Microstructure Investigation on Nano-Geopolymer Cement Cured under HPHT Condition

by

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Dissertation submitted in partial fulfilment of
the requirements for the
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CERTIFICATION OF APPROVAL

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Approved by, Approved by,

(Dr. Syahrir Ridha) (Mr. Asif Zamir)

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TRONOH, PERAK
MAY 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MUHAMMAD AKMALLUDIN BIN ABD HAIR

ABSTRACT

Drilling in high pressure and high temperature (HPHT) conditions place extreme stresses on the cement sheath and affect the integrity of the cement. It such conditions, the design of the cement is important and it must possess properties to ensure the cement slurry to remain pumpable long enough to allow placement and also have sufficient density to overbalance the formation pressure. Apart from that, the cement also should be environmentally friendly and should not cause damage or contamination to underground formation.

Utilizing industrial waste such as fly ash as raw materials, geopolymer cement has been highlighted as a better alternative to widely used, Ordinary Portland Cement (OPC). Manufacturing process of OPC proven to emit large amount of carbon dioxide (CO_2), one of the main greenhouse effect (GHG). While, in terms of performance, OPC creates high permeability between cement particles when exposes to HPHT conditions inside the wellbore. Despite proven to have superior mechanical properties, geopolymer cement still encountered problems when applied in the same condition.

The objectives of the paper are to develop nano-geopolymer cement and investigate the microstructure change of the cement cured in HPHT condition, including strength development and pore structure. The paper describes an experimental approach to study effects of nanoparticles in the strength development of the cement. It is performed by changing the composition of geopolymer cement by introducing nano-silica, SiO_s. The compressive strength of the cement was tested using compressive strength tester, while the microstructural analysis was studied using Scanning Electorn Microscope (SEM) and X-Ray Diffraction (XRD).

With the inclusion of nanomaterial in geoploymer, nano-geopolymer cement showed significant improvement in terms pore distribution and structure. Ultra-fined SiO_s fills the void spaces between particles which results in uniform and compact cement matrix. With low porosity and permeability, this microstructure analysis reflects the high compressive strength obtained by nano-geopolymer as compared to OPC and base geopolymer.

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CHAPTER 1

INTRODUCTION

1.0 Background Study

The fundamental function of oil well cementing is to restrict fluid movement between zones within the formation. The formation is isolates not only to protect the aquifers, but also to prevent flow of fluid from high pressure to low pressure formation. This is to avoid excessive water production or any loss of hydrocarbon. The cement also bond and provide structural support for the casing. Apart from these, oil well cementing prevents the fluid from raising to the surface which will cause blowout. The cement also protects the casing from shock load while drilling in deeper formation and also guards against corrosion.

Oil well cementing is performed when the cement slurry is pumped from the surface to the target location in the well through the drill string. The cement slurry displaced the drilling fluids which still located within the well and eventually filled in the space between the annulus and the casing.

There are two types of cementing process involve in oil well operation:

1. Primary cementing: To fulfill the objective of cementing such as providing zonal isolation between casing and formation.
2. Remedial cementing: Repair the primary cementing or treat the condition arising after wellbore has been constructed.

As oil and gas companies continue to search in new or unexplored areas due to the growing demand, the exploration is getting extreme in terms of depth, temperature and pressure. In high temperature and pressure well, for example, the condition requires the cement slurry to remain pumpable long enough to allow placement and must have enough density to overbalance the underground formation pressure. Such conditions also put extreme stresses on the cement sheath and affect the integrity of the cement [1].

While in deepwater wells, accelerators are added to the cement slurry as additives to counter the low temperature which can lengthen the wait-on-cement (WOC) time and potentially increasing the cost of operations.

Hence, the design of cement slurry is important in facing extreme exploration challenges due to the wide range of depths, pressure and temperature to which it is subjected. The cement slurry designed must possess properties that ensure the durability and long term integrity of cement sheath as well as environmentally friendly and should not cause any contamination or damage to underground formation [4].

1.1 Problems Statement

1. Ordinary Portland Cement (OPC) creates high permeability between cement particles when exposes to HPHT conditions inside the wellbore. As a result, it undergoes significant phase change that result in substantial decrease in compressive strength.

2. Despite the property enhancement, geopolymer cement still encountered some problems when it is applied in wellbore under HPHT conditions. At high curing temperature (>100^{o}C), there is a possibility of breaking up the intergranular structure of geopolymer that could lead to strength reduction.

Hence, this study will introduce nanomaterial to geopolymer cement to enhance strength development under HPHT conditions. The study will also focuses on microstructure of the nano-geopolymer cement in terms of pore structure.

1.2 Objectives

The main objectives of this project are:

1. To investigate strength development of nano-geopolymer cement.
2. To investigate the microstructure change in of nano-geopolymer cement cured under HPHT condition, including:
   - Strength development
   - Pore structure

1.3 Scope of Study

The project investigates the microstructure of nano-geopolymer cement cured under HPHT environments. This study will utilize OFITE automated compressive strength tester, Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD) techniques.

The investigation on strength development of nano-geopolymer cement will use OFITE automated compressive strength tester. The results obtained will determine the ability to bear imposed stresses and also the integrity of the cement.

Scanning Electron Microscope (SEM) will be employed to study the pore structure and topography of the nano-geopolymer cement. The cement hydration and phase change will be analyze at ambient temperature and HPHT conditions.

While, X-Ray Diffraction (XRD) will be employed to investigate the nano-geopolymer cement composition when cured at HPHT conditions at various curing duration. Several compounds in hydrated cement paste such as calcium hydroxide (CH), belite (C2S), alite (C3S), ettringite (AFT), calcium silicate hydrate (C-S-H) and tobermorite etc can be detected using XRD spectra.

1.4 Feasibility of study within scope and time frame

This project is feasible to be done within 8 months, from January 2015 till August 2015, which consists of Final Year Project 1 and 2. The project includes the cement slurry preparation, cement curing, laboratory test and microstructure investigation.. The study will be held in the cementing laboratory. The experiment will be carried out from May 2015 till August 2015. All precautions and safety are taken to ensure the experiments are done according to the standard.

