Reinforcing Effects of Graphene Oxide in Oil Well Cement Used for CO2 Storage

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***Abstract*— CCS or Carbon Capture and Storage is one of the method to conserve environment by reduce the CO2 gas emission to the atmosphere by the process of separation and capture of carbon dioxide and safely store the CO2 into deep geologic formations. Wellbore and cement integrity need to be maximize for safely and permanently storing of carbon dioxide (CO2) in the subsurface for a very long term of duration. The chemical interactions between CO2 in carbonic acid and cements will form calcium carbonate that easily leachable or susceptible to further reaction that could potentially diminish the strength of the cement and increase the cement degradation rate that can lead to leakage. The reinforcing effects of graphene oxide (GO) in oil well cement used for CO2 storage was investigated in this experimental study. GO was prepared by oxidization and ultrasonic dispersion. Effects of GO on mechanical properties of cement cubes after been exposed to carbonic acid for 10 days were investigated by determining the compressive strength and mass losses of the cement cubes and the results were compared with neat cement without GO. It is discovered that when 0.10 wt.% by weight of GO was added into the cement paste, compressive strength was increased by more than 24% and it due to the refinement of the porosity of the cement matrix caused by strong covalent bond that form flower-like crystal regulated by GO and can reduce the degradation rate of the cement by more than 32% because GO have various oxygen-containing functional groups that make GO highly attractive for cement hydration that needed in order to get strong and lower degradable compound of cement. The overall results show that GO can be an effective nanomaterials for reinforcing the mechanical properties of Ordinary Portland Cement (OPC) used for CO_2 storage.**

Keywords*— *graphene oxide, oil well cement, CO2 storage, compressive strength, degradation rate, agglomeration

I. INTRODUCTION

Carbon storage is one of the method to conserve environment by safely store the CO2 into deep geologic formations to avoid it from escaped and cements act as sealant in wellbore used for carbon storage. Wellbore and cement integrity need to be maximize for safely and permanently storing of carbon dioxide (CO2) in the subsurface for a very long term of duration. The loss of well integrity often cause by the geological environment in down hole formations due to supercritical CO2 and carbonic brine that responsible for cement degradation, leading to rapid CO2 leakage [1].Carbon dioxide saturated with brine underground will deteriorates the wellbore's cement used in CO2 storage that occur in the cement structures that have been set in order to support the well casing either in the annulus between the casing and rock or at the interface between the casing and cement well plug that will lead to leakage [2]. Cement exposed to CO_2 in carbonic acid will undergoes combination of processes which include chemical shrinkage and hydration, thermally induced pressurization and expansion, structural transformation of calcium silicates and decalcification. Besides that, carbonation, bi-carbonation and mineral leaching also will happen when cement exposed to CO2 in carbonic acid [3]. Thus, the role of cement as sealing agent can be compromised when exposed to carbonic acid which leads to increment in the rate of cement degradation.

The chemical interactions between CO2 in carbonic acid and cements will form calcium carbonate that easily leachable or susceptible to further reaction that could potentially induce the cement degradation and lead to leakage [4]. The progressive dissolution of calcium carbonate creates a high-porosity 'dissolution front' in the cement. The degradation rate of the cement increases as porosity of the cement increases and thus lowering the compressive strength of the cement[5]. Thus, cement needs some additives that can dispersed well in the morphology of the cement in such way to enhance the mechanical strength of the cement. The present inventors have determined that graphene oxide sheets can be readily dispersed throughout cementitious material pastes such that the cementitious matrix formed upon curing exhibits significantly improved mechanical qualities compared to an equivalent cementitious material matrix that does not include graphene oxide [6]. Development of high compressive strength of oil well cement become an important role in CO_2 storage and also drilling program. Achievement of enough and sufficient compressive strength of oil well cement in CO_2 storage give sufficient structural support for the underground well and providing hydraulic/mechanical isolation of borehole intervals.

