The Islamic University Gaza
Higher Education Deanship
Faculty of Engineering
Civil Engineering Department
Design and Rehabilitation of Structures Program

الجامعة الإسلامية بغزة
عمادة الدراسات العليا
كلية الهندسة
قسم الهندسة المدنية
برنامج تصميم وتأهيل المنشآت

M.SC. THESIS

The Effect of a Group of Nano Materials on the Mechanical Properties of Fresh and Hardened Concrete

تأثير مجموعة من المواد المالئة على الخواص الميكانيكية للخرسانة الطازجة والمتصلبة

Researcher

Bassam S. Dabbour

Supervision

Dr. Mohammed Arafa

Dr. Mamoun Alqedra

A Thesis Submitted in Partial Fulfillment of the Requirements for the Master Degree in Design and Rehabilitation of Structures at the Islamic University Gaza

September

1435-2014

إقـــــــــرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

The Effect of a Group of Nano Materials on the Mechanical Properties of Fresh and Hardened Concrete.

أقر بأن ما اشتملت عليه هذه الرسالة إنما هو نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وإن هذه الرسالة ككل أو أي جزء منها لم يقدم من قبل لنيل درجة أو لقب علمي أو بحثي لدى أي مؤسسة تعليمية أو بحثية أخرى.

DECLARATION

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student's name: Bassam S. Dabbour

Signature:

Date: 27/09/2014

اسم الطالب: بسام سليمان دبور

التوقيع:

التاريخ: 27/09/2014

بسم الله الرحمن الرحيم

الجامعة الإسلامية – غزة
The Islamic University - Gaza

مكتب نائب الرئيس للبحث العلمي والدراسات العليا   هاتف داخلي 1150

الرقم ج س غ/35/ Ref

التاريخ 2014/09/15 Date

نتيجة الحكم على أطروحة ماجستير

بناءً على موافقة شئون البحث العلمي والدراسات العليا بالجامعة الإسلامية بغزة على تشكيل لجنة الحكم على أطروحة الباحث/ **بسام سليمان علي دبور** لنيل درجة الماجستير في **كلية *الهندسة* قسم الهندسة المدنية – تصميم وتأهيل المنشآت** وموضوعها:

تأثير مجموعة من المواد المالئة على الخواص الميكانيكية للخرسانة الطازجة والمتصلبة

The Effect of a Group of Nano Materials on the Mechanical Properties of Fresh and Hardened Concrete

وبعد المناقشة التي تمت اليوم الاثنين 20 ذو القعدة 1435هـ، الموافق 2014/09/15م الساعة العاشرة صباحاً، اجتمعت لجنة الحكم على الأطروحة والمكونة من:

د. محمد حسني عرفة	**مشرفاً ورئيساً**	....
د. مأمون عبد الحميد القدرة	**مشرفاً**	....
أ.د. سمير محمد شحادة	**مناقشاً داخلياً**	....
د. علي إبراهيم تايه	**مناقشاً خارجياً**	....

وبعد المداولة أوصت اللجنة بمنح الباحث درجة الماجستير في **كلية *الهندسة*/** قسم **الهندسة المدنية – تصميم وتأهيل المنشآت**.

واللجنة إذ تمنحه هذه الدرجة فإنها توصيه بتقوى الله ولزوم طاعته وأن يسخر علمه في خدمة دينه ووطنه.

والله ولي التوفيق،،،

مساعد نائب الرئيس للبحث العلمي وللدراسات العليا

أ.د. فؤاد علي العاجز

ص.ب. 108 الرمال. غزة. فلسطين هاتف Tel: +970 (8) 286 0700 فاكس fax: +970 (8) 286 0800 P.O. Box 108, Rimal, Gaza, Palestine
public@iugaza.edu.ps www.iugaza.edu.ps

Abstract:

The Nano materials (NM) are being used in several fields of civil engineering due to their significant impact on the properties of that field. Particularly, the NM have been widely used in concrete industry to produce a concrete with specific fresh and hardened properties; such as high strength, self-compactness, durability…etc.

The main objective of this research is to study the effect of several nano mineral materials (NM) on the mechanical properties of concrete in order to produce high strength concrete of about 50 MPa with good workability. The NM materials used in the research were not heavily used in the production of concrete.

Normal concrete was applied to study the effect of the NM materials on the mechanical fresh and hardened properties. The applied NM materials in research were brown iron oxide (BIO), yellow iron oxide (YIO), Titanium dioxide (TiO), Barium sulfate (BaS), Kaolin (CCK) and acid poly acrylic (PAA). These materials are considered as filler materials. This means that they do not generally react with concrete components.

The mechanical properties of fresh and hardened concrete have been studied for normal strength concrete without any NM and with 6 NM materials. Five contents were applied for each NM materials. These ratios were ranging from 0.5% to 2.5% of BIO and BaS and range from 1% to 5% of YIO, TiO, PAA and CCK. Also, the current research studied the case of considering PAA as a main gradient and adding each of the remaining five NM materials individually, in order to improve workability. The slump tests, compressive strength tests were conducted for all specimens with and without NM materials. The indirect tensile strength, flexure strength, shear strength and modulus of elasticity were carried out for concrete specimens having 2.5% BIO and those with concrete specimens having 2.5% BIO with 5% of PAA.

The results showed that PAA improves the workability of fresh concrete also can be used BIO, YIO, TiO and BaS to improving the mechanical properties of the hardened concrete with varying degrees. The results also indicated that using 2.5% of BIO by cement weight enhances the compressive strength of hardened concrete from 37.37 MPa to up to 50 MPa and the workability improved from 90 to 105 mm. The results also revealed that using 5% of BIO by cement weight and 2.5% of PAA enhances the compressive strength from 37.37 MPa to up to 49.35 MPa and workability of fresh concrete about from 90 to 170 mm.

Arabic Abstract:

تستخدم مواد النانو في مجالات عديدة وخصوصاً في مجال الهندسة المدنية وذلك بسبب تأثيرها الكبير في هذا المجال، ويبرز استخدامها على نطاق واسع في صناعة الخرسانة وذلك لإنتاج خرسانة ذات خصائص خاصة للخرسانة الطازجة والمتصلبة، مثل قدرة التحمل العالية للإجهاد الرأسي وذاتية الدمك والديمومة ... الخ.

الهدف الرئيسي من هذا البحث دراسة تأثير العديد من مواد النانو المعدنية على الخواص الميكانيكية للخرسانة بهدف إنتاج خرسانة عالية الإجهاد بقدرة تحمل نحو 50 ميجا باسكال وبتشغيلية جيدة، كما أن المواد المستخدمة في هذا البحث قليلة الاستخدام في مجال إنتاج الخرسانة.

تم تجهيز عينات من الخرسانة بدون أي إضافات كعينات قياسية للمقارنة وذلك من أجل دراسة تأثير مواد النانو المعدنية على الخواص الميكانيكية للخرسانة الطازجة و المتصلبة، علماً بأن المواد المستخدمة في هذا البحث كمواد نانو معدنية هي أكسيد الحديد البني وأكسيد الحديد الأصفر وثاني أكسيد التيتانيوم وكبريتات الباريوم والكولين وحمض البولي أكريلك، تعمل تلك المواد كمواد مالئة وغالبا ليس لها أي تفاعلات كيميائية مع مكونات الخرسانة.

تم دراسة الخواص الميكانيكية للخرسانة الطازجة والمتصلبة وذلك للخرسانة العادية بدون إضافة مواد النانو المعدنية، كما تم دراسة تلك الخواص مع إضافة ستة مواد مختلفة من مواد النانو المعدنية وبشكل منفرد فتم إضافتها بخمس نسب مختلفة تتراوح ما بين 0.5% إلى 2.5% لمادتي أكسيد الحديد البني وكبريتات الباريوم، و تتراوح النسبة ما بين 1% إلى 5% لمواد أكسيد الحديد الأصفر وثاني أكسيد التيتانيوم والكولين وحمض البولي أكريلك.

تم دراسة استخدام حمض البولي أكريلك مضافاً إلى المواد الخمسة الأخرى بشكل منفرد وذلك كمادة أساسية لتحسين التشغيلية للخليط الخرساني، كما أجري اختبار الهطول واختبار تحمل الخرسانة للإجهاد الرأسي لجميع العينات سواء كانت تحتوي على مواد النانو المعدنية أو لا تحتوي عليها، كذلك أجري اختبار الشد الغير مباشر وعزم الانحناء وإجهاد القص ومعامل المرونة لعينات الخرسانة العادية والخرسانة التي تحتوي على مادة أكسيد الحديد البني بنسبة 2.5% والعينات التي تحتوي على مادتي أكسيد الحديد البني بنسبة 2.5% و حمض البولي أكريلك بنسبة 5% مجتمعتين.

لقد أوضحت النتائج أن حمض البولي أكريلك يحسن التشغيلية للخرسانة الطازجة، كما يمكن استخدام كل من أكسيد الحديد البني وأكسيد الحديد الأصفر وثاني أكسيد التيتانيوم وكبريتات الباريوم في تحسين الخواص الميكانيكية للخرسانة المتصلبة ولكن بنسب مختلفة، كما أوضحت النتائج أنه عند استخدام نسبة 2.5% من وزن الإسمنت من أوكسيد الحديد البني يحسن قدرة تحمل الخرسانة للإجهاد الرأسي من 37.37 ميجا باسكال إلى 50.2 ميجا باسكال وكذلك تحسين التشغيلية للخرسانة من 90 مم إلى 105 مم. كما أن النتائج أثبتت أنه عند استخدام نسبة 2.5% من وزن الإسمنت من أكسيد الحديد البني و 5% من وزن الإسمنت من حمض البولي أكريلك معاً يحسنا قدرة تحمل الخرسانة للإجهاد الرأسي من 37.37 ميجا باسكال إلى 49.35 ميجا باسكال وكذلك يحسنا التشغيلية للخرسانة من 90 مم إلى 170 مم.

Dedication:

I would like to dedicate this work to my family specially my mother and father whose loved and raised me and to my loving wife and daughters and son and to my brothers and sisters, for their sacrifice and endless support and to whom I belong.

Acknowledgment:

I would like to express my sincere appreciation to ***Dr. Mohammed Arafa and Dr. Mamoun Alqedra*** from the Department of Civil Engineering at The Islamic University of Gaza, for their help, guidance and assistance in all stages of this research. The constant encouragement, support and inspiration they offered were fundamental to the completion of this research.

Special thanks go to ***College of science and technology- Khanyounes***, for their logistic facilitations and their continuous support.

Special thanks for ***Dr. Mohammed Alaskalany*** to his help, guidance and assistance in all stages of this research. The constant encouragement, support and inspiration they offered were fundamental to the completion of this research.

Finally, I would like to thank everyone who gave advice or assistance that contributed to complete this research.

Abbreviations

ACI	American Concrete Institute
ASTM	American Society for Testing and Material
NC	Normal Concrete
HSC	High Strength Concrete
HPC	High Performance concrete
NM	Nano material
NMM	Nano mineral material
YIO	Yellow Iron Oxide
BIO	Brown iron Oxide
TiO	Titanium Dioxide
BaS	Barium Sulfate
CCK	China clay "Kaolin"
PAA	Poly Acrylic Acid
W/C	Water Cement Ratio

Table of Contents:

List of Tables:

List of Figures:

Chapter (1)

Introduction

1.1 Introduction:

The repeated aggression on Gaza Strip by the Israeli army left large number of damaged buildings. The damaged buildings need strengthening with high quality concrete such as High Strength Concrete "HSC" or High Strength Self Compacting Concrete "HSSCC". This type of concrete cannot be produced in Gaza strip economically. Therefore, normal concrete was using with normal strength and the workability was adjusted by increasing the water cement ratio and cement quantity. These adjustments will cause many problems as large repair cross- section, segregation, honeycombing, bleeding, and shrinkage of concrete.

Recent studies showed that using of Nano material "NM" in concrete have very strong effect on properties of concrete.

This research will focus on the effect of group of Nano mineral materials “NMM “ as Yellow, brown Iron oxide, Titanium dioxide, Barium sulfate, china clay" kaolin or meta kaolin" and poly acrylic acid on the properties of fresh and hardened concrete to obtain the suitable NMM to improve the properties of concrete.

1.2 Definition of Nano material:

According to the latest recommendation of the EU Commission, "nanomaterial" means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range between 1 nm and 100 nm.

The Nano mineral material (NMM) was an important part of nano material. The NMM was almost an inert material and does not react chemically in normal condition and need special condition to react as very high temperature. The NMM had wide use in manufacturing, for example colored iron oxide can be used as pigment in normal concrete, interlock and plastering.

1.3 Problem Statement:

High strength concrete "HSC" concrete is always preferred in construction especially in high-rise buildings and strengthening. However, producing HSC to HSSCC required addition of expensive material such as silica fume, basalt aggregate, more quantity of super plasticizer, quarts and high strength cement. In this research, the HSC will produce using cheap available materials with Nano material.

1.4 Aim and Objectives of This Research:

1.4.1 Aim of works:

The aim of this work is to study the effect of several NMM on the mechanical properties of fresh and hardened concrete to reach to high strength concrete as possible with the optimum workability.

1.4.2 Objectives:

The objectives of this study are to investigate the effect of several NMM on the mechanical properties of fresh and hardened concrete. The following objectives were identified to achieve the aim of the study:

1. Identifying the types of NMM, that will be used to enhance concrete mixes.
2. Investigation the effect of each identified NMM on the mechanical properties of fresh and hardened concrete.
3. Identify the optimum mechanical properties of concrete with each NM.
4. Investigation the effect of mixes of NMM's on the mechanical property of fresh and hardens concrete.

1.5 Methodology:

The following methodology was followed:

1. Literature review from books, papers and researches which are related to this objects "using NMM in concrete", and conduct visits to concrete laboratories in Gaza strip to collect data.

2. Making test program and identifying the physical properties of raw materials of concrete such as aggregate, cement, sand and water, identifying the mechanical properties of fresh and hardened concrete for every NMM.

3. Analysis of obtained data for each NMM and their mixes.

4. Recording the date and make recommendation and conclusions.

1.6 Scope of work:

In order to assess the characteristics of fresh normal concrete and concrete with NMM, the following aspects are considered:

- Mix design.
- Workability.
- Homogeneity.

The tests below will be made to establish the mechanical properties of normal concrete and concrete with NMM:

- Compressive strength
- Indirect tension of concrete “Splitting tensile strength”.
- Flexural strength
- Hardened density.

1.7 Thesis structure:

The research consists of five chapters, references and Appendices arranged as shown below with brief description.

- **Chapter 1 (Introduction):**

  This chapter talks about general background about HSC, problem statement, aim and objective of research, scope of work, and the methodology adopted.

- **Chapter 2 (Literature review):**

  This chapter gives general review of previous research related to using the Nano mineral material in concrete and its effects in mechanical properties of fresh and hardened concrete.

- **Chapter 3 (Constituent Material and Experimental Program):**

  This chapter discusses types of laboratory tests, standards, adopted procedures, materials properties, curing condition and schedules of the testing program.

- **Chapter 4 (Result and discussion):**

  Chapter 4 includes test results, analysis of the results and discussion.

- **Chapter 5 (Conclusion and recommendations):**

  General conclusion and recommendations from this research work are stated.

- **References**

Chapter (2)
Literature Review

2.1 Introduction:

This chapter reviews available previous studies which deal with nano material and nano mineral material in concrete. The effects of these materials on the mechanical properties of fresh and hardened concrete are also reviewed.

2.2 Definition of Nano material:

National Institute for Occupational Safety and Health was defined the Nanomaterial's as materials with at least one external dimension in the size range from approximately 1-100 nanometers. Nanoparticles are objects with all three external dimensions at the nano scale. Engineering nanoparticles are intentionally produced and designed with very specific properties related to shape, size, surface properties and chemistry. These properties are reflected in aerosols, colloids, or powders. The behavior of nanomaterial may depend more on surface area than particle composition itself. The relative-surface area is one of the principal factors that enhance its reactivity, strength and electrical properties.

Buzea, et. Al., 2007, defined the Nanomaterial's as a materials of which a single unit is sized (in at least one dimension) between 1 and 1000 nanometers (10^{-9} meter) but is usually 1—100 nanometers.

Some additive materials as nano material, nano mineral material and microstructure were used in concrete to production several types of concrete as self- compact concrete, high strength concrete, ultra high strength concrete and high performance concrete. For every type of concrete there was some group of additive material was added to enhancing the mechanical property of fresh and hardened concrete. The most mechanical property which enhanced by additive as workability, compressive strength, flexure strength, tension strength, shear strength, resistance of wearing and durability.

The following paragraphs explain the effect of several nano materials.

2.3 Mechanism of effect of several NM on concrete properties:

The mechanism of effect of nano material on the concrete property was discussed in many researches which explain below.

- Lazaro1, et al. , 2013, studied the effect of Nano-silica on concrete and cement paste, was reached to that the nano silica can effects on cement pastes and concrete mixes as acceleration of the setting time, cement matrix densification and improvement of the inter-particle transition zone of aggregates (filling effect). Because of the pozzolanic reaction, micro-silica or nano silica can replace cement (1 part silica instead of 3 to 4 parts cement) for medium-strength concrete, while the strength is unaffected by the replacement. Considering that the main difference between Nano-silica and micro-silica is their particle sizes, assuming pozzolanic behaviors in each are similar—Nano-silica will react faster with the cement due to its smaller particles. In addition, the largest use of micro-silica is for producing concrete with enhanced properties, such as high early strength or low permeability.

- Sanghchulie, et al., 2010, studied adding Nano-Silicate to the concrete mixture will result the active SiO_2 to mix with the free calcium hydroxide available in the micro holes of the concrete and produce insoluble calcium silicate, and finally cause the structure of the cement to become more dense and become less penetrable causing the concrete to be more resistant.

  - Mehta, et al., 2008, discussed the general principles of design the high-strength concrete mixtures, it is apparent that high strengths are made possible by reducing porosity, homogeneity, and micro-cracks in the hydrated cement paste and the transition zone. The utilization of fine pozzolanic materials in high strength concrete leads to a reduction of the size of the crystalline compounds, particularly, calcium hydroxide. Consequently, there is a reduction of the thickness of the interfacial transition zone in high-strength concrete. The densification of the interfacial transition zone allows for efficient load transfer between the cement mortar and the coarse aggregate, contributing to the strength of the concrete. For very high-strength concrete where the matrix is extremely dense, a weak aggregate may become the weak link in concrete strength. Almost any ASTM Portland cement type can be used to obtain concrete with adequate rheology and with compressive strength up to 60 MPa. In order to obtain higher strength mixtures while maintaining good workability, it is necessary to study carefully the cement composition and fineness and its compatibility with the chemical admixtures. Experience has shown that low-C3A cements generally produce concrete with improved rheology. In high-strength concrete, the aggregate plays an important role on the strength of concrete. The low-water to cement ratio used in high strength concrete causes densification in both the matrix and interfacial transition zone, and the aggregate may become the weak link in the development of the mechanical strength. Extreme care is necessary, therefore, in the selection of aggregate to be used in very high strength concrete.

- Birgisson, et al., 2012, studied the effect of addition of nano fine particles on concrete. The study conclude that the nano fine particles can improve the properties of concrete due to the effect increased surface area has on reactivity and through filling the nano pores of the cement paste. Nano silica and nano titanium dioxide are probably the most reported additives used in nano modified concrete. Nano materials can improve the compressive strength and ductility of concrete. Carbon nano tubes or nano fibers (CNT-CNF) have also been used to modify strength, modulus and ductility of concretes. CNFs can act as bridges across voids and cracks that ensure load transfer in tension. Ultra high-performance concretes (UHPC) used in current practice and found in the research literature have mainly been developed using some type of nano modification or the use of an admixture developed using nanotechnology methods. Some of the ways nanotechnology can be used to affect concrete include modifying the cement properties through nano modification, modifying the cement paste itself through admixtures, or affecting the concrete mixture using nano porous thin film (NPTF) coatings for the aggregates themselves. Durability of concretes can also be improved through reduced permeability and improved shrinkage properties. These effects can be accomplished through nano modified cements or the use of nano developed additives to the paste.

- Wei, et al., 2011, concluded that, there are many effect factors of mix proportion on anti-permeability and anti-freezing durability of high performance concrete containing nano-particles, such as the dosage of cement, nano materials, mineral fine admixture, chemical admixture and the value of water-binder ratio and sand ratio. The aim of this study was to evaluate the effect of these effect factors on durability of high performance concrete containing nano-particles and find out the main factors. Applying grey relational analysis method, the relational grades between the effect factors and diffusion coefficient of Cl-, and the relational grades between the effect factors and anti-freezing durability coefficient of high performance concrete containing nano-particles were calculated. Besides, the sequence results of influencing degree of the factors to affect the anti-permeability and freezing-thawing resistance were obtained. The results indicate that water-binder ratio, dosage of cement and dosage of nano- particles have the greatest influence on chloride permeability and freeze-thaw resistance of high performance concrete containing nano- particles among the 7 selected parameters of design of mix proportion. In order to improve anti-permeability of Cl- and freeze-thaw resistance of high performance concrete containing nano-particles, water-binder ratio, the dosage of cement and nano-materials must be controlled strictly. It had better decrease water-binder ratio and the dosage of cement, besides increase the dosage of nano-materials.

2.4 Previous studies for using Nano material in concrete:

Several investigations have been conducted to study the effect of use Nano material on concrete to enhancing the mechanical properties of fresh and hardened concrete, the studies below explain that.

2.4.1 Using of nano silica and fly ash in concrete:

- Maghsoudi, et al. , 2010, concluded that, it can enhance the stability of self -compacting mixes by using nano silica (in a form of colloidal silica solution) and lime stone powder with average particle size of 50 nm and 0.3 mm respectively were used in mixtures.

- Arulraj, et al., 2011, concluded that the 28th day strength of concrete with 10%-30% of nano-fly ash was found to be 17 to 21% higher than that of normal cement concrete. M20 concrete had the highest increase in strength whereas M50 concrete had the least increase in strength.

- Quercia, et al., 2012, studied the effect of nano silica on some property of concrete. The study had been reported that nano-silica (NS) addition increases the compressive strength and reduces the overall permeability of hardened concrete due to the pozzolanic properties which are resulting in finer hydrated phases (C-S-H gel) and identified microstructure (nano-filler and anti-leaching effects).

