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MICROSTRUCTURE INVESTIGATIONS ON NANO-GEOPOLYMER CEMENT CURED UNDER HPHT CONDITIONS

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ABSTRACT

Utilizing industrial by-products such as fly ash as raw materials for geopolymer cement has been highlighted as a better alternative to widely used comparing to Ordinary Portland Cement (OPC). Manufacturing process of OPC are proven emitting large amount of carbon dioxide (CO_2), one of the main greenhouse effect. While, in terms of performance, OPC creates high permeability between cement particles when exposes to High Pressure High Temperature (HPHT) conditions inside the wellbore. Despite proven to have superior mechanical properties, basic geopolymer cement still encountered problems when applied in the same condition. This paper investigates the strength development of geopolymer cement admixed with nano-silica, SiO_2 cured under temperature of 120°C and pressure of 4000 psi. It encompasses the microstructure change of the cement in terms of pore structures. The compressive strength development is tested using compressive strength tester, while the microstructural analysis are studied using Scanning Electorn Microscope (SEM) and X-Ray Diffraction (XRD). Results indicated that substantial increase in compressive strengthonce nano-silica is admixed. Pore distribution is improved due to nano-silica in geopolymer cement. This nanomaterial in geoploymer cement has better performance under HPHT condition than standard OPC and base geopolymer cement.

Keywords: microstructure, geopolymer, cement, nano-SiO_2, HPHT.

INTRODUCTION

Ordinary Portland Cement (OPC) has been the most widely used cement in oil well cementing for decades. It easily mixed with water and prepared at the recommended water-to-cement ratio 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. However, when exposed to HPHT condition inside the wellbore, it undergoes significant phase changes that create high permeability between cement particles and reduce its strength. This phenomenon called strength retrogression results in substantial decrease in compressive strength.

Apart from that, as the environmental regulation is more stringent from time to time, the demand for environment friendly material in oil and gas exploration is increasing. Raw materials of OPC are proven emitting high amount of CO_2, one of major greenhouse gases (GHG), which is accounting for 82% of the total [1]. In reducing GHG emission from cementing process, several initiative can be done including improving the energy conversion efficiency of fossil fuels, shifting energy production to low carbon sources, enhancing uptake by terrestrial and marine biomass, and capturing and storing CO_2 deep underground [2].

Research on alternative cement material has been carried out since OPC has weaknesses associated with environment interferences. As a concern, greener alternative inorganic polymer cement with similar performance as OPC is studied to substitute the using of OPC named Geopolymer cement. Geopolymer is alkali activated aluminosilicate cement which has been gone through geopolymerization as chemical process in reacting aluminosilicates with aqueous alkaline solutions to produce a new class of inorganic binders. Test experiments proved that fly ash based geopolymer cement has excellent compressive strength and good acid resistance which have been indicated at atmospheric pressure and temperature.

Although geopolymer cement has some advantages over OPC; it still encountered several problems when it applied in wellbore or high temperature high pressure (HTHP) condition. It is stated that geopolymer cement possesses better performance than Class G cement in term of compressive strength [2]. However, it must be noted that there is a possibility of breaking up inter granular structure of geopolymer at very high curing temperatures (>100°C) and hence it could lead to strength reduction [3]. In consequences of this phenomenon, nano-scale particle of silica is admixed to geopolymer cement as it is reliable in property enhancement. Hence, the strength reduction when high pressure and high temperature applies can be less than base geopolymer.

MATERIALS AND METHODS

Geopolymer cement

In response to environmental and industrial demand towards more sustainable oil and gas exploration, greener cement has been developed which is Geopolymer

[4]. Geopolymer cement is a low calcium, alkali activated aluminosilicate cement which has been gone through geopolymerization as chemical process in reacting aluminosilicates with aqueous alkaline solutions to produce a new class of inorganic binders. There are several categories of geopolymer cement including slag-based, rock-based, fly ash-based and ferro-sialate-based. The low calcium fly ash in geopolymer is considered as a waste material from combustion and relatively cheaper than the Portland cement. Some studies have been found that geopolymer possesses higher strength, excellent acid resistant characteristics, very little shrinkage compared to OPC, and has higher pumpability compared to OPC [2, 5].

The geopolymerization process involves three separate processes and during initial mixing, the alkaline solution dissolves silicon and aluminium ions in the raw material (fly ash, slag, silica fume, bentonite, etc.) [6]. In this research, the mixture of fly ash and silica fume will act as the base of geopolymer with the composition of 70:30 with addition of nano silica, respectively.

