



# Impact of wet supercritical CO<sub>2</sub> injection on fly ash geopolymer cement under elevated temperatures for well cement applications

Syahrir Ridha<sup>1</sup> · Riau Andriana Setiawan<sup>1</sup> · Astra Agus Pramana<sup>2</sup> · Muslim Abdurrahman<sup>3</sup>

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## Abstract

An alternative cement system created through geopolymerization of fly ash offers favorable properties such as able to resist acidic fluids and possess high compressive strength. However, the application of fly ash geopolymer as wellbore cement under carbon dioxide (CO<sub>2</sub>) environment at elevated temperature is not well recorded in the literature. This paper characterizes the fly ash-based geopolymer cement and experimentally investigates its mechanical and microstructure changes after exposed to CO<sub>2</sub> under elevated temperature. Microstructure identification on the altered cement paste was conducted by the analysis of XRD and SEM. In this study, fly ash-based alkali-activated cement was made using 8 molal sodium hydroxide and sodium silicate as alkali activators. The results found that crystal-like shape identified as calcium carbonate was formed at the surface of spherical fly ash particle after carbonation formation. The strength of geopolymer cement was found not to be decreased although carbonation process was occurred. Microstructure analysis revealed that zeolite was formed during CO<sub>2</sub> acid exposure for geopolymer cement which contributes to the strength development.

**Keywords** Fly ash · Oil well cement · Alkali activated · Microstructure · Wet supercritical CO<sub>2</sub>

## Abbreviations

GC60	Geopolymer cement cured at 60 °C and 17.23 MPa
GC130	Geopolymer cement cured at 130 °C and 24.13 MPa
96GC130w	Geopolymer cement after wet CO <sub>2</sub> exposure at 130 °C and 24.13 MPa for 96 h
72GC60w	Geopolymer cement after wet CO <sub>2</sub> exposure at 60 °C and 17.23 MPa for 72 h
24GC130w	Geopolymer cement after wet CO <sub>2</sub> exposure at 130 °C and 24.13 MPa for 24 h

## Introduction

Enhance oil recovery (EOR) is aimed to increase the percentage of oil production from unrecovered reservoirs. This is a well-established method which not only offers economic benefit in term of oil production but also reduces the cost of CO<sub>2</sub> storage (Dai et al. 2016). Although EOR operation may reduce CO<sub>2</sub> in the atmosphere, proper action should be addressed to avoid leakage into the surface. Good cement system is one of key element for well integrity to sustain CO<sub>2</sub> in the formation and prevent uncontrolled fluids seep to the surface (Ridha et al. 2018a, b). This was early indicated by Benson et al. (2003) that incompatible well construction materials have major role causing failure of injection wells. Good cement materials and slurry design are important factor of having good wellbore integrity (Velayati et al. 2015).

The interactions between wet CO<sub>2</sub>, neat cement, and pozzolanic material had been investigated by Kutchko et al. (2008), Sauki and Irawan (2010), Jacquemet et al. (2012) and Chindaprasirt et al. (2013) using ordinary Portland cement (OPC)-based cement. However, there is limited reference on the investigation of wet CO<sub>2</sub>, brine and geopolymer cement interactions under elevated temperatures. These reactions may increase porosity and permeability and

✉ Riau Andriana Setiawan  
riauandriana@gmail.com

<sup>1</sup> Petroleum Engineering Department, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Malaysia

<sup>2</sup> Petroleum Engineering Department, Universitas Pertamina, Jakarta 12220, Indonesia

<sup>3</sup> Petroleum Engineering Department, Universitas Islam Riau, Pekanbaru 28284, Indonesia

decrease compressive strength of the cement paste (Omosebi et al. 2016; Ridha et al. 2018a, b).

Class G oil well cement (OPC-based cement) is most commonly used in oil and gas industry due to their compatibility and ability to mix with series of additives (Smith 1990). However, the major concern is that OPC cement is not stable in CO<sub>2</sub>-rich environment due to durability issues. In the presence of CO<sub>2</sub>, calcium hydroxide as one of the products from OPC hydration was altered into calcium bicarbonate which is easily dissolved in water. As the effect, this may lead to integrity problem of wellbore that may cause potential fluids leak paths which lead to contamination of freshwater aquifers and groundwater. The possible leakage pathway would be from the reservoir to the shallower formation to the wellbore cement.

