15 cm are commonly used (Figure 7). The concrete is poured in the mold and tempered properly so as not to have any voids. After 24 hours these molds are removed and test specimens are put in water for curing. The top surface of these specimens should be made even and smooth. This is done by putting cement paste and spreading smoothly on whole area of specimen.

The specimens are tested by compression testing machine (Figure 6) after 7 days curing or 28 days curing. Load should be applied gradually at the rate of 140 kg/cm2 per minute till the Specimens fails. Load at the failure divided by area of specimen gives the compressive strength of concrete (Figure).

Figure 6: Specimen Tested for Compressive Strength

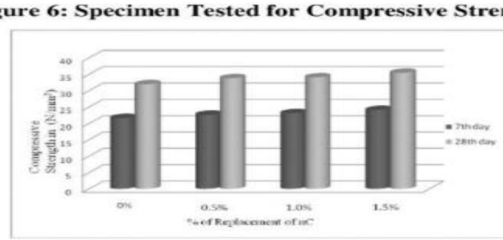

Figure 7: Compressive Strength of Concrete with and without nC (0 - 1.5 %) [36]

Figure 8 Specimen Tested for compressive Strenth

Split Tensile Strength

The concrete is fill in the cylinder mold in four layers each of approximately 75 mm and ram each layer more than 35 times with evenly distributed strokes. Remove the specimens from the mold after 24 hours and immerse them in water for the final curing.

The test is usually conducted at the age of 7-28 days. Apply the load without shock and increase it continuously at the rate to produce a split tensile stress of approximately 1.4 to 2.1 N/mni2/min Compute the split tensile strength of the specimen to the nearest 0.25 N/mm2 (Figure 8).

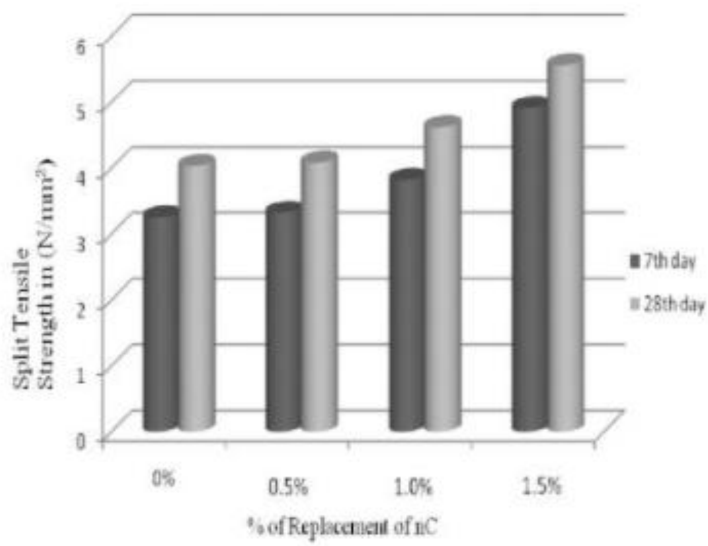

Figure 8: Split Tensile Strength of Concrete with and without nC (0 – 1.5 %) [36]

Figure 9 Tensile Strength of concrete with and without nC (0-15%)

Flexural Strength

Beams shall be fabricated in sets of three (3) beams for each test age. Before each use, apply a release agent such as a light coat of fresh oil to all inside surfaces of the mold. Place the concrete in the molds. Vibrate the concrete.

The duration of vibration required will depend upon the workability of the concrete and the effectiveness of the vibrator. Cover the beams with an insulating blanket to hold the heat and moisture in the beams while they cure. Apply the load continuously at a rate that constantly increases the extreme fiber stress from 0.85 MPa to 1.2 N/mm2/min, until rupture occurs (Figure 9). The average of these three Specimens is listed.

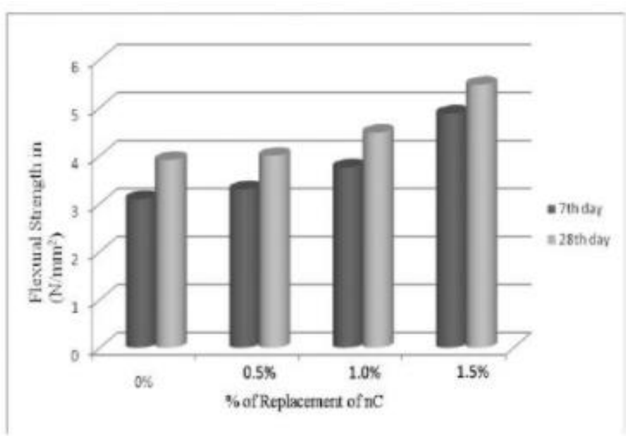

Figure 9: Flexural Strength of Concrete with and without nC (0 – 1.5 %)

Figure 10 Flexural Strength of Concrete with and without nC (0-15%)

The nano Clay based concrete structure fill all micro holes, because it's thousand times smaller than in the case of traditional concrete materials. This allows the reduction of the cement used and gives the compression needed to reduce over 90 % of the additives used in the production of concrete.

Core concrete allows saving some percentage of the used cement. The use of nano Clay help in modifying properties of concrete both in plastic and hardened stage and thus results into a more durable concrete. It has been recognized that the addition of small, closely spaced and uniformly dispersed nano Clay to concrete would act as crack arrester and would substantially improve its static and dynamic properties. Addition of nano Clay enhances the ductility performance, post-crack tensile strength, fatigue strength and impact strength of concrete structures.

The main purpose of this investigation is to study the effects of nano Clay on the workability, compressive strength, spilt tensile and flexural strength of M20 grade concrete.

For comparison, reference specimens were tested. Experimental results show that the workability of concrete reduces with the addition of nano Clay in concrete and also the results show that the nano Clay concrete specimen's gives higher compressive, split tensile and flexural strength.