CHAPTER 2

LITERATURE REVIEW

2.1 Ordinary Portland Cement (OPC)

OPC has been widely used in oil well cementing for decades. It easily mixed with water and prepared at the recommended water-to-cement ration to produce a readily pumpable slurry that can be placed anywhere within hydrostatic pressure constraints of a wellbore. OPC satisfies the fundamental objective which hydraulically isolating the formations. It is readily available worldwide and is not expensive [6]. OPC can be divided into several classes with different properties and depths as indicated in Table 1 [7]:

Table 1: Different classes of OPC: Class A until Class J

Cement Class	Depth, ft	Descriptions
A	0 – 6000	No special properties are required
B	0 – 6000	Required for moderate to high sulfate resistance
C	0 – 6000	Required for high early strength
D	6000 - 10,000	Required for high pressure high temperature
E	10,000 - 14,000	Required for high pressure high temperature
F	10,000 - 16,000	Required for extremely high pressure high temperature

G & H	0 – 8000	Used with accelerators & retarders to cover a wide range of well depths and temperatures.
J	12,000 - 16,000	Required for extremely high pressure high temperature. Used with accelerators & retarders to cover a wide range of well depths and temperatures

Apart from amount and types of solids and water, the conventional cement's performance is also influence by chemical additives. Numerous types of additives are normally used for the optimum cement mixture design to provide desired characteristics to the slurry mixture. Weighing agents increase the slurry density while extenders decrease it. The rheology is control by dispersants that break larger particles into smaller ones which can reduce viscosity. Other types of additives is as shown in Table 2.

Table 2: Different Types of Additives & Functions

Type of Additives	Function
Accelerator - Calcium chloride - Sodium chloride - Gypsum	1. Reducing WOC time 2. Setting surface pipe 3. Setting cement plugs 4. Combating lost circulation
Retarder - Lignosulfonates - Organic acids	1. Increasing thickening time for placement 2. Reducing slurry viscosity

Filtration-Control Additives - Polymers - Dispersants - Latex	1. Squeeze cementing 2. Setting long liners 3. Cementing in water-sensitive formation
Lost Circulation Control Agents - Gypsum cement - Bentonite/diesel oil - Gilsonite	1. Bridging 2. Increasing fill-up 3. Combating lost circulation 4. Fast-setting system

However, when subjected to high temperatures (in excess of 110^{o}C), hydrated OPC suffers significant phase changes. This phenomenon, known as strength retrogression, result in substantial decrease in compressive strength of the cement slurry [2 - 3]. Hence, cementing under high temperature high pressure condition requires the addition of special materials to counteract the degradation of compressive strength.

2.2 Geopolymer cement

As companies are moving towards more sustainable oil and gas exploration, the demand for environmentally friendly material increases. In response, a sustainable cement has been developed which is Geopolymer. Geopolymer technology involves the converting of byproduct to valuable product. There several categories of geopolymer cement including (1) slag-based, (2) rock-based, (3) fly ash-based and (4) ferro-sialate-based.

2.2.1 Geopolymerisation Process

Using industrial waste such as fly ash and slag as source materials, geopolymer is produced by the reaction of aluminosilicate oxides (Si_2O_5, Al_2O_2) with alkali polysilicates yielding polymeric Si-O-Al bond. This chemical process is called geopolymerisation process. The alkaline solution dissolves silicon and aluminium ions in the raw material during the initial mixing [14]. The cement is reported can harden rapidly at room temperature and can gain the compressive strength up to 2900psi in 1 day. It looks alike and performs a similar function to Portland cement.

The difference between geopolymer cement and OPC lies in the different of energy uses for activation process. OPC uses high energy to activate the material before reacting with low energy material, such as water during calcination process. While, geopolymer use low energy material such as fly ash to react with small amount of high energy solution, for example sodium hydroxide to create the reaction between those materials. Due to low energy required for manufacturing, the applications of geopolymer foresees the reduction of global warming due to less carbon dioxide emission from cement plants [15]

2.2.2 Fly Ash

Fly ash is a by-product obtained from coal combustion in thermal coal electricity generating power plan. Finely divided material, fly ash has been identified as an environmental pollutant. Fly ash makes up from coal impurities that is thermally treated, combined with small amounts of unburned coal. The chemical properties is depending on the type of coal burned as well as the handling and storage methods [9]. Collectively contains greater than 70% of silica, alumina, ferrous oxide and calcium oxide, Malaysian fly ash is categorized as class F fly ash.

The presence of calcium content in fly ash is the key element in compressive strength development. The calcium ion’s presence delivers a faster reactivity and hence yields good hardening of geopolymer in shorter curing time. Apart from that, with small particle size, fly ash is more reactive and major portion is in amorphous form. It will take part in geopolymer synthesis and produces good quality geoplymer material. Hence, fly ash is a right source material for geopolymer cement. [10]

2.2.3 Silica Fumes

Silica fume is an amorphous, non-crystalline silica with an average particle size of 150nm. It is a by-product of the silicon and ferrosilicon alloy production. The benefits of adding silica fumes to OPC mixtures has been widely known as it improves the mechanical properties and abrasion resistance.

There are 2 factors that attributes to the enhancement of cement property by silica fumes mechanism. Firstly, silica fumes acts as a filler material to fill the interstitial space between cement particles. This subsequently results in a higher packing density and lower porosity. Secondly, the amorphous silica chemically react with calcium hydroxide to form calcium silicate hydrate, C-S-H. Calcium silicate hydrate, C-S-H, is the hydration product that contributes to the strength gain of cementitious materials. The reaction is known as pozzolanic effect [2].

In this research, the mixture of fly ash and silica fumes will act as the base of geopolymer cement with the composition of 70:30 respectively.

2.3 Nanotechnology

Nanotechnology encompasses an extensive range of disciplines and nanomaterials are recently used as commercially viable solution to technical challenges in industries including electronics, bio-medicine as well as oil and gas.

2.3.1 Nanomaterials

Nanomaterials have extensively attracted considerable scientific interest due to its potential uses in nanometer scale (10^{-9}m). Recently, several research groups in the oil and gas industry has begun their investigation on the application of nanomaterials to solve problems in oilwell cementing. These nanomaterials are largely used to improve mechanical properties of the cement such as corrosion resistance, crack resistance, compressive strength and tensile strength [15].

Among the applications of nanomaterials in oilwell cementing are [2]:

1. Nanosilica and nanoalumnia as potential accelerators
2. Carbon nanotubes (CNT's) with high aspect ratio to enhance mechanical properties
3. Nanomaterials to decrease permeability/porosity
4. Nanomaterials to increase thermal and/or electrical conductivity

However, the optimum percentage of nanoparticle in geopolymer cement system is not well-documented. For this study, the use of nanosilica will be investigated to enhance the properties of oilwell cement.

