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ORIGINAL PAPER-EXPLORATION ENGINEERING

Experimental investigation of the effects of temperature on the morphological characteristics of geopolymer binders

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Abstract
Since the beginning of this century, assessment of the environmental impacts and the global warming potential of industrial practices and technologies are on the top agenda. Therefore, many construction materials such as cement systems are being designed for reducing the environmental impacts and greenhouse gas emissions. For that purpose, the petroleum industry is also striving for developing environmentally friendly cementing systems for oil well application; for example, a better alternative to the class-G cement, which is consumed in a tremendous amount worldwide. In finding the greener alternative to class-G cement, geopolymer binders are being researched for possible applications for oil-well cementing jobs. This paper presents the experimental investigation of the effects of temperature on the morphological characteristics of geopolymer binders. For that purpose, sodium silicate and sodium hydroxide were used as the alkaline activator with fly ash as the precursor. Fifteen samples were prepared with a density of 10, 11, 13, 15 and 17 ppg (3 samples for each value of density). The samples were subjected to a temperature of 30, 60, and 90 °C and cured in a water bath for 24 h. Morphological and microstructural characteristics were analyzed using XRD and FESEM. In an overview, increases in temperature significantly impact the geopolymerization process where the microstructure in geopolymer cement produces more reacted particles, which results in excellent mechanical strength. Generally, the strength of geopolymers is associated with the fly ash dissolution FESEM image for 17 ppg mixture cured at 90 °C clearly shows that it underwent extensive geopolymerization with the formation of continuous alumino-silicate gel and almost entirely reacted fly ash particles, resulting in relatively dense geopolymer matrix.

Keywords Fly ash · Geopolymer · Field emission scanning electron microscope (FESEM) analysis · Fourier transform infrared (FTIR) analysis · X-ray diffraction (XRD)

Introduction

Oil well cementing is an essential operation for the completion of a wellbore and ensuring its integrity throughout the service life. The operation is performed using cement slurry, which is traditionally made of Ordinary Portland Cement (OPC) or API class-G cement, water, and performance controlling agents called admixtures, which are added to smoothly place the slurry to several thousand feet below the ground level. Every year, the global oil and gas industry consumes a tremendous amount of cement for cementing operation. The cement industry worldwide is facing extensive criticism because of the consumption of massive quantities of natural resources and greenhouse gas emissions. It is estimated that for every ton of OPC cement mass-produced, nearly one ton of CO_2 is being discharged to the air inducing the greenhouse effect (Natural Resources Canada Climate Change, 2006). In last few years, oil well-cementing experts are working to develop environmentally useful material for replacing the class-G cement that offers the required performance at a minimum level of emission of greenhouse gases (GHG); researchers have identified fly ash, natural pozzolans, rock, blast furnace slag, and rice husk ash as the partial substitution to cement. In other efforts, Devidovits (1989) presented the concept of geopolymer cement, which can be prepared using the precursors containing silica and alumina rich mineral composition with the application of alkali activators containing sodium hydroxide and sodium silicate or potassium hydroxide and potassium silicate.

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According to Mahmoudkhani et al. (2008), the geopolymeric binders reduce the GHG emissions along being a cost-effective substance compared to OPC. With the early development of geopolymer binders, most of the applications focused on the construction industry. Whereas, the oil and gas industry is also focusing on the possible application of geopolymer binders for the oil-well cementing jobs. However, research findings have some limitations also the specified characteristics of materials restricting its applications for well cementing. Therefore, further studies are recommended for developing geopolymer binders that can enhance the integrity of the oil-well system. This assumption was supported by Dam (2010) that stated the geopolymer could either be fully or partially replace OPC depending on the industrial residue.

The principal objective of this paper was to investigate the effects of temperature (30, 60, and 90 °C) on the morphological characteristics of geopolymer cement made of fly ash as the precursor and sodium silicate and sodium hydroxide solution as the alkaline activator. The slurry was prepared for 5 different density values, 10, 11, 13, 15, and 17 ppg. A set of samples composing of each of the five density values was cured in a water bath at 30, 60, and 90 °C. When fly ash is exposed to the alkaline solution, a reaction chain of alumina, silica, and oxygen molecules is formed that is called polymerization or geopolymer. The characteristics of such a molecular bond were studied using Fourier Transformation Infrared Spectroscopy or FTIR, which is an essential morphological test that determines the completion of the polymerization process. Therefore, FTIR analysis facilitates for studying the structural evolution of amorphous aluminosilicates that exhibits high heterogeneity.