It is relevant and important to study the effects of reinforced additives of cement on the integrity of oil well cement because wells that supported by cements represent a potential leakage pathway in wellbore used for CO2 storage. A new cement with some additives materials in purpose to gain better CO2 resistance is compared with a neat cement using methodology and experimental procedure simulating the interaction of set cement with carbonic acid to investigate the effect of carbonic acid on compressive strength and the degradation rate of oil well cement at different amount of graphene oxide as additive. Graphene oxide can become promising nanomaterial that will act as nucleation site for the cement hydration product in order to overcome the increment of cement's porosity that become the negative effect of carbonic acid towards cement's mechanical strength in CO_2 storage. Therefore, due to the problems regarding cement in carbonic acid environment during carbon storage, this research will proves that graphene oxide can influence the compressive strength and degradation rate of the cement in carbonic acid environment in a positive way [7].

II. METHODOLOGY

A. Materials Preparation

Graphite powders (Mw=12.01, COMAK) were used as substrate of GO. Sulphuric acid, H_2SO_4 (95-98%, R&M Chemicals), sodium nitrate, $NaNO_3$ (84.99 g/mol, SYSTERM), potassium permanganate, $KMnO_4$ (158.05 g/mol, R&M Chemicals), hydrogen peroxide, H_2O_2 (30%, Merck) were used as received and for washing method, distilled water and HCL were used. In sample preparation, deionized water (DI) was used. Class G cement was used as subject of experiment. Dry ice was used to prepare the carbonic acid solution.

B. Synthesis of GO

Synthesized via exfoliation of graphite. This process was performed through a colloidal suspension route. By using a modified Hummers method, natural graphite powders were oxidized to graphene oxide. About 2.5 g sodium nitrate ($NaNO_3$) and 5 g graphite powder were added into 1000 ml beaker at an ice bath condition. After that, 200 ml of concentrated sulfuric acid (98.08g/mol) were added into the previous beaker and the mixture were stirred for 1 hour using magnetic stirrer obtaining a black slurry. Then, 30 g potassium permanganate ($KMnO_4$) was gradually added and the mixture was stirred within 2h while the temperature was kept less than 15°C using an ice bath to prevent explosion due to overheating. For another 2h, the mixture was continued stirred at temperature below 15°C. The mixture was kept stirred at 24°C (room temperature) for 20h after ice bath was removed. Then, the mixture was heated up to 70°C and continued stirred for 2h and 100 ml of distilled water (H_2O) was added into the mixture very slowly. Again, the mixture was heated to 90°C and kept stirred for another 1h while another 100 ml of distilled water (H_2O) was slowly added and kept stirred for 1h. To ensure the termination of the oxidation reaction, the solution was further treated with 30 ml of 30% of hydrogen peroxide solution (H_2O_2). The resulting mixture was repeatedly washed until it formed gel like solution and pH neutral by centrifugation with HCL and distilled water (H_2O) for several times. After the purification stage, to ensure the complete exfoliation of graphene oxide sheets, the solution was sonicated for one hour and then part of the aqueous solution has been dried in an oven at 60°C for 24 hours which is enough to eliminate all the water but not to degrade the GO.

C. Characterization of GO

The GO was tested using the Fourier Transform Infrared Spectroscopy (FT-IR), in order to identify the compositions and distribution of GO. GO also characterized by using X-ray Diffraction (XRD). The GO sample was grounded into tiny powder for measurement and the crystalline structure of GO was investigated by using Rigaku model of X-Ray Diffractometer (XRD) equipment in order to confirm the formation of graphene oxide from graphite powder. The measurement was performed by using scanning range of 40 Kv, 40 mA, 5-8°, and (2°/min).