Several studies have been conducted to find alternative cement system for wellbore application, including partial or total replacement of OPC cementing material with alkali-activated cement (Ryu et al. 2013; Ridha et al. 2018a, b; Khalifeh et al. 2014) which is known as geopolymer cement system. This material is rich in silica, alumina, and calcium that possess good character as a cementing material. Geopolymer cement is known as a product of the reaction between solid source material rich with alumina-silica and solution of alkali hydroxide and/or alkali silicate activator. Metakaolin, fly ash, slag and silica fume had been identified as solid source materials (Ridha et al. 2017). The most commonly used alkali activators are sodium silicate, potassium silicate, sodium hydroxide and potassium hydroxide (Duxson et al. 2007). The use of source materials containing high calcium content such as fly ash makes geopolymer cement susceptible to calcium carbonate formation. However, the main structure framework (Si–O–Al–O–Si) of geopolymer cement is expected to be able to withstand the negative effects of CO<sub>2</sub> attack.

Geopolymer cement has been showed potential utilization in oil well cementing operations due to having high compressive strength, low shrinkage and an excellent resistance to acid attack (Phair and Van Deventer 2002; Palomo et al. 1999). However, its changes in term of microstructure and mineralogical during accelerated carbonation by wet supercritical CO<sub>2</sub> were not fully studied. Therefore, this research was carried out to investigate the effect of alteration of geopolymer cement by wet supercritical CO<sub>2</sub> injection under elevated temperature condition.

## Materials and methods

The materials used for experiment were fly ash, sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>), and sodium hydroxide (NaOH). Fly ash was obtained from Manjung power plant located at Manjung, Perak, Malaysia. The chemical composition of fly ash

is shown in Table 1 as obtained from X-ray fluorescence (XRF) analysis. The total element content of pozzolans (Si, Fe, and Al) in fly ash was 63.82%.

## Materials

The ratio of fly ash to alkali activator and the ratio of sodium silicate to sodium hydroxide were maintained at 2.27 and 2.5, respectively (Ridha and Yerikania 2015). The 8 molal concentration of sodium hydroxide was diluted to a definite amount of NaOH pellets in distilled water. Geopolymer cement slurry was prepared by gently pouring sodium silicate into the mixer that had been filled with sodium hydroxide solution for about 10 s. The fly ash was then poured into alkali solution with speed mixer for 15 s at 4000 rpm and continued for 35 s at 12,000 rpm based on API standard (API RP-10B-2, 2005).

Once the slurry has been prepared, it was poured into a 2×2×2-inch steel cubic mold which has been coated with grease. The molds were then located inside curing chamber for 24 h with pressures and temperatures at 17.2 MPa and 60 °C, and 24.1 MPa and 130 °C. The hardened cement pastes were then exposed into CO<sub>2</sub> wet supercritical. These experiments were conducted by placing the hardened cement samples in the pressure vessel with half-filled of brine solution. The vessel was subsequently pressurized with CO<sub>2</sub> gas to simulate pre-determined reservoir pressures and temperatures. At these conditions, the CO<sub>2</sub> was in a supercritical state. The experiments were carried out under static conditions for 24, 72, and 96 h to determine the effect of acid gas attack on the cement samples.

## Methods

The compressive strength was measured according to ASTM C 109 (2016) using compression machines ELE ADR 3000 with 3000 kN capacity, and the loading rate of the plate had been set to 0.9 kN/s. All the debris and powder of each sample were collected and properly labeled for further testing to investigated microstructure and mineralogical degradation of the cement samples.

The degradation of the geopolymer cement after exposed to wet supercritical CO<sub>2</sub> after 24, 72 and 96 h was

**Table 1** Chemical composition of fly ash

Composition	Element (%.wt)
Si	23
Al	9.32
Fe	31.5
Ca	25
Na	0.72
Others	10.46

investigated using scanning electron microscopy (SEM) and X-ray diffraction (XRD). SEM gave the visual appearance of different phase inside the sample from millimeters to micrometers to produce information such as good physical and mechanical description of the microstructure of crystalline and amorphous materials. Prior to SEM analysis, sample with approximate size of 220 mm<sup>2</sup> area and 3 mm thickness was located inside sputter coater machine together with additional thin layer (~ 10 nm) of a conductor material (gold). Due to their insulating nature, cement surface acts as an electron trap and this accumulation of electrons on the surface is called charging which creates extra white regions on the sample image. To overcome charging phenomena, lower vacuum pressure up to  $1 \times 10^{-5}$  atm in the SEM chamber and gold sputter have been introduced to all samples. The XRD diffractogram was acquired by scanning the sample in steps of 0.01 ( $2\theta$ ) at range of 5° to 80°  $2\theta$ .

## Results and discussion

### Fly ash characteristics

The fly ash was categorized as class C high calcium fly ash because the percentage components of Si, Fe and Al in fly ash were 68.2%, while the Ca was 20.66% (Table 1). This may be attributed to the presence of lime, crystalline tricalcium aluminate, crystalline tricalcium silicate (belite and/or alite). The high calcium content of fly ash leads to higher reactivity as compared to the low calcium fly ash, and this can be seen from the short thickening time in geopolymer paste measured using consistometer or Vicat needle apparatus (Ridha et al. 2017).