CHAPTER 3

METHODOLOGY

3.1 Preparation of cement slurries

Cement slurries are mixed using Constant Speed Mixer and prepared based on American Petroleum Institute API-10B-2 procedure. Three types of cement were studied namely Class G (OPC), Geopolymer cement (GC) and Nano Geopolymer cement (GPC) respectively. Each sample has certain composition of cement slurries as shown in Table 3. The mass for each material is showed in Table 4. No additive is included in the samples.

Table 3: Composition of Cement Samples (percentage, %)

Samples	Cement Component			
	Class G	Fly Ash	Silica Fume	Nano-Silica
OPC	100%	-	-	-
GPC	-	70%	30%	-
GPC1	-	70%	29%	1%
GPC2	-	70%	27%	3%
GPC3	-	70%	25%	5%

Table 4: Mass of Fly Ash, Silica Fumes, Class G Cement, Nano-Silica, Sodium Silicate, Water and Sodium Hydroxide (grams, g)

Samples	Class G	Fly Ash	Silica Fume	Nano-Silica	Sodium Silicate	Sodium Hydroxide	Water
OPC	500	0	-	-	71.43	18.94	259.77
GPC	0	350	150	-			
GPC1	0	350	145	5			
GPC2	0	350	135	15			
GPC3	0	350	125	25			

3.1.1 Cement Slurries Mixing Procedure

a. All materials are weighted using mass balance based on Table 4.
b. The mixer is switched on. Wet materials are filled in mixing container. The container is then placed on the mixer motor.
c. The mixer is set for rotation of 4000 r/min ± 200 r/m for 15 seconds. Dry materials are then poured.
d. After 15 seconds, the mixer is set for rotation of 120000 r/min ± 500 r/min for another 35 seconds.
e. Cement slurry is complete.

Figure 1: Class G

Figure 2: Fly Ash

Figure 3: Silica fumes

Figure 4: Nano-Silica

Figure 5: Constant Speed Mixer

Figure 6: Sodium Hydroxide Pellet

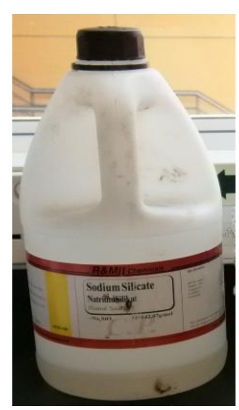


Figure 7 Sodium Silicate

3.2 Laboratories Test

3.2.1 Cement Slurry Density Test

Based on procedure specified in API Spec 10B-6, density test is conducted to determine hydrostatic head of cement slurry. Conducted at standard pressure and temperature, the test used pressurized mud balance (Figure 8). The test procedure as below:

i. Cement slurries is filled in the sample cup to a level slightly below the upper edge of the cup. [6 mm ± 0.5 mm (1/4 in)]
ii. Lid is placed on the cup with the check valve in open position and pushed downward until excess slurry expel through check valve.
iii. Sample cup is pressurized by keeping downward force on the pump cylinder housing. This is to hold check valve open and force piston rod inward.
iv. Cleaned the exterior of the sample cup. Moved the sliding weight until the beam is balanced. This can be seen from the centered attached bubble between two scribed marks.
v. The density is read from calibrated scales on the arrow side of the sliding weight.

3.2.2 Cement Slurry pH Test

Cement slurries were also tested on pH Meter to determine its pH value

Figure 8: Pressurized Mud Density Balance

Figure 9: pH Meter

3.2.3 Cement curing under HPHT condition

The cement slurries were cured in curing chamber at 4000psi and 120^{o}C to simulate the wellbore condition under HPHT condition for the duration of 1 and 3 days. The curing procedure is as shown below:

i. Before assemble, curing molds are greased on the inner surface. (Figure 11).

ii. Mixed cement slurry is poured into the assembled molds in three layers.

iii. Molds are clamped using the threaded rod (Figure 13).

Figure 10: Curing Chamber

Figure 11: Greased Curing Molds

Figure 12: Cement is stirred

iii. Next, curing chamber is switched on.

iv. Molds are lowered into the pressure vessel (Figure 14). The cylinder plug thread is lubricated using grease and threaded into the cylinder (Figure 15). The set screws on top of the cylinder thread are tightened using spanner three different torques (15, 30 and 40 ft-lbs).

v. A thermocouple is inserted through the hole on top of cylinder plug and is tied loosely (Figure 13).

vi. Air supply is released and flow of oil into pressure vessel is observed through oil cylinder (Figure 14). The thermocouple is tightened with a spannerwhen the oil expelled from the thermocouple.

vii. The pump is set to pressure of 4000 psi.

viii. The temperature is set in the program list. In this project, 120 ℃ is chosen as the temperature.

ix. The heater is switched on and followed by the timer.

x. Next, auto and run button is switched on to start the operation. The durations of the operation are 24 hours, 48 hours and 72 hours

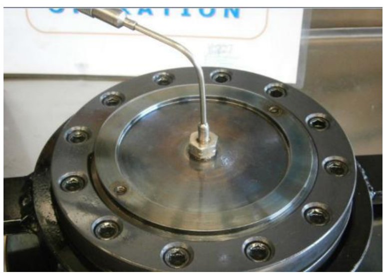


Figure 13: Thermocouple inserted into pressure vessel

Figure 14: Molds tied using thread

Figure 15: Molds inserted into pressure

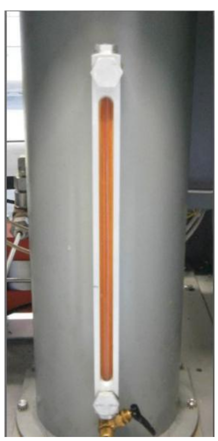


Figure 16: Oil Cylinder

Figure 17: Cylinder plug is threaded into pressure vessel

3.2.4 Cement Slurry Compressive Strength Test

The cement cubes is placed in OFITE automated compressive strength tester to study its strength development. The result determine the integrity and ability to withstand stresses imposed.

3.3 Microstructure Investigations

The microstructure investigations of the cement cube samples will be carried out through Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD). These tests require:

3.3.1 Scanning Electron Microscope (SEM)

The microstructure of cement slurry will be studied using SEM to analysis the composition, topography and pore structure. Small pieces of nano-geopolymer cement obtained from the cube samples were analyzed to investigate the effects of nanomaterial admixed cement on the pore distribution and permeability reduction. The result is compared to the microstructure of Class G Cement. Uniform pore distribution and a densely packed structure with low porosity and permeability indicates the high compressive strength of the cement.