2.4.2 Using of Titanium dioxide in concrete:

- Li, et al., 2007, studied the effect of Nano-TiO_2 and Nano-SiO_2 on concrete and the ability to use their as additive on concrete. The researchers conclude that the nano-TiO_2 and nano-SiO_2 can used as additives and the flexural fatigue performance of concretes containing Nano-particles as TiO_2 and SiO_2 enhanced significantly and the sensitivity of their fatigue lives to the change of stress is increased. The study proved that the concrete containing 1% of Nano-TiO_2 by weight of cement have the best flexural fatigue performance, and better than that of the concrete containing Polypropylene fibers.

- Shekari, et al., 2011, concluded that, nano particles can be very effective in improvement of both mechanical properties and durability of concrete. The using of nano ZrO_2, Fe_3O_4, TiO_2 and Al_2O_3 with constant content will enhance the mechanical properties of fresh and hardened concrete as compressive strength, indirect tensile strength and durability.

- Li, et al., 2006, concluded that, it can use nano TiO2 and SiO2 as additives. The abrasion resistance of plain concrete contains Nano particles as TiO_2 and SiO_2 will be enhanced. The effect of TiO2 for enhancing the abrasion resistance of concrete will be better than the containing of the same amount of nano-SiO_2, but the enhancing will be decreasing with extended amount of Nano TiO_2 or SiO_2.

- Jalal, et al., 2013, indicated that using of flay ash with percent 15% from cement weight and TiO_2 with percent 5% from cement weight will enhance the mechanical properties of fresh and hardened concrete as concrete flow, durability, compressive strength, flexure strength , indirect tensile strength.

- Broekhuizen, et al., 2011, studied the effect of nano TiO_2 in concrete, the study conclude that the TiO_2 can enhance the durability of concrete and maintain whiteness throughout the entire lifetime of the construct. It is claimed that organic pollutants, microorganisms and NO_x are broken down by the photo-catalytic activity of TiO_2. The efficient performance of nano TiO_2 for road coating systems or coating of acoustic fencing along motorways has not been substantiated in practice.

2.4.3 Using of barium sulfate in concrete:

- Tsuyuki, et al. , 2000, studied the using of barium sulfate" BaSO4" in fresh concrete and conclude that the BaSO4 will fix the chloride ion in the hydration of C3A . The study explained that concrete contain BaSO4 have low permeability of chloride ion so it will increase the durability of concrete.

- Karatasios, et al., 2008, concluded that, using of barium hydroxide ($BrSO_4$) in fresh concrete will increases the durability of hardened mixtures against sulphate attack.

2.4.4 Using of Kaolin or meta- kaolin in concrete:

- Azeredo, et al., 2013, concluded that, the kaolin wastes with super plasticizer can be used to product a self-compacting concrete.

- Mermerdaş, et al., 2013 concluded that, using of meta-kaolin in concrete will be decrease the drying shrinkage and weight loss of concrete.

- Badogiannis, et al., 2009 studied the using of meta-kaolin in concrete, the study concluded that, using of meta-kaolin with specific percent will enhancing durability, decrease permeability and porosity and enhance pore size distribution of concrete.

2.4.5 Using of poly or Meta Acrylic Acid in concrete:

- Son, et al., 2012, concluded that, it can be used meth-acrylic acid (MAA) as binder in order to develop the polymer concrete that can be used at low temperatures. The using of meth-acrylic acid (MAA) in concrete with specific percent will enhance the mechanical properties of fresh and hardened concrete.

- Al-Mishhadani1, et al., 2013, investigated the effect of nano meta-kaolin (NMK) on some mechanical properties as compressive strength, splitting tensile strength & water absorption of concrete. The ordinary Portland cement was partially substituted by NMK of (3, 5 & 10%) by weight of cement. The Water absorption was tested at 28 days while the tests (compressive strength, splitting tensile strength) were tested at ages of (7, 28, 60 & 90) days. The compressive strength and splitting tensile strength of concrete with NMK were higher than that of reference concrete with the same W/c ratio. The improvement in the compressive strength when using NMK was (42.2, 55.8 , 63.1%) at age 28 days for (3%, 5%, &10%) replacement of NMK respectively here as the improvement in the splitting tensile strength was (0% , 36% & 46.8 %) at age of 28 days when using (3%, 5%, &10%) NMK respectively. The improvement in the water absorption was (16.6%, 21.79%, &25.6) when using (3, 5, &10%) NMK.

2.4.6 Using of Iron oxide in concrete:

- Lee, et al., 2003, concluded that, it can be used iron oxide as pigment with percent less than 4% in concrete. The iron oxide will enhance some of mechanical properties of hardened concrete as compressive and flexure strength.

2.5 Application of nano material:

There are many applications of nano material in production of several type of concrete. These types of concrete were manufactured by adding one or more of additive as microstructure and nano material to enhance the mechanical property of concrete. These types of concrete were classified according to their mechanical property as below:

2.5.1 Self-compact concrete (SCC):

Self-Compacting Concrete (SCC) is an innovative concrete that does not require vibration process to its placing. SCC is able to flow under its own weight, enables it to meet or filling formwork and reached its highest density. SCC requires a mineral admixture such as fly ash, super-plasticizer and other compounds such as iron slag waste from steel mill wastes in the form of fine aggregate in order to meet the specified flow-ability. Some trial mixtures containing fly ash, silica fume, Policarboxilate based of super-plasticizer, and iron slag have been performed that aims to determine the SC ability, viscosity and segregation were conducted using slump cone, L-box and V-funnel.

2.5.2 High strength concrete:

According to the American Concrete Institute, high strength is defined as that over 41 MPa compressive strength “cylindrical samples”. This value was adopted by ACI in 1984, but is not yet hard and fast, because ACI recognizes that the definition of high strength varies on a geographical basis. Prof. J. Francis Young of the University of Illinois at Champaign-Urbana has developed a strength classification system that, though not yet adopted by a recognized authority, is a helpful tool for describing high strength concretes, see Table (2.1).

2.5.3 High performance concrete:

ACI defined high-performance concrete as a concrete meeting special combinations of performance and uniformity requirements that cannot always be achieved routinely using conventional constituents and normal mixing, placing, and curing practice. The definition of high-performance concrete is more controversial, Mehta and Aitcin used the term, high performance concrete (HPC) for concrete mixtures possessing high workability, high durability and high ultimate strength.

Table 2.1 : Strength classification of concrete and property.

Item	Conventional concrete	High-strength concrete	Very-high strength concrete	Ultra-high strength concrete
Strength, MPa	< 50	50-100	100-150	> 150
Water-cement ratio	>0.45	0.45-0.3	0.3-.25	<0.25
Chemical admixtures	Not necessary	Water reducing admixture or high-range water reducer	high-range water reducer	high-range water reducer
Mineral admixtures	Not necessary	Fly ash & Silica fume	Fly ash & Silica fume	Fly ash & Silica fume
Permeability coefficient (cm/s)	$>10^{-10}$	10^{-11}	10^{-12}	$< 10^{-13}$
Freeze-thaw protection	Needs air entrainment	Needs air entrainment	Needs air entrainment	No freezable water

2.6 Hydration of Portland cement

When Portland cement is mixed with water, its constituent compounds undergo a series of chemical reactions that are responsible for the final hardening of concrete. Reactions with water are named as hydration, and the new solids formed on hydration are collectively referred to as hydration products. Figure (2.1) shows schematically the sequence of structure formation as hydration proceeds. This involves the replacement of water that separates individual cement grains in the fluid paste (Figure 3.2a) with solid hydration products that form a continuous matrix and bind the 40 residual cement grains together over a period of time, as illustrated in Figure 3.2(b-d). The calcium silicates provide most of the strength developed by Portland cement. C3S provides most of the early strength (in the first three to four weeks) and both C3S and C2S contribute equally to ultimate strength.

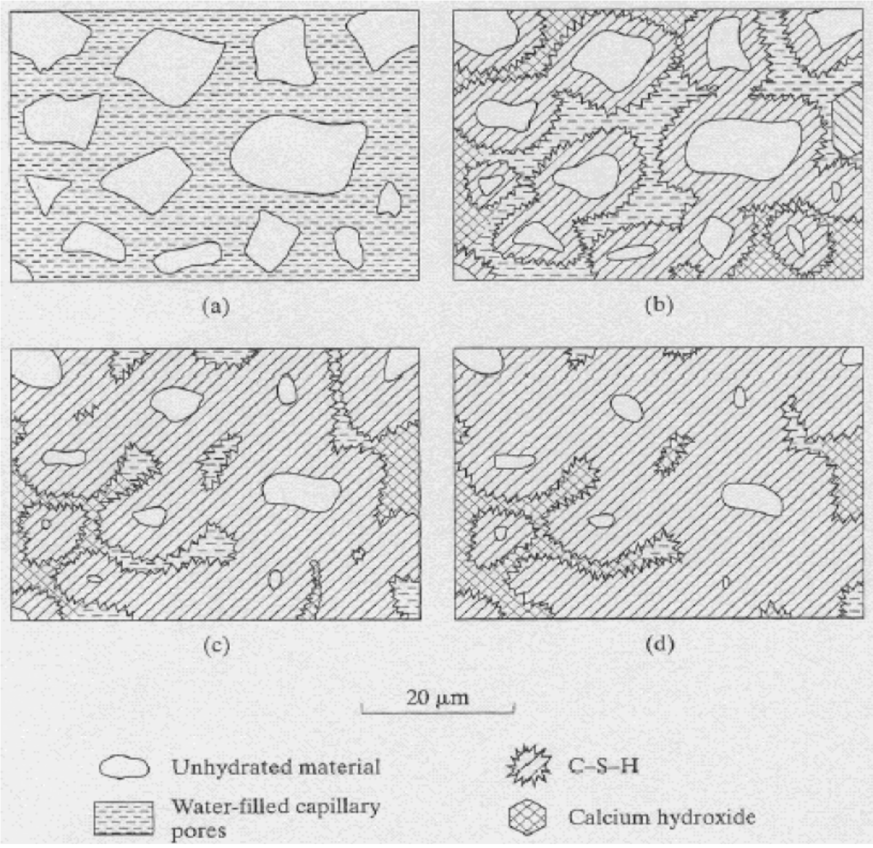

Figure 2.1: Microstructural development in Portland cement pastes.

In commercial cements, the calcium silicates contain small impurities of some oxides present in the clinker, which have a strong effect on the properties of the calcium silicate hydrate (C-S-H). Calcium silicate hydrate is essentially amorphous and develops as a mass of extremely small irregular particles of indefinite morphology. The particles are so small that 41 they can be studied only by scanning electron microscope and even cannot be completely resolved.

Tricalcium silicate and dicalcium silicate present in the cement, on hydration give rise to calcium silicate hydrates and calcium hydroxide as shown in Equations (3.5) and (3.6).

$2\ (3\ CaO.\ SiO_2) + 6\ H_2O \longrightarrow 3CaO.\ 2SiO_2\ 3\ H_2O + 3Ca\ (OH)_2$

Tricalcium silicate+ water$\longrightarrow$ Calcium Silicate Hydrates + Calcium Hydroxide (3.5)

$2(2\ CaO.\ SiO_2) + 4H_2O \longrightarrow 3CaO.\ 2SiO_2\ 3\ H_2O + Ca\ (OH)_2$

Dicalcium Silicate+ water $\longrightarrow$ Calcium Silicate Hydrates+ Calcium Hydroxide (3.6)

The nano mineral material does not soluble in water and inert material does not react with the above component of cement hydration but will be as filling material. The NMM will be fill the pore in the cement mortar and may be reduce the internal friction between aggregate particles. Also the NMM will be decrease the permeability of concrete and increase the bulk density.

Chapter (3)

Experimental Program and Constituent Material

3.1 Introduction:

This chapter presents the experimental program which was carried out in the current study. The experimental program consists of checking the specifications of the components of concrete mix as aggregate, sand, cement and the Nano mineral materials "NMM" and compares the results to standard specifications. The tests for coarse aggregate are unit weight, specific gravity, absorption, grain size distribution, fineness modulus, loss Anglos, flakiness, elongation and soundness but the test for cement is normal constancy ,initial and final set, fineness and compressive strength. This chapter also discusses the procedure of testing fresh and hardened concrete. The fresh concrete was tested using slump test to measure its workability. Also the used to compare slump result between normal concrete and concrete with adding several type and percent of NMM and measure the amount of workability. The testing on hardened concrete was made according to the ASTM and by British Standard. These tests are cylindrical and cubic compressive strength, modulus of rupture, indirect tension and modulus of elasticity of hardened concrete.

3.2 Experimental program:

Six nano mineral materials have been selected for this study which was brown iron oxide, yellow iron oxide, Titanium dioxide, Barium Sulfate, Poly acrylic acid and Kaolin (china clay) based on availability in the Gaza Strip, where they are used in the paints manufacturing. The six materials were from the same group of inert mineral materials in natural conditions and they need very high temperatures more than 1000°c to start the reaction. Also concrete composite material as cement, three types of aggregates which had different gradients with three sizes, clean sand and water were selected according to ASTM specification.

All physical tests were made for aggregate, sand and cement to ensure conformity to international standards (ASTM). The result of physical test will be used in design of concrete job mix. The main test for aggregate and sand were as specific gravity in three form, absorption, sieve analysis, fineness modulus of sand, Soundness, Loss angles, elongation, flakiness, and density. All results were in the range according to the specifications. The tests for cement were such as fineness, normal consistency, initial and final set and compressive strength. All cement tests were according to ASTM specification.

After insuring that all materials used were conform to standard specifications , it will be used to design the concrete job mix with standard cylinder compressive about 30 MPa and slump about 50-100 mm, the job mix was achieved after two trials.

The testing program will be include studying the effect of each nano mineral material (NMM) with different ratios in the mechanical property of fresh and hardened concrete as well as using of some NMM together. From basic test the optimal percent for each material can be defined. These tests were as cubic compressive strength for hardened concrete, and slump test for fresh concrete. The testing program steps were explained as follows:

3.2.1 Determination of the optimal ratios of each NMM:

1. **Brown iron oxide:**

   Brown iron oxide was used in mix which was added with the cement during the mixing of concrete components with different ratios as 0.5-1.0-1.5-2.0-2.5% by cement weight. The different ratios were added to study the amount and rate of changing in compressive strength when testing 8 cubes with size 150 mm (4 samples at 7 days age and 4 samples at 28 days). As well as measuring the change in slump value of fresh concrete for each ratios. By knowing the rate of increase in compressive strength and slump value the optimum value of NMM which achieve the best value of compressive strength.

2. **Yellow Iron oxide:**

   The same tests were done using yellow iron oxide but using the following ratios 1, 2, 3, 4 and 5 % by cement weights.

3. Titanium dioxide:

When adding Titanium dioxide the same tests with the same ratios as YIO ie.1, 2, 3, 4 and 5 % by cement weights was used.

4. Barium Sulphate:

The same test were done using Barium Sulphate but using the following ratios 0.5, 1, 1.5, 2 and 2.5 5 % by cement weights.

5. China Clay (Kaolin):

When adding China clay the same tests with the same ratios as YIO ie.1, 2, 3, 4 and 5 % by cement weights was used.

6. Poly acrylic acid

Poly acrylic acid was added was with ratios 1, 2, 3, 4 and 5 % by cement weights and the same test as YIO was done.

3.2.2 Select the best materials to improve compressive strength and slump:

After the cubic compressive strength results of hardened concrete at 28 days age came out, it can be defined the best percent for each NMM, which in that percent can be enhance the compressive strength with highest percent.

During testing of workability of fresh concrete using slump test can be defined the best percent and the ideal NMM from the six materials which can be enhancing the workability with maximum value of slump.

3.2.3 Mixing two or more NMM together with the concrete mix:

In this stage will be define the best NMM to enhancing the compressive strength of hardened concrete and the other NMM will be selected to enhancing the workability of fresh concrete. The two materials can be used together in the same mix to study the behavior of the new mix. The mechanical property of fresh concrete which will be studied was workability using slump test, but for studying the mechanical property of hardened concrete will be testing the cube compressive strength, indirect tension strength, modulus of rupture, modulus of elasticity and calculation of shear strength.

The last test will be done for the following mixes:

- Standard mix without any additional NMM.
- Mix that contains the best material for enhancing the compressive strength.
- Concrete mix was contained the best two material, the first to enhancing the compressive strength and the second material for enhancing the workability.

Results can be analyzed and then can conclude the impact of these NMM on the mechanical properties of fresh and hardened concrete, and then can be make a recommendation. The experimental program is explained in Figure (3.1).

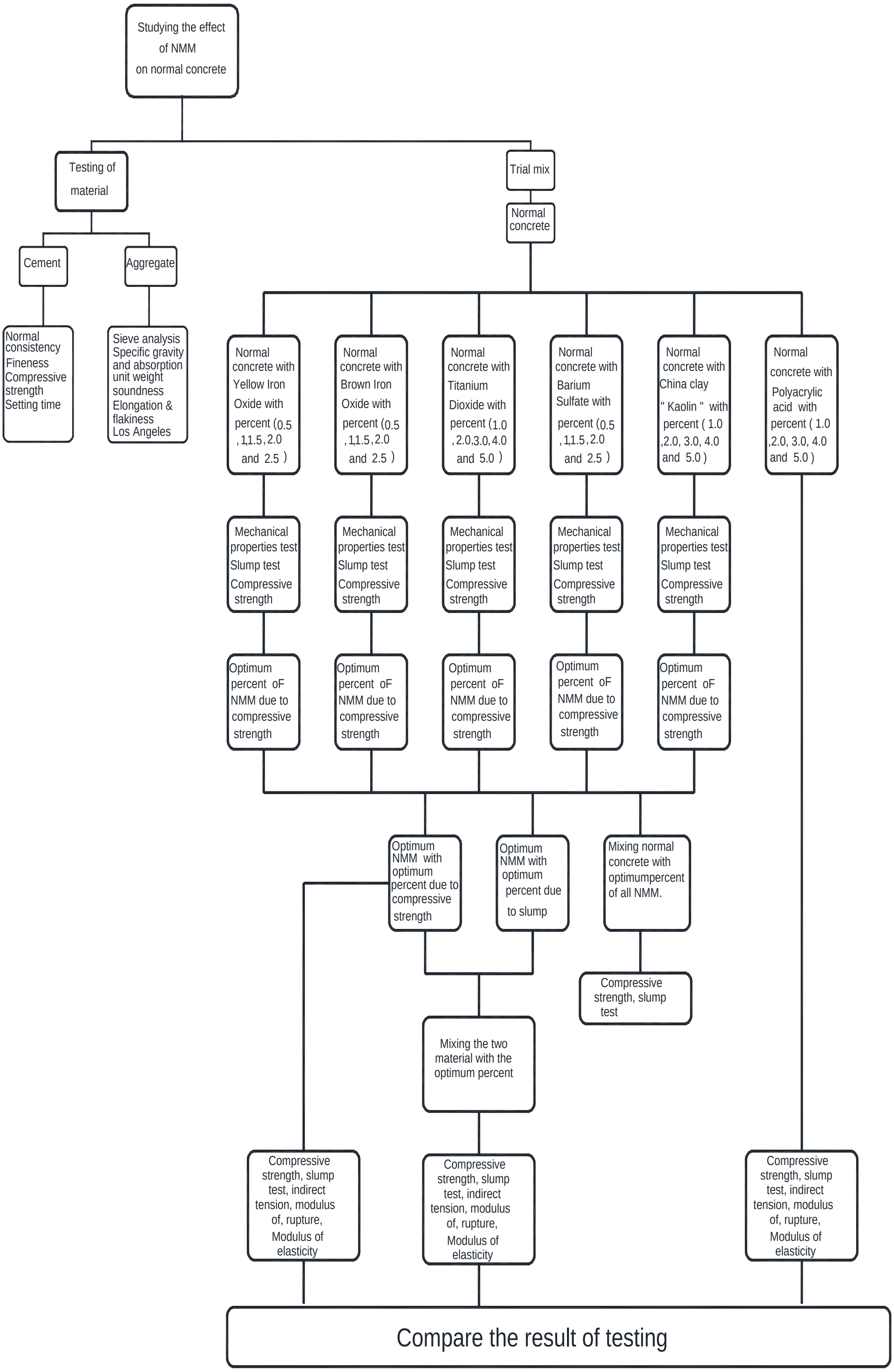

Figure 3. 1: Test program chart

3.3 Properties of Nano mineral material:

3.3.1 Nano Mineral material

Nano material is described as a material the single units of which is sized in at least one dimension between 1 and 1000 nanometers (10^{-9} meter) but is usually 1—100 nm.

In this research, six Nano mineral materials were used to study their mechanical properties on fresh and hardened concrete, and defined the best percent and material, which can enhance the workability and the compressive strength of concrete. The Nano mineral material, which used was Yellow Iron Oxide, Brown Iron Oxide, barium sulfate, titanium dioxide, Kaolin “china clay” and poly acrylic acid. All of last material was as pigment in the paint industrial and colored concrete as concrete interlock tile.

The characteristic of these materials was inert and stable material in normal heat and conditions. In addition, it was needed very high temperatures and special circumstances to begin to decompose and then interact with other component, it's also often had a neutral PH “nearly 7” or it was alkalinity material that means it doesn't effect on the alkalinity of concrete and the reinforcement.

3.3.2 Yellow and Brown Iron oxide:

JECFA, 2008, mention that the Iron oxide is a nano mineral materials have particles with diameters between about 1 to 100 nanometers. The two main forms of iron are magnetite (Fe_3O_4) and its oxidized form maghemite (γ-Fe_2O_3). Iron oxides produced from ferrous sulfate by heat soaking, removal of water, decomposition, washing, filtration, drying and grinding. They produced in either anhydrous or hydrated forms. Their range of hues includes yellows, reds, browns and blacks.

The main manufacture physical property was listed in Table (3.1) according to Huzhou Siyuan Pigment Co., Ltd.

Table 3.1: Manufactured physical property of Yellow and Brown iron oxide:

Item	Iron oxide Yellow	Iron oxide Brown
Molecular formula $Fe_2O_3/Fe_3O_4 \geq$ %	86	92
Appearance	Yellow Powder	Brown Powder
Toxicity	Not toxic	Not toxic
Residue on 45 μm ≤ %	0.3	0.30
Normal Size (nm)	< 100	< 100
PH-value	7	7
Density approx. g/ cm^3	4.0-4.3	4.8

3.3.3 Titanium dioxide

Kuznesof, et al., 2013, explained that Titanium dioxide, also known as Titanium (IV) oxide or Titania, is the naturally occurring oxide of titanium, chemical formula TiO_2. Generally it is sourced from Ilmenite, rutile and Anatase. The main manufacture physical property according to Shandong Jinhua Titanium Industry Co., Ltd. was listed in Table (3.2).