Fly ash

Identified as environmental pollutant, fly ash is a by-product obtained from coal combustion in power plant. It contains more than 70% of silica, alumina, ferrous oxide and calcium dioxide. The presence of calcium is the key element in strength development as calcium ions delivers a faster reactivity and yields good hardening of geopolymer in shorter curing period [7].

Silica fumes

By-product of silicon and ferrosilicon allow production, addition of silica to cement mixture has been widely known to improve mechanical strength and abrasion resistance. Silica acts as a filler material to fill the voids between particles which results in higher packing density and lower porosity [8].

Nanotechnology

Recently, extensive investigation has been carried out by several research groups in oil and gas industry on the application of nanomaterials to solve problems in oilwell cementing [9]. Inclusion of nanomaterial in cement system has various advantages in overcoming poor crack resistance, acid resistance and low strength. Common nanomaterials used in cement system are nano-SiO_2, ZnO_2, Al_2O_3, TiO_2, carbon nanotubes, nano-clays, carbon nanofibers and other nanomaterials [9].

Among those types of nanomaterials, this study will utilize nano-SiO_2 whereas it gives enhanced mechanical properties (compressive strength), lower porosity and permeability [10]. The amounts of admixed nano-SiO_2 in three geopolymer cement samples are 1%, 3% and 5%

Class G cement

In this study, Portland Class G cement is selected as the base line cement to specify the performance of nano-SiO_2 geopolymer in HPHT wellbore conditions. Class G cement is conventional and commercial cement material and made from raw materials such as clay and limestone [11]. It easily mixed with water and prepared at the recommended water-to-cement ration. Class G cement satisfies the fundamental objective which hydraulically isolating the formations and applicable as basic oil well cement from surface of earth to the depth of 8000 ft. (2440 m) [12, 13].

General experiment procedure

There are six stages in the procedures conducted in this experiment. The stages involved preparation of cement cube samples, determination of cement slurry, pressurized density and pH, determination of compressive strength and microstructure investigations.

The first procedure of experiment was the preparation of cement cubes based on American Petroleum Institute API-10B-2 using Constant Speed Mixer under the curing conditions of 4000 psi/120°C for 24 and 48 hours. In this study, three types of cement were used namely Class G, geopolymer and nano-SiO_2 geopolymer cement. Each sample has certain composition of cement slurries as defined in Table-1. In each sample, 259.772 g of water, 18.94 g of NaOH and 71.428 g of Na_2SiO_3 were added to produce cement slurries.

Table-1. Composition of cement samples.

Samples	**Cement** (500 g)			
	Class G	**Fly ash**	**Silica fume**	**Nano-SiO_2**
OPC	100%	-	-	-
GPC	-	70%	30%	-
NGPC1	-	70%	29%	1%
NGPC2	-	70%	27%	3%
NGPC3	-	70%	25%	5%

The density of the cement is determined based on procedure specified in API Spec 10B-6 using pressurized mud balance. The determination of compressive strength was using OFITE automated compressive strength tester with the loading rate of 4000 psi/min. The microstructure investigations of the cement cube samples was carried out through Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) tests. These tests required two slices with 3 mm in thickness of cement cube samples.

RESULTS AND DISCUSSIONS

Density test for all samples was done using pressurized mud balance at standard condition. Densities for Class G cement and geopolimer samples areshown in Figure 1. It indicated that the density of geopolymer decreases as the percentage of nano-SiO_2 increases.

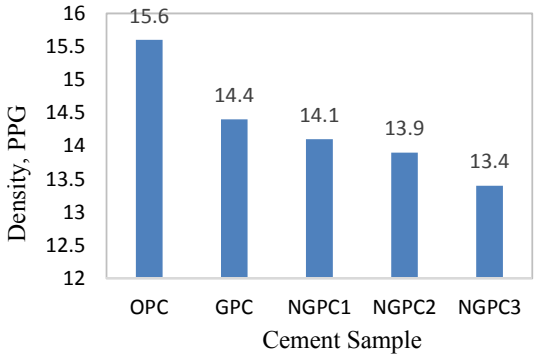

Figure-1. Density of cement samples.

GPC has the highest density, 14.4 ppg while NPGC3 shows the lowest density, 13.4 ppg. The difference between both densities is 15.83%. The difference in density for each samples due to differences in specific gravity in the mixture compositions. Materials with high specific gravity lead to high density.

Compressive strength

It is clearly indicated in Figure 2 that pure geopolymer cement with the composition of 70% fly ash and 30% silica fume had the lowest strength. Though the compressive strength value was lower strength than class G but it still was exceeding the minimum requirement of cement strength which is 1500 psi. According to previous research, GPC possessed the lowest strength due to the possibility of breaking up inter granular structure of geopolymer at very high curing temperatures (>100ºC). Therefore, this may lead to higher strength reduction [3].