Whereas, the microstructure of the samples was studied using FESEM–EDX technique, and due to the amorphous character of geopolymers, XRD analysis was done to identify the newly formed phases, that defines the degree to which the precursor materials have reacted, and the level of amorphic character of the final product is also assessed. All tests were performed according to the procedures described in the American Petroleum Institute API-10B-R2.

Concept and description of geopolymer binders

Geopolymer and geopolymerization

In the year 1978, an alternative binder to cement called geopolymer was introduced to the researchers were working on the development of green cement binders. The concept of geopolymer was first established and patented by Davidovits (1982), which is consisted of polymeric (a chain of molecular reaction) silicon-oxygen-aluminium framework structure. In other words, alkaline liquid that is used to react with alumina (Al) and silica (Si) available in the precursor, which are usually derived from materials of geological origin, for example, fly ash is the byproduct obtained from coal firing in a power stations and slag is the byproduct of steel processing in the blast furnace (Davidovits 1989), both coal and iron ores are of geological origin, and such byproducts are rich in silica and alumina. Mahmoudkhani et al. (2008) and Nasvi et al. (2012) concurred with the concept of Davidovits (1989) that the formation of a geopolymer or in other words, alkali-activated alumino-silicate cementitious material is the result of the reaction of aluminosilicate material with the alkaline solution. In some research on geopolymer binders, rice husk ash is used as a precursor, which is also rich in alumina and silica (Ridha and Yerikania 2014).

Geopolymerization is a process comprising of occurring of a rapid chemical reaction of aluminium–silicate compounds with the alkaline solution, which gives the outcome of a three-D polymeric chain reaction consisting of silicon-oxygen-aluminium (Si–O-Al) framework structure (Srinivasan and Sivakumar 2013). There are three critical steps of geopolymerization that ultimately form geopolymer gel, which is (a) Separation or Dissolution of Silicon (Si) and Aluminium (Al) when aluminosilicate in touch with sodium hydroxide, (b) Transportation or Orientation when the particles move in sequences and (c) Poly-condensation or Chemical Compression of aluminosilicate materials, Davidovits (1989). Figure 1 describes the theoretical model of the geopolymerization process (Palomo et al., 1999, Duxson et al., 2007).

Fly ash

The pulverization of coal in a thermal power plant results in the production of a massive amount of fly ash, which is considered a byproduct. The analytical findings of the union of concerned scientists (2008) estimated that approximately 75% mass of the produced fly ash is disposed-off in the landfills, which causes adverse effects on the ambient environment. By realizing the substantial amount of silica and alumina present in fly ash, the idea of developing geopolymer cement using the fly ash with the alkali activators is considered a value-added solution of the problem (Izquierdo et al. 2009). Similarly, Badur and Chaudhary (2008) also discussed the beneficial effects of fly ash as cement raw material; such as improving the sulfate resistance, workability, and an increase in concrete strength. A partial substation of Portland cement with fly ash can results in a cost-effective solution as compared to the cost incurred for disposing-off into the landfill deposits. Therefore, the usage of fly ash as a partial substitution of cement in the cementitious composite can appreciably reduce the greenhouse emission effects as caused by massive consumption