Table 3.2: Physical property of Titanium Dioxide:

Item	Characteristic
Molecular formula	TiO2
Appearance	White solid
Toxicity	Not toxic
Residue on 45 μm < (%)	0.05 max
Normal Size (nm)	<100
PH Value	7-8.5
Density	4.23 g/cm^3 (Rutile) & 3.78 g/cm^3 (Anatase)

3.3.4 Barium sulfate:

Barium sulfate is the inorganic compound with the chemical formula BaSO4. A white crystalline solid is odorless and insoluble in water. It occurs as the mineral barite, which is the main commercial source of barium and materials prepared from it. The white opaque appearance and its high density were exploited in its main applications. The main manufacture physical property according to Industrial Grade Super-Fine Barium Sulfate Shanghai Yuejiang Titanium Chemical Manufacturer Co., Ltd. was listed in Table (33).

Table 3. 3: Physical property of Barium sulfate:

Item	Characteristic
Molecular formula	$BaSO_4$
Appearance	white crystalline
Toxicity	Not toxic
Residue on 45 μm < (%)	0
Normal size nm	< 100
PH Value of Aqueous Suspension	6.5-8.0
Density	4.5 g/cm^3

3.3.5 China clay (Kaolin):

Kaolinite is a clay mineral, part of the group of industrial minerals, with the chemical composition $Al_2Si_2O_5(OH)_4$. The name was derived from Chinese Kao-Ling, a village near Jingdezhen, Jiangxi province, China. The main manufacture physical property according to Guangzhou Changing Trading Co., Ltd. was listed in Table (3.4).

Table 3. 4: Physical property of China clay " Kaolinite":

Item	**Characteristic**
Molecular formula	$Al_2(Si_2O_5)(OH)_4$
Appearance	White
Toxicity	Not toxic
Residue on 45 μm < (%)	0.003 max
Normal size (nm)	< 100
PH Value	7-8.5
Density	2.54-2.6 g/cm^3

3.3.6 Poly acrylic Acid:

The poly acrylic acid is component from pure acrylic emulation, which used in paint manufacturing. In this research used the product with good weather resistance, pulverization resistance and color change resistant properties because the polymer membrane has excellent balance between internal cohesion and adhesion. The main manufacture physical property according to was listed in Table (3.5).

Table 3. 5: Physical property of Poly Acrylic Acid:

Item	**Characteristic**
Molecular formula	(C8H8.C3H4O2)x
Appearance	White
Toxicity	Not toxic
Normal size (nm)	<100
PH Value	9-10
Density	1.08 g/cm^3

3.4 Characteristic of concrete constituent:

3.4.1Cement:

In this research, the Combined Portland cement type CEM II/B-V 42.5 N "Portland fly ash cement" was used. The cement tested according to ASTM C109, C187, C191 and C204 and the result are accepted according to the specification of ASTM C150. The results physical and a mechanical properties and the specification requirement according to ASTM C150 of the cement was mentioned in Table (3.6).

Table 3. 6: Cement characteristic according to testing and (ASTM C150):

Type of test	Related ASTM specification	Characteristic	Result	Type II Cement ASTM C150
Setting time using Vicat test (minutes)	C191	Initial	105	>60
		final	315	<600
Mortar compressive strength (MPa)	C109	At age 3 days	13.5	Min 12
		At age 7 days	29.6	Min 17
		At age 28 days	47.3	No limit
Blain fineness (cm^2/g)	C204	-	3035	Min. 2800
Water demand (%)	C187	-	27.5	No limit

3.4.2 Aggregate:

The physical property of fine and coarse aggregate are listed as below:

1. Sieve analysis:

The sieve analysis of fine and coarse aggregate was made according to ASTM C136, the result was listed in the Table (3.7), and Figure (3.2), the fineness modulus of sand is 2.504.

Table 3. 7: Sieve analysis results for fine and coarse aggregate:

Sieve (#)	Sieve Size (mm)	Sample Name			
		Type I	Type II	Type III	Type IV (Sand)
1.5	37.5	100.00			
1"	25	92.60			
3/4"	19	77.44	100.00		
1/2"	12.5	33.78	56.03	100.00	
3/8"	9.5	10.27	21.83	95.51	
#4	4.75	0.80	2.33	20.54	
#8	2.36	0.27	0.37	0.71	100.00
#16	1.19				88.40
#30	0.6				41.60
#100	0.15				2.00
#200	0.075				

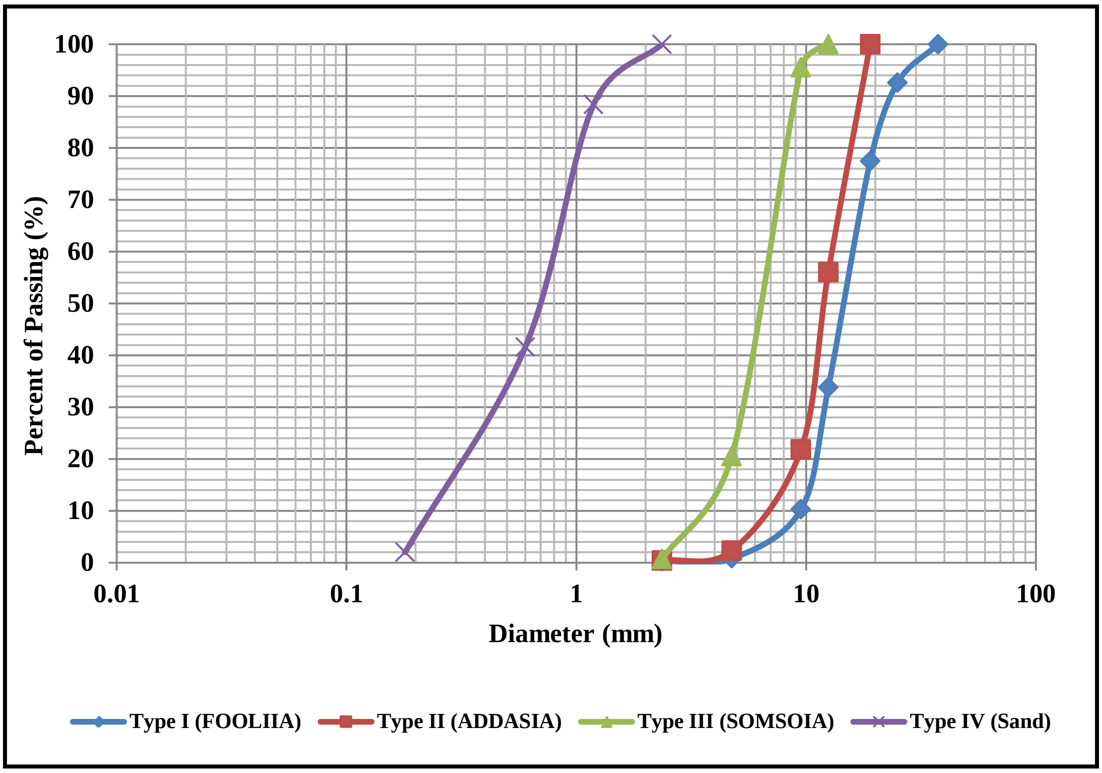

Figure 3. 2: Aggregate graduation of fine and coarse aggregate

2. Absorption and Specific Gravity:

The Absorption and specific gravity of fine and coarse aggregate was made according to ASTM C 128 & ASTM C 127 and the results are presented in Table (3.8).

Table 3. 8: Absorption and specific gravity of fine and coarse aggregate.

Sample Name	Absorption After 24 hour	Absorption After 1.5 hour*	Specification	Apparent specific gravity	Bulk specific gravity	Bulk specific gravity in SSD
Type I	1.58%	1.03%	Max. 2%	2.647	2.541	2.581
Type II	0.97%	0.71%	Max. 2%	2.666	2.598	2.624
Type III	1.97%	1.24%	Max. 2%	2.706	2.569	2.620
Type IV (Sand)	1.27%	0.73%	Max. 2%	2.664	2.577	2.610

3. Flakiness:

The Flakiness of coarse aggregate was made according to ASTM D4791 and the results were listed in the Table (3.9).

Table 3. 9: Flakiness result of coarse aggregate

Sample Name	Normal Average Flakiness (%)	Average Flakiness due to percent of retain in each sieve	Specification
Type I	17.84%	17.87%	0- 20%
Type II	17.58%	17.08%	0- 20%
Type II	16.86%	18.15%	0- 20%
Type IV (Sand)	-	-	-

4. Elongation:

The Elongation of coarse aggregate was made according to ASTM D4791 and the results were listed in the Table (3.10).

Table 3. 10: Elongation result of coarse aggregate

Sample Name	Normal Average Elongation (%)	Average Elongation due to percent of retain in each sieve	Specification
Type I	9.61%	8.87%	0- 35%
Type II	9.15%	6.91%	0- 35%
Type III	7.09%	6.85%	0- 35%
Type IV (Sand)	-	-	-

5. Soundness of Aggregate by Use Sodium Sulfate or Magnesium Sulfate:

The Soundness of Aggregate by using sodium sulfate or magnesium sulfate of coarse aggregate was done according to ASTM C 88 and the final result was listed in the Table (3.11).

Table 3. 11: Soundness result of coarse aggregate:

Sample Name	Soundness (%)	Specification
Type I	0.57%	ASTM C 88 Less than 12%
Type II	0.64%	ASTM C 88 Less than 12%
Type III	1.44%	ASTM C 88 Less than 12%

6. Resistance to degradation of coarse aggregate by abrasion and impact in the Los Angeles machine:

The Resistance to degradation of coarse aggregate by abrasion and Impact in the Los Angeles machine was done according to ASTM C 131 and the final result was listed in the Table (3.12).

Table 3. 12: Resistance to degradation result of coarse aggregate.

Sample Name	Los Angeles (%)	Specification
Type I	27.8	ASTM C 131 Less than 45%
Type II	30.4	ASTM C 131 Less than 45%
Type III	29.82	ASTM C 131 Less than 45%

3.4.3 Water:

Drinkable water was used for all mixing and curing of concrete.

3.5 Mix Design:

Against finishing of all tests for concrete constituent and ensure that all material as water, aggregate , sand and cement are according to ASTM specification will designed the concrete with strength 30 MPA at 28 days age. The job mix will be designed according to Standard Practice for Selecting Proportions for Normal, Heavyweight, and Mass Concrete (ACI 211.1-91). The design criteria which used in the current study are as:

1. **Compressive strength:** The most strength of normal concrete for general use was 30 MPa for cubic strength and ***25 MPa*** for cylinder strength so the mix will be design for that strength.

2. **Slump:** The most slump of normal concrete for general use is between 25 to 100 mm and the mix was designed for slump around 75 to 100 mm.

3. **Nominal maximum aggregate size:** The nominal maximum aggregate size in the job mix was 25 mm.

4. **Water cement ratio:** The water cement ratio in the job mix was 0.569.

5. **The final average weight for job mix:** The final average weight for the job mix was listed in Table (3.13).

Table 3. 13: The final average weight for the job mix

Material	Weight (kg)	Volume (m3)
Entrapped air	0	0.0150
Water	182	0.1650
Cement	320	0. 1016
Coarse aggregate	1161	0.4519
Fine aggregate	687	0.2665
Total	**2350**	**1.000**

6. **The aggregate graduation:** Final material weight of concrete job mix and final graduation of aggregate as mentioned in the Table (3.14) and figure (3.3).

Table 3. 14: concrete aggregate graduation

Material	aggregate						
	Type 1 1”	Type 2 ¾”	Type 3 ½”	Sand #8	Cement	Water	Total kg
Weight (kg)	468	375	318	687	320	182	2350

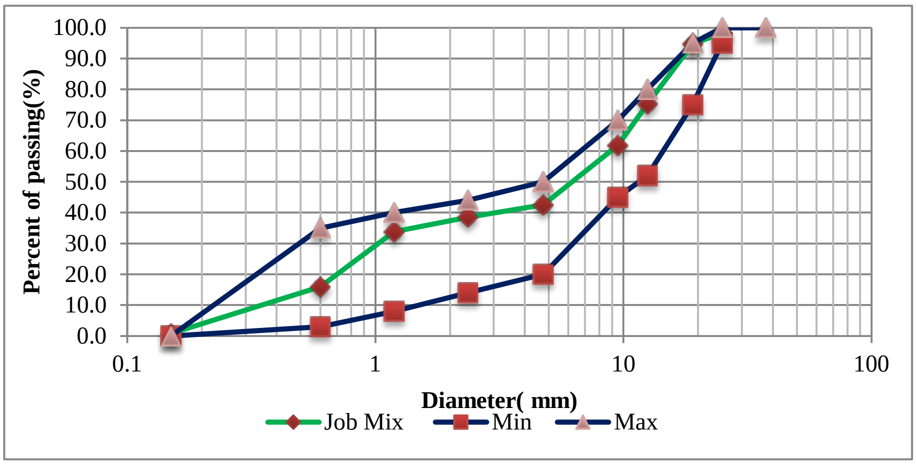

Figure 3. 3: Concrete Job Mix Graduation and Specifications

7. **Material weight for batch concrete with volume 0.03 m3:**

Material	Weight (kg)	Volume (liter)
Entrapped air	-	0.450
Water	5.437	4.944
Cement	9.600	3.048
Coarse aggregate		
Type 1	14.041	5.525
Type 2	11.233	4.323
Type 3	9.548	3.716
Fine aggregate “sand”	20.597	7.994
Total	**70.456**	**30**

8. **First result of mechanical property of fresh and hardened concrete:**

- Batching: from mixing the material batching to check the slump was found about 90 mm without any segregation.
- The average compressive strength was 26.24 MPa at 7 days age for cubic sample and 20.99 MPa or cylinder sample.
- The average compressive strength was 37.37 MPa at 28 days age for cubic sample and 29.90 MPa or cylinder sample.

3.6 Mix Proportion with Nano Mineral Material:

After check the compressive strength of normal designed concrete at 28 days age will add the Nano mineral material to the normal concrete with different percent. The percent and weight of Nano mineral material and the weight of the main material of concrete were listed in Table (3.15).

Table 3. 15: Mix proportions with NMM'S:

NMM Name	NMM Percent (NMM/Cement)/NMM Weight(Kg)						
Yellow iron oxide (YIO)	0%	1% (3.2 Kg)	2% (6.4 Kg)	3% (9.6 Kg)	4% (12.8 Kg)	5% (16.0 Kg)	Nano Mineral Materials
Brown iron oxide (BIO)	0%	0.5% (1.6 Kg)	1.0% (3.2 Kg)	1.5% (4.8 Kg)	2.0% (6.4 Kg)	2.5% (8.0 Kg)	
Titanium dioxide (TiO)	0%	1% (3.2 Kg)	2% (6.4 Kg)	3% (9.6 Kg)	4% (12.8 Kg)	5% (16.0 Kg)	
Barium Sulfate (BaS)	0%	0.5% (1.6 Kg)	1.0% (3.2 Kg)	1.5% (4.8 Kg)	2.0% (6.4 Kg)	2.5% (8.0 Kg)	
Poly Acrylic Acid (PAA)	0%	1% (3.2 Kg)	2% (6.4 Kg)	3% (9.6 Kg)	4% (12.8 Kg)	5% (16.0 Kg)	
China Clay ”Kaolin" (CCK)	0%	1% (3.2 Kg)	2% (6.4 Kg)	3% (9.6 Kg)	4% (12.8 Kg)	5% (16.0 Kg)	
Cement (Kg)	320	320	320	320	320	320	Main Concrete Constituents
Water (Kg)	182	182	182	182	182	182	
Aggregate type I (Kg)	468	468	468	468	468	468	
Aggregate type I (Kg)	374	374	374	374	374	374	
Aggregate type I (Kg)	318	318	318	318	318	318	
Sand (Kg)	687	687	687	687	687	687	

3.7 Preparation of concrete specimen:

3.7.1 Mixing procedure:

The concrete will mixed according to Standard Method of Making and Curing Test Specimens in the Laboratory ASTM C 192. Firstly will be adding the coarse aggregate with some of the mixing water then starting rotation of the mixer. A after that will be adding the fine aggregate, cement and remain water. The powder nano mineral material will be adding to mix with cement powder but the liquid NMM will be adding with water. The concrete will be mix for 3 minutes after all constituent of concrete in the mixer then will be followed by a 3-min rest, followed by a 2-min final mixing. Note that the open end or top of the mixer will be covered to prevent evaporation during the rest period. It must be Take precautions to compensate for mortar retained by the mixer so that the discharged batch, as used, will be correctly proportioned. To eliminate segregation, deposit machine-mixed concrete in the clean, damp mixing pan and remix by shovel or trowel until it appears to be uniform.

3.7.2 Curing of hardened concrete:

After 20-40 hour, the hardened concrete will be removed from the molds with very carefully to prevent any defect in the samples. After that the samples will be placing in curing water tank at temperature 21-25°C until the period of testing.

3.8 Testing program:

As mentioned in chapter 1 of this research , the main aim of this research is to study the effect of Nano mineral material on the mechanical properties of fresh and hardened concrete and find the ability to obtain high strength concrete using component as limestone aggregate, sand, cement and Nano mineral material which valuable in local market. To study the effects of NMM on the mechanical property of fresh and hardened concrete should be flow many testes on fresh and hardened concrete, these test explained as follow.

3.8.1 Fresh concrete test and sampling:

After completing the mixing of fresh concrete there are many test can be done to measure the workability of concrete and the flow ability of concrete. This test as slum test, T500 test, V- Funnel test and …etc.. In this research will depend on slump test only to measure the workability.

1. **Slump Test according to ASTM C143:**

   The test was made to measure the workability of fresh is slump test according to standard Test Method for Slump of Portland Cement Concrete ASTM C 143, the scope of this test is determination of slump of hydraulic-cement concrete.

2. **Sampling of fresh concrete in several molds according to ASTM C192:**

   All test of hardened concrete must be made on specific mold shape and size for example the compressive strength of hardened concrete made by crushing a cube with size 100 mm or 150 mm, all mold shape, size and test are listed in Table (3.21).

Table 3. 16: Mold shape, size and related test

No.	Mold shape	size	Test
1	Cubic	100*100*100 150*150*150	Compressive strength
2	Cylinder	D150 *H300	Compressive strength, Young's modulus of elasticity, splitting tensile strength and creep.
3	Prism Beam	100*100*500 150*150*750	flexural strength, prisms for freezing and thawing, bond, length change, volume change

The procedure of placing the fresh concrete in molds are according to a specific method under number C192 in ASTM which explain the method of placing and tamping the fresh concrete in several layers in molds. Number of strokes for each layer, size of tamping rod and all date for filling the mold by fresh concrete was listed in Table (3.22).

Table 3. 17: Mold shape, size and tamping rode size, number of layers and strokes

No.	Mold shape	Size	Number of layer	Rod size	Number of Strokes/Layer
1	Cubic	100*100*100 150*150*150	2 3	D=16 mm and L=600 mm	25 25
2	Cylinder	D150 *H300	3		25
3	Prism Beam	100*100*500 150*150*750	2 3		36 80

3.8.2 Testing of hardened concrete:

After completing the curing process for hardened concrete as mention previously, there are many tests should be made to study the mechanical property of hardened concrete as compressive strength, indirect tension, modulus of rupture, shear strength and modulus of elasticity. These tests must be made according to ASTM specification as mention below.

1. **Compressive strength According to ASTM C39 and BS 1881, Part 127:**

The main Objective of compressive strength test of hardened concrete is knowing the ability of cubic or cylinder samples of hardened concrete to withstand the vertical stress at several ages at 7,14 and 28 days. This test can made by continuous loading with rate 0.15 to 0.35 MPa/s on a concrete sample until the sample collapse, and by knowing the dimensions of the mold and maximum crushing load can calculate the maximum stress whish the sample can carry, the calculation equation as below:

For cubic sample according to BS 1881 PART 127:

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

Where: σ is normal stress in N/mm^2 or MPa, P is normal crushing force in N and A is area in mm^2.

For cylinder sample according ASTM C39:

$$\sigma = \frac{PK}{A}$$

Where: σ is normal stress in N/mm^2 or MPa, P is normal crushing force in N, A is area in mm^2 and K is correction factor depend on the diameter and height of sample as listed in Table (3.23).

Table 3. 18: Diameter/Height of sample and correction factor K:

L/D	2	1.75	1.5	1.25	1
Correction factor (K)	1	0.98	0.96	0.93	0.87

Notes: To convert the normal stress for cylinder sample to cubic sample will multiplied by constant 1.25.

2. Splitting Cylinder Test According to ASTM C496:

This test method covers the determination of the splitting tensile strength of cylindrical concrete specimens according to ASTM C496. This test method consists of applying a diametric compressive force along the length of a cylindrical concrete specimen with rate 0.7 to 1.4 MPa/min until failure occurs. Calculate the indirect tensile test according to below equation:

$$T = \frac{2P}{\pi DL}$$

Where: T is splitting tensile strength in N/mm^2, P is maximum applied load indicated by the testing machine, in N, L is length of the specimen, in mm and D is diameter of the specimen, in mm.

3. Flexure strength for beam Test according to ASTM C78:

This test method covers the determination of the flexural strength of concrete by the use of a simple beam with third-point loading. The test procedure don by place the test specimen on its smooth flat side with respect to its position as molded and center it on the support blocks then center the loading system in relation to the applied force. The load will be applied in specimen continuously and without shock with rate 0.86 to 1.21 MPa/min until rupture occurs.

If the fracture initiates in the tension surface within the middle third of the span length, calculate the modulus of rupture as follows:

$$R = \frac{PL}{bd^2}$$

Where: R is a modulus of rupture (MPa), P is maximum applied load indicated by the testing machine (N), L is span length (mm), b = average width of specimen (mm) at the fracture, and d is average depth of specimen (mm) at the fracture.

If the fracture occurs in the tension surface outside of the middle third of the span length by not more than 5 % of the span length, calculate the modulus of rupture as follows:

$$R = \frac{3Pa}{bd^2}$$

Where: a is average distance between line of fracture and the nearest support measured on the tension surface of the beam, mm.