3.3.2 X-Ray Diffraction (XRD)

The cement composition and hydration process will be studied using XRD. Compounds in hydrated cement paste such as calcium hydroxide (CH, portlandite), belite (C2S), alite (C3S), ettringite (AFT) calcium silicate hydrate (C-S-H) and tobermorite etc can be detected using XRD spectra. A fully transformed compound, for example portlandite to calcium silicate hydrate on reaction with silica, causes high compressive strength of the cement.

CHAPTER 4

RESULT AND DISCUSSION

4.1 PRESSURIZED DENSITY TEST

Density test for all samples are done using pressurized mud balance at standard condition.

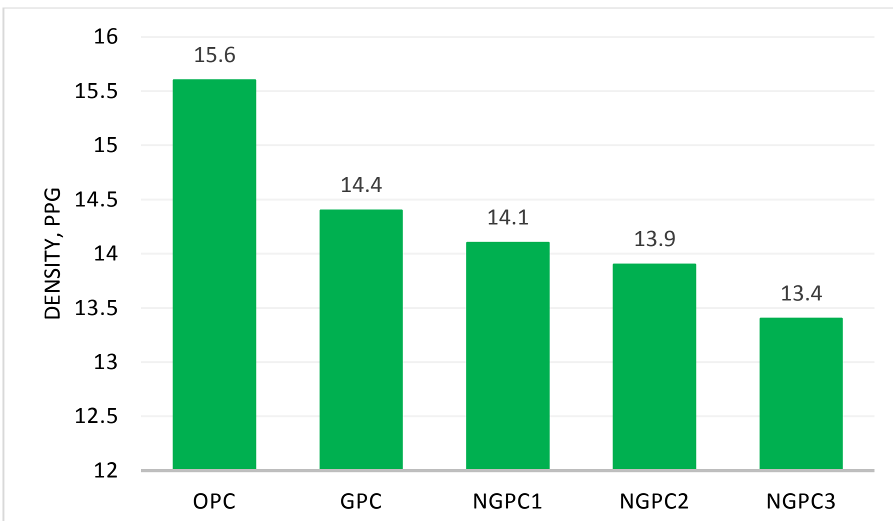


Figure 18: Density for OPC, GPC and NGPC

Material	Specific gravity	Density Difference with OPC				
		OPC	GPC	NGPC1	NGPC2	NGPC3
Portland Cement	3.15	0%	7.69%	10.42%	12.06%	15.83%
Fly Ash	2.38					
Silica Fumes	2.22					
Nano Silica	1.2					

Table 5: Specific Gravity of Cement Materials & Density Difference

Based on Figure 18, it is observed that the density of cement samples decreases as the percentage of Nano-silica increases and the percentage of class F fly ash reduces. OPC (Class G Cement) has the highest density, 15.6 ppg while NPGC3 which consist of 70% fly ash, 35% silica fumes and 5% Nano-silica shows the lowest density, 13.4 ppg. The difference between both densities is 15.83%.

The difference in density for each samples is the result of differences in specific gravity of each material in the mixture compositions. Materials with high specific gravity lead to high density cement samples. Table 4.1 shows Nano-silica has the lowest specific gravity, 1.2, followed by silica fumes, fly ash and OPC. Hence, NGPC3 with highest percentage of Nano-silica has the lowest density.

4.2 PH TEST

The pH test was conducted as per the procedure mentioned in ASTM E70, Standard Test Method for pH of Aqueous Solutions with the Glass Electrode. The pH value of the cement samples are shown in Table 6.

Sample	GPC	NGPC1	NGPC2	NGPC3	**Average**
pH value	11.53	11.52	11.50	11.51	**11.515**

Table 6: pH Value of Geopolymer Cement

The base pH value is highly contributed by the alkaline reagent, which are the wet mix of sodium hydroxide, calcium silicate and water, which react with the dry mix (fly ash, silica fumes and Nano-silica) through Geopolymerisation process.

Component	**pH value**
Sodium Hydroxide (NaOH)	11.95
Sodium Silicate (Na_2SiO_3)	11
Water	7

Table 7: pH Value of Wet Mix

4.3 COMPRESSIVE STRENGTH TEST

After cured at 4000psi and 120°C, compressive strength test were conducted for all samples using OFITE automated compressive strength tester. The results are as follows:

Sample	**Fly Ash : Silica Fumes : Nano Silica**	**Compressive Strength (psi)**	
		1 Day Curing	**3 Day Curing**
GPC	70 : 30 : 0	1595.4	2175.6
NGPC1	70 : 29 : 1	1740.5	2610.7
NGPC2	70 : 27 : 3	2320.6	3190.8
NGPC3	70 : 25 : 5	3045.8	4351.1

Table 8: Compressive Strength Test Result

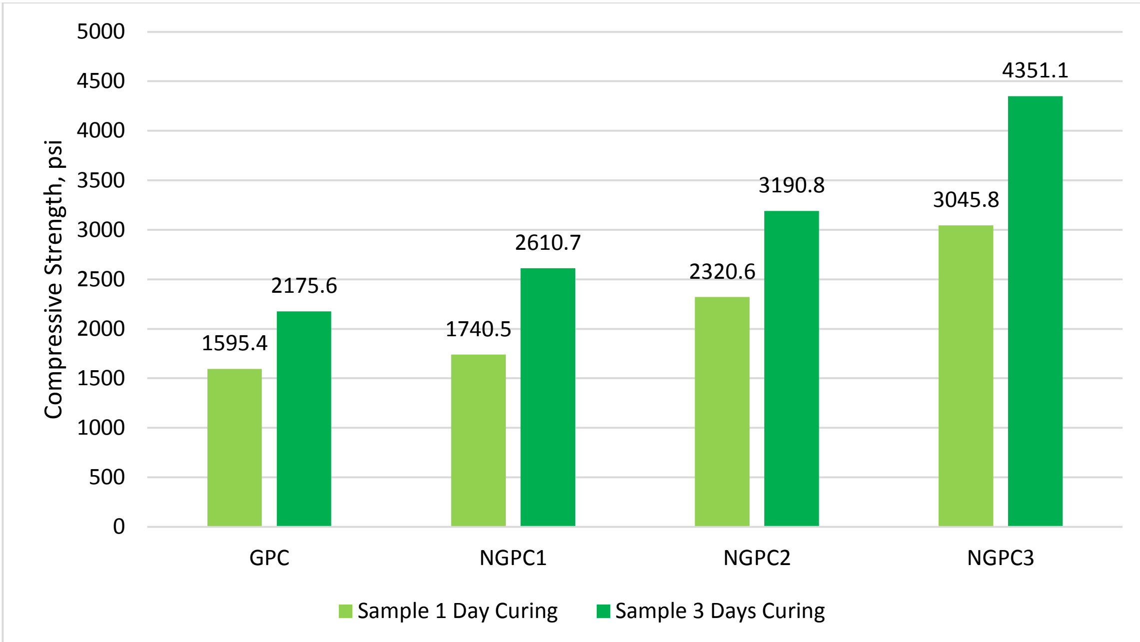


Figure 19: Compressive Strength of Cement cured for 1 Day and 3 days

Based on the compressive strength test result for 1 day curing, the highest reading recorded was 3045.8 psi with 5% Nano-silica addition. Followed by 3% Nano-silica addition which the result recorded was 2320.6 psi. 1% Nano-silica addition and 0% Nano-silica addition gave 1740.5 psi and 1595.4 psi respectively.