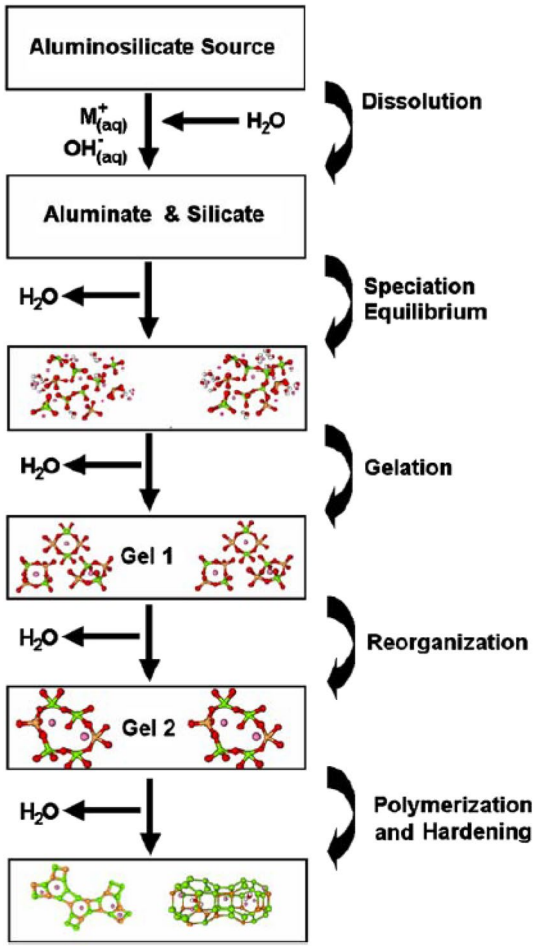

Fig. 1 Conceptual model for geopolymerization [Duxson et al. 2007]

of Portland cement (Malhotra and Mehta 2008). Since global oil and gas industry consumes a handsome amount of Portland class-G cement for well construction and maintenance, therefore, the application of geopolymer binder for well construction can further reduce the negative impacts to the environment (Malhotra and Mehta 2008, and Barsoum et al. 2006). ASTM C-618 classified fly ash into two classes; i.e. class-F and class-C. In many sample tests, the chemical analysis of class-F fly-ash showed that the total amount of SiO_2, Al_2O_3 and Fe_2O_3 being higher than 70% and the CaO is less than 10%.

Methodology

Experimental procedure

The first part of the experiment is to test the slurry density and obtain five different compositions with a density range of 10 ppg to 17 ppg of geopolymer cement by mixing with alkaline activator solution. Alkaline activator is a concoction of sodium hydroxide and sodium silicate and needs to be prepared just before the experiment. Research done by (Xu et al. 2000) concluded that by adding sodium silicate, the geopolymerization process is enhanced. In total, there will be twelve samples where twelve prepared with fly ash, alkaline activator, additives, lightweight material, and weighting material. The second part of the experiment will be the curing process of the cement slurry under different temperatures, namely 30 °C, 60 °C, and 90 °C, and cured for 24 h as per industry standard. The last part is to analyze the effect of temperature on the morphology of all geopolymer samples by carrying out FESEM, XRD, and FTIR tests.

Table 1 shows the composition (fly ash and alkaline) of five different mixes used in this investigation. The mixes are designated with the density value achieved, e.g. GP10 means geopolymer mix holding a density value of 10 ppg. All five groups were cured at three different temperature regimes; 30, 60, and 90 °C. The curing temperature influenced the rheological properties and the compressive strength of all mixes. In the case of oil-well cementing operation; controlling two rheological properties is essential, which are fluid loss and the thickening time. It can be seen that for low density mixes at 10 and 11 ppg, the maximum fluid loss was observed at 60 °C curing. Whereas, high-density mixes showed highest fluid loss at 30 °C curing. Similarly, curing at 30 °C delayed the thickening of the paste, in this curing regime the maximum thickening time was obtained as 22 h for 17 ppg samples. Whereas, low-density sample showed a thickening time of 5 h 16 min, which is an acceptable value. When investigating the compressive strength of the hardened pastes; high-density pastes cured at 30 °C showed the highest compressive strength value. The samples hold a density of 17 ppg and cured at 30 °C showed a compressive strength value of 4159 psi, and GP10 samples showed a compressive strength of 2278 psi.

Field emission scanning electron microscopy (FESEM)

Field Emission Scanning Electron Microscopy (FESEM) was performed using FESEM Zeiss Supra 55 VP available in the central analytical laboratory at University Teknologi PETRONAS, Malaysia, Perak (UTP) for investigating the microstructural characteristics of geopolymer cement when subjected to different temperature regimes. Geopolymer samples were crushed into particles of approximately 1 mm to 3 mm and were mounted on the test plate in the machine. As geopolymers are naturally non- conductive samples, before testing, they were coated using a gold sputter coater to ensure that there was no image uncertainty during the micrograph testing collection. Basically, the test was conducted using secondary and backscattered electron detectors.