4. Static modulus of elasticity according to ASTM C469:

This test can made by applying continuously load without shock and with loading rate 0.241±0.034 MPa/s on cylindrical sample with size 150*300 mm. Through operation of testing will record the load and the strain related to that load, the reading will stopped if the applied load and longitudinal strain at the point when the longitudinal strain is 0.000050 and when the applied load is equal to 40 % of the ultimate load. To draw the stress-strain curve it must take more point of elongation dial gage related to applied loads until 40% of compressive strength then we will reduce the load to zero with the same rate at which it was applied, complete the loading cycle and then repeat it. When intermediate readings taken will plot the results of each of the three tests with the longitudinal strain as the abscissa and the compressive stress as the ordinate then will calculate the compressive stress by dividing the quotient of the testing machine load by the cross-sectional area of the specimen. The calculate modulus of elasticity of cylinder sample in compression as follows:

$$E = (S_2 - S_1)/(\varepsilon_2 - 0.000050)$$

E= Slope of the first line (0 to 40% of compressive strength)

where: E = chord modulus of elasticity (MPa), S_2 is stress corresponding to 40 % of ultimate load, S_1 is stress corresponding to a longitudinal strain, ε1, of 0.000050 , MPa or MP and ε_2 is longitudinal strain produced by stress S_2.

Chapter (4)

Test Results and Discussion

4.1 Introduction:

The performed experimental program was carried to obtain and evaluate the mechanical properties of fresh and hardened concrete under several nano mineral materials. This chapter discusses the results obtained using slump test, compressive strength, indirect tension, flexure strength and modulus of elasticity. For each Nano mineral material “NMM” five ratios were added to the normal job mix to obtain the optimum ratios.

Table 4.1 shows the mixture proportion and one cubic meter ingredient of the best result obtained mixture of normal concrete.

Table 4. 1: mixture proportion and one cubic meter ingredient

Material	Ingredient/cement	Weight	Volume
Entrapped air	0.00	0	0.0150
Water	0.57	182	0.1650
Cement	1.00	320	0. 1016
Coarse aggregate	3.63	1161	0.4519
Fine aggregate	2.15	687	0.2665
Additive (NMM)	-	-	-
Total	**-**	**2350 Kg**	**1.000 m^3**

4.2 Normal concrete:

A normal concrete was prepared to serve as a control mix. The control mix does not have any NMM. The slump value of the control mix was 90 mm with true shape, and the compressive strength was 26.2 MPa and 37.37 MPa at 7 and 28 days respectively.

4.3 Concrete with yellow iron oxide “YIO”:

This mix is prepared by adding Yellow Iron Oxide ‘YIO’ as Nano Mineral Material “NMM”. The effect of NMM in the mechanical properties of fresh and hardened concrete explained as below:

4.3.1 Mechanical properties of fresh concrete “Slump”:

While the slump value of normal concrete mix was 90 mm with true shape, the slump of the YIO mix was between 20 to 80 mm and has also a true shape. The slump values of mixes having 1%, 2%, 3%, 4% and 5% of YIO material by cement content are shown in Figure (4.1).

Figure (4.1) represents an adverse relation between slump and the increasing percentage of YIO. This decrease range was from 90 mm for the control mix to 20 mm for 5% of YIO. This represents a decrease of 20% in slump for each 1% of YIO material.

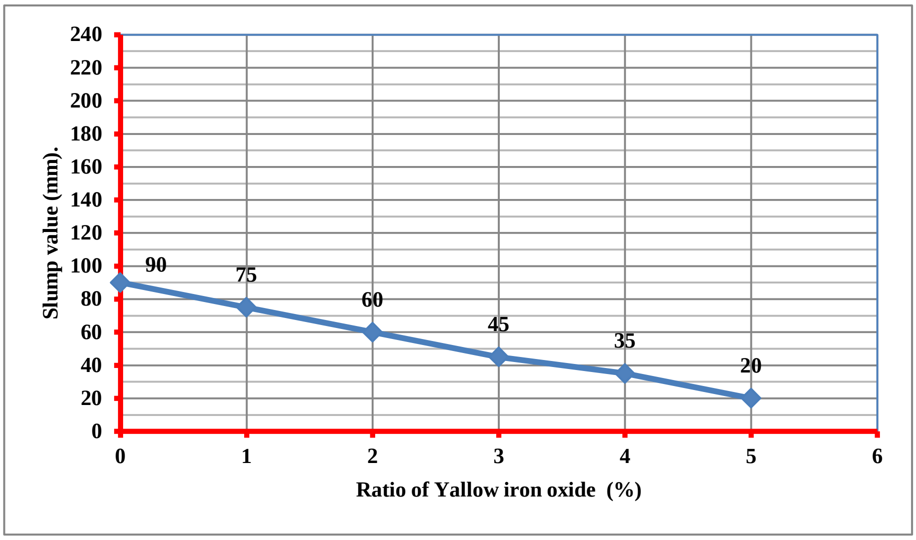

Figure 4. 1 Relation between the ratio of YIO and slump value.

4.3.2 Mechanical properties of hardened concrete:

4.3.2.1 Compressive strength 7 days age:

The 7 days compressive strength of concrete mixes having 0%, 1%, 2%, 3%, 4% and 5% of YIO material by cement content are shown in Figure (4.2).

Figure (4.2) reveals that there was a very slight increase in compressive strength from 29.2 MPa to 31.7 MPa at 1%to 5% respectively, with increasing rate of 2.14%. However, the reasonable increasing of strength occurred when adding 1% of YIO by cement content. The strength increased from 26.2 MPa to 29.2 MPa with a percent of 11.1%. Afterward, adding 4% of YIO by cement content does show any significant improve to strength (not more than 10% in total).

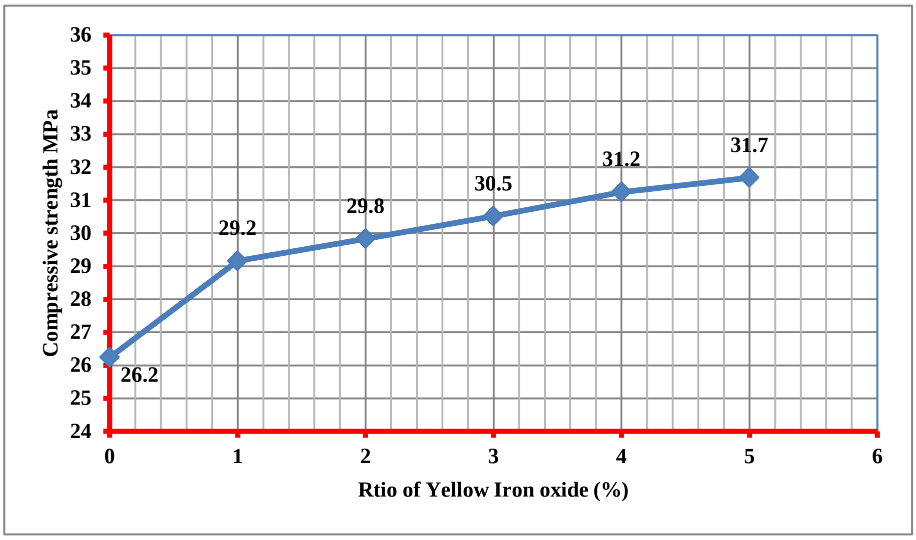

Figure 4. 2: Relation between the ratio of YIO and 7 days compressive strength

4.3.2.2 Compressive strength 28 days age:

The compressive strength of concrete mixes having 0%, 1%, 2%, 3%, 4% and 5% of YIO by cement content are shown in Figure (4.3).

Figure (4.3) represented almost increasing linear relation between the strength and YIO content. The compressive strength increased from 37.37 MPa at 0% of YIO to 43.9 MPa at 5% of YIO. This means that adding every 1% of YIO increase the compressive strength by about 3.5%.

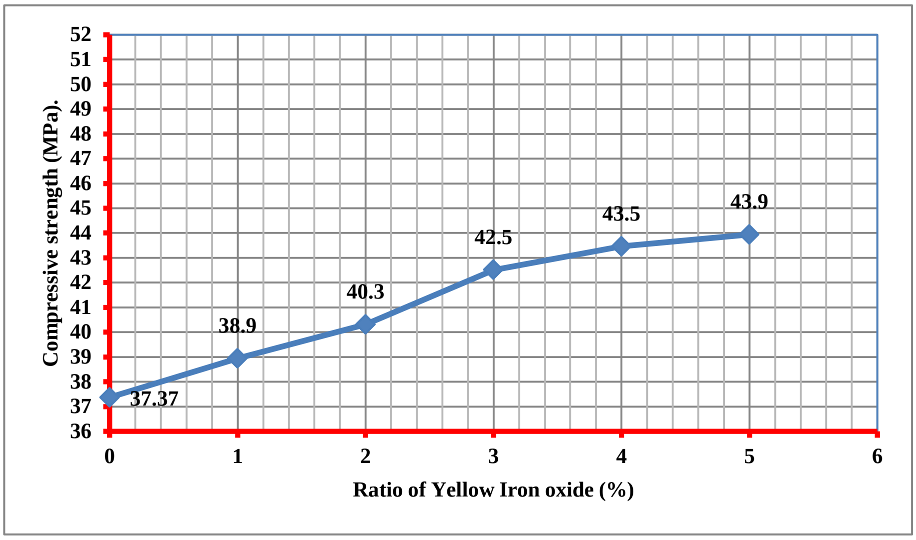

Figure 4. 3: Relation between the ratio of YIO and 28 days compressive strength.

4.3.3 Justification of Results:

Lazaro1, et al. , 2013, conclude that the YIO is extremely fine with particles less than 1 μm in diameter and with an average diameter of about 0.1 μm or less (100nm or less), about 100 times smaller than average cement particles. Then the behavior will correspond to silica fume as a filling material which cleared by slump and compressive strength results as pointed above.

4.4 Concrete with Brown iron oxide "BIO":

This mix is prepared by adding Brown Iron Oxide 'BIO' as Nano Mineral Material "NMM". The effect of NMM in the mechanical properties of fresh and hardened concrete explained as below.

4.4.1 Mechanical properties of fresh concrete "Slump":

While the slump value of normal concrete mix was 90 mm with true shape, the slump of the BIO mix was between 90 to 105 mm and has a true shape. The slump values of mixes having 0.5%, 1%, 1.5%, 2.0% and 2.5% of BIO material by cement content are shown in Figure (4.4).

Figure (4.4) represents nearly constant relation between slump and the increasing percentage of BIO. This increase was range from 90 mm for the control mix to 105 mm for 2.5% of BIO. This represents about 6.7% increase in slump for each 0.5% of BIO material.

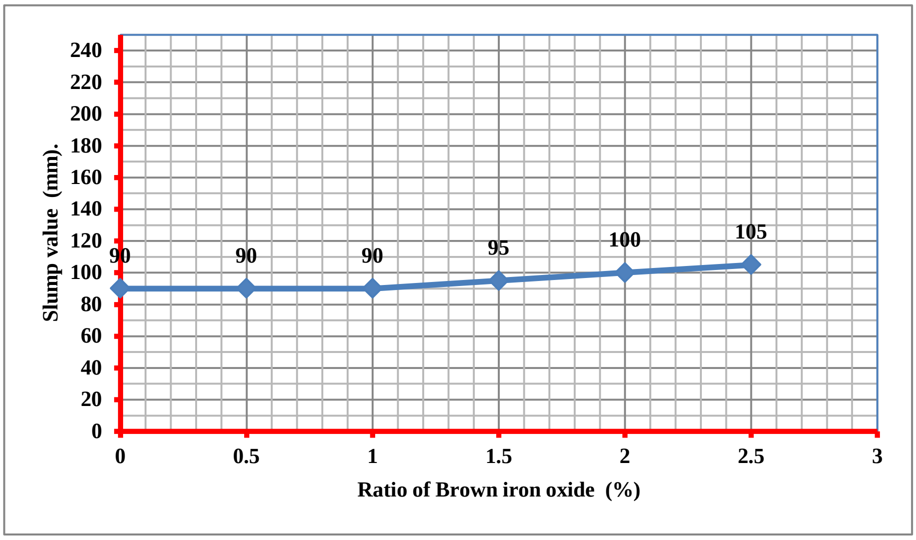

Figure 4. 4: Relation between the ratio of BIO and slump value.

4.4.2 Mechanical properties of hardened concrete

4.4.2.1 Compressive strength 7 days age:

The 7 days compressive strength of concrete mixes having 0%, 0.5%, 1%, 1.5%, 2% and 2.5% of BIO by cement weight are shown in Figure (4.5).

Figure (4.5) reveals that there was high increase in compressive strength from 26.24 MPa to 34.62 MPa at 0% to 2.5% respectively, with average increasing rate of 6.38% for every 0.5% of BIO material. However, the reasonable increasing of strength occurred when adding 1.5% of BIO by cement content. The strength increased from 26.24 MPa to 32.66 MPa with increasing percent of 24.5%. Afterward, adding additional 1% of BIO by cement content does show any significant improve to strength (not more than 7.4% in total).

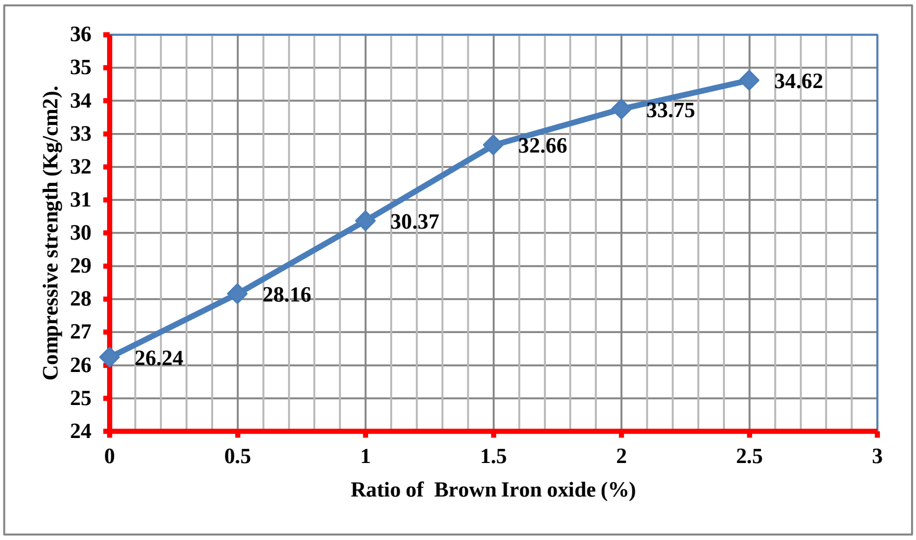

Figure 4. 5: Relation between the ratio of BIO and 7 days compressive strength.

4.4.2.2 Compressive strength 28 days age:

The compressive strength of concrete mixes having 0%, 0.5%, 1%, 1.5%, 2% and 2.5% of BIO by cement content are shown in Figure (4.6).

Figure (4.6) represented almost increasing relation between the compressive strength and BIO content. The compressive strength increased from 37.37 MPa at 0% BIO to 50.20 MPa at 2.5% of BIO. This means that adding every 0.5% of BIO will increase the compressive strength by about 6.86%. The increasing rate of compressive strength was nearly constant and the totally increasing ratio in compressive strength was 34.3%.

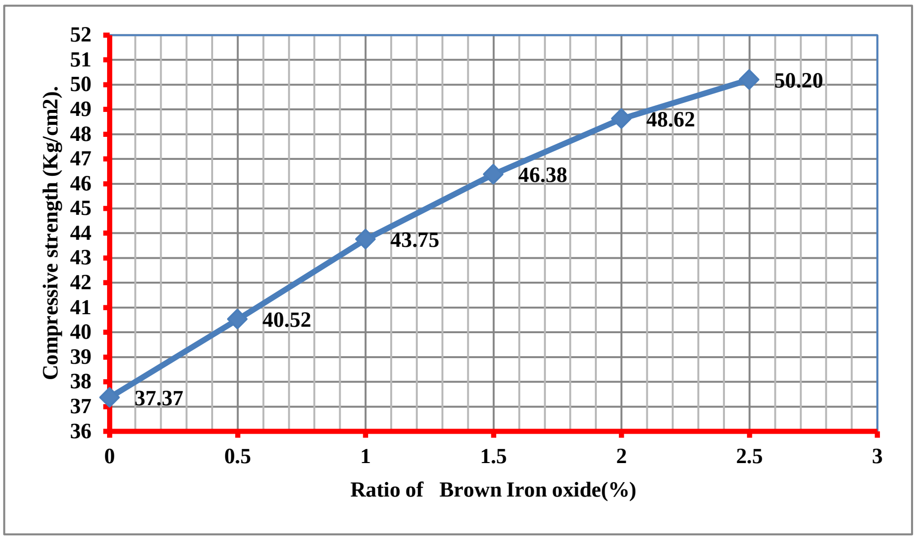

Figure 4. 6: Relation between the ratio of BIO and 28 days compressive strength value.

4.4.3 Justification of Results:

We noted from the results outlined above that we facing another behavior of nano materials now the effect also corresponding to pozzolanic materials not only the filling is the only one but also the effect of reaction rate and velocity of C-S-H gel, the slump test results for BIO indicate that there is small effect of BIO to retard the hydration of C-S-H gel, but from the compressive strength data the effect of pozzolanic is very clear as done in YIO.

4.5 Concrete with Titanium dioxide “TiO”:

This mix is prepared by adding Titanium Dioxide ‘TiO’ as Nano Mineral Material “NMM”. The effect of NMM in the mechanical properties of fresh and hardened concrete explained as below.

4.5.1 Mechanical properties of fresh concrete “Slump”:

While the slump value of normal concrete mix was 90 mm with true shape, the slump of the TiO mix was between 90 to 100 mm and has also a true shape. The slump values of mixes having 1%, 2%, 3%, 4% and 5% of TiO material by cement content are shown in Figure (4.7).

Figure (4.7) reveals that the slump was not affected at 1 and 2% of TiO by increasing the ratio of TiO from 3 to 5% the slump was increased by a rate of 3.3% of each 1% increase in TiO.

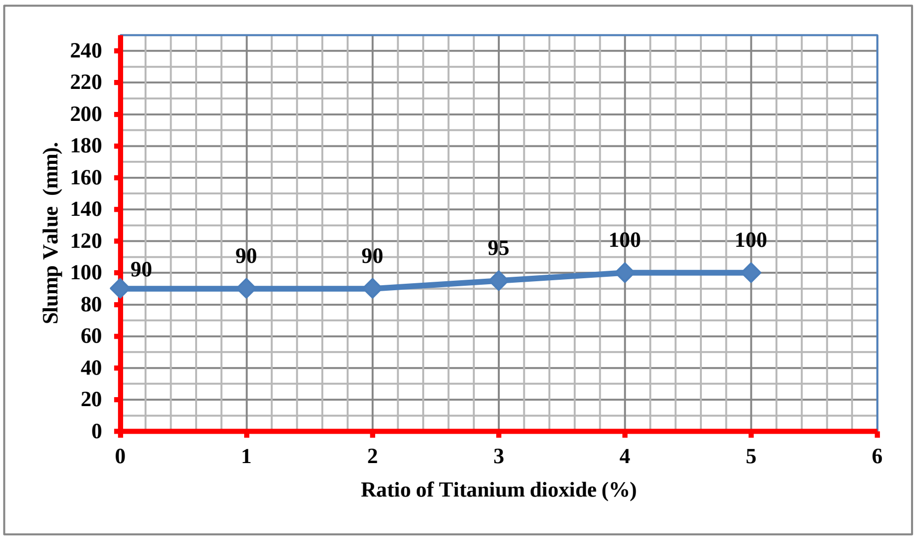

Figure 4. 7: Relation between the Ratio of TiO and slump value.

4.5.2 Mechanical properties of hardened concrete:

4.5.2.1 Compressive strength 7 days age:

The 7 days compressive strength of concrete mixes having 0%, 1%, 2%, 3%, 4% and 5% of TiO by cement content are shown in Figure (4.8).

Figure (4.8) reveals that there was high increase in compressive strength from 26.24 MPa to 31.08 MPa at 0% to 1% of TiO respectively, with increasing rate of 18.45% for the first ratio. Afterward, adding additional 1% of TiO by cement content does not show any significant improve to compressive strength, but there was decrease in the compressive strength with very low rate -0.78% for each 1% of TiO.

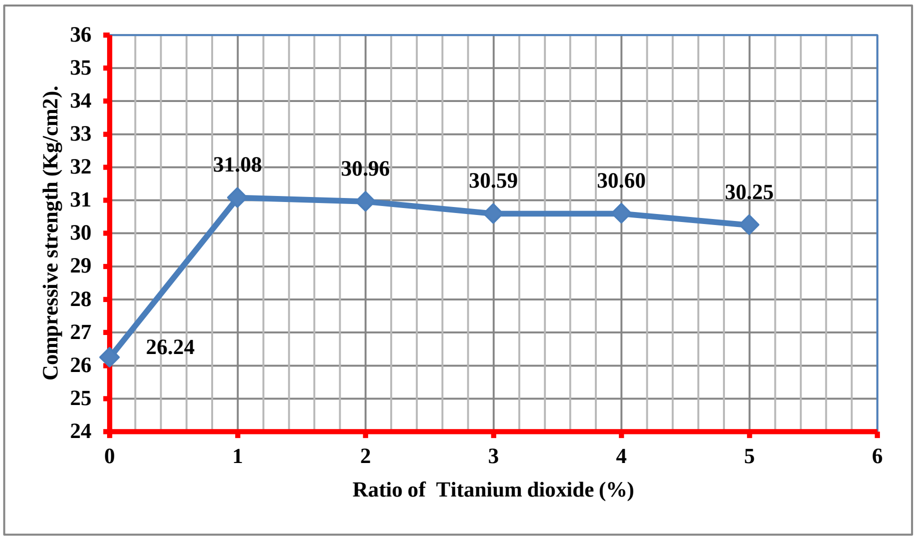

Figure 4. 8: Relation between the ratio of TiO and 7 days compressive strength.

4.5.2.2 Compressive strength 28 days age:

The compressive strength of concrete mixes having 0%, 1%, 2%, 3%, 4% and 5% of TiO by cement content are shown in Figure (4.9).

Figure (4.9) represented the relation between the compressive strength and TiO content. The compressive strength increased from 37.37 MPa at 0% of TiO to 43.37 MPa at 1% of TiO. Afterward, adding additional 1% of TiO by cement content does show any significant improve to compressive strength but it was decrease the compressive strength with very low rate -2.18% for each 1% of TiO.