From the compressive strength test result for 3 days curing shown in Figure 19, the highest reading recorded was 4351.1 psi with 5% Nano-silica addition. Followed by 3% Nano-silica addition which the result recorded was 3190.8 psi. 1% Nano-silica addition and 0% Nano-silica addition gave 2610.7 psi and 2175.6 psi respectively. As the percentage of Nano-silica in the cement composition increases, the compressive strength also increases. Apart from that, the compressive strength with longer curing time showed higher reading. For example, for sample with 3% of Nano-silica (NGPC2), the compressive strength for 1 day is 2320.6 psi while for 3 days is 3190.8 psi.

Table 9 shows the percentage differences in compressive strength for all cement sample cured for 1 day to the control mix which was 0% Nano-silica.

Samples	Percentage Difference Compared to Control Mix for 1 Day Curing (%)
GPC (0% Nano-silica)	-
NGPC1 (1% Nano-silica)	9.09
NGPC 2 (3% Nano-silica)	33.33
NGPC 3 (5% Nano-silica)	31.25

Table 9: Percentage Difference Compared to Control Mix for 1 Day Curing

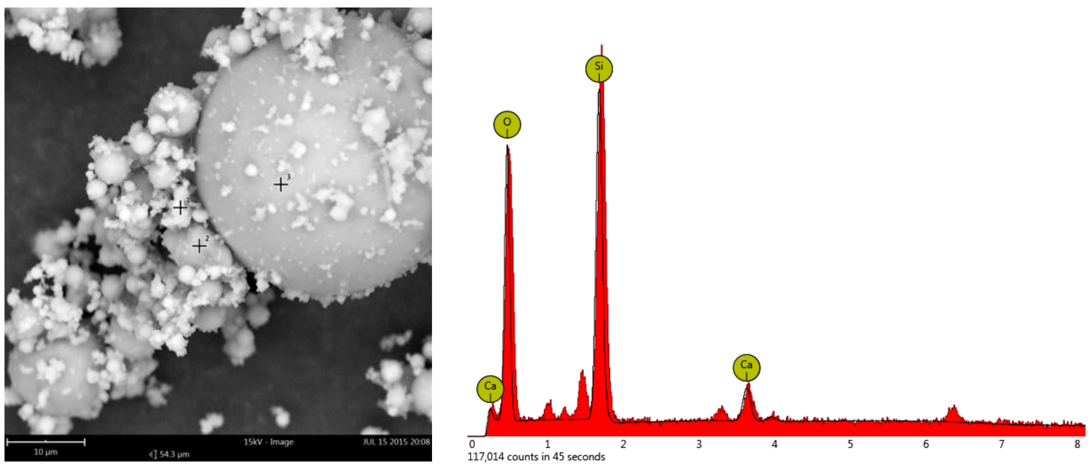
Table 10 shows the percentage differences in compressive strength for all cement sample cured for 3 days to the control mix which was 0% Nano-silica.

Samples	Percentage Difference Compared to Control Mix for 3 Days Curing (%)
GPC (0% Nano-silica)	-
NGPC1 (1% Nano-silica)	20.00
NGPC 2 (3% Nano-silica)	22.22
NGPC 3 (5% Nano-silica)	36.36

Table 10: Percentage Difference Compared to Control Mix for 3 Days Curing

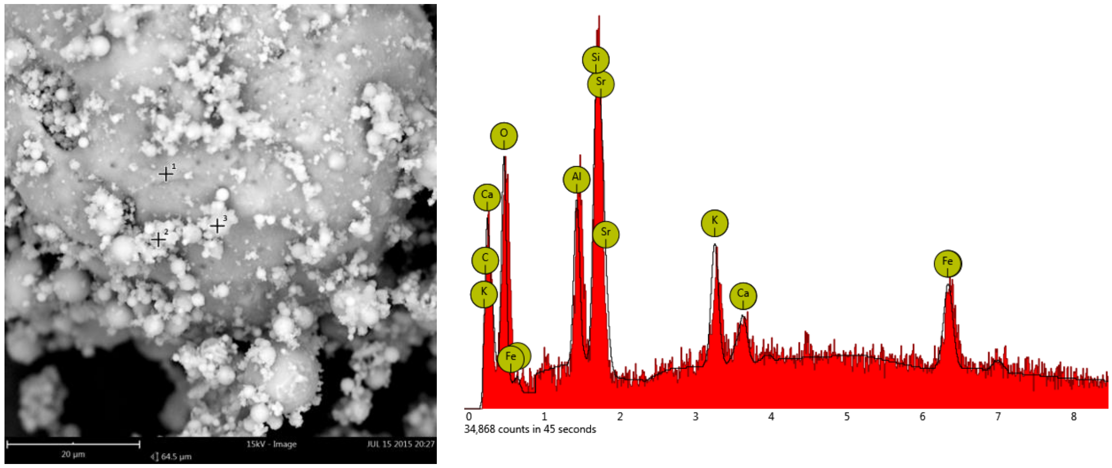
4.4 SCANNING ELECTRON MICROSCOPE (SEM)

The small pieces of cement obtained from cube samples were examined using Scanning Electron Microscopy (SEM) for microstructural analysis to investigate the effects of Nano-silica admixed geopolymer cement on the pore distribution and permeability reduction.