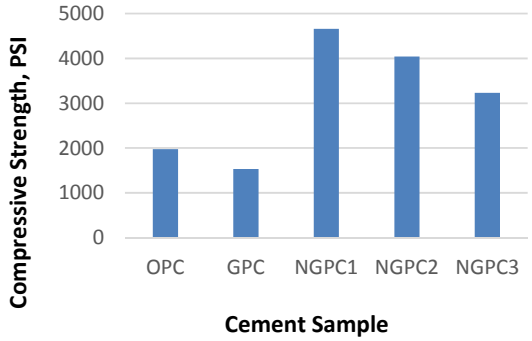

Figure-2. Compressive strength of cement samples.

However, geopolymer with addition of 1% nano-SiO_2 (NGPC1) possessed highest strength which is 4655.71 psi. Nanoscale particles are known to affect the porosity/permeability, strength, durability, shrinkage, and corrosion resistant [14]. This nano size particles can fill the spaces between gel formed by geopolymerization system and act as nanofiller to reduce effective porosity and permeability [9]. By the results obtained, it proved that nano-SiO_2 has the function in enhancing mechanical properties (compressive strength) of the cement whereas compressive strength increased about twice with 1% nano-SiO_2.

Furthermore, geopolymer with addition of 2% and 3% nano-SiO_2 (NG3) had lower value than NGPC1. This phenomenon occurred because this percentage might exceed the optimal amount of nano-SiO_2 used. It is important to acknowledge threshold of nanomaterial contents to improve hardened cement properties by pozzolanic reaction [15-16]. As such, the resulting of unreacted nanosilica might produce a strain-softening like effect in the cement-nanosilica composite. Such behavior has been reported by nano-glass particles [17] and is yet to be studied in oilwell cement materials.

Microstructure properties

Figure-3 presents the microstructure of geopolymer cement which indicates the presence of air bubble shaped concave-circular like hole. The air bubbles are believed as resulted from oxidation reaction in the samples. This reaction has substantially fast chemical under alkaline conditions with Si and Al minerals. As a result, it create a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds called geopolymerization.

It is indicated from the SEM image, GP samples produced small amount of air bubbles that assigned to the less polymerization process were occurred. It can be seen from unreacted fly ash presented in the microstructure imaging too.

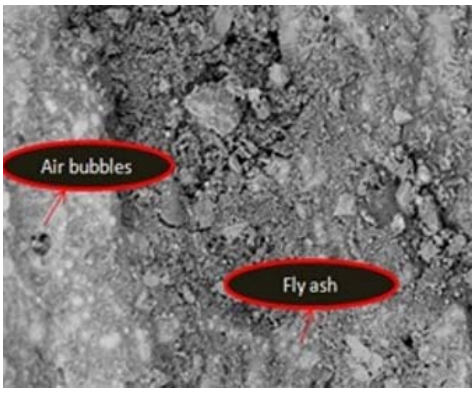

Figure-3. SEM image of GPC.

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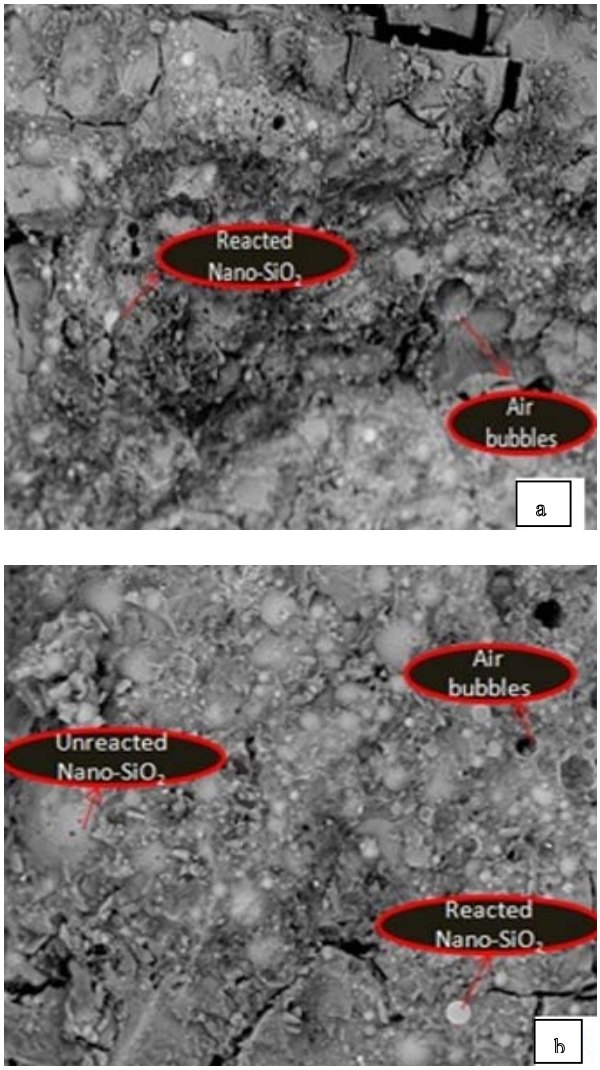