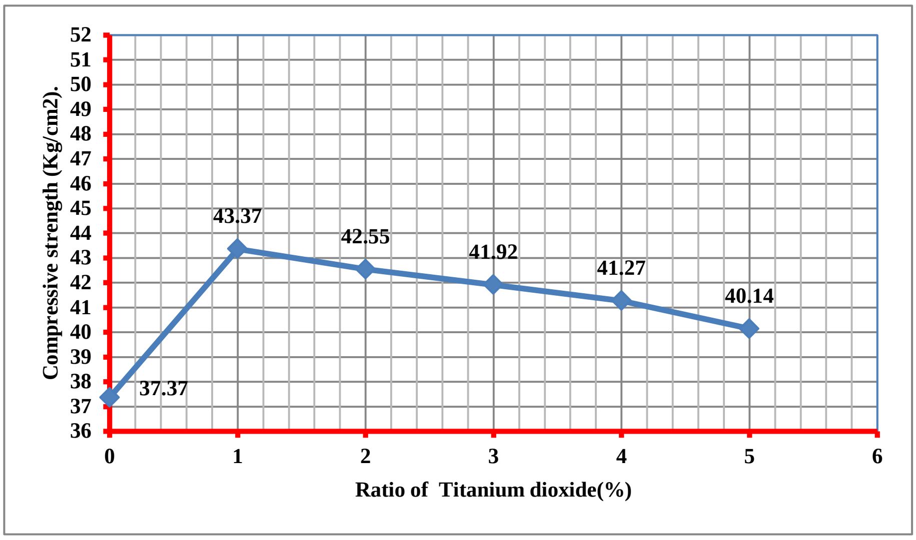

Figure 4. 9: Relation between the ratio of TiO and 28 days compressive strength value.

4.5.3 Justification of Results:

Jayapalan, et al., 2010, studied the effect of chemically nonreactive Anatase TiO_2 nanoparticles on early-age hydration of cement. 2010. The effects of different percentage rates of added TiO_2 to Portland cement on early age behavior were examined, and influence of TiO_2 on hydration of C_3S phase, this study showed that, an increase in addition rates of TiO_2 accelerates the rate of cement hydration. Li, et al., 2007, discussed the effect of Nano-TiO_2 and Nano-SiO_2 on concrete and the ability to use their as additive on concrete, the study proved that the concrete containing 1% of Nano-TiO_2 by weight of cement have the best flexural fatigue performance, and better than that of the concrete containing Polypropylene fibers. From these two studies can conclude that the TiO_2 may increase the hydration rate but in high percentage and this indicated by slump result plot which indicate that up to 5% of TiO_2 there is no increasing on the hydration rate and the main increasing of the hydration occur on C_3S which response to the final strength of concrete which not observed at 28-dayes in very clear fashion. But from the second study the percentage 1% of Nano-TiO_2 by weight of cement have the best flexural fatigue performance, and this will explain that we have the best compressive strength at 1% that may indicate that the content of fine nano particles in TiO_2 is more than BIO or YIO which make the increasing of TiO_2 percentage with no meaning and may alter to compressive strength negatively.

4.6 Concrete with Barium Sulfate “BaS”:

This mix is prepared by adding Barium Sulfate (BaS) as NMM. The effect of NMM in the mechanical properties of fresh and hardened concrete explained as below.

4.6.1 Mechanical properties of fresh concrete “Slump”:

While the slump value of normal concrete mix was 90 mm with true shape, the slump of the BaS mix was between 90 to 105 mm and has a true shape. The slump values of mixes having 0.5%, 1%, 1.5%, 2% and 2.5% of BaS material by cement content are shown in Figure (4.10).

Figure (4.10) reveals that there was a very slight increase in slump from 90 mm to 105 mm at 0% to 5% of BaS respectively with increasing rate 3.3% for each 0.5% of BaS material.

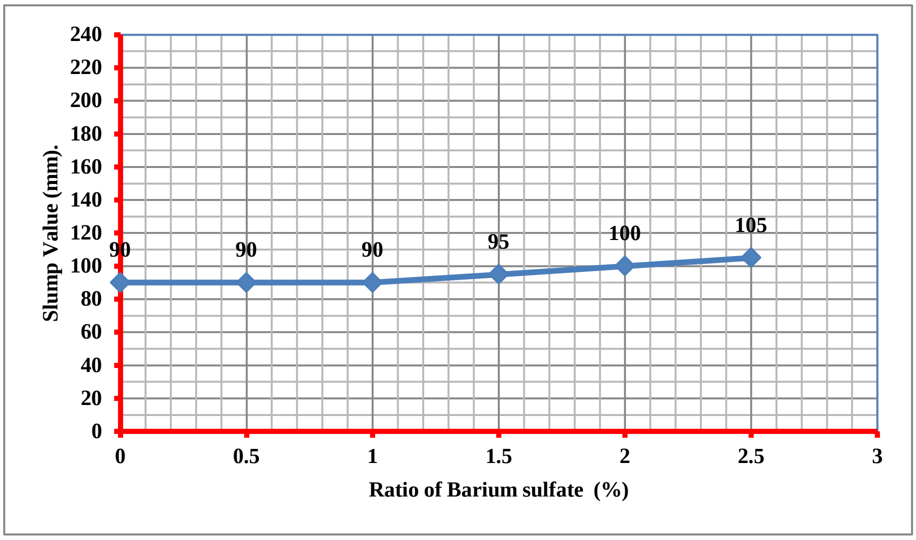

Figure 4. 10: Relation between the ratio of BaS and slump value.

4.6.2 Mechanical properties of hardened concrete:

4.6.2.1 Compressive strength 7 days age:

The 7 days compressive strength of concrete mixes having 0%, 0.5%, 1%, 1.5%, 2% and 2.5% of BaS by cement content are shown in Figure (4.11).

Figure (4.11) reveals that there was low increase in compressive strength from 26.24 MPa to 28.65 MPa at 0% and 1% of BaS respectively, with increasing rate of 9.2% for the first ratio. Afterward, adding additional 0.5% of BaS by cement content does show any significant improve to compressive strength. The average increasing rate of compressive strength was 2.3% for each additional 0.5% of BaS, but the total increase percent of compressive strength was 16.7% at 2.5% of BaS. The correlation between the compressive strength and the ratio of BaS in the mix was nearly positive linear correlation.

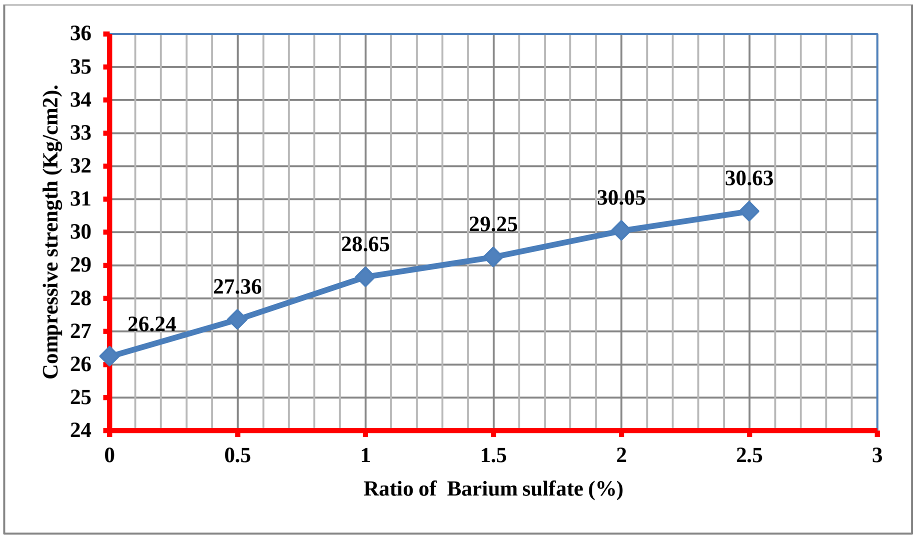

Figure 4. 11: Relation between the ratio of BaS and 7 days compressive strength value.

4.6.2.1 Compressive strength 28 days age:

The compressive strength of concrete mixes having 0%, 0.5%, 1%, 1.5%, 2% and 2.5% of BaS by cement content are shown in Figure (4.12).

Figure (4.12) represented a non-uniform relation between the compressive strength and BaS content, in the first two ratios 0.5% and 1% of BaS the compressive strength increased with slightly rate 1.6% and 2.4% respectively, but the compressive strength was increased from 37.37 MPa at 0% of BaS to 41.97 MPa at 1.5% of BaS with increasing rate 12.3%. Afterward, adding additional 0.5% of BaS by cement content does not show any significant improve to compressive strength and it was increase the compressive strength with very slightly rate 1% for each 0.5% of BaS.

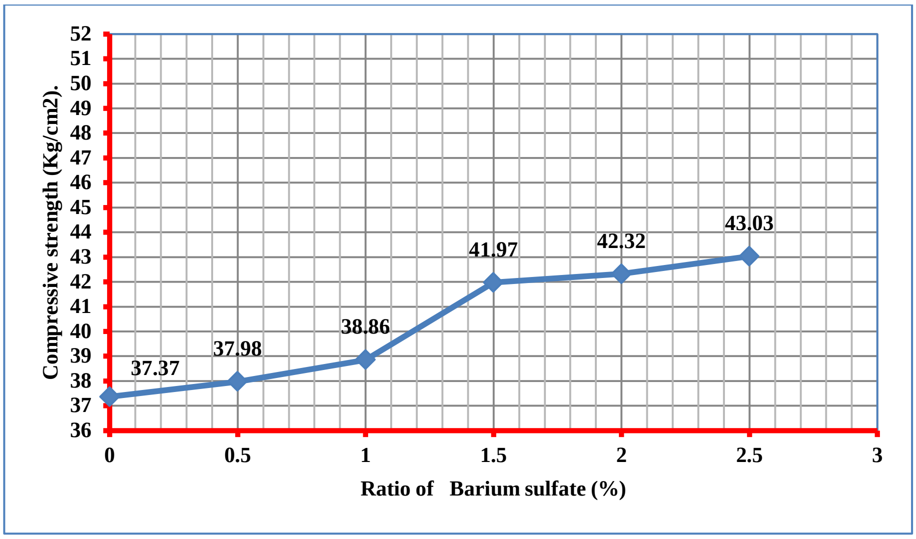

Figure 4. 12: Relation between the ratio of BaS and 28 days compressive strength.

4.6.3 Justification of Results:

The behavior of BS was very closed to BIO and this may indicate that most nano materials will behave the same behavior especially for compressive strength.

4.7 Concrete with Poly Acrylic Acid "PAA":

This mix is prepared by adding Poly Acrylic Acid (PAA) as NMM. The effect of NMM in the mechanical properties of fresh and hardened concrete explained as below.

4.7.1 Mechanical properties of fresh concrete "Slump":

While the slump value of normal concrete mix was 90 mm with true shape, the slump of the PAA mix was between 90 to 210 mm and has a true shape. The slump values of mixes having 1%, 2%, 3%, 4% and 5% of PAA material by cement content are shown in Figure (4.13).

Figure (4.13) reveals that there was very high increase in slump from 90 mm to 210 mm at 0% to 5% respectively with increasing rate 26.7% for each 1% of PAA material, the total increasing percent in slump value was 133.3% at 5% PAA.

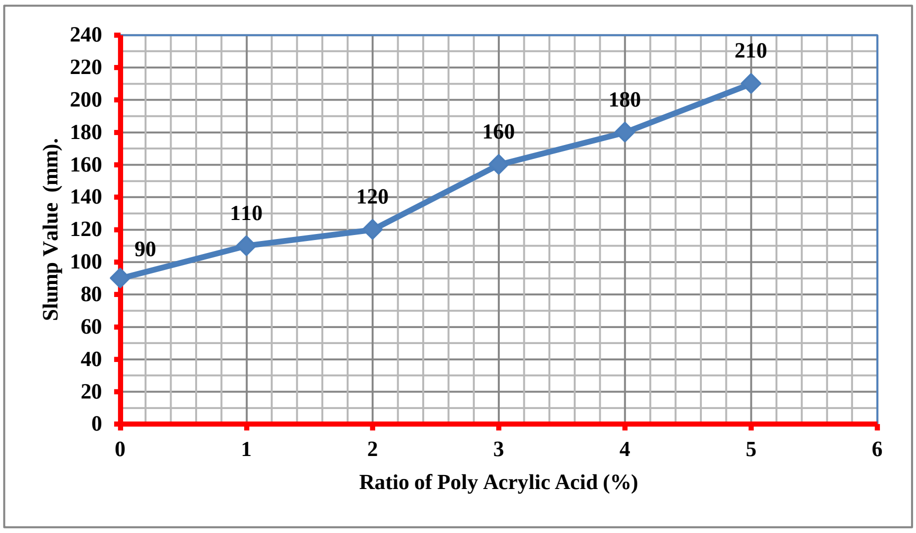

Figure 4. 13: Relation between the ratio of PAA and slump value.

4.7.2 Mechanical properties of hardened concrete:

4.7.2.1 Compressive strength 7 days age:

The 7 days compressive strength of concrete mixes having 0%, 1%, 2%, 3%, 4% and 2.5% of PAA by cement content are shown in Figure (4.14).

Figure (4.14) reveals that there was low increase in compressive strength from 26.24 MPa to 27.87 MPa at 0% to 1% respectively, with increasing rate of 6.2% for the first ratio. Afterward, adding additional values of PAA by cement content does show any significant improve to compressive strength but it was decrease the compressive strength with very low rate -1.56% for each 1% of PAA. At ratio 5% of PAA from cement content nearly does not effect in compressive strength and remain the compressive strength as 0% of PAA.

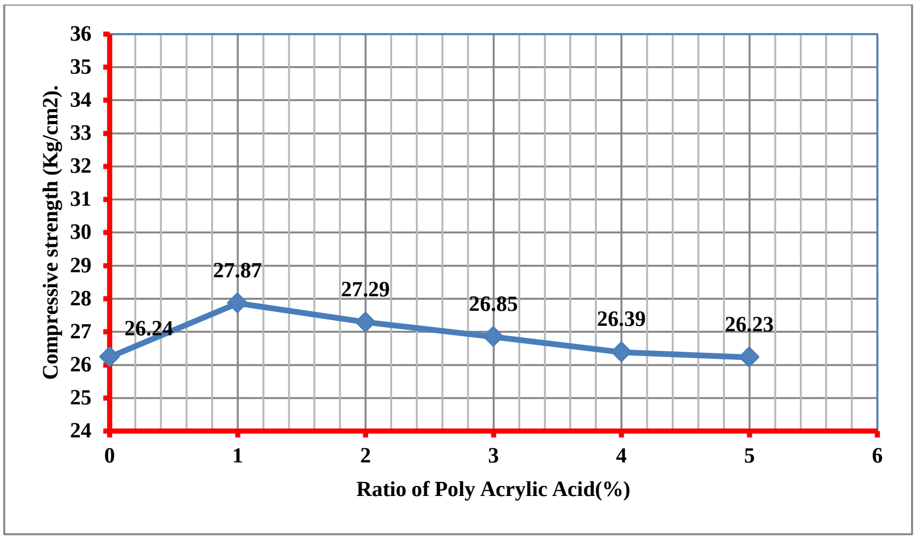

Figure 4. 14: Relation between the ratio of PAA and 7 days compressive strength value.

4.7.2.2 Compressive strength 28 days age:

The compressive strength of concrete mixes having 0%, 1%, 2%, 3%, 4% and 5% of PAA by cement content are shown in Figure (4.15).

Figure (4.15) represented almost very slightly increase relation in compressive strength at the first three ratio 1%, 2% and 3% of PAA material, then very slightly decrease relation at latest two ratio 4% and 5% of PAA material. In the first ratio 1% of PAA the compressive strength was 38.69 MPa with increasing ratio 3.6%, and then the increasing rate was decrease to 2.5% at 2% of PAA. At percent 5% of PAA the compressive strength decreases to 36.34 MPa with decreasing ratio -2.7%.

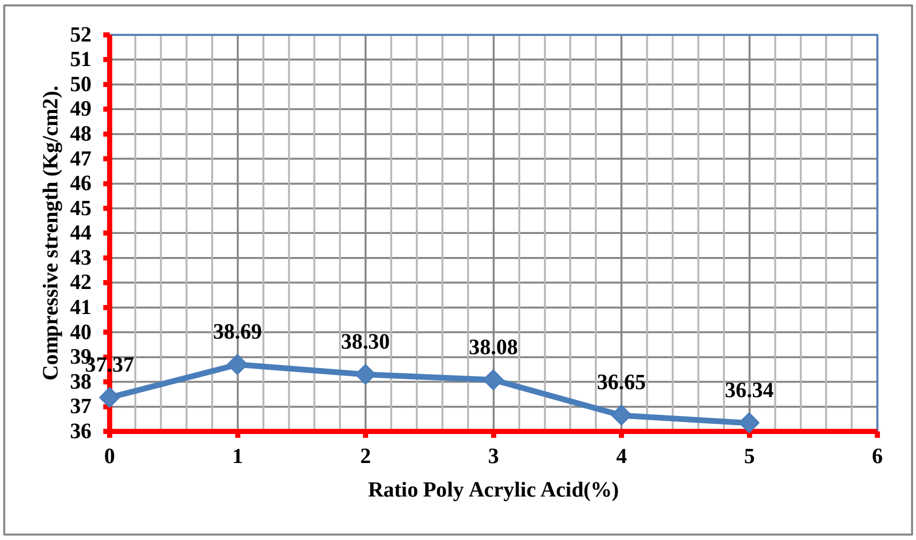

Figure 4. 15: Relation between the ratio of PAA and 28 days compressive strength value.

4.7.3 Justification of Results:

Nmai, et al., 1998, concluded that the effect of PAA is very close to super plasticizer. PAA is considered as mid-range water reducing admixture owing to slump which achieved in this study (90mm to 210mm) and from point view of chemical composition PAA is considered as poly carboxylates and this family of chemical compounds classified as Super plasticizers according to (ASTM C 1017, Type 1). Percentage of 3-4% may be the effective one to make a compromise between slump loss and compressive strength.

4.8 Concrete with China Clay "Kaolin" "CCK":

This mix is prepared by adding Kaolin (CCK) as NMM. The effect of NMM in the mechanical properties of fresh and hardened concrete explained as below:

4.8.1 Mechanical properties of fresh concrete "Slump":

While the slump value of normal concrete mix was 90 mm with true shape, the slump of the CCK mix was between 90 to 60 mm and has also a true shape. The slump values of mixes having 1%, 2%, 3%, 4% and 5% of CCK material by cement content are shown in Figure (4.16).

Figure (4.16) reveals that there was very slightly decrease in slump from 90 mm to 60 mm at 0% to 5% respectively with decreasing rate 6.7% for each 1% of CCK material, the total decreasing percent in slump value was 33.3% at 5% of CCK.

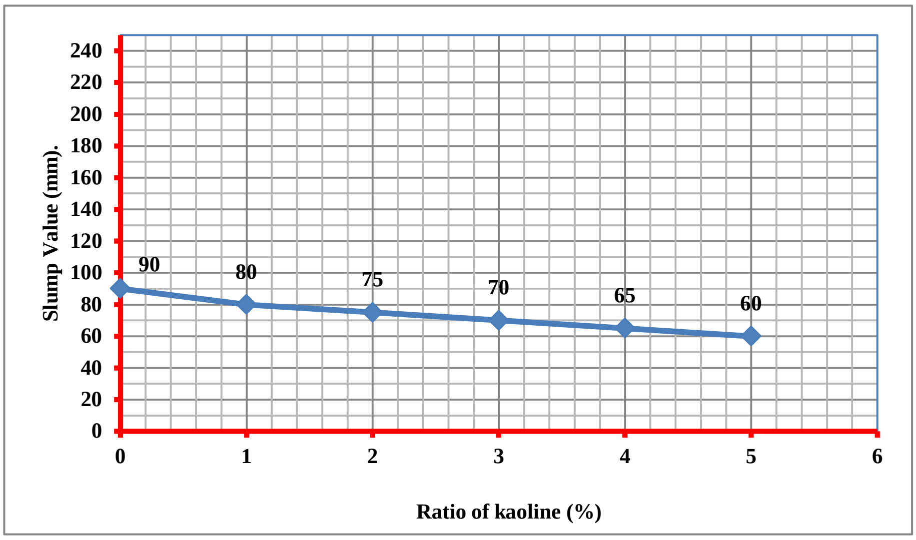

Figure 4. 16: Relation between the ratio of CCK and slump value.

4.8.2 Mechanical properties of hardened concrete:

4.8.2.1 Compressive strength 7 days age:

The 7 days compressive strength of concrete mixes having 0%, 1%, 2%, 3%, 4% and 2.5% of CCK by cement content are shown in Figure (4.17).

Figure (4.17) reveals that there was low increase in compressive strength from 26.24 MPa to 29.86 MPa at 0% and 1% of CCK respectively, with increasing rate of 13.8% for the first ratio. Afterward, adding additional 1% of CCK by cement content does not show any significant improve to compressive strength but it was decrease the increase of compressive strength with very low rate -1.93% for each 1% of CCK.

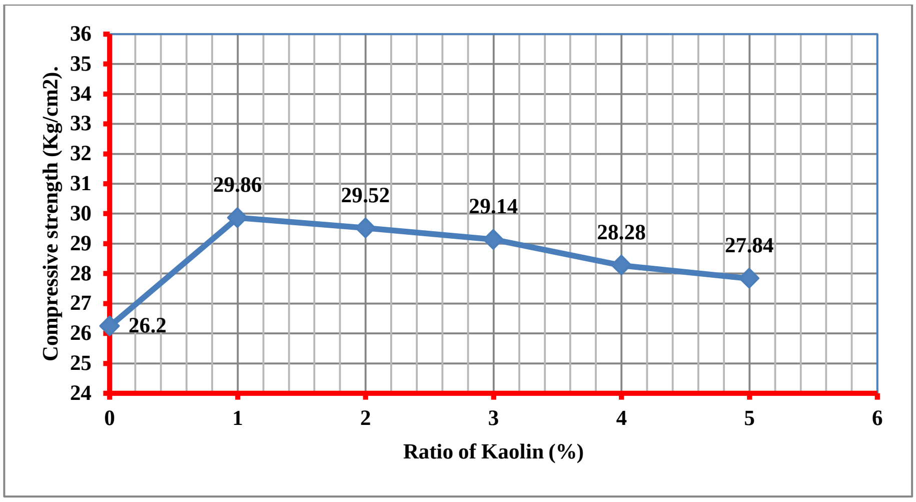

Figure 4. 17: Relation between the ratio of CCK and 7 days compressive strength value.

4.8.2.2 Compressive strength 28 days age:

The compressive strength of concrete mixes having 0%, 1%, 2%, 3%, 4% and 5% of CCK by cement content are shown in Figure (4.18).