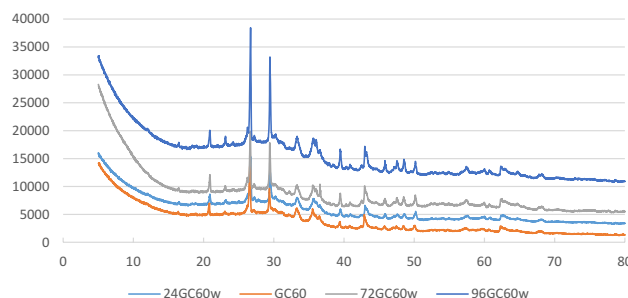
The major phases of oxides in the fly ash were quartz (SiO<sub>2</sub>), mullite (3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>), maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>), rutile (TiO<sub>2</sub>). Minor impurities such as sulfur, phosphorus, boron, and calcium silicate phases are often present in fly ash in low concentrations. Furthermore, cement slurry requires high curing temperature to boost the acceleration rate in geopolymer reaction, whereas high calcium content in fly ash yields the chemical structure of calcium aluminate silicate hydrate (C–A–S–H) gel that undergoes higher acceleration rate in geopolymer reaction as compared to low calcium fly ash and provides a shorter thickening time in cement paste.

### Compressive strength

Table 2 shows the compressive strength development of geopolymer and class G cement before and after exposure into wet supercritical CO<sub>2</sub> at 60 °C and 130 °C. The effect of wet supercritical CO<sub>2</sub> on the compressive strength of geopolymer cement has different profile with particular at 130 °C where

**Table 2** Compressive strength development of geopolymer and class G cement expose into wet supercritical CO<sub>2</sub> at 60 °C and 130 °C

Aging time (h)	Compressive strength (MPa)			
	GC60w	GC130w	PC60w	PC130w
0	50	99	53	42
24	77	77	19	40
72	83	114	49	28
96	82	78	44	23



**Fig. 1** XRD pattern before and after CO<sub>2</sub> exposure

it experienced sudden decrease after 24 h of exposure due to carbonation process accelerated by higher temperature. However, as some of ettringite was formed during exposure, the strength was further increased. For class G cement, the strength was decreased as a function of temperature and aging time. It can be seen that geopolymer cements have a better compressive strength as compared to class G cement for both before and after expose into wet supercritical CO<sub>2</sub>.

### XRD analysis

Figure 1 identifies prominent twin peaks located at 26.5°  $2\theta$  denoted the presence of geopolymer network in all sample. The wet supercritical CO<sub>2</sub> (96GC60w) experiences higher carbonation rate as indicated at peak intensity of calcium carbonate at  $2\theta$  23° and 29.4°. The reason behind this could be the ability of wet supercritical CO<sub>2</sub> to penetrate deep inside the smallest pore of the sample and then attacking calcium fraction of the fly ash.

The presence of quartz and mullite was obtained by observing a peak at 20.8°  $2\theta$  (4.26 Å) and 16.4°  $2\theta$  (5.39 Å), respectively. These wavelengths were chosen because there is no overlap between these peaks and those of any peaks belong to hematite, magnetite or maghemite. Most of these presence peaks in the geopolymer cement indicate that crystalline phases were inactive and act as fillers in the geopolymer synthesis. Inactive means the phases did not react with alkali solution or CO<sub>2</sub>, or not affected by elevated temperature or exposure duration.

The XRD line at  $32.3^\circ 2\theta$  ( $2.77 \text{ \AA}$ ) is indicative of  $\gamma\text{-Fe}_2\text{O}_3$  which magnetic phase of a crystal structure is closely related to that of magnetite. All other lines in the XRD pattern of  $\gamma\text{-Fe}_2\text{O}_3$  overlap with the line of magnetite (Hansen et al. 1981).

### SEM analysis

Figure 2a depicts more crystalline area in the gel phase of the 72GC60w geopolimer. It shows the existence of calcium carbonate crystal as a dominant carbonation product. This finding was in agreement with XRD diffractogram at which  $\text{CaCO}_3$  was produced due to supercritical  $\text{CO}_2$  exposure. From XRD identification, carbonate phases were aragonite and calcite. The crystal shape of carbonate was similar with the previous research of Zhang et al. (2012).

Calcium carbonate crystal appears as the pyramidal white crystalline. More calcium carbonate crystal formed in the samples exposed by wet supercritical  $\text{CO}_2$  seems having less contribution to the strength development as mentioned earlier by Scherer et al. (2011) because it only acts as a filler in concave and pore space of the cement. Corresponding to the phenomena of gismondine produced in Fig. 2b, the small particles reside in the surface of concave change their morphology along with increasing temperature and the presence of brine. The quasi-spherical aggregate particles were formed with the diameter of  $0.5 \mu\text{m}$  at  $135^\circ\text{C}$ . It is believed that the cracks (breakage) shown in Fig. 2b were generated due to the load received by the sample during compressive strength testing.