Table 1 Details of mix composition and physical and mechanical properties

Mix	Fly Ash Content (ml)	Alkaline Water (ml)	Density (ppg)	Temperature (°C)	Fluid Loss (ml)	Thickening Time (hrs, mins)	Compressive Strength (psi)
GP10	300	300	10	30	48	5, 16	2278
				60	208	2, 30	211
				90	86	4, 24	1129
GP11	400	300	11	30	118	6, 0	2834
				60	278	5, 16	688
				90	64	2, 9	515
GP13	400	600	13	30	322	11, 14	1019
				60	53	6, 50	380
				90	85	5, 1	896
GP15	600	300	15	30	208	19, 25	3573
				60	186	8, 3	695
				90	145	3, 9	2287
GP17	600	300	17	30	240	22, 0	4159
				60	192	5, 8	1241
				90	154	6, 11	2708

FESEM analysis was done at the accelerating voltage of 20 kV and with a magnification factor up to × 25,000.

X-ray diffraction (XRD) test

Bench Top X-ray Diffractometer (XRD) was performed using XRD Bruker D2 Phaser in University Teknologi PETRONAS Malaysia Perak (UTP) to detect new-formed phases, define the extent to which materials have started to be reacted and assess the level of amorphic of the final products. The X-ray diffractometer using CuKα radiation was used, and samples went through testing in the range of 2θ, ranging from 5° to 90° and in steps of 0.035/s. The purpose of conducting XRD for paste samples was to examine the morphological characteristics, which usually control the fresh and hardened state behaviour of the system. Amorphous morphology indicates that the samples will show the highest performance in the fresh and hardened state. Whereas, occurrence crystals indicate the weak performance of the system.

Fourier transform infrared spectroscopy test (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was performed using FTIR Perkin Elmer in University Teknologi PETRONAS Malaysia Perak (UTP) to study the organic materials by delivering data on chemical bonds and molecular structure. Analysis of geopolymers focuses on the structural development of amorphous aluminosilicates that generally possess high heterogeneity and emphasis on significant reaction zones of Si–O and AL-O of cement paste.

Results and discussion

FESEM analysis

Figure 1 shows the image of the original fly ash consists of cenospheres, magnetic spheres, and quartz. Ceno representing a Greek word means empty. Cenospheres generally forms a large ratio of the lightweight elements due to their hollow characteristic, as stated by Blissett and Rowson (2012). Magnetic spheres are the solid spheres containing

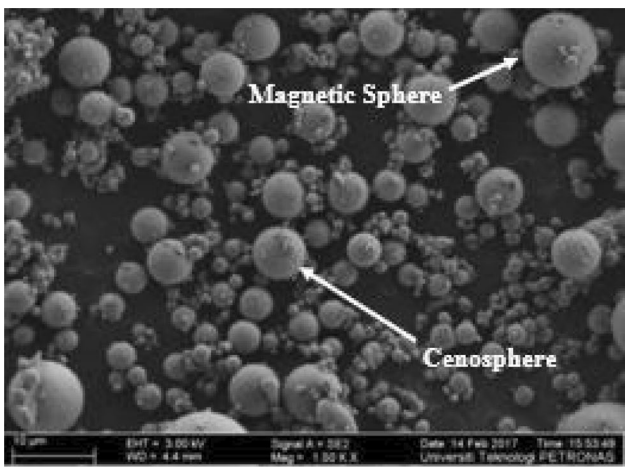

Fig. 2 300 × Magnification of the sample tested at 40 °C

the iron crystals covered by amorphous alumina and silica that actively participate in the geopolymerization process. A common difference between cenospheres and magnetic spheres is that the surface of cenosphere is smooth while the magnetic sphere has a somewhat rough surface (Fig. 2).