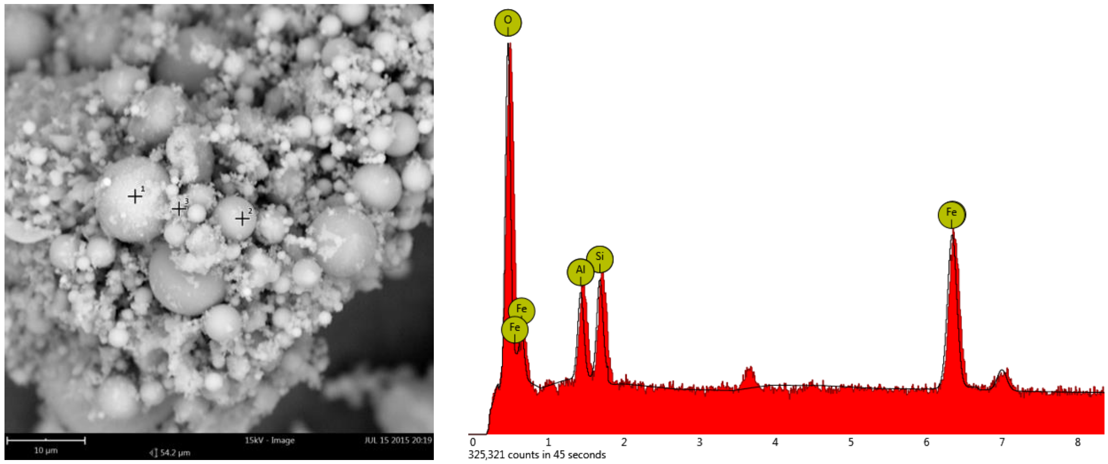
Element Number	Element Symbol	Element Name	Weight Concentration
14	Si	Silicon	27.3
8	O	Oxygen	67.3
20	Ca	Calcium	5.5

Figure 20: SEM Images for GPC and its Components (0% Nano-silica) – 1 Day



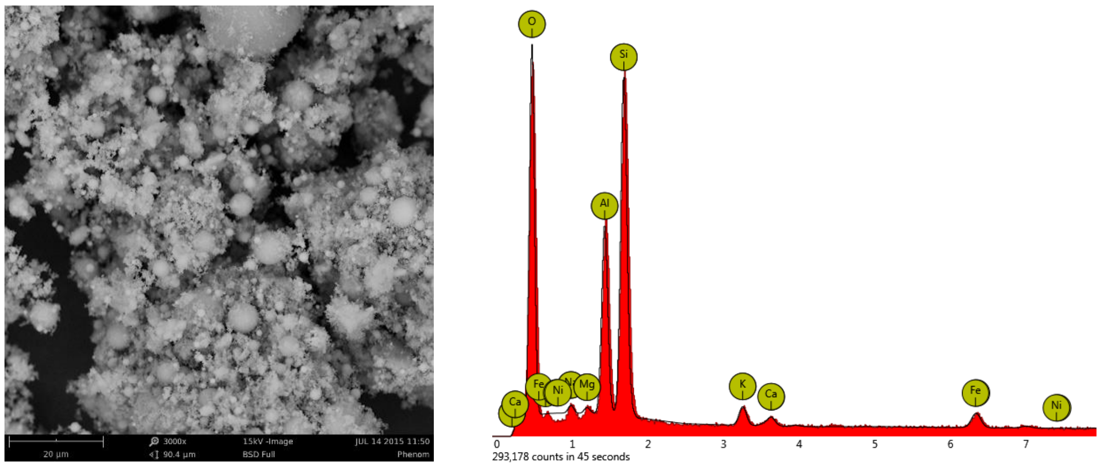
Element Number	Element Symbol	Element Name	Weight Concentration
38	Sr	Strontium	13.9
14	Si	Silicon	5.8
8	O	Oxygen	28.2

Figure 21: SEM Images for NGPC1 and its Components (1% Nano-silica) – 1 Day



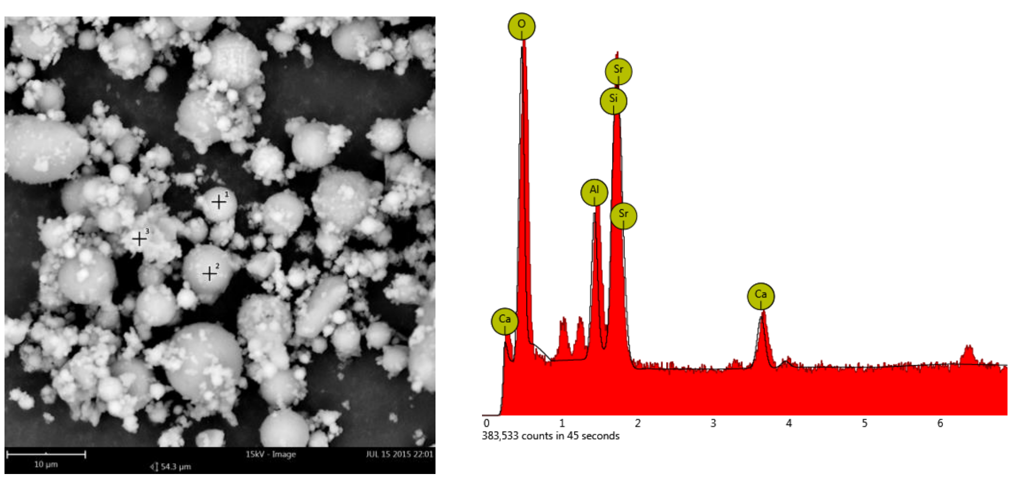
Element Number	Element Symbol	Element Name	Weight Concentration
8	O	Oxygen	33.4
26	Fe	Iron	52.0
14	Si	Silicon	7.2
13	Al	Aluminum	7.4

Figure 22: SEM Images for NGPC2 and its Components (3% Nano-silica) – 1 Day



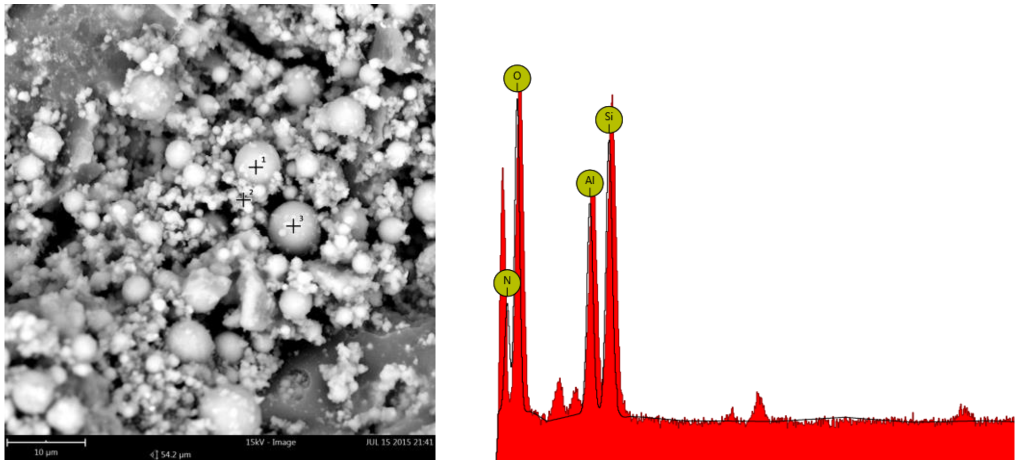
Element Number	Element Symbol	Element Name	Weight Concentration
14	Si	Silicon	22.1
8	O	Oxygen	55.7
13	Al	Aluminium	12.5
20	Ca	Calcium	0.9