D. Preparation of cement slurries

Class G oil well cement was used in this project. Samples were made by mixing class G cement with distilled water and graphene oxide. Cement slurries were prepared with 0.44 water to cement ratio (w/c). One sample of cement without GO (neat cement) that served as a reference sample was prepared and another samples were containing different amounts of GO of 0.05, 0.10, 0.15, and 0.20 wt.% by of cement. The cements were mixed according to API specifications 10B. Constant Speed Mixer, Model 686CS was used to mix the samples. The dry constituents were prepared and weighed. The cement powder was dry mixed with accurate amount of graphene oxide powder. These mixture were placed near the mixer where they can be quickly added during the mixing phase. Then, 32-oz container of constant speed mixer was filled with water to the proper level. The water was stirred until the speed reaches 4000 RPM. When the speed reaches 4000 RPM, the dry ingredients that been prepared earlier as described in the API specification was added into the container quickly and the mixer will begin counting down to 15 seconds only when the 4000 RPM was achieved. Right after the 15-second mixing step was elapsed, the button labelled 12000 was pressed and the mixer was accelerated to 12,000 RPM. The mixer was counted up to 35 seconds when the speed stabilized at 12,000 RPM. After 35 seconds, the mixer was slow down and stopped. When the display shows 0 RPM and the fluid stops swirling, the mixer container was removed. The cement sample was ready for curing.

E. Curing

After preparation of cement slurries, right after mixing, the samples were molded in 50mm x 50mm x 50mm cubic molds that have been put grease on it. The mixing materials were left in the mold and cured in a water bath at 60°C for 24 hours. After 24 h, the cement cubes were demolded and rest in the water bath at room temperature until the analysis was ready to begin.

F. CO2 Exposure

After curing period, the samples were demolded and in order to remove grease from their surface, the cubes were washed. Half of the cubic samples were cored to obtain 20mm diameter cylindrical samples with 40mm length and another half of the cubic samples was kept in 50mm cubic shape prior to carbonic acid exposure. The carbonic acid was prepared by putting some of dry ice into a beaker containing distilled water. Diluted HCL solution was slightly put into the carbonic acid formed to reduce the pH of the carbonic acid into pH 4. Aging cell was used in order to expose cement core samples (20mm diameter x 40mm length) for 10 days. The set of screws in the outer cap was tighten by using Allen wrench. The valve stem with the O-rings in place was completely tighten after been inserted into the inner cap. The aging cell was connected to the pressure line of the gas tank. The valve stem was loosened approximately one half turn before pressurizing. The safety pin was attached to the aging cell for safety issue during the experiment. The aging cell was pressurized. When the desired pressure which is 500 psi was reached, the valve stem was closed by tightening it with a wrench. The pressure of the tank was completely released. The aging cell was placed inside the oven and adjusted to the desired temperature which is 60ºC.All steps of aging with carbonic acid and samples was repeated every 2 days until 10 days.

Because the compressive strength tester only can run on the 50 mm cubic samples. The 50mm cubes were exposed to CO_2 using water bath. All cubic samples were put into the beaker together with carbonic acid. The beaker containing the carbonic acid and samples was put into the water bath at 60ºC pH was adjusted to pH 4 using HCL. The beaker was adjusted slightly higher than water bath interface to avoid flow of fluid between the carbonic acid and water bath. The beaker was left in the water bath for 10 days. After 10 days, the cubic samples were ready for compressive strength test.

G. Compressive Strength Test

After the samples have been exposed to the carbonic acid for 10 days, the samples undergo compressive strength test by using standard compressive strength tester (ELE ADR Touch 3000 BS EN). After specified time, the samples were removed from carbonated brine and excess fluid was wiped out from the surface. First of all, the bearing surface of the compressive strength tester where samples were placed when testing was cleaned. Then, the cubic cement was placed in the machine in such a manner that the load can be applied to the opposite sides of the cube cast. The load was applied gradually and continuously at the rate of 140 kg/cm^2/minute without shock till the sample breaks and fails. The maximum load where the samples can hold was recorded. By using formula (Compressive Strength of cement = Maximum compressive load / Cross Sectional Area of the cement cube), the compressive strength of the cement pastes was calculated.