Figure 3a–c shows the microstructure of 11 ppg, 13 ppg, and 17 ppg cured at 30 °C. In general, the compactness of microstructure is enhanced by the formation of a higher amount of alumino-silicate gel. The samples cured at 30 °C clearly show there is a less amorphous gel, and partially reacted fly ash spheres are seen to be lesser. Large particles of fly ash still did not completely. Figure 4a and b shows the microstructure of 15 ppg and 17 ppg cured at 60 °C. This samples at 60 °C clearly shows that a better reaction has taken place compared to samples at 30 °C. Morphological changes were observed due to the dissolution of SiO2

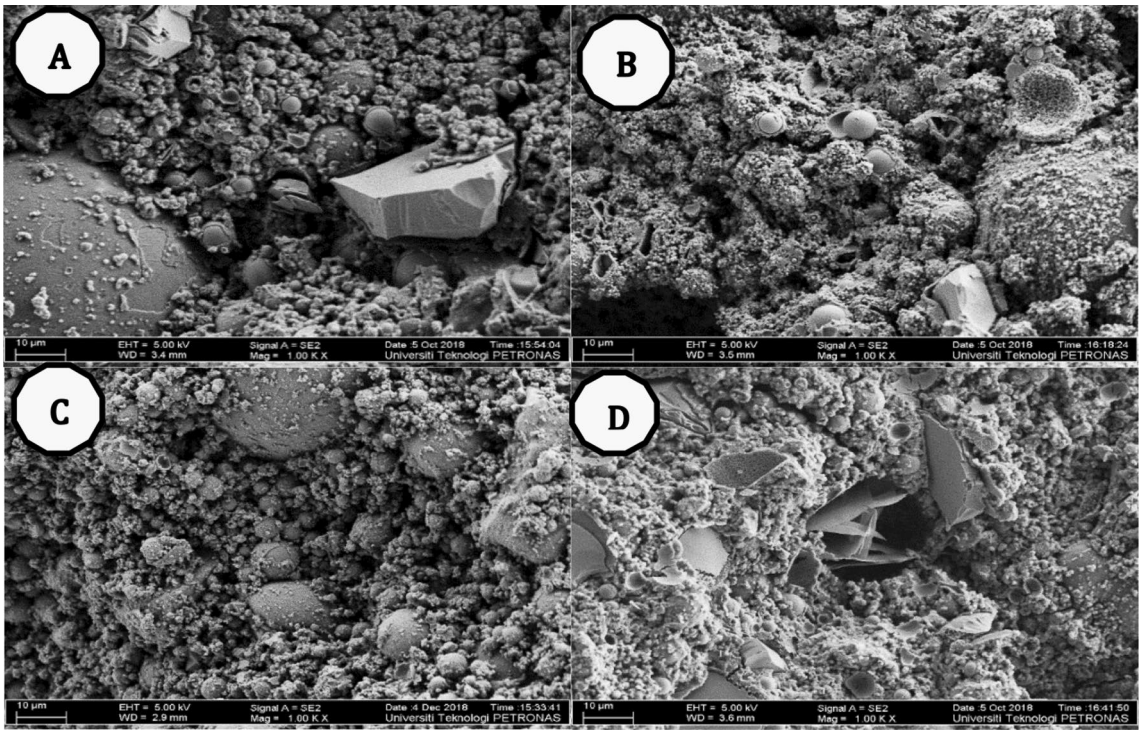

Fig. 3 100×Magnification of FESEM of geopolymer samples of **a** 11ppg, **b** 13ppg, **c** 15ppg and **d** 17ppg at 30 °C