SELF HEALING PROCESS IN CONCRETE WITH NANO CEMENT

Experimentation is also underway on self-healing concrete USING NANOCEMENT. When self-healing concrete cracks, embedded microcapsules rupture and release a healing agent into the damaged region through capillary action.

The released healing agent contacts an embedded catalyst, polymerizing to bond the crack face closed. In fracture tests, self-healed composites recovered as much as 75 percent of their original strength.

They could increase the life of structural components by as much as two or three times. When cracks form in this self-healing concrete, they rupture microcapsules, releasing a healing agent which then contacts a catalyst; triggering polymerization that bonds the crack closed Figure 10.

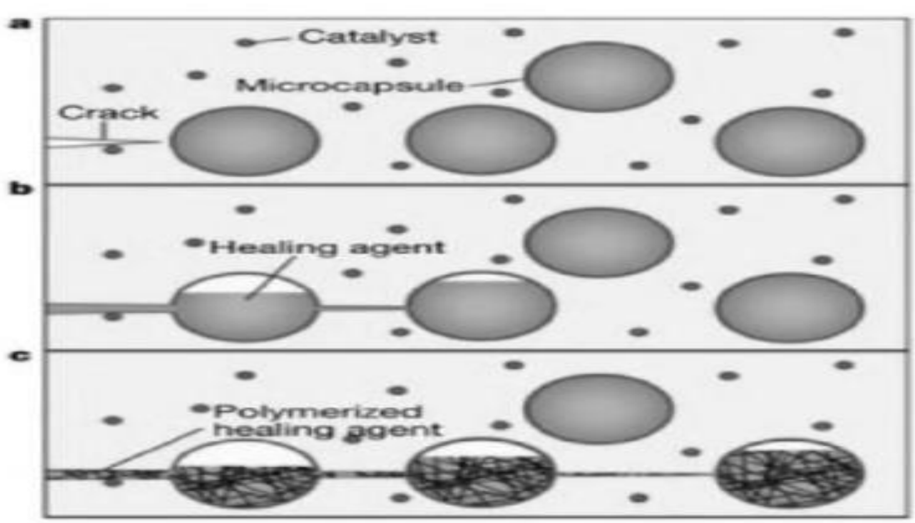

Figure 10: Mechanism of Self Healing Concrete [36]

Figure 11 Mechanism of Self-Healing Concrete

The compressive strength results of series CO and N mixtures are shown in Comparison of the results from the 7-, 28- and 90-days samples shows that the compressive strength increases with nano-Zr02 particles chemical up to 1.0% replacement (N2) and then it decreases, although the results of 2.0% replacement (N4) is still higher than those of the plain cement concrete (CO). It was shown that the use of 2.0% nano-Zr02 particles decreases the compressive strength to a value which is near to the control concrete. This may be due to the fact that the quantity of nano-Zr02 particles (pozzolan) present in the mix is higher than the amount required to combine with the liberated lime during the process of hydration thus leading to excess silica leaching out and causing a deficiency in strength as it replaces part of the cementitious material but does not contribute to strength. Also, it may be due to the defects generated in dispersion of nanoparticles that causes weak zones.

ACID RESISTANCE NANOCEMENT

The risk of acid attack on concrete can be minimized by providing due consideration to concrete porosity. Lesser the porosity, lesser will be the chances of acid attack on concrete.

In general, it is said that all high-performance concrete mixtures show a better resistance against acid attack than the reference ordinary type concrete. By High performance concrete is meant a concrete with superior qualities including low permeability and low diffusion. In another way, the concrete resistance to acids can also be provided by giving its surface an acid resistant coating. In construction materials, the materials density and strengths are the most important properties in which the experts are interested.

The High-performance concrete is quite effective against acid attack. However, it is a common observation that materials having high strengths are also associated with higher densities and thus the dead weight of the structure considerably increases.

Conclusions

The role and mechanism of the nano particles of various oxides with cementitious materials have been reviewed and discussed in detail. Most of the authors concluded that inclusion of nano particles will impart more uniform and compact microstructure inside the concrete. The improvement in mechanical properties such as compressive-, flexural- and split- tensile strength of concrete containing nano particles have been reviewed by several researchers.

According to researchers, following is a list of areas, where the construction industry could benefit from nano-technology.

1- Replacement of steel cables by much stronger carbon nanotubes in suspension bridges and cable-stayed bridges.
2- Use of nano-silica, to produce dense cement composite materials.
3- Incorporation of resistive carbon nanofibers in concrete roads in snowy areas.
4- Incorporation of nano-titania, to produce photocatalytic concrete.
5- Use of nano-calcite particles in sealants to protect the structures from aggressive elements of the surrounding environment.
6- Use of nano-clays in concrete to enhance its plasticity and flow ability.
7- Urban air quality could be improved by if the civil structures are treated with nano Ti02.

8- The nano-particles act as filler and increase the density by filling the micro-voids between cement grains.

9- The well-dispersed nano-particles act as crystallization booster to the cement hydrates, therefore accelerating the hydration process.

10- The nano-particles improve the structure of the aggregates contact zone, i.e. the interfacial transition zone between aggregates and mortar, resulting in a better bond between aggregates and cement paste.

11- The crack arrest and interlocking effects between the slip planes provided by the nano-particles improve the toughness, shear, tensile and flexural strength of cement-based materials

Although, several studies are reported, there is no clear mechanism on the Form-Structure-Function of materials as it's intended to use them in cement or concrete.

Further, the manufacturing of nano cement in Iraq confirms that the establishment of nano cement production line within existing cement factory is feasible.

The new product can reduce the unit price of cement by US$25 and improve the quality of the cement.

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