THESIS APPROVAL

GRADUATE SCHOOL, KASETSART UNIVERSITY

Master of Engineering (Civil Engineering)
DEGREE

Civil Engineering
FIELD

Civil Engineering
DEPARTMENT

TITLE: The Role of Sodium Hydroxide Concentration in Fly ash-Based Geopolymer

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THESIS

THE ROLE OF SODIUM HYDROXIDE CONCENTRATION IN FLY ASH-BASED GEOPOLYMER

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A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Engineering (Civil Engineering)
Graduate School, Kasetsart University
2009

Yudthana Leelathawornsuk 2009: The Role of Sodium Hydroxide Concentration in Fly ash-Based Geopolymer. Master of Engineering (Civil Engineering), Major Field: Civil Engineering, Department of Civil Engineering. Thesis Advisor: Associate Professor: Prasert Suwanvitaya, Ph.D. 88 pages.

The purpose of this study is to determine the effect of concentration of sodium hydroxide solution on fly ash-based geopolymer. This experiment, class C and class F fly ash in accordance with ASTM C618 were used. The fly ash samples were suspended in 4M sodium hydroxide solution. The dissolution samples with different proportions were analyzed with inductively coupled plasma emission spectrometer to determine the amount of silica, alumina and calcium dissolutions. Compressive strength and setting time of geopolymer were also tested. The compressive tests were conducted after aging the specimen at 1, 3, 7, 14 and 28 days. The mineralogical composition and microstructural of the geopolymer were determine by using X-ray diffraction and Scanning electron microscopy.

From the experiment results, the solubility of fly ash depending on the proportions and properties of fly ash. Class F fly ash containing higher amount of silica and alumina than class C fly ash but calcium ion was more dissolved from class C fly ash than class F fly ash. After the sodium silicate was added in the dissolution liquid, it had no formation because of the precipitation of fly ash was helpfully for the formation of geopolymer. Class C fly ash-based geopolymer produced higher compressive strength than class F fly ash-based geopolymer. High compressive strength was obtained with the use of 60% fly ash and 40% solution by weight. Scanning electron microscopy (SEM) of the geopolymer indicated that high percentage of fly ash produced low porosity and high density of geopolymer.

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ACKNOWLEDGEMENTS

The author wishes to express his profound gratitude and sincerest appreciation to his advisor Assoc.Prof.Dr. Prasert Suwanvitaya for his advice at all stages of work, strong support, and continuous encouragement throughout this research. His deepest and sincere gratitude is sincerely extended to Assoc.Prof.Dr. Trakool Aramraks and Dr. Barames Vardanabhuthi for useful suggestions and tremendous help in the aspect of the research. The acknowledgements are also extended to Assoc.Prof. Patcharaporn Suwanvitaya of faculty of Environmental Engineering, Kasetsart University for invaluable suggestions, support with the experimental facilities and help during his experimental work.

A special thanks is given to Parames Kamhangrittirong lecturer of Faculty of Architecture, Kasetsart University for sharing ideas, suggestions and the donation of fly ash materials.

The author wishes to express his great appreciation to the International Graduate Program of Civil Engineering for the opportunity to study. The author also wishes to express his thanks to Kasetsart University for the great opportunity over the years.

Finally, the author is deeply grateful to his parents for their encouragement throughout the course of his study. No acknowledgement can ever do justice to their continuous support. The author would like to dedicate this thesis to them.

Yudthana Leelathawornsuk
May 2009

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LIST OF ABBREVIATIONS

Al = Aluminium
ASTM = American Standard Testing Method
Ca = Calcium
FA = Fly ash
ICP-OES = Inductive Coupled Plasma Optical Emission Spectrometer
ksc = Kilogram per square centimeter
NaOH = Sodium hydroxide
SEM = American Standard Testing Method
Si = Silicon
Sol = Solution
XRD = X-ray Diffractometer
XRF = X-Ray Fluorescence

THE ROLE OF SODIUM HYDROXIDE CONCENTRATION IN FLY ASH – BASED GEOPOLYMER

INTRODUCTION

Geopolymer are a relatively new group of materials, which were developed by Joseph Davidovits in St. Quentin, France, in the 1970s. Fly ash based geopolymers are one branch in the Geopolymer family and these have attracted more attention since the 1990s. As a novel binder, the performance of fly ash based geopolymer is promising, especially in some aggressive situations where Portland cement concretes are vulnerable.