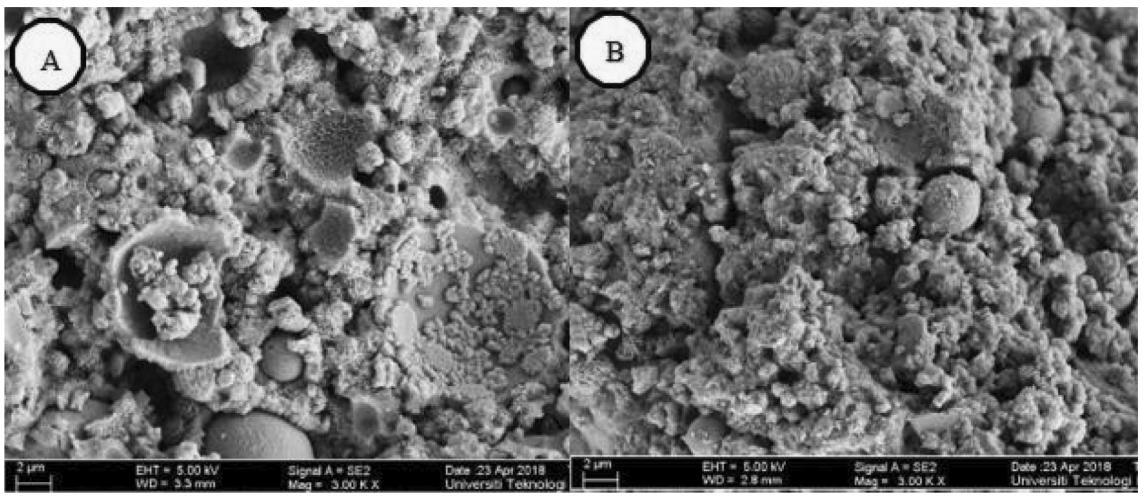

Fig. 4 FESEM of geopolymer samples of **a** 15ppg, **b** 17ppg at 60°

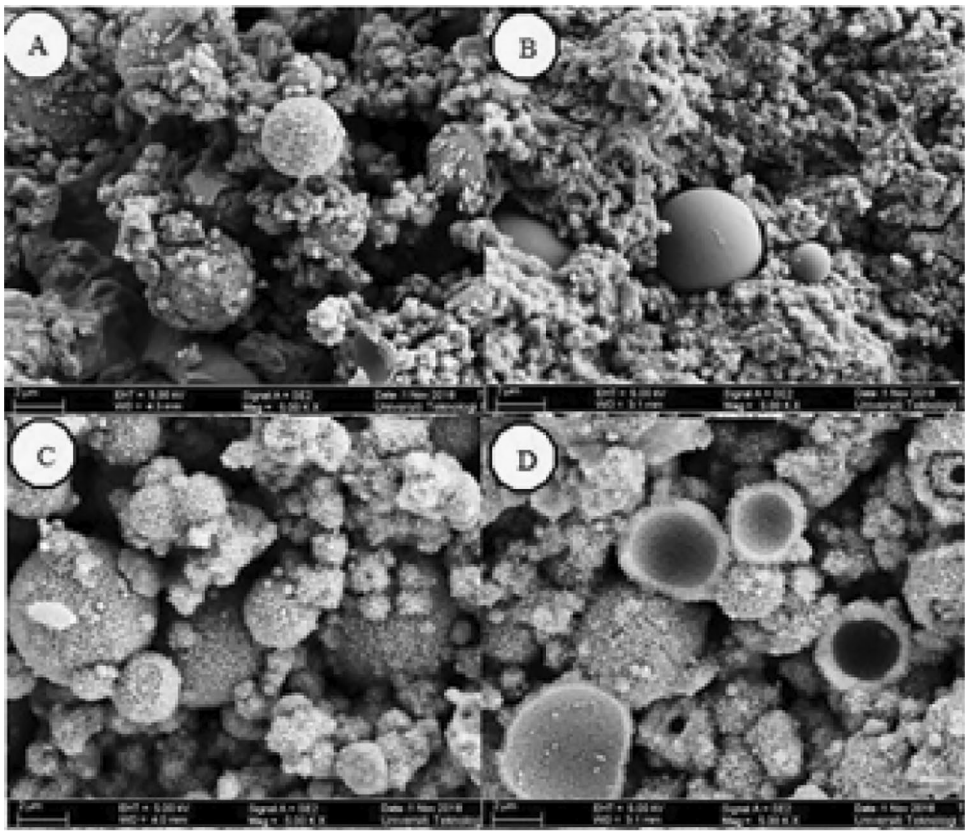

Fig. 5 FESEM micrographs of the samples cured at 90 °C, and possessed different density **a** 11ppg, **b** 13ppg, **c** 15ppg, **d** 17ppg

and Al2O3 that leads to the creation of aluminosilicate gel as mentioned by Murayama et al. (2002), which then turns as a precursor to geopolymer development. Figure 5a–d shows the microstructure of 11 ppg, 13 ppg, 15 ppg, and 17 ppg cured at 90 °C. Samples of 90 °C indicate that the geopolymerization of fly ash was extensive and full mode as a compact structure can be seen, although unreacted spherical fly ash particles were visibly present. Highlights of this test on 17 ppg cured at 90 °C, there was a surface continuity resembling a gel type of the reaction products, implying the high mechanical characteristics (Fernández-Jiménez et al. 2005).