H. Degradation Rate Evaluation

The cores were weighed to measure its mass before CO_2 exposure. After the exposure, visual inspection has been done by taking a picture of degraded specimens. The cores were also was weighed after exposure. By using the rate of corrosion formula, the mass loss rate was calculated in order to know the degradation rate of the cement. The rate of corrosion formula that be used was shown in the figure 1 below. The steps were done every 2 days of exposure until 10 days.

$$R = \frac{K(m_b - m_a)}{A \cdot \Delta t \cdot \rho}$$

R = penetration rate (mm/yr or mils/yr)
m_b = mass before exposure (gram)
m_a = mass after exposure (gram)
A = total exposed surface area (in^2 or mm^2)
Δt = total exposure time (hours)
ρ = density (grams/cm^3)
K = unit conversion constant

Figure 1: The rate of corrosion formula

III. RESULTS AND DISCUSSION

A. Characterization of GO (X-Ray Diffraction, XRD)

Figure 2 shows that sharp reflection peak appear at 2Θ = 9.92° which indicates that the graphite was altered after oxidation to form graphene oxide completely.

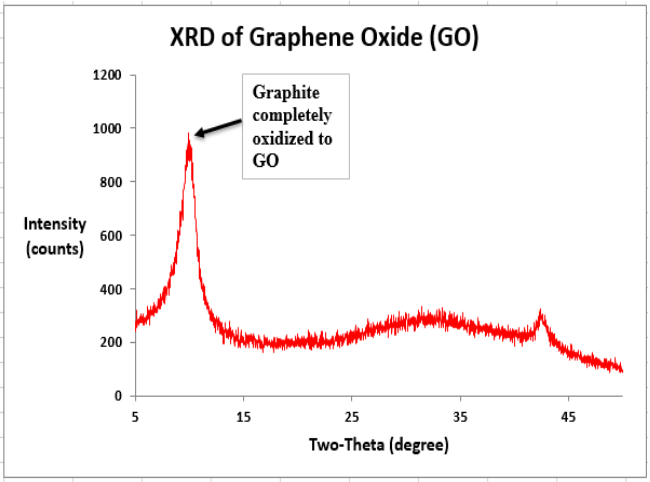

Figure 2: XRD of Graphene Oxide (GO)

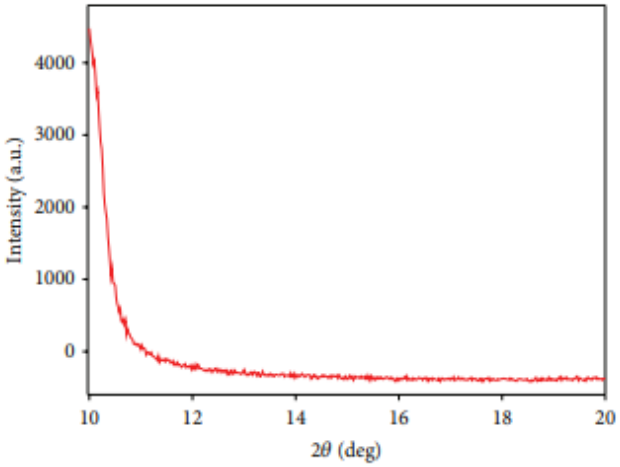

Figure 3: XRD of Graphene Oxide (GO) from other researcher[8]

By using FT-IR analysis, the presence of oxygen functional groups in GO was verified. GO shows some characteristic peaks that confirm the groups of carbonyl and carboxyl which approving the successful of oxidation of graphite. A peak at 3228.92 cm^{-1} represents the O-H stretching automatically indicates the hydroxyl group. A peak signal at 1716.55 cm^{-1} shows the C=O stretching of the carboxyl group (COOH) whereas at 1622.72 cm^{-1} and 1052 cm^{-1} indicates the aromatic, C=C and C-O stretching of alkyl groups respectively.