Figure 23: SEM Images for NGPC3 and its Components (5% Nano-silica) – 1 Day



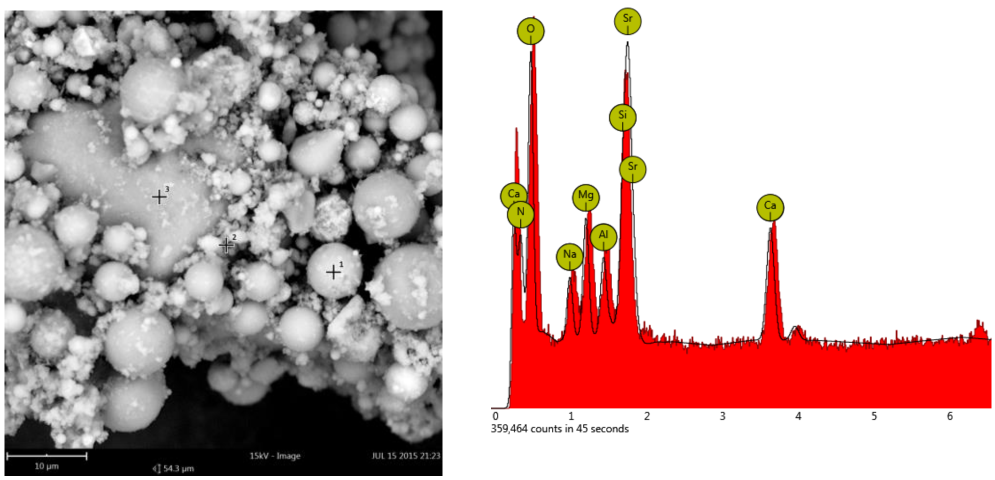
Element Number	Element Symbol	Element Name	Weight Concentration
38	Sr	Strontium	28.6
14	Si	Silicon	8.3
8	O	Oxygen	51.3
13	Al	Aluminium	7.2

Figure 24: SEM Images for GPC and its Components (0% Nano-silica) – 3 Days



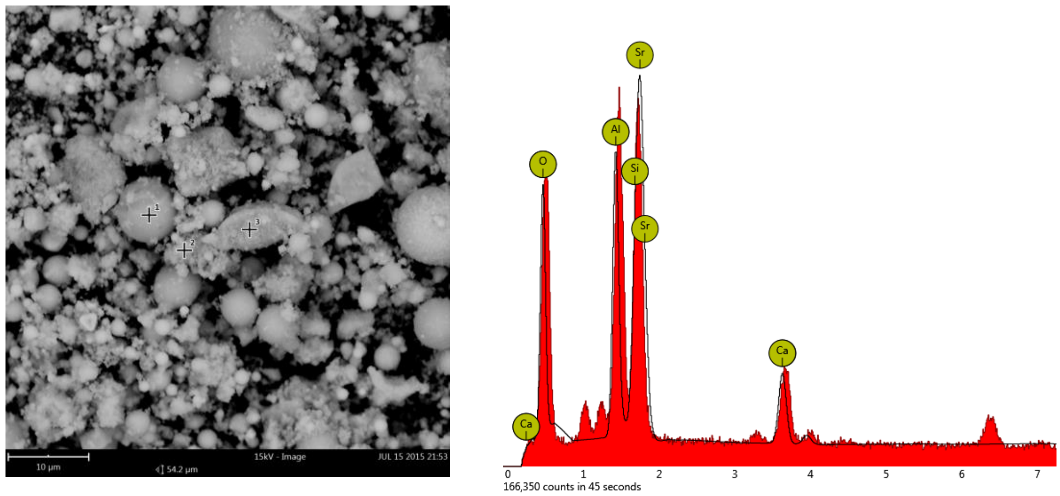
Element Number	Element Symbol	Element Name	Weight Concentration
14	Si	Silicon	11.4
8	O	Oxygen	55.9
13	Al	Aluminium	9.5
7	N	Nitrogen	23.2

Figure 25: SEM Images for NGPC1 and its Components (1% Nano-silica) – 3 Days



Element Number	Element Symbol	Element Name	Weight Concentration
38	Sr	Strontium	18.3
8	O	Oxygen	40.2
14	Si	Silicon	3.1
20	Ca	Calcium	5.3

Figure 26: SEM Images for NGPC2 and its Components (3% Nano-silica) – 3 Days



Element Number	Element Symbol	Element Name	Weight Concentration
38	Sr	Strontium	36.0
13	Al	Aluminium	11.3
14	Si	Silicon	6.3
8	O	Oxygen	41.1
20	Ca	Calcium	5.4

Figure 27: SEM Images for NGPC3 and its Components (5% Nano-silica) – 3 Days

The SEM images for GPC shows that the pores distribution is not uniform. The empty spaces between pores are also visible which results in high permeability and porosity. Refer to figure 20. However, with the increment of Nano-silica to the cement mix, the volume of permeable pore space decreases gradually. In NGPC3 slurry, the SEM images shows the least visible empty spaces between pores as well as uniform pore distribution. A densely packed strong structure is evident as shown in Figure27. This leads to low porosity and permeability.

Pore distribution and permeability reduction observed from SEM images reflect the compressive strength obtained in **4.3**. A densely packed, uniform pore distribution and less empty spaces leads to higher compressive strength. This is shown in Figure 19, where the value for NGPC3 is 3.0 kN/mm^2 as compared on GPC, 1.5 kN/mm^2.

The nanomaterial added, Nano-silica (SiO_2), improve the strength property of the geopolymer cement due to their ultra-fined particle properties. Nano-silica acts as filler that fills the void between larger cement particles, resulting in a dense and solid matrix. With lower porosity and permeability, this leads to high compressive strength.