X-ray diffraction (XRD) test

Class F fly ash X-ray spectra are shown in Fig. 6. Peaks at 21° and 27°θ represent quartz (SiO2), and peaks at 34° and 43° 2θ represent mullite (3 Al_2O_3.2 SiO_2) while the peak

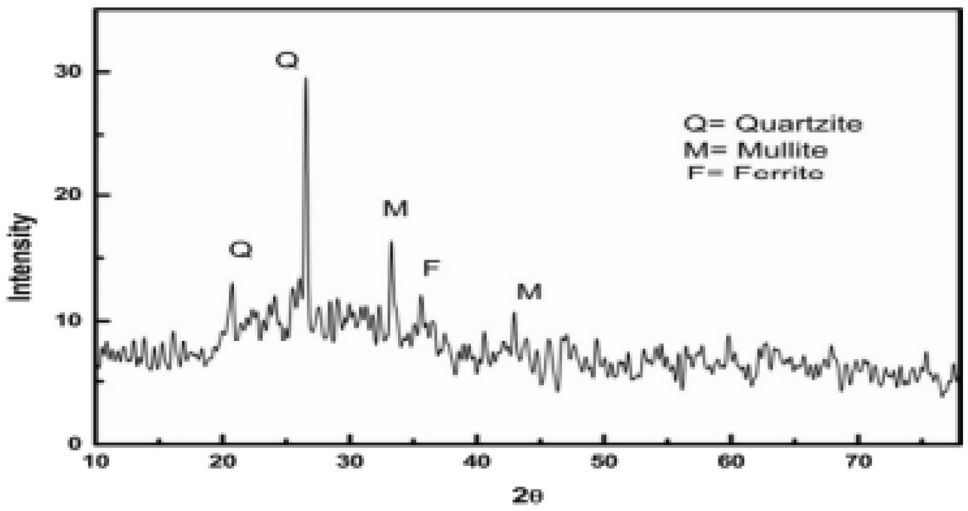

Fig. 6 XRD analysis of fly ash (Siyal et al. 2016)

at 36° 2θ is for ferrite (Fe_2O_3). The XRD pattern generally reveals peaks at various intensities, usually crystalline zones such as hematite, quartz, mullite, and a few types of zeolites that are formed due to the reaction between fly ash and the alkaline activator.

XRD diffractograms for fly ash-based geopolymers of 15 ppg and 17 ppg cured at three different temperatures presented in Figs. 7 and 8. From the XRD results for both densities, it is seen clearly that peaks of mullite ($3Al_2O_3.2\ SiO_2$) and quartz (SiO_2) remains the same as compared to XRD pattern of fly ash in Fig. 6. The vast and diffusive reflective from the interval of 25° to 35° 2θ confirms the presence of alumina- silicates with an amorphous structure. In 17ppg samples, zeolite type crystalline compounds are formed from the slightest dissolution of crystalline compounds forming the amorphous phase. Dissolution of amorphous compounds are more natural compared to crystalline compounds, and this concludes that higher content of amorphous compound leads to higher amounts of reactive SiO_2 and Al_2O_3 to blend during the geopolymeric reaction. Therefore, resulting in a higher degree of geopolymerization and, consequently, higher mechanical strength. Van Jaarsveld et al. (2003) also stated that the degree of crystallinity or the amorphous nature in a geopolymer affects the compressive strength.

Conclusion

Geopolymerization process is greatly affected by constraints like alkali activator ratio, curing time, the effect of mechanical activation, silica ratio, and effect of mixing time that was studied in the past researches. This research focuses on temperature that plays a significant role as a reaction accelerator.