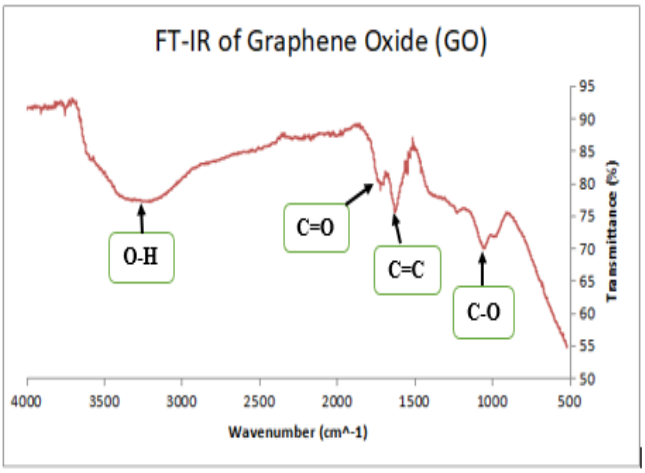

Figure 4: FT-IR of Graphene Oxide (GO)

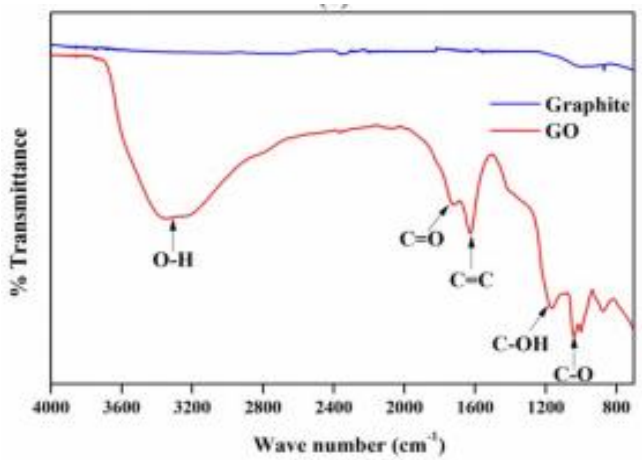

Figure 5: FT-IR of Graphene Oxide (GO) from other researcher[9]

B. *Compressive Strength*

Based on the figure 6, the cement cubes that have been exposed for 10 days in the carbonic acid solution at 60ºC show that samples with GO experience higher compressive strength than the neat cement. The increment of compressive strength of the cement was as much as 24% between the neat cement and the 0.1 wt. % GO reinforced cement. However, the compressive strength of the graphene oxide reinforced cement starts to decrease when the concentration of the GO was increased to 0.15 wt.% and 0.20 wt.% caused by agglomeration of the GO that hinder the potential of GO to reduce the porosity of the cement structure.

In CO2-rich environments, which is carbonic acid environment, the carbonation of portlandite initiate CO2 attack on the cement [10]. When portlandite is consumed as time passes, $CaCO_3$ and silica gel that easily leachable or susceptible was formed by decomposition of calcium silicate hydrate (C-S-H phases) which reduction of the cement's strength occurred that could potentially induce the cement weakening and lead to leakage [11]. The progressive dissolution of calcium carbonate creates a high-porosity 'dissolution front' in the cement and make the compressive strength of the cement was decreased [12]. The graphene oxide, due to its unique features of a two-dimensional materials, with several oxygen groups spread over it surface and can regulate formation of "flower-like crystals" that will increase the compressive strength of the corresponding cement paste by filled into the porous part of the cement and create a very good bonding between the particles of the cement[6].

The strength of the cement improved also may be gained from refinement of pore structure gave by GO nanostructure that filled in the graphene oxide reinforced cement. Good dispersion of the GO gained by the "oxygen-bearing functional groups" of the GO that are desirable for homogeneous dispersion in cement and nucleation of C–S–H while effects of GO on pore, hydration, and "crack-bridging" will lead to increment of compressive strength of the cement. By having high reinforcing effect of GO, GO become an effective reinforcement for cementitious materials shown by the improvement in strength of cement cubes [13]. The cause of reduction in the compressive strength of the graphene oxide reinforced cement cubes at 0.15 and 0.2 wt% was because the GO start to agglomerate and was not well-dispersed. For GO additives, agglomeration of GO become the limitation that hinders their potential to improve the mechanical properties of the cement. Due to GO agglomeration, the workability of the cement paste was reduced caused by water that have been trapped in GO agglomerates and then reduce the strength of the cement cubes [7]. Hydration of cement paste was not improved significantly and the porosity of cement paste also was not refined notably since GO was agglomerated [14].