Figure (4.18) represented almost decrease relation between the compressive strength and CCK content. The compressive strength decreased from 37.37 MPa at 0% of CCK to 32.84 MPa at 5% of CCK. This means that adding every 1% of CCK will decrease the compressive strength by about 2.42%. The decreasing rate of compressive strength related to CCK content was nearly constant and the totally decreasing ratio in compressive strength was -12.1%.

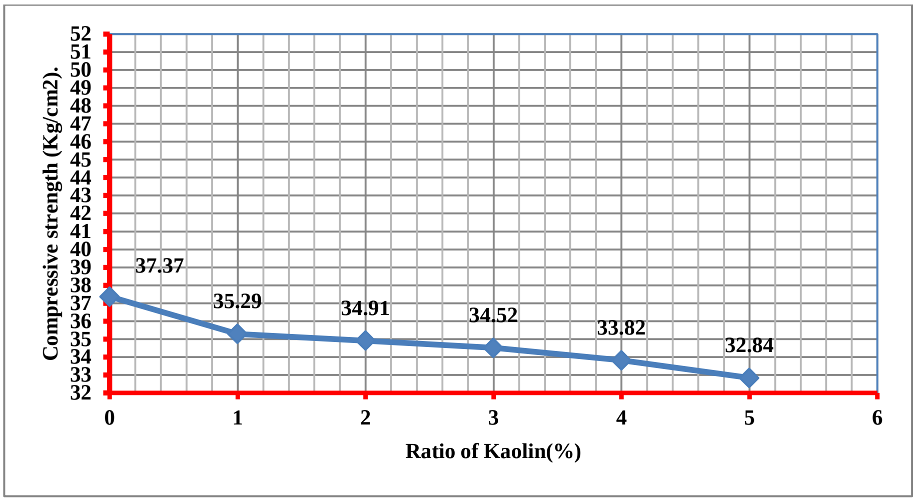

Figure 4. 18: Relation between the ratio of CCK and 28 days compressive strength value.

4.8.3 Justification of Results:

According to PCA (Design and Control of Concrete Mixtures, fourteenth edition), Kosmatka, et al., 2002, Meta kaolin, a special calcined clay, is produced by low temperature calcination of high purity kaolin clay. The product is ground to an average particle size of about 1 to 2 micrometers. Meta kaolin is used in special applications where very low permeability or very high strength is required. In these applications, meta-kaolin is used more as an additive to the concrete rather than a replacement of cement; typical additions are around 10% of the cement mass. This indicate that

1) Kaolin is classified as a clay material and this lead to be water absorbing material because all clays are layered materials(lamella) and then absorbed the water to their inter-layer spaces and this produce, the first one is slump loss will increase by increasing the percent of kaolin.

2) at early curing days (7-days) the kaolin control the hydration process which result as increasing the efficiency of hydration process and reducing the hydration temperature and then make enhancement of concrete strength which outlined by the present study

3) at more later curing days (28- days) the concrete affected negatively by this controlling behavior and also by increasing of kaolin size, which also shown by the above plots. Finally owing to these unparalleled actions of kaolin the popular form of kaolin used is the meta-kaolin.

4.9 Comparison between the influences of the six tested NMM:

4.9.1 Mechanical propriety of fresh concrete “Slump”:

The slump value of all mixes with YIO, CCK, TiO, BIO, PAA and BaS nano materials at ratio ranging from 0%, to 5% or 0 to 2.5 with an increasing of 1% and 0.5 respectively are presented in Figure (4.19), Figure (4.20) and Table (4.2).

Table (4.2) shows that the PAA material gives the highest rate of increasing in slump value with 26.7% for each 1% adding of PAA, although at ratio 5% of PAA the compressive strength decreased by 2.7%. The worst performance was showed by YIO which obtained a decrease rate of slump 15.6% at each 1% increase of YIO.

Figure (4.20) explains the relation between the best percent of NMM which can give better enhancing of compressive strength and slump values.

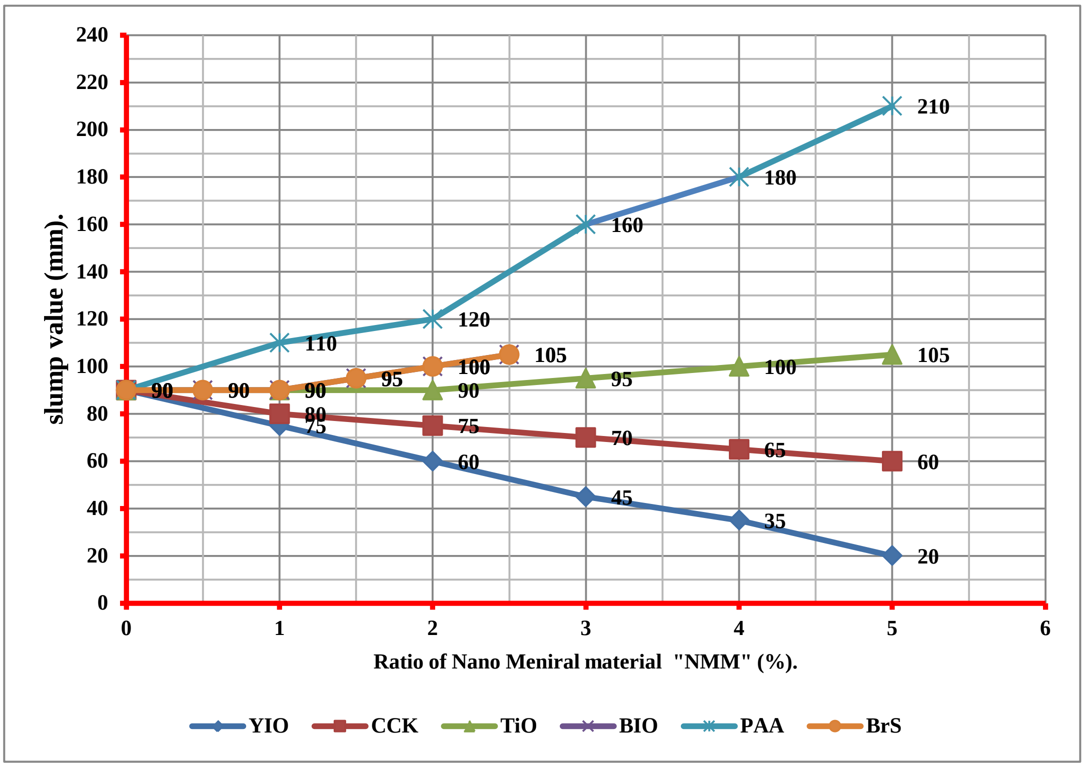

Figure 4. 19: Relation between several NMM with several percent and slump value.

Table 4. 2: optimum percent of NMM and slump value

No.	Name of NMM	Ratio of NMM at highest compressive strength (%)	Slump Value (mm)	Average Changing Rate of slump = $(100*(S-S_0)/S_0)/D$
1	Normal concrete, NC	-	90	0
2	Yellow iron oxide, YIO	5	20	-15.6%
3	Brown iron oxide, BIO	2.5	105	+6.7%
4	Titanium dioxide, TiO	1	105	+2.2%
5	Barium sulfate, BaS	2.5	105	+6.7%
6	***Poly acrylic acid, PAA***	***5***	***210***	***+26.7%***
7	Kaolin, CCK	1	80	-6.7%

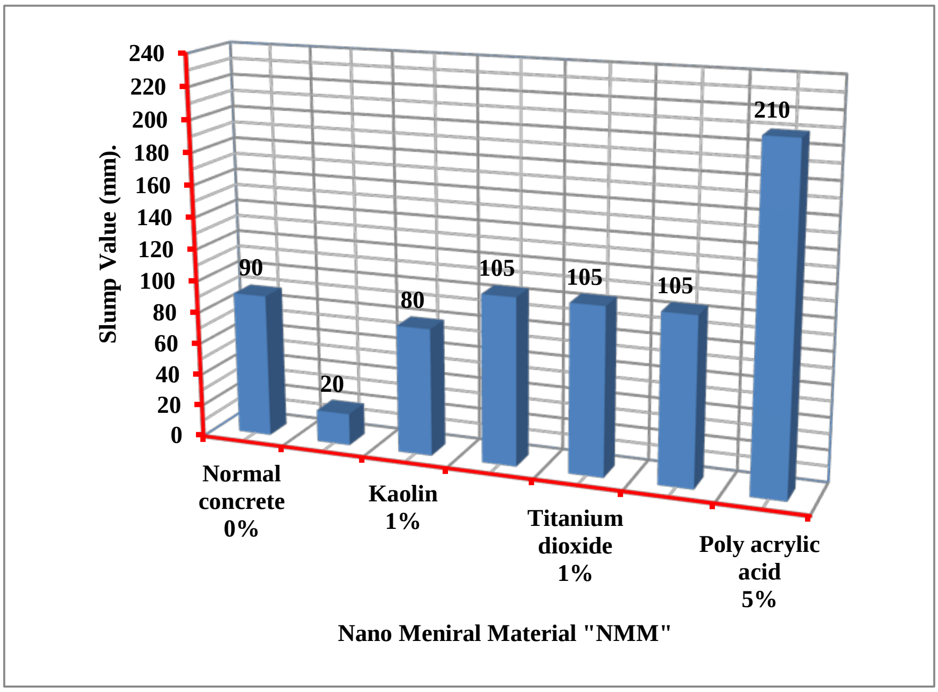

Figure 4. 20: Relation between best percent of several NMM and slump value

4.9.2 Mechanical propriety of hardened concrete "compressive strength":

The compressive strength, 7 days and 28 days of 6 NMM which applied in this study are presented in Figure (4.21) and Figure (4.22) respectively. The analysis of the results presented in Figure (4.21) to Figure (4.22) and Table (4.3) and comparing them with corresponding slump value, the following points are found:

1. Yellow iron oxide enhanced the compressive strength of concrete from 37.37 MPa to 43.90 MPa with a percent of 17.6%. However the slump value was reduced from 90 mm to 20 mm.

2. Titanium dioxide improved the compressive strength of concrete from 37.37 MPa to 43.37 MPa with a percent of 16.1%. At the same time, enhance the slump value increased from 90 mm to 105 mm with a percent of 16.7%.

3. Barium sulfate enhanced the compressive strength of concrete from 37.37 MPa to 43.03 MPa with a percent of 15.2%. Also, the slump value increased from 90 mm to 105 mm with a percent of 16.7%.

4. Titanium dioxide and Barium sulfate nearly hade a similar effect in enhancing the workability and compressive strength.

5. China clay “Kaolin” enhanced the initial time set, the compressive strength decrease from 37.37 MPa to 35.3 MPa with a percent of 15.2%. In addition. Also the slump value decrease from 90 mm to 80 mm with a percent of 11.11%.

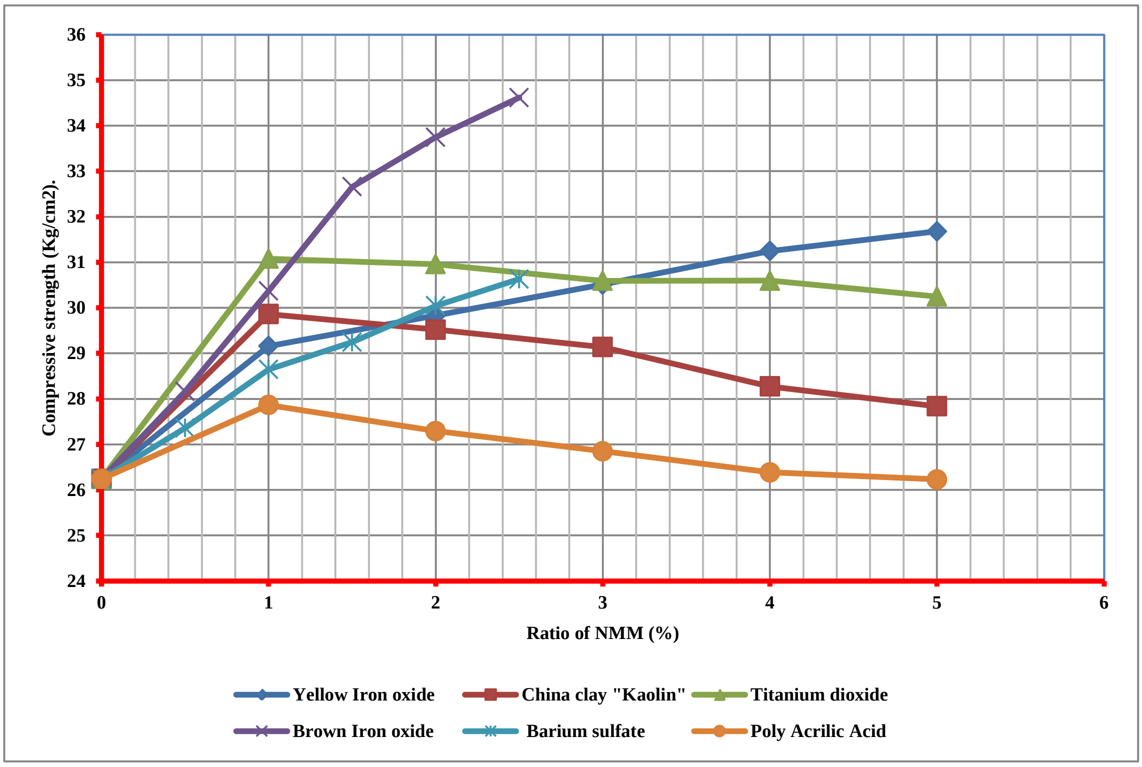

Figure 4. 21: Comparison between 7 days age compressive strength for several NMM’s contents.

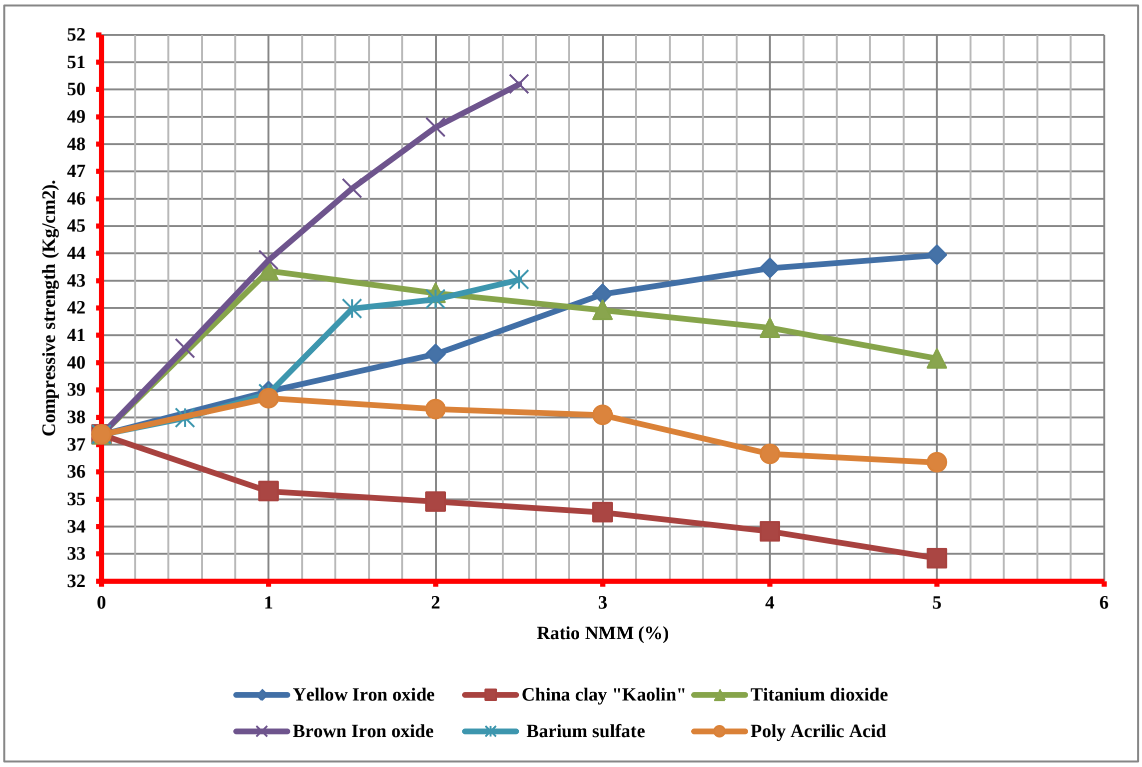

Figure 4. 22: Comparison between 28 days age compressive strength for several NMM’s contents.

Table 4. 3: Best percent of each NMM's, compressive strength and increasing percent.

No.	Name of NMM	Ratio of NMM from Cement content (%)	Compressive Strength 7 Days Age (MPa)	Increasing percent (%)	Compressive Strength 28 Days Age (MPa)	Increasing percent (%)
1	Normal concrete, NC	-	26.24	-	37.37	-
6	Poly acrylic acid, PAA	5	26.23	**-0.04**	36.34	**-2.76**
7	Kaolin, CCK	1	29.86	**13.80**	35.3	**-5.54**
5	Barium sulfate, BS	2.5	30.63	**16.73**	43.03	**15.15**
4	Titanium dioxide, TiO	1	31.08	**18.45**	43.37	**16.06**
2	Yellow iron oxide, YIO	5	31.70	**20.81**	43.90	**17.47**
3	Brown iron oxide, BIO	2.5	36.62	**39.56**	50.20	**34.33**

4.10 Effect of adding two or more NMM's together:

The performance of the concrete with more than one NMM's on the mechanical properties is investigated in this study. The aim of these tests is to investigate the possibility of adding up the individual advantage of the tested NMM's. An optimum percent of each NMM is first identified from the obtained results.

Table (4.4) presents the optimum NMM contents of the concrete mixes. It is decided to use the max content of PAA in all mixes as this NMM significantly improve workability of the mix. Four new mixes were prepared having 5% of PAA and 5% of YIO, 2.5% of BIO, 1% of TiO, and 2.5% of BaS. The fifth mix was prepared using the four NMM at their optimum content.

The slump values and compressive strength of the new 5 mixes are included in table (4.5).

Table (4.5) and comparing them with corresponding slump value, the following points are found:

1. Adding PAA to the YIO mix will improve the slump with a percent 300% compare with YIO alone , however the compressive strength will be decrease with a percent of -1.74% at 7 days age and -8.41% at 28 days age.

2. Adding PAA to the BIO mix will improve the slump with a percent 61.90% in comparison with BIO alone , but the compressive strength will be decrease with a percent of -5.93% at 7 days age and -1.69% at 28 days age.

3. Adding PAA to the TiO mix will improve the slump with a percent 38.10% in comparison with TiO alone , also the compressive strength will be very slightly increase with a percent of .35% at 7 days age and 1.73% at 28 days age.

4. Adding PAA to the BaS mix will improve the slump with a percent 42.86% comparing with BaS alone , however the compressive strength will be decrease with a percent of -7.44% at 7 days age and -8.69% at 28 days age.

5. Adding PAA to all other NMM will decrease the slump with a percent 4.76% comparing with BIO alone , also the compressive strength will be decrease with a percent of -19.91% at 7 days age and -21.75% at 28 days age comparing with BIO mix.

Table 4. 4: Optimum percent of NMM and compressive strength value

No	The Nano Mineral Materials		Percent of Poly Acrylic Acid	Name of mix
	Name	Percent of adding		
1	Yellow iron oxide, YIO	5	5	YIOPAA
2	Brown iron oxide, BIO	2.5	5	BIOBIO
3	Titanium dioxide, TiO	1	5	TiOPAA
4	Barium sulfate, BS	2.5	5	BaSPAA
5	Mixing all NMM, YIO, BIO, TiO & BS	All optimum percent of NMM	5	TMIX

Table 4. 5: Compressive strength and slump value for the mixing of some NMM together:

No.	Name of mix	Slump value for primary NMM	Slump value	Shape of slump	Compressive strength at 7 days age Kg/cm^2	Compressive strength at 28 days age Kg/cm^2
1	NC	90	90	True Shape	26.24	37.37
2	YIOPAA	20	80	True Shape	31.15	40.21
3	**BIO,PAA**	**105**	**170**	**True Shape**	34.45	49.35
4	TiOPAA	105	145	True Shape	31.19	44.12
5	BaSPAA	105	150	True Shape	28.35	39.29
6	TMIX	-	100	True Shape	29.33	39.28

4.11 Influence of NMM at optimum contents on other mechanical properties:

Several mixes were prepared and tested to obtain the influence of the proposed NMM at this optimum content on flexure strength, shear strength, indirect tensile strength and modulus of elasticity.

4.11.1 Effect on Flexure strength:

The ACI 318-11 talked about the relation between the cylinder compressive strength and the modulus of rupture and mention an empirical equation as below:

$$R = 0.62\sqrt{f'c}$$

Where: f'_c was the cylinder compressive strength.

The flexure strength test was done by using three beam concrete samples with size 150* 150* 750 mm or with size 100*100* 500 mm, in this research the first size was selected.

Table (4.6) discussed the result of flexure strength of normal concrete (control mix), concrete mix with 2.5% of BIO and concrete mix with 2.5% of BIO with 5% of PAA. And from table (4.6) the following points are found:

1. Normal concrete: The flexure strength of the normal concrete at 28 days age was 3.80 MPa and the fracture was normal in the one-third middle span. But the flexure strength due to ACI318 was 3.39 with changing percent of 10.79%.

2. Concrete with BIO material: The tested flexure strength of concrete with 2.5% of BIO for beams at 28 days age was 4.60 MPa, with increasing percent of 21.05% form the normal concrete flexure strength. Also the fracture was normal in the one-third middle span.

3. Concrete with BIO and PAA material: The flexure strength of concrete with2.5% of BIO and 5% of PAA at 28 days age was 4.72 MPa with increasing percent of 24.21% form the normal concrete flexure strength.

4. The BIO material enhance the flexure strength with percent 21.0% but when adding PAA to the mix can enhance the mix to percent 24.1% so the PAA have appositive effect in enhancing the flexure strength.