4.5 X-RAY DIFFRACTION (XRD)

Apart from that, small pieces of cement obtained from OPC admixed with Nano-silica samples were also investigated using X-ray Diffraction technique (XRD) to study the cement composition and hydration as well as the effect on addition of the nanoparticles. Among compounds in hydrated cement paste that can be detected includes tobermorite, alite (C_3S), belite (C_2S), ettringite (Aft), calcium silicate hydrate (C-S-H) and calcium hydroxide (CH, portlandite).

Alite (C_3S) and Belite (C_2S) are the fundamental components that contributes to compressive strength development. When react with water, C_3S and C_2S form CH and C-S-H gel which acts as a binder, consolidate the matrix and contribute strength to cement. The inclusion of silica further accelerate the formation of C-S-H gel, hence assisting the cement gain early strength.

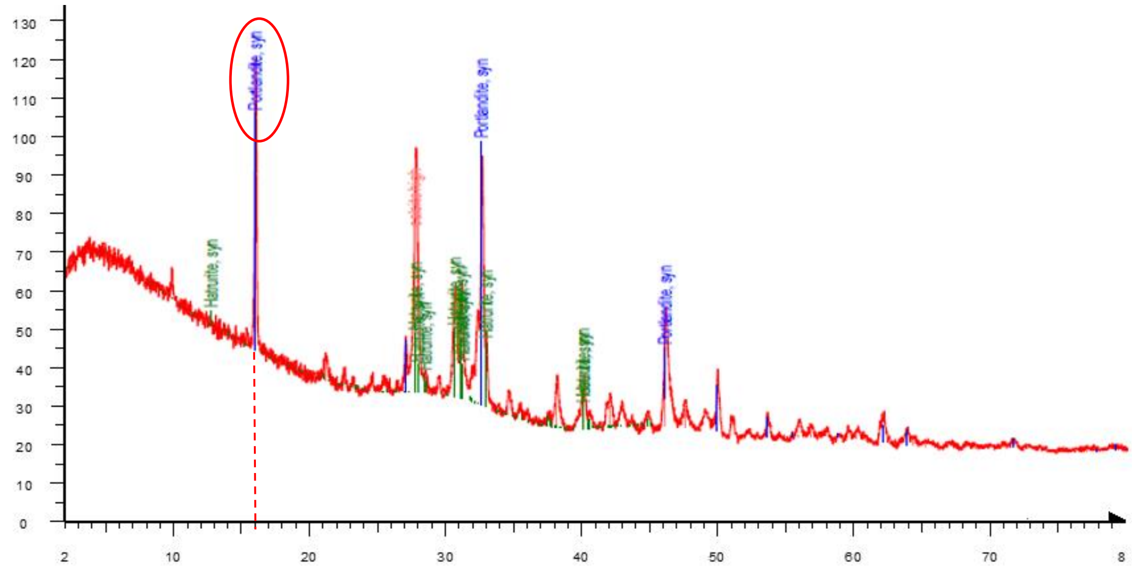


Figure 28: XRD Spectra without Nano-silica

Figure 28 shows the spectrum of hydrated cement pastes without addition of Nano-silica. In can be observed that the calcium hydroxide (CH/portlandite) peaks at 16°. However, when Nano-silica is added as shown in Figure 29, the portlandite peak is no longer visible. This indicates that the portlandite was not fully consumed earlier due to lack of silicon dioxide. While, after addition of Nano-silica, CH was fully transformed to C-S-H hydrate and causes the high compressive strength.

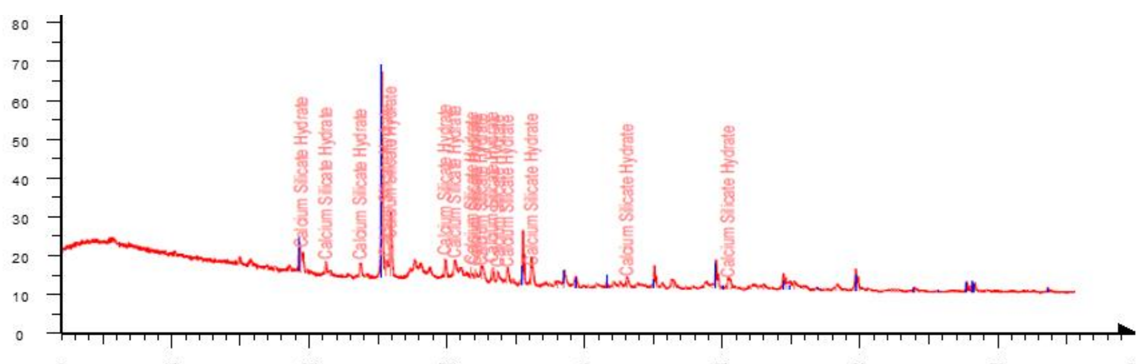


Figure 29: XRD Spectra of OPC admixed Nano-silica

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

From the data obtained, the following conclusions can be drawn:

- GPC, NGPC1, NGPC2 and NGPC3 (0%, 1%, 3% and 5% of Nano-silica) can replaced OPC in high pressure high temperature (HPHT) well (4000psi and 120^{o}C).
- Nano-silica reduced the density of geopolymer cement due to its low specific weight as compared to fly ash, class G cement and silica fumes.
- Addition on Nano-silica also results in a substantial increase in compressive strength. Increase in curing time also leads to the same result.
- XRD analysis of the cement mix with silica shows that the addition of Nano-silica transform the portlandite (CH) to calcium silicate hydrate (C-S-H) and tobermorite at HPHT condition. This show that nanoparticles assist in preventing strength retrogression and provides low permeability to the cement.
- Addition of Nano-silica has significant effect in improving the pore distribution of the geopolymer cement. SEM analysis shows that the ultra-fined particle fills the void spaces between particles which result in uniform, less voids and compact cement matrix.
- SEM images reflect the graph of compressive strength of the cement. As the volume of void spaces between particles reduces (permeability reduction) with increment of percentage of Nano-silica in the cement mix, the compressive strength reading also increases.

5.2 RECOMMENDATION

For further investigation, it is recommended:

1. To vary the curing time of the cement for a longer period as the cement microstructure might weaken. This might lead to increase in permeability.
2. To increase the curing temperature from 120 ◦C to 200 ◦C to observe the effect of temperature on cement performance as Nano-silica might degrade and cause high permeability.
3. To immerse the cement cubes in acidic solution to simulate the condition at which the cement encounter acidic formation. The cement integrity and strength might compromise when encounter this situation

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