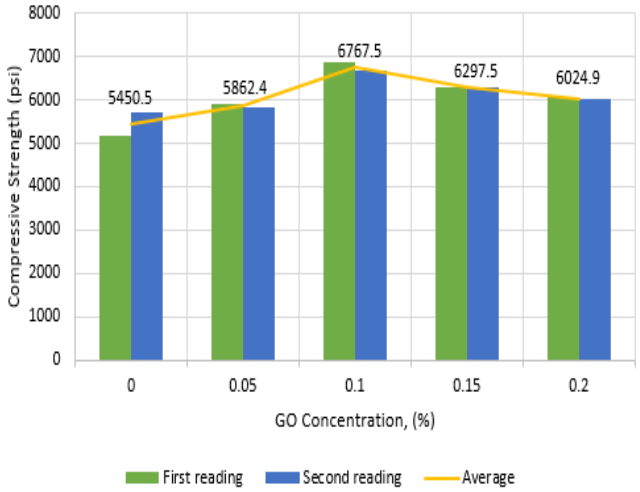

Figure 6: Compressive strength development of cement cubes after 10 days of CO_2 exposure

C. *Degradation Rate*

Based on the figure 7, when the cements were exposed to the carbonic acid at 60ºC and 500 psi respectively, the degradation rate of the cement was increased as the time moving. Although the degradation rate increases but the rate of increment become the promising parameter that need to be stated to differentiate between the neat cement and graphene oxide reinforced cement in term of durability. From the figure, based on average degradation rate, the highest rate of degradation was at 0.2 % wt. GO reinforced cement which is 0.645 cm/year while the lowest rate of degradation was at 0.1 % wt. GO reinforced cement which is 0.407 cm/year. Thus, the optimum concentration of GO that will give the lowest degradation rate of the cement that exposed to the carbonic acid environment is 0.1 % wt. in order to increase the durability of the cement.

Cement exposed to carbonic acid will undergoes combination of processes which include hydration and chemical shrinkage, expansion and thermally induced pressurization, structural transformation of calcium silicates, decalcification, carbonation, bi-carbonation and mineral leaching which will happen when cement exposed to carbonic acid that could potentially induce the cement degradation and lead to leakage [15].GO is the highly oxidized derivative of graphene possessing various oxygen-containing functional groups such as carbonyl, hydroxyl, epoxy and carboxyl and these groups make graphene oxide highly attractive and can attracts C3S, C3A and C2S as it plays a major role in increment of degree of hydration. Higher degree of hydration was produced by GO also due to the large total surface area [6]. Improved degree of hydration in the GO reinforced cement become the reason in reduction of porosity of the cement paste and lowering the degradation rate of cement. GO only works efficiently as hydration inducer for cement structure to reduce the porosity of the cement matrix in order to get stable and lower degradable compound when GO addition was in an optimum concentration which is at 0.1 wt.%.

After the optimum concentration of GO was exceeded, the degradation rate of the cement start to increase more than neat cement caused by agglomeration of the GO where GO start to accumulate and did not well-dispersed [7]. In other words, increasing GO content create difficulty to the cement structure in providing suitable workability for the cement and then make GO

within the matrix of the cement hard to disperse well caused by the presence of hydrophilic groups on the GO surfaces that means GO flakes will absorb a huge amount of water, diminish the hydration of the cement paste and last induce them to agglomerate in the form of clumps and form large voids due to agglomerates within the cement matrix and stresses cannot be transferred across the bundles. Furthermore, when the GO agglomerate, they are no longer remain within the nanoscale range therefore GO will gather between the products of cement hydration and later induce zones of weakness in the cement matrix rather than filling the void spaces within the cement grains. This is the major reason for the increment of degradation rate of the cement after excessive GO concentration was applied.