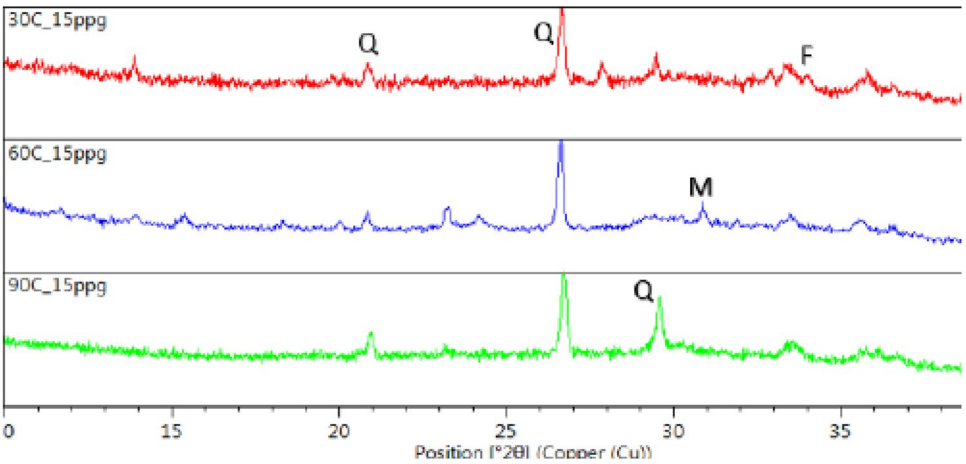

Fig. 7 XRD pattern of 15ppg geopolymer cured for 24 h at 30, 60 and 90 °C

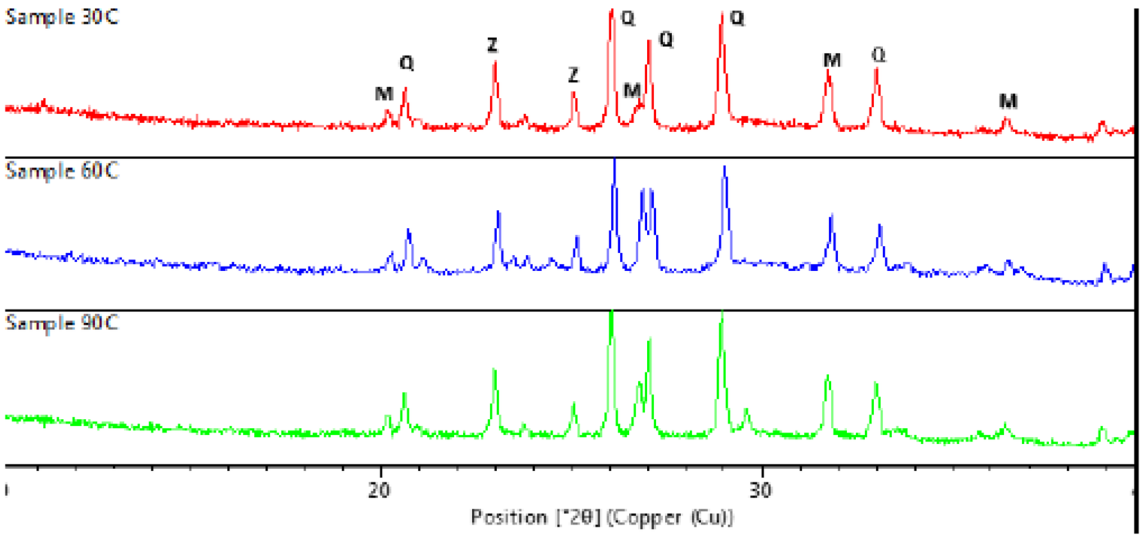

Fig. 8 XRD pattern of 17ppg geopolymer cured for 24 h at 30°, 60°, and 90 °C

In an overview, increases in temperature significantly impact the geopolymerization process where the microstructure in geopolymer cement produces more reacted particles, which results in excellent mechanical strength. This is achievable when all the other factors are kept constant.

In this research, the characterization of geopolymer obtained by four different composition alkali activation of fly ash (class F) have been investigated, with three varying curing temperatures. The techniques of FESEM and XRD give invaluable support and complement each other, and consecutively, these results can be linked to the physical and chemical properties of a geopolymer.

Generally, the strength of geopolymers is associated with the fly ash dissolution FESEM image for 17 ppg mixture cured at 90 °C clearly shows that it underwent extensive geopolymerization with the formation of continuous aluminosilicate gel and almost entirely reacted fly ash particles, resulting in relatively dense geopolymer matrix.

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