Table 4. 6: Flexure strength value for the mixing of some NMM together:

Type of Concrete	Cubic Compressive strength (MPa)	Cylinder compressive strength $f'_c=f_c/1.25$	Modulus of Rupture (MPa)	Increasing or decreasing percent of Modulus of Rupture (%)	Modulus of Rupture According to ACI, $f_r=0.62(f'_c)^{0.5*}$ (MPa)	Increasing or decreasing percent of Modulus of Rupture due to ACI (%)
NC	***37.37***	***29.90***	***3.80***	-	3.39	10.79%
NC with BIO	50.19	40.15	4.60	21.05%	3.93	14.56%
NC with BIO &PAA	49.15	39.32	4.72	24.21%	3.89	17.58%

* **f'_c in the equation is cylindrical compressive strength in MPa**

4.11.2 Shear strength 28 days age:

The ACI Code 318.11 clause 11.2.1.1 was taking about the relation between the cylinder compressive strength and the Shear strength and mentions an empirical equation as below:

$$Vc = 0.53\sqrt{f'c}\, bd$$

Where: f'c was the cylinder compressive strength.

The shear strength test don by using three beam concrete samples with size 150* 150* 750 mm or with size 100*100* 500 mm, in this research the sample size were 150* 150* 750 mm.

Table (4.7) discussed the result of shear strength of normal concrete (control mix), concrete mix with 2.5% of BIO and concrete mix with 2.5% of BIO with 5% of PAA. And from table (4.7) the following points are found:

1. The shear strength of normal concrete was 949.6 KPa, this value was calculated from flexural strength test using simple beam with third point loading but the

2. nominal shear strength of normal concrete according to ACI Code 318.11 clause 11.2.1.1 was 907.4 KPa thus the deference between the nominal shear strength and calculated shear by testing is +4.44%. The Value of shear strength represented of 2.54% from cubic compressive strength.

3. The shear strength of concrete mix with 2.5% of BIO was 1162.5 KPa. The Value of shear strength represented to 2.32% of compressive strength. In another way, the BIO can enhance the shear strength with a percent of 22.41%.

4. The shear strength of concrete mix with 2.5% of BIO and 5% PAA was 1190.0 KPa. The value of shear strength represented to 2.42% of compressive strength. In another way, the BIO can enhance the shear strength with a percent of 25.31%.

Table 4. 7: Shear strength results for NC, NC with BIO and NC with BIO and PAA together.

Type of concrete	Compressive strength (MPa)	Shear strength calculated from Modulus of rupture test (KPa)	Increasing or decreasing percent of Shear Strength (%)
Normal concrete	***37.37***	***949.6***	-
Normal concrete with BIO	50.19	1162.5	22.41
Normal concrete with BIO &PAA	49.35	1190.0	25.31

4.11.3 Indirect tensile strength:

A better correlation found between the various measures of tensile strength and the square root of the compressive strength. A number of empirical formulae connecting f_t and fc´ have been suggested, many of them of the following type:

1. The American Concrete Institute was used the formula $\mathbf{f_t = k\ (f_c)^n}$, where k and n are coefficients. The values of n between ½ and ¾ have been suggested.

2. Gardner was used the former value, and Poon found a value near the later value (ACI), cylinders being used in both cases. Probably the best-fit overall is given by the expression, $\mathbf{f_t = 0.3\ (f_c)^{2/3}}$, Where, f_t is the splitting strength, and fc´ is the compressive strength of cylinders, both in mega Pascal.

3. The BS 8007:1987 mention an mathematical formulae to find the indirect tension of concrete related to cubic compressive strength was $\mathbf{f_t = 0.12\ (fc)^{0.7}}$.

The indirect tension test don by using three cylindrical concrete samples with size 150mm diameter and 300 mm in height.

Table (4.8) and Table (4.9) discussed the result of indirect tension strength of normal concrete (control mix), concrete mix with 2.5% of BIO and concrete mix with 2.5% of BIO with 5% of PAA. And from table (4.8) the following points are found:

1. The result of indirect tensile strength of normal concrete (control mix) was 3.05 MPa, this value represented to 8.17% of cubic compressive strength.

2. The result of indirect tensile strength of concrete with 2.5% of BIO was 3.48 MPa with increasing percent of 14.21% from control mix. Thus the indirect tension of BIO mix was represented to 6.93% from the cubic compressive strength.

3. The result of indirect tensile strength of concrete with 2.5% of BIO and 5% PAA was 3.52 MPa with increasing percent of 15.31% from control mix. Thus the indirect tension of BIO mix was represented to 7.13% from the cubic compressive strength

4. All result located between the minimum and maximum range according to American concrete institute and between Raphael equation and Oluokun equation of indirect tensile strength.

5. The BIO can enhance the indirect tension strength with percent 14.07% and when adding PAA to the mix will increase the indirect tension strength to 15.16% percent from the normal concrete indirect tension.

Table 4. 8: Indirect tension strength and compressive strength values of NC, NC with BIO and with BIO &PAA.

Type of concrete	Compressive strength (MPa)	indirect tension strength (MPa)	Increasing or decreasing percent of indirect tension Strength (%)
NC	***37.37***	3.05	-
NC with BIO	50.19	3.48	14.21%
NC with BIO &PAA	49.35	3.52	15.31%

Table 4. 9: Indirect tension strength value of NC, NC with BIO and with BIO &PAA and comparing with ASTM, Raphaeal equation and Oluokum equation

Concrete type	Cylindrical Compressive strength	Experimental value of indirect tensile strength	Mathematical value of indirect tensile strength According to American Concrete Institute		Mathematical value of indirect tensile strength	
			Min. equation $f_t = [0.3(f_c)^{1/2}]$	Max. equation $f_t = [0.3(f_c)^{3/4}]$	Raphael Equation $f_t = [0.313(f_c)^{0.667}]$	Oluokun Equation $f_t = [0.294(f_c)^{0.69}]$
	MPA	MPA	MPA	MPA	MPA	MPA
NC	29.89	3.05	3.06	3.84	3.02	3.07
NC with BIO	40.16	3.48	3.55	4.79	3.68	3.76
NC with BIO & PAA	39.48	3.52	3.52	4.73	3.63	3.71

4.11.3 Modulus of Elasticity at 28 days age:

The ACI 318 Clause 8.5 was taking about the relation between the cylinder compressive strength and the modulus of elasticity and mentions an empirical equation as below:

$$E_n = 4700\sqrt{f'c}$$

Where: f’c was the cylinder compressive strength.

Nine cylindrical sample withe size 150 mm diameters and 300 mm height were tested. The nine samples was made for three types of concrete which was normal concrete (control mix), concrete with 2.5% of BIO and finally concrete with 2.5% of BIO and 5% of PAA. The samples were made to measure and calculate the modulus of elasticity of concrete and the result mentioned in Table (4.10) and discussed in the paragraph below.

1- Normal Concrete: The modulus of elasticity at 28 days age of normal concrete (control mix) is 24373 MPa and the nominal value of modulus of elasticity according to ACI 319 Clause 8.5 is 25697 MPa with difference ratio 5.43% from the tested samples, Figure (4.23) explain the result of modulus of elasticity testing for normal concrete.

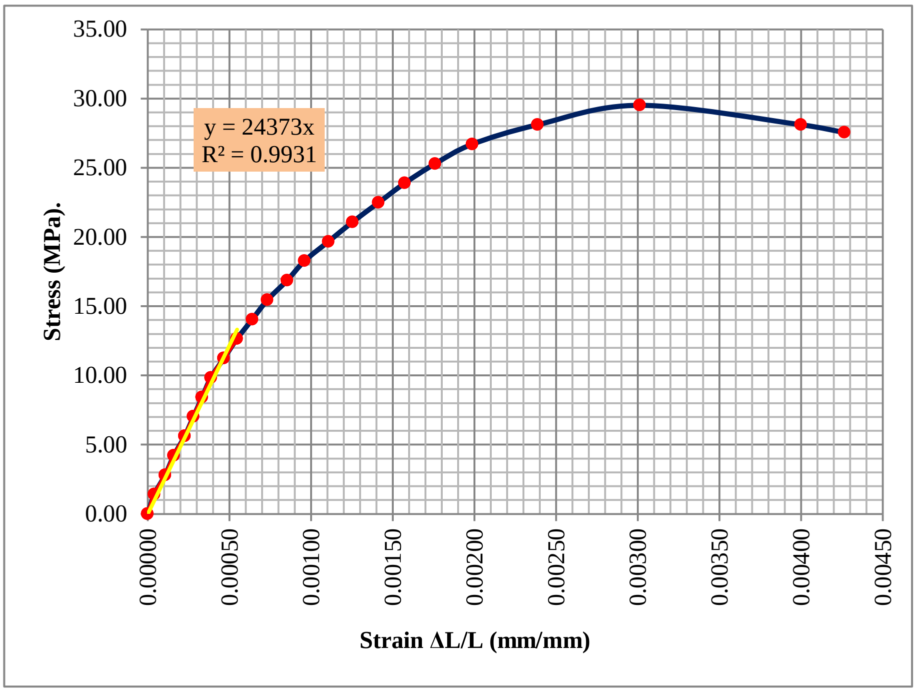

Figure 4. 23: Strain – stress diagram for normal concrete

2- Normal concrete with BIO: The modulus of elasticity at 28 days age of the concrete with 2.5% of BIO was 28671 MPa. The BIO was enhanced the modulus of elasticity of concrete with a percent of 17.63%. Figure (4.24) explain the result of modulus of elasticity testing for concrete with 2.5% of BIO.

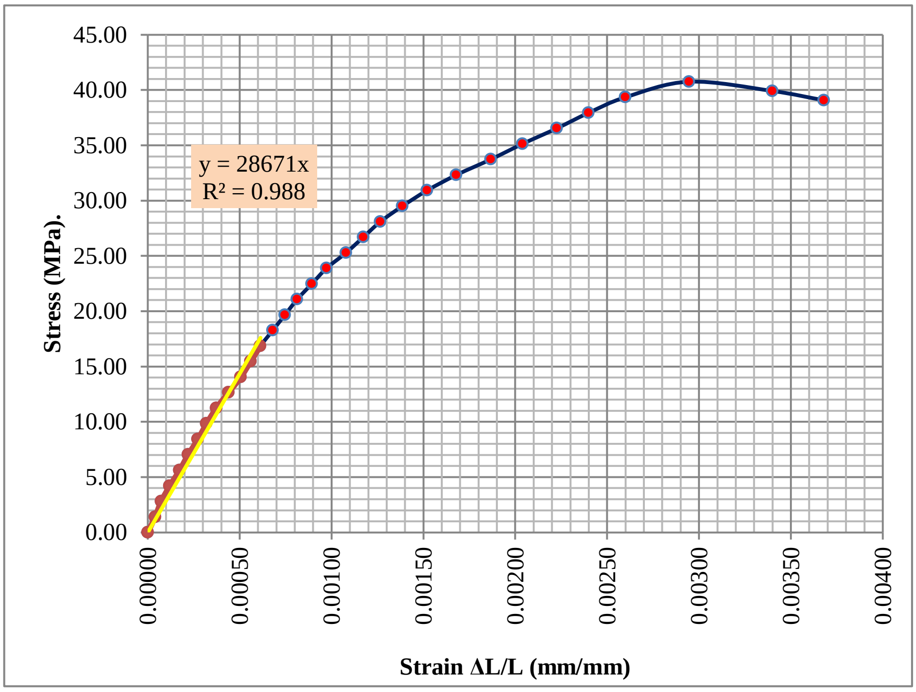

Figure 4. 24: Strain stress diagram for normal concrete with BIO.

3- Concrete with BIO and PAA: The modulus of elasticity at 28 days age of concrete with 2.5% of BIO and 5% of PAA was 25875 MPa. The BIO with PAA was enhanced the modulus of elasticity of concrete with a percent of 14.57%, thus the PAA reduce the modulus of elasticity with a percent of 3.06%. Figure (4.25) and Figure (4.26) were explained the result of modulus of elasticity testing for normal concrete with BIO and PAA and the comparisons of the three type of concrete ,NC, BIO and BIOPAA.

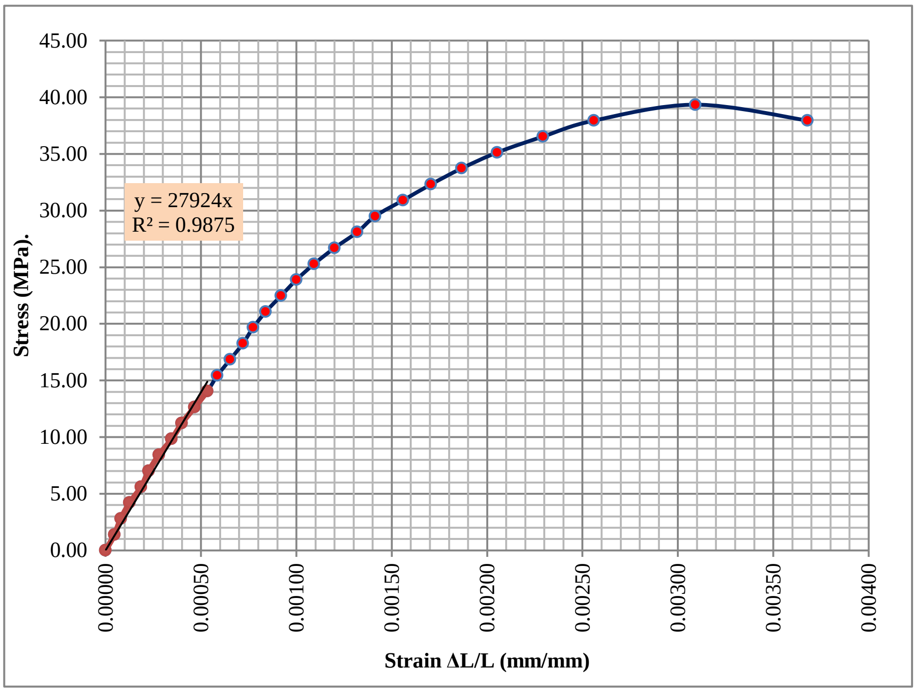

Figure 4. 25: Strain stress diagram for normal concrete with BIO and PAA.

Table 4. 10: modulus of elasticity value of normal concrete and with mixing of some NMM together.

Type of concrete	Compressive strength (MPa)	Modulus of Elasticity (MPa)	Increasing or decreasing percent of Modulus of Elasticity (%)
Normal concrete	***380.9***	***24373***	-
Normal concrete with BIO	50.19	28671	17.63%
Normal concrete with BIO &PAA	49.35	27924	14.57%

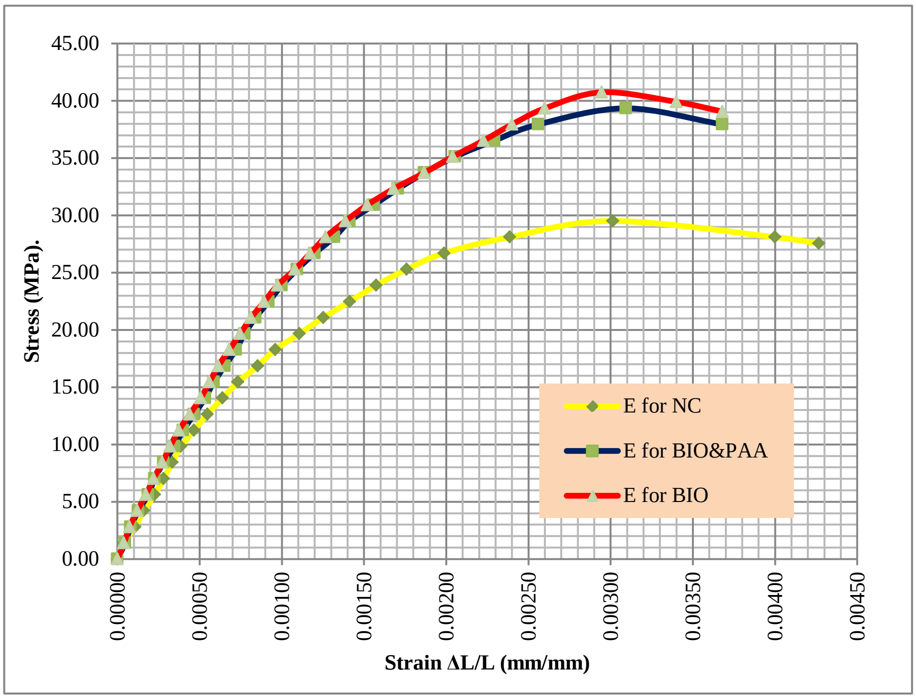

Figure 4. 26: Result of modulus of elasticity testing for NC, NC with BIO and NC with BIO&PAA.

4.11.4 Compressive strength and time relationship:

4.11.4.1 Compressive strength and time relationship in ACI206:

In most concrete, the compressive strength increase related with time. The compressive strength in the first 7 days may be reach to 65 – 75% from 28 days compressive strength but the compressive strength at age 7 to 14 days can reach to 80-90% from 28 days compressive strength. The ACI committee 206 clause 2.2.1 predicts the compressive strength at any time as mention in this equation:

$$(f'_c)_t = [t*(f'_c)_{28}]/[\alpha+\beta*t]$$

Where: $(f'_c)_t$ Predicted compressive strength at t time, t time in days " age of concrete", $(f'_c)_{28}$ compressive strength at 28 days, α in days and equal to 4 for type I cement, β factor depend on the type of curing and equal to 0.85 for moist curing.

4.11.4.2 Compressive strength and time relationship for the tested samples:

From the result of compressive strength for normal concrete and concrete with NMM at age 7, 14 and 28 day, which listed in table (4.11) and figure (4.27) , can calculate the percent between the 7 and 14 day's compressive strength to 28 days compressive strength, all result listed in table (4.11). The ratio of fc_7/fc_{28} and fc_{14}/fc_{28} for normal concrete was 70.2% and 88.4% respectively which according to ACI209 these ratios are 70.4% and 88.1% respectively.

In concrete with NMM, the ratio became between 69.8 and 77.5% for fc_7/fc_{28} and 86.8 to 89.8 for fc_{14}/fc_{28} . The main reason of deviation between ACI and work results is the type of the cement which ACI depend on cement type I but in this work type II cement was used, also the effect of the NMM additives .

Table 4. 11: Compressive strength at 7,14 and 28 days age and percent of fct/fc28 for normal and with NMM concrete:

Concrete Type	compressive strength at age (MPa)			fc_t/fc_{28} (%)			fc/fc28 According to ACI206		
	7 days	14 days	28 days	7 days	14 days	28 days	7	14	28
Normal concrete	26.24	33.03	37.37	70.2	88.4	100	70.4	88.1	100
Concrete with YIO	31.68	39.18	43.94	72.1	89.2	100			
Concrete with TiO	31.08	38.48	43.37	71.7	88.7	100			
Concrete with BIO	34.62	43.58	50.20	69.0	86.8	100			
Concrete with BrS	30.63	37.70	43.03	71.2	87.6	100			
Concrete with PAA	26.23	32.33	36.34	72.2	88.9	100			
Concrete with YIOPAA	31.15	36.10	40.21	77.5	89.8	100			
Concrete with BIOPAA	*34.45*	43.32	*49.35*	69.8	87.8	100			
Concrete with TiOPAA	31.19	39.23	44.12	70.7	88.9	100			
Concrete with BrSPAA	28.35	34.52	39.29	72.1	87.8	100			
Concrete with all NMM	29.33	35.10	39.28	74.7	89.3	100			

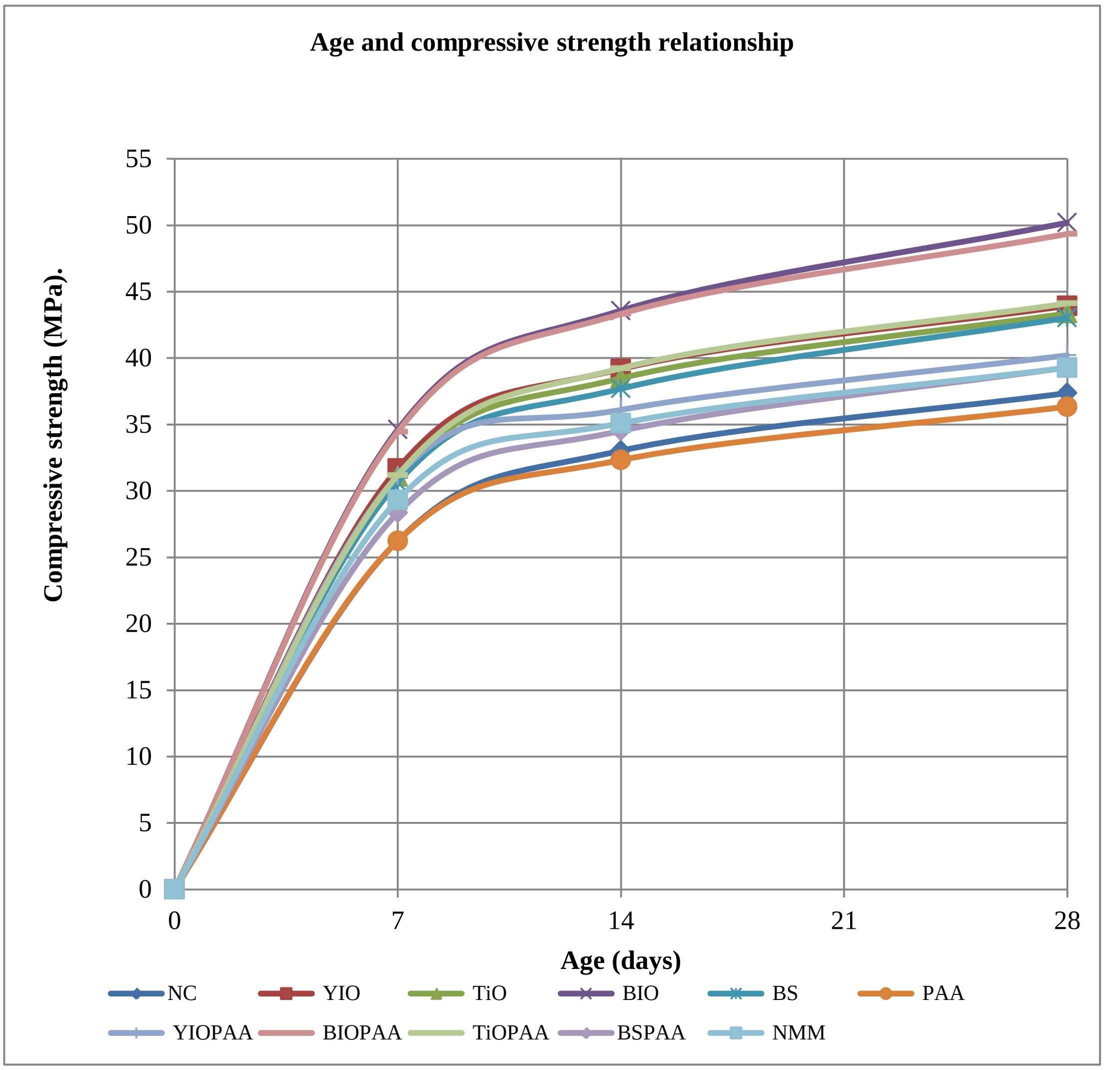

Figure 4. 27: Age and compressive strength relationship for normal concrete and with NMM.