Polymerization process of fly ash – based geopolymer involves a chemical reaction of alumino-silicate oxides (Si_2O_5, Al_2O_2) with alkali polysilicates and yields polymeric Si – O – Al bonds. Polysilicates are generally sodium or potassium silicate supplied by chemical industry or manufactured fine silica powder as a by-product of ferro-silicon metal industry. Unlike ordinary Portland pozzolanic cements, geopolymers do not form calcium-silicate-hydrates (CSHs) for matrix formation and strength, but utilize polycondensation of silica and alumina precursors and a high alkali content to attain structural strength. Therefore, geopolymers are sometimes referred to as alkali activated alumino silicate binders. Chemical composition of geopolymers material is similar to natural zeolites materials, but its microstructure is amorphous.

Two main constituents of geopolymers are source materials and alkaline liquids. Source materials for geopolymers based on alumino-silicate should be rich in silicon (Si) and aluminium (Al). These could be natural minerals such as kaolinite, clays, micas, andalousite, spinel whose empirical formula contains Si, Al, and oxygen. Alternatively, by product materials such as fly ash, silica fume, slag, rice-husk ash, red mud could be used as source materials. The choice of source materials for making geopolymers depends on factor such as availability, cost, and type of application and specific demand of end users. Alkaline liquids are from soluble alkali metals that are usually sodium or potassium based. The most common alkaline liquids used in geopolymerisation are combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate.

Particle size, calcium content, alkali metal content, amorphous content, morphology and origin of fly ash affected the properties of geopolymers. Calcium content in fly ash plays a significant role in strength development. Its content in fly ash in significant quantities could interfere with polymerization setting rate and alters the microstructure. Therefore, it appears that the use of low calcium (ASTM Class F) fly ash is preferable to high calcium (ASTM Class C) fly ash as a source material to make geopolymer.

Due to heat being a reaction accelerator, curing of fresh geopolymer is performed mostly at an elevated temperature. When curing at elevated temperatures, loss of water should be taken care of. However, curing at room temperature has successfully been carried out by using calcined source material of pure geological origin.

OBJECTIVES

The main purpose of this study is to investigate, through experimental testing, the effect of proportion of sodium hydroxide on fly ash in geopolymer. This research study includes the following objectives:

1. To determine the proportion of sodium hydroxide, which effect the dissolution of silica, alumina, and calcium ions from fly ash.

2. To determine the factors affecting geopolymer formation.

3. To determine the geopolymer properties namely compressive strength and setting time in various proportional.

4. To determine the microstructure of geopolymer having difference proportions of NaOH.

Scope of Study

The study consist of laboratory tests on fly ash based – geopolymer mixed with fly ash type C and type F;

1. Dissolution ions : mainly to determine the silica alumina and calcium ions dissolution by sodium hydroxide from various proportional and difference class of fly ash.

2. Compressive strength test : mainly to determine the strength gain with time, using sodium hydroxide, sodium silicate and fly ash with various proportional and difference class of fly ash.

3. X-Ray diffraction and Scanning electron microscopy (SEM) analysis was performed on the fly ash-based geopolymer.

4. Fly ash used in this study are class C and class F fly ash.

LITERATURE REVIEW

1. Synthesis of Geopolymers

Before discussing the terminology, reaction mechanism and structure formation of geopolymers, it is necessary to briefly discuss the formation of zeolites as they follow very much the same route. This view is supported by Davidovits (1982, 1994, 1988, 1999) who stated that aluminosilicate geopolymers have a three dimension structure and belong to the category of zeolites and feldspathoids.

Zeolites are based on a crystalline aluminosilicate framework and are three dimensional network inorganic polymers built up of $(Si,Al)O_4$ tetrahedra linked by sharing oxygen atoms into ring and cages. The stoichiometry of zeolites can be represented by the general formula (Bell 1999):

$$M^{n+}\ [(AlO_2)(SiO_2)_x]\ .zH_2O \tag{1}$$

Where x represents the atomic ratio of Si:Al. The extra lattice cation M^{n+} such as H^+, Na^+, K^+, Cu^+ and $[Fe(OH)_2]^+$ is required for charge compensation. Zeolites are found naturally but can also be synthesized hydrothermally from a caustic mixture of sodium silicate, aluminium hydroxide and an organic templating agent. The framework of zeolites is formed by corner sharing of SiO_4 and AlO_4 tetrahedra. Figure 1 shows the structure of faujasite which is a representative of zeolite X (Si:Al = 1) and zeolite Y (Si : Al = 2.5) in which Si or Al atom is located at the vertices and O atoms are located on the line segments joining the vertices.