Figure-4. SEM image of NGPC3.

Figures 4(a) and 4(b) exhibited the particles structure of sample NGPC1 and NGPC3. NGPC1 that contained 1% nano-SiO_2 in geopolymer cement was showing more rigid structure with much more air bubbles and the workability appearance of nano-SiO_2 in filling the empty spaces and strengthening the cement samples. With much more air bubbles presented, it was assumed that nano-SiO_2 aided the geopolymerization process.

NGPC3 in Figure 4(b) contained 3% nano-SiO_2 likewise indicated the presence of air bubbles and nano-SiO_2 that have been reacted to fill the empty spaces. Nevertheless, the unreacted nano-SiO_2 were also visible whereas this unreacted ones were just covering the surface of the cement without merging or reacting with the other chemical compositions and much probably did not enhance the mechanical properties of the cement samples. The SEM images obtained were in a certain way synchronized with the compressive strength results.

Small pieces of cement obtained from OPC admixed with Nano-SiO_2 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.

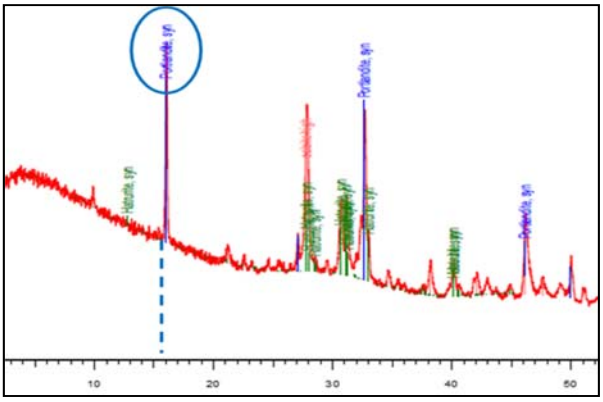

Figure-5. XRD spectra of OPC.

Figure-5 shows the spectrum of hydrated OPC pastes without addition of nano-silica. It can be observed that the calcium hydroxide (CH/portlandite) peaks at 16°. However, when nano-silica is added, the portlandite peak is no longer visible as shown in Figure-6. 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 high compressive strength.

By means of the inclusion of nanomaterial in geopolymer, it is expected that the nano-SiO_2 will aid the performance of geopolymer chemically under high pressure and high temperature since it encountered strength problem in this kind of curing conditions which could also be proved in microstructure investigations. When nano particles are added, the size of the empty spaces is greatly reduced, yielding smaller pore sizes and high mechanical strength and density.

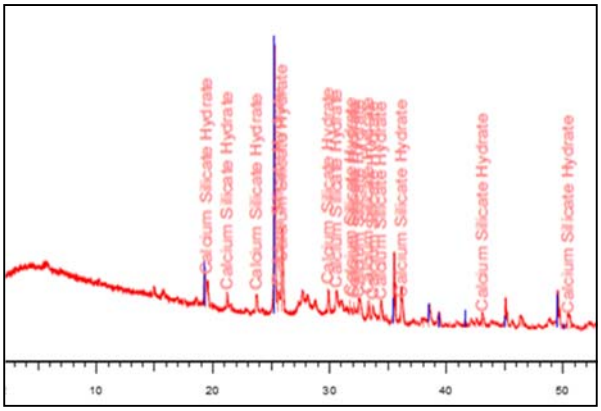

Figure-6. XRD spectra of OPC admixed nano-silica.

CONCLUSIONS

The results found that 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 results in a substantial increase in compressive strength. As indicated in XRD analysis that the addition of nano-SiO_2 transform the portlandite (CH) to calcium silicate hydrate (C-S-H) and tobermorite at HPHT condition. This phenomena assist in preventing strength retrogression and provides low permeability. Furthermore, it contribute to fills the void spaces between particles which result in uniform, less voids and compact cement matrix. This has potential application in replacing conventional OPC for oilwell cement.

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