Chapter (5)

Conclusion & Recommendations

5.1 Introduction:

This research investigates the effect of six Nano mineral materials which are Yellow Iron oxide (YIO), Brown Iron oxide (BIO), Titanium dioxide (TiO), Barium Sulfate (BaS), Kaolin (CCK) and Poky Acrylic Acid (PAA) on the mechanical property of fresh and hardened concrete. This investigation made by adding five different percent form each NMM to normal concrete. The mechanical property of fresh concrete made by conducting slump test for every mix “42 mixes”. The primary mechanical property of hardened concrete “compressive strength” made by crushing 4 cubic molds for investigation compressive strength for every age (7 and 28 days). Then the optimum ratio of NMM to enhance the workability and the compressive strength can be defined. The remaining tests for investigating the mechanical property “indirect tension strength, flexure strength, shear strength and modulus of elasticity” were made for normal concrete and the concrete with optimum two NMM ratios for compressive strength and workability. In this research the minimum samples number for compressive strength was four cubes for compressive strength and three samples for indirect tension and flexure strength and modulus of elasticity

5.2 Conclusion:

The result of this research showed that some of Nano mineral material as YIO, BIO, TiO, BS and PAA can enhance the mechanical property of fresh and hardened concrete as slump, compressive strength, indirect tension, flexure strength and modulus of elasticity with different percent of enhancing. The used NMM is considered a low cost material. The next concluding remarks were got from the obtained experimental observation:

5.2.1 Effect of single NMM on mechanical properties of concrete:

1. The compressive strength of normal concrete "Control Samples" was 26.24 MPa at 7 days age and 37.37 MPa at 28 days age. The flexural strength of NC was 3.80 MPa and the fracture was normal in the one-third middle span. The

calculated shear strength of NC was 949.6 KPa also the indirect tension was 3.05 MPa at 28 days age. The slump value of NC was 90 mm with true shape.

2. The most used NMM in the study except CCK and YIO can enhance the workability “slump” with several ratios.

3. The most used NMM in the study except CCK and PAA can enhance the compressive strength with several ratios.

4. PAA was the best material that enhance the slump value of concrete with true shape and without segregation, the increase of slump compared with standard sample was 133.33% and with a little or no reduction in compressive strength. Therefore, it can be concluded that in this study depended in PAA to enhance the workability “slump value”.

5. Adding YIO with a ratio of 5% can enhance the compressive of concrete to reach to 31.70 MPa at 7 days age and 43.90 MPa at 28 days age with increasing 20.7% and 17.60% at 7 and 28 days age respectively compared with normal concrete samples. The slump value at this percent was 20 mm with decreasing of 77.8% compared with normal concrete.

6. Adding 1% of TiO enhanced the compressive of concrete to reach to 31.08 MPa at 7 days age and 43.37 MPa at 28 days respectively. The increasing of compressive strength was 18.4% and 16.1% at 7 and 28 days age respectively compared with normal concrete. Thus TiO enhanced the slump value to reach to 105 mm with increasing of 16.7% compared with normal concrete.

7. The effect of BaS with a ratio of 2.5% can enhance the compressive of concrete to reach to 30.63 MPa at 7 days age and 43.03 MPa at 28 days age and with increasing 16.7% and 15.2% at 7 and 28 days age respectively compare with normal concrete. The slump value was 105 mm with increasing of 16.7%.

8. BIO founded to be the best material from the six NMM, which used in this research to enhance the compressive strength of concrete. BIO increased the compressive strength at optimum percent 2.5% to reach to 36.62 MPa at 7 days age and 50.20 at 28 days age with increasing of 39.6% and 34.3% at 7 and 28

days age compare with normal concrete. The slump value was 105 mm with increasing of 16.7%.

9. BIO with ratio 2.5% can enhance the flexure strength of concrete to reach to 4.60 MPa with increasing of 21.05% compare with normal concrete.
10. BIO with ratio 2.5% can enhance the shear strength of concrete to reach to 1162.5 KPa with increasing of 22.41% compare with normal concrete.
11. BIO with ratio 2.5% can enhance the indirect tension strength of concrete to reach to 3.48 MPa with increasing of 14.07% compare with normal concrete.
12. The modulus of elasticity of normal concrete was 24373 MPa according the tested samples and 25697 MPa according ACI 319 with difference percent 5.43%, which is acceptable difference ratio.
13. BIO with ratio 2.5% can enhance the modulus of elasticity of concrete to reach to 28671 MPa with increasing of 11.57% compare with normal concrete and 29784 MPa according ACI 319 with difference percent 3.883%, which is acceptable difference ratio.

5.2.2 Effect of using two or more NMM on mechanical properties of concrete:

1. Adding 5% of YIO and 5% of PAA enhanced the compressive of concrete to reach to 31.15 MPa at 7 days age and 40.21 MPa at 28 days age. The increase in compressive strength was 18.7% and 7.6% at 7 and 28 days respectively compared with normal concrete. The slump value was 80 mm, which mean a decrease of 11.11% compared with normal concrete.
2. YIO was more efficient in enhancing the compressive strength. When adding PAA the slump enhanced with a 300% compared with YIO In other hand, the existence of PAA reduced the compressive strength by 9.18% at age 28 days but will conserve on the slump compare with normal concrete.
3. A percent of 1% of TiO and 5% of PAA improve the compressive of concrete by 31.19 MPa at 7 days age and 44.12 MPa at 28 days respectively. The increasing percent of compressive strength was 18.9% and 18.1% at 7 and 28 days age respectively compared with normal concrete. Thus the slump value was 145 mm

with increasing percent of 61.1% compared with normal concrete. The TiO was compatible with PAA, where the PAA was not made side effect in compressive strength, the main effect of PAA in this mix was in slump.

4. Adding 2.5% of BaS and 5% of PAA together enhanced the compressive strength of concrete to reach to 28.35 MPa at 7 days age and 39.29 MPa at 28 days age. The increasing percent are 8.0% and of 5.1% at 7 and 28 days age respectively compared with normal concrete, also the slump value enhanced to reach to 150 mm with increasing percent of 66.7% compared with normal concrete. The PAA reduce the compressive strength when used with BaS with percent of 7.4% at 7 days age and 9.5% at 28 days age that meant BaS was not compatible with PAA.

5. By Adding 2.5% of BIO and 5% of PAA improved the compressive of concrete to reach to 34.45 MPa at 7 days age and 49.35 MPa at 28 days age with increasing percent of 31.3% and 32.1% at 7 and 28 days age respectively compared with normal concrete. The slump value was 170 mm with increasing of 88.9% compare with normal concrete. The BIO was compatible with PAA, where the PAA was not made side effect in compressive strength, the main effect of PAA in this mix was in slump.

6. When adding all six NMM in the normal concrete with the optimum percent of each the compressive strength improved with slightly value which reach to 29.33 MPa at 7 days age and 39.28 MPa at 28 days age with increasing of 11.7% and 5.1% respectively. The slump value was 100 mm with increasing percent of 11.11% so not efficient to use more than two NMM in the mix.

7. A ratio 2.5% of BIO and 5% of PAA increased the flexure strength of concrete by 24.21% compare with normal concrete. That means the BIO and PAA was compactible together.

8. Adding 2.5% of BIO and 5% of PAA increased the shear strength of concrete by 24.31% compare with normal concrete and increased the indirect tension strength of concrete by 15.31% compare with normal concrete.

9. A ratio 2.5% of BIO and 5% of PAA enhanced the modulus of elasticity of concrete to reach to 27924 MPa with increasing percent 14.57% compare with normal concrete and 27420 MPa according ACI 319 equation.

10. The compressive strength ratio at 7 days to 28 days age for all concrete with NMM except concrete with YIO was between 69% to 72.2% but the percent was 70.40% according to ACI 209 that means all result in the range of ACI206.

11. The ratio of 14 to 28 days compressive strength for all concrete with NMM between 86.8%- 89.8% but 88.1% this rate is according to ACI 209 equation, which indicates a good agreement between the test result and ACI209 equation.

12. The ratio of 14 to 28 days compressive strength for concrete with YIO was around 77.5% but this ratio was 70.1 according to ACI 209 equation that mean YIO can enhance the early compressive strength.

5.3 Recommendation for further studies:

The following recommendations are purposed for further research:

1. The type of cement used in this research was CEM II/B-V 42.5 N, which contain fly ash with percent 21-35% and it may be effect in the behavior of the added NMM so it recommended using normal cement type I in the future study and using white cement. (The cement type which used in this research was available in Gaza Stripe at the period of research).

2. Study the performance of normal concrete and concrete with NMM under freezing and thawing condition .

3. Study the effect of adding NMM on the porosity and permeability of concrete.

4. Investigate the fire resistant of normal concrete and concrete with NMM.

5. Study the effect of adding NMM to concrete on reinforcement corrosion.

6. Investigate the durability of concrete with NMM with time.

7. Investigate the thermal transfer of concrete with NMM.

8. Study the effect of adding NMM to concrete on sound absorption.

9. Identified the chemical resistance of normal concrete and concrete with NMM.

10. Study the effect of adding NMM on the compressive strength at long time (1 and 2 years).

11. Study the effect of these NMM on higher grades of concrete (high strength, ultra high strength … etc.).

References:

Al-Mishhadani, S. A., Ibrahem, A. M., & Naji, Z. H. (2013, March). The effect of Nano Metakaolin material on some properties of concrete. *Diyala Journal of Engineering Sciences*, pp. 50-61.

American Society for Testing and Material . (2004). *ASTM C496 Test Method for Splitting Tensile Strength of Cylindrical Concrete Specimens.* Philadelphia, Pennsylvania: American Society for Testing and Material .

American Society for Testing and Material. (2004). *ASTM C187 Test Method for Normal Consistency of Hydraulic Cement.* Philadelphia, Pennsylvania: American Society for Testing and Material.

Arulraj, G. P., & Carmichael, M. J. (2011, July). Effect of Nano-Flyash on Strength of Concrete. *International Journal of Civil & Structural Engineering*, p. 475.

Badogiannis , E., & Tsivilis , S. (2009, February). Exploitation of poor Greek kaolins: Durability of metakaolin concrete. *Cement and Concrete Composites*, pp. 128–133.

Buzea, C., Blandino, I. I., & Robbie, K. (2007, 4). Nanomaterials and nanoparticles:. *Biointerphases*, pp. 17-172.

FP7 ERA-NET on Nanosafety. (2011, October 18). *http://www.siinn.eu/en/news-events/recommendation-of-the-eu-commission-on-the-definition-of-nanomaterials-2011-696-eu,3,6*. Retrieved from SIINN.

Li, H., Zhang , M. H., & Ou , J. P. (2006, June 30). Abrasion resistance of concrete containing nano-particles for pavement. *Wear*, pp. 1262–1266.

Li, H., Zhang , M.-h., & Ou, J.-p. (2007, July 7). Flexural fatigue performance of concrete containing nano-particles for pavement. *International Journal of Fatigue*, pp. 1292–1301.

Nmai, , Schlagbaum, & Violetta. (1998, April). American Concrete Institute. *A History of Mid-Range Water-Reducing Admixtures*, p. 45 to 50.

Quercia, G., Spiesz, P., Hüsken, G., & Brouwers, J. (2012). Effects of Amorphous Nano Silica additions on mechanical and durability performance of SCC mixtures. *International Congress on durability of concrete(ICDC).*, pp. 1-15.

Son , S. W., & Yeon , J. H. (2012, December). Mechanical properties of acrylic polymer concrete containing methacrylic acid as an additive. *Construction and Building Materials*, pp. 669–679.

Tsuyuki , N., Watan, R., Koizumi, K., Umemura , Y., & Machinaga , O. (2000, September). Effects of barium salt on the fixation of chloride ions in hardened mortars. *Cement and Concrete Research*, pp. 1435–1442.

A., Lazaro; Quercia, G.; Brouwers, H. J.; Geus, J. W.;. (2013, September 1). Synthesis of a Green Nano-Silica Material Using Beneficiated Waste Dunites and Its Application in Concrete. *World Journal of Nano Science and Engineering*, pp. 41-51.

acrylic polymer emulsion manufacturers/Styrene acrylic Emulsion. (2002). *http://www.alibaba.com/product-detail/acrylic-polymer-emulsion-manufacturers-Styrene-acrylic_1405535696.html*.

American concrete institute Committee 318. (2011). *ACI Committee 318,Building Code Requirements for Structural Concrete and Commentary.* Farmington Hills: American concrete institute (ACI).

American Concrete Institute Committee 209. (1997). *ACI Committee 209 Prediction of Creep, Shrinkage, and Temperature Effects in Concrete Structures chapter 2 and chapter 9.* Farmington Hills: American Concrete Institute.

American Concrete Institute Committee 211. (2002). *ACI Committee 211 Standard Practice for Selecting Proportions for Normal, Heavyweight, and Mass Concrete.* Farmington Hills: American Concrete Institute (ACI).

American Society for Testing and Material . (2001). *ASTM C150 Specification for Portland Cement.* Philadelphia, Pennsylvania: American Society for Testing and Material .

American Society for Testing and Material . (2002). *ASTM C469 Test Method for Static Modulus of Elasticity and Poisson's Ratio of Concrete in Compression.* Philadelphia, Pennsylvania: American Society for Testing and Material .

American Society for Testing and Material . (2005). *ASTM C192 Practice for Making and Curing Concrete Test Specimens in the Laboratory.* Philadelphia, Pennsylvania: American Society for Testing and Material .

American Society for Testing and Material. (1999). *ASTM C88 Test Method for Soundness of Aggregates by Use of Sodium Sulfate or Magnesium Sulfate.* Philadelphia, Pennsylvania.: American Society for Testing and Material.

American Society for Testing and Material. (1999). *ASTM D4791 Test Method for Flat Particles, Elongated Particles, or Flat and Elongated Particles in Coarse Aggregate.* Philadelphia, Pennsylvania: American Society for Testing and Material.

American Society for Testing and Material. (2000). *ASTM C204 Test Method for Fineness of Hydraulic Cement by Air-Permeability Apparatus.* Philadelphia, Pennsylvania.: American Society for Testing and Material.

American Society for Testing and Material. (2002). *ASTM C109 Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens.* Philadelphia, Pennsylvania: American Society for Testing and Material.

American Society for Testing and Material. (2002). *ASTM C78 Test Method for Flexural Strength of Concrete Using Simple Beam with Third-Point Loading.* Philadelphia, Pennsylvania: American Society for Testing and Material.

American Society for Testing and Material. (2003). *ASTM C131 Test Method for Resistance to Degradation of Small-Size Coarse Aggregate by Abrasion and Impact in the Los Angeles Machine.* Philadelphia, Pennsylvania: American Society for Testing and Material.

American Society for Testing and Material. (2004). *ASTM C127 Test Method for Density, Relative Density (Specific Gravity), and Absorption of Coarse Aggregate.* Philadelphia, Pennsylvania: American Society for Testing and Material.

American Society for Testing and Material. (2004). *ASTM C128 Test Method for Density, Relative Density (Specific Gravity), and Absorption of Fine Aggregate.* Philadelphia, Pennsylvania: American Society for Testing and Material.

American Society for Testing and Material. (2004). *ASTM C191 Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle.* Philadelphia, Pennsylvania: American Society for Testing and Material.

American Society for Testing and Material. (2004). *ASTM C39 Test Method for Compressive Strength of Cylindrical Concrete Specimens.* Philadelphia, Pennsylvania: American Society for Testing and Material.

American Society for Testing and Material. (2005). *ASTM C0136 Test Method for Sieve Analysis of Fine and Coarse Aggregates.* Philadelphia, Pennsylvania.: American Society for Testing and Material.

American Society for Testing and Material. (2005). *ASTM C0143 Test Method for Slump of Hydraulic-Cement Concrete.* Philadelphia, Pennsylvania: American Society for Testing and Material.

Arιoglu, N., Girgin, Z. C., & Arιoglu, E. (2006, January-February). Evaluation of Ratio between Splitting Tensile Strength and Compressive Strength for Concretes up to 120 MPa and its Application in Strength Criterion. *ACI Material Journal*, pp. 18-24.

Azeredo , G., & Diniz , M. (2013, January). Self-compacting concrete obtained by the use of kaolin wastes. *Construction and Building Materials*, pp. 515–523.

Bianchi , G. Q., & Brouwers, J. (2010). Application of nano-silica (nS) in concrete mixtures. *8th fib PhD Symposium in Civil Engineering*, (pp. 431-436). Lyngby, Denmark.

Birgisson, B., Mukhopadhyay, A. K., Geary, G., Khan, M., & Sobolev, K. (2012, December). *Nanotechnology in Concrete Materials.* Washington, D.C.: Task Force on Nanotechnology-Based Concrete Materials Transportation Research Board.

Broekhuizen, P., Broekhuizen, F., Corneliss, R., & Reijnders, L. (2011, February). Use of nanomaterials in the European construction industry and some occupational health aspects thereof. *Journal of Nanoparticle Research*, p. 447.

BSI. (1990). *BS 1881-127 Testing concrete. Method of verifying the performance of a concrete cube compression machine using the comparative cube test.* Britain: Business Standards Company .

Buzea, C., Blandino, I. I., & Robbie, K. (2007). Nanomaterials and nanoparticles:Sources and toxicity. *Biointerphases*, pp. 17-172.

China.com, M. i. (2013). *http://sdjinhua.en.made-in-china.com/*. (Shandong Jinhua Titanium Industry Co., Ltd.)

Department of Health and Human sevices, Centers for Disease Control and Prevention,National Institute for Occupational Safety and Health. (March 2009). *Approaches to Safe Nanotechnology Managing the Health and Safety Concerns Associated with Engineered Nanomaterials.* Columbia Parkway: Department of Health and Human sevices.

FP7 ERA-NET on Nanosafety Safe Implementation of Innovative Nanoscience and Nanotechnology. (2011, October 18). *http://www.siinn.eu/en/news-events/recommendation-of-the-eu-commission-on-the-definition-of-nanomaterials-2011-696-eu,3,6*. Retrieved from SIINN- FP7 ERA-NET on Nanosafety Safe Implementation of Innovative Nanoscience and Nanotechnology.

Huzhou Siyuan Pigment Co., L. (2012). *http://sypigment.en.made-in-china.com/*. Retrieved from Made- in-China.com.

Huzhou Siyuan Pigment Co., Ltd. (2012). *http://sypigment.en.made-in-china.com/*. Retrieved from Made in china.com.

Institution, B. S. (1987). *British Standard code of practice for Design of Concrete structure.* Britain: BSI.

Jalal , M., Fathi, M., & Farzad , M. (2013, July 15). Effects of fly ash and TiO2 nanoparticles on rheological, mechanical, microstructural and thermal properties of high strength self compacting concrete. *Mechanics of Materials*, pp. 11-27.

Jayapalan, A. R., Lee, Y., & F., S. M. (2010). Influence of Additions of Anatase TiO2 Nanoparticles on Early-Age Properties of Cement-Based Materials. *Transportation Research Record: Journal of the Transportation Resea*, pp. 41-46.

JFAO/WHO. (2004, June). Iron Oxides. *Compendium of Food Additive Specifications*, (pp. 33-34). Geneva, switzerland.

Kaolin Nano Al2O3 powder. (2013). *http://www.alibaba.com/product-detail/Kaolin-Nano-Al2O3-powder_999302591.html*.

Karatasios, I., Kilikoglou , V., Theoulakis, P., Colston, B., & Watt , D. (2008, October). Sulphate resistance of lime-based barium mortars. *Cement and Concrete Composites*, pp. 815–821.

Kosmatka, S. H., & Kerkhoff, B. (2002). *Design and Control of Concrete Mixtures.*

Krishna, M. N., Narasimha , R. A., Ramana, V. R., & sekhar, V. (2012, September). Mix Design Procedure for Self Compacting Concrete. *IOSR Journal of Engineering*, pp. 33-41.

Kuznesof, P. M. (2006). *Titanium_dioxide Chemical and Technical Assessment.*

Lee , H. S., Lee , J. Y., & Yu , M. Y. (2003, November). Influence of iron oxide pigments on the properties of concrete interlocking blocks. *Cement and Concrete Research*, pp. 1889–1896.

Maghsoudi, A. A., Maghsoudi, M., & Noori, M. (2010). Effect of Nano Particles on SCC. *Second International Conference on Sustainable Construction Materials and Technologies.*

Ancona, Italy.: Civil Eng. Department,, Shahid Bahonar University of Kerman & International Center for Science, High Technology & Environmental Sciences,,Kerman.

Mehtaand, P. K., & Monteiro, P. J. (2008). Concrete:Microstructure, Properties, and Materials. Hari Prasad.

Mermerdaş , K., Güneyisi , E., Gesoğlu , M., & Özturan , T. (2013, June). Experimental evaluation and modeling of drying shrinkage behavior of metakaolin and calcined kaolin blended concretes. *Construction and Building Materials*, pp. 337–347.

Qing, Y., Zhang, Z., Deyu, K., & Chen, R. (2005, October). Influence of nano-SiO2 addition on properties of hardened cement paste as compared with silica fume. *Construction and Building MATERIALS*, pp. 539–545.

Sanghchulie, T., Faghihirad, S., & Husseini, Y. K. (2010). *An experimental study for the application of nano concrete to reduce roughness coefficient.* Iran: Water Research Institute, Ministry of Energy, IRAN.

SENG, A. Y. (2008, October 18). *http://www.scribd.com/doc/7281495/HSC-HPC-RPC-SCC*.

Shanghai Yuejiang Titanium Chemical Manufacturer Co., Ltd. . (n.d.). *http://yuejiangchem.en.made-in-china.com/product/OoaENVzAlFkZ/China-Superfine-Barium-Sulfate-3000mesh-with-White-Powder.html*. (Made in China.com)

Shekari, A. H., & Razzaghi, M. S. (2011, October 1). Influence of Nano Particles on Durability and Mechanical Properties of High Performance Concrete. *Procedia Engineering*, pp. 3036–3041.

Wei, X., Zhang, P., & Zhou, Z. (2011, August). Sensitivity Analysis for Durability of High Performance Concrete Containing Nano-particles based on Grey Relational Grade. *Modern Applied Science*, pp. 68-73.