According to EDX result in Fig. 3, the spotted analysis to the crystal shows three major elements of calcium, carbon and oxygen with percentage of 20.1, 20.4, and 52.6%.

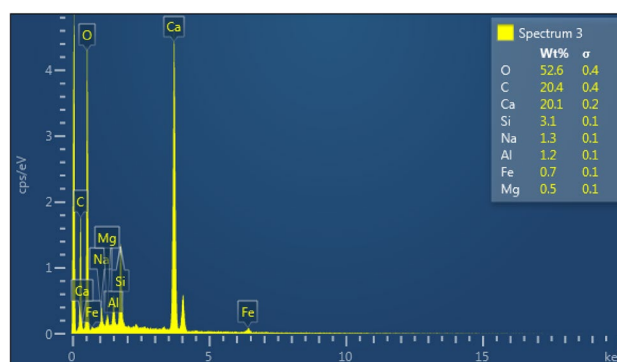


Fig. 3 Modest element identification in the 72GC60w

Carbon weight percentage of GC60 was 10.1% and then increased to 20.4% in 72GC60b, or experienced 100% changes indicating  $\text{CO}_2$  attack on the cement.

### Conclusions

XRD analysis of cement samples exposed to wet supercritical  $\text{CO}_2$  shows geopolimer network of  $\text{Si-O-Al-Si-O}$  and calcium carbonate phase with prominent peaks at  $2\theta$   $26.5^\circ$  and  $29.5^\circ$ . Carbonation occurred in the geopolimer cement due to higher calcium content of Class C fly ash in the presence of  $\text{CO}_2$ . Since the main framework of geopolimer cement was  $\text{Si-O-Al-O-Si}$  so that the formation of carbonate compounds on calcium does not impose the cement to lose its strength. Under elevated temperature and pressure, strength development continues to build up by producing zeolite which is beneficial as a filler in a pore. The

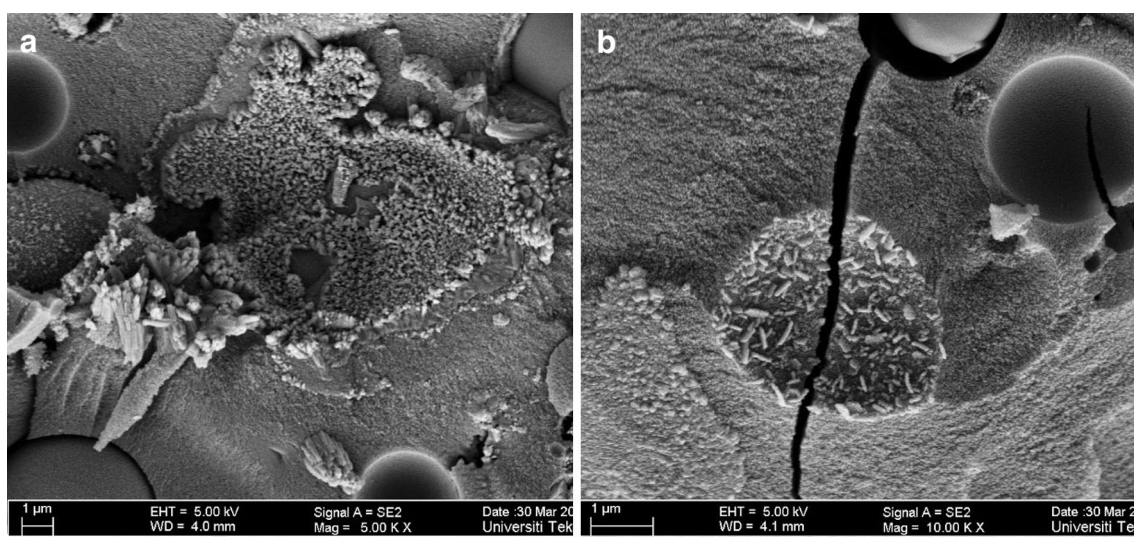


Fig. 2 SEM images after wet supercritical  $\text{CO}_2$  exposure a 72GC60w, b zeolite Na-P1 and  $\text{CaCO}_3$  formed in the surface of concave



peaks with higher intensities and ranges can be integrated smaller adjacent peaks and formed the overlap peak with broader and higher intensity. Fly ash is potentially used as a binder in oil well cement for CO<sub>2</sub> injection wells or wells with naturally rich CO<sub>2</sub>.

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