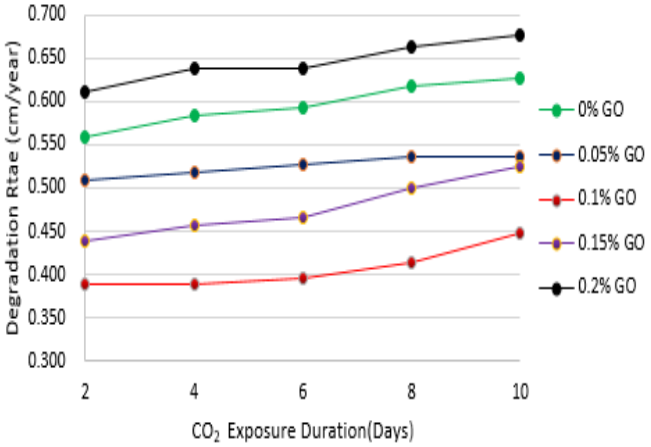

Figure 7: Summary of degradation rate of the cement after carbonic acid exposure

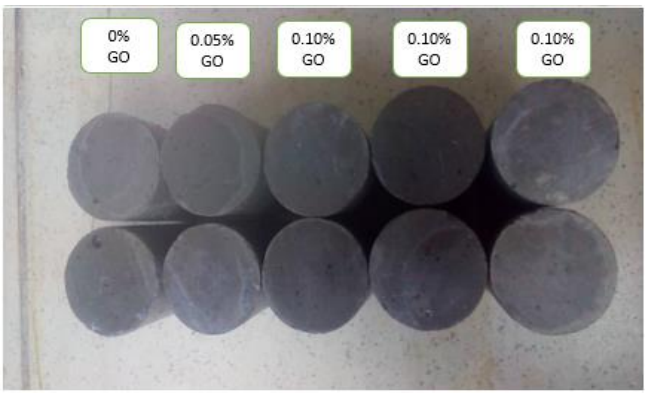

Figure 8: Cement cores before 10 days of CO_2 exposure

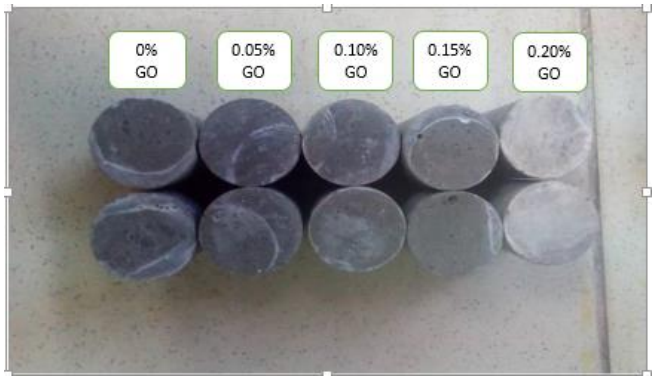

Figure 9: Cement cores after 10 days of CO_2 exposure

IV. Conclusion

In this study, GO was synthesized via graphite through oxidation and ultrasonic treatment. The effects of GO nanomaterials on the degradation rate and mechanical strength of cement samples were investigated after exposed to the carbonic acid that related to CO2 storage environment. The progressive dissolution of calcium carbonate that formed when CO2 in carbonic acid and cements interacts will creates a high-porosity 'dissolution front' in the cement that reduce the compressive strength of the cement and lead to high degradation rate of cement. Cement with 0.10 wt. % of GO exhibited remarkable increase in compressive strength (24%) and experience in reduction of degradation rate (32%) comparing with those without GO. When excessive addition of GO, adverse impact will be experienced by the cement that shown by increment in degradation rate and reduction in the compressive strength of the cement when the content of GO was 0.20 wt% caused by agglomeration of GO.

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