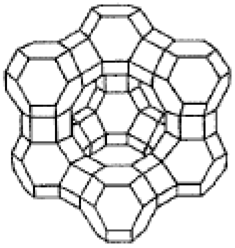


Figure 1 The crystal structure of faujasite, where Si or Al are at the corner of framework and these are linked by oxygen bridges represented by the lines.

Zeolite synthesis depends on the use of highly reactive starting materials, a relatively high pH, a high degree of saturation resulting in large numbers of nuclei, and a relatively low temperature. Zeolites are most commonly synthesised by sol-gel techniques. In a typical procedure, a soluble source of Al is dissolved in a highly alkaline solution of sodium silicate resulting in an amorphous aluminosilicate gel. Crystallisation is normally carried out in the temperature range of 100 – 180 °C for a few hours to a few days. During this period the amorphous gel undergoes continual dissolution and reconstruction, and the crystalline zeolite phase grows (Ray, 1978; Bell, 1999).

The silica content in zeolites is an important parameter that determines the acidity, density and the thermal resilience of zeolites. Aluminosilicate clays have been utilized to obtain high-silica zeolites. Synthesis of zeolite for example is obtained from hydrothermal treatment of kaolinite (metakaolinite) in a caustic solution at 100°C (Hos, 2000).

2. Geopolymer

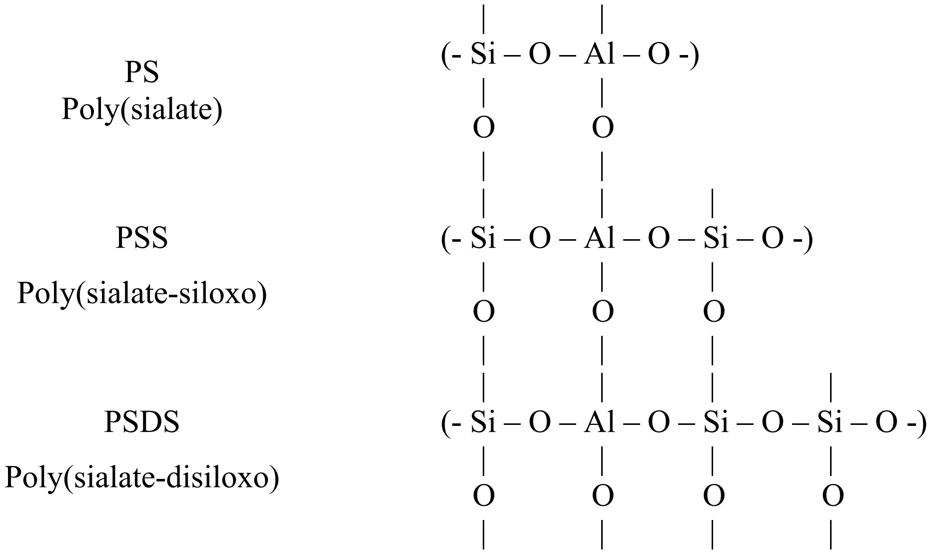
As early as the 1980s, Davidovits developed amorphous to semi-crystalline aluminosilicate inorganic polymers, now known as geopolymers (mineral polymers resulting from geochemistry). The geological interest of aluminosilicate is particularly based on their natural abundance in Si-Al minerals such as kaolinite ($Al_2Si_2O_5(OH)_4$).

Geopolymerisation involves a chemical reaction between various aluminosilicate oxides (Al^{3+} in IV-fold coordination) with silicates under highly alkaline conditions, yielding polymeric –Si-O-Al-O- bonds (Davidovits, 1982; Davidovits, 1991; Davidovits, 1994a; Rahier, 1996; van Jaarsveld, van Deventer & Lorenzen, 1997; Xu & van Deventer, 2000).

The family of geopolymers based on aluminosilicate is called poly(sialates) comprising an amorphous network of AlO_4 and SiO_4 tetrahedara linked alternately by sharing all the oxygens. Sialate is an abbreviation for silicon-oxo-alumminate (-Si-O-Al-O-). The presence of positive ions, such as Na^+, K^+, Li^+ and Ca^{++}, in the framework is necessary to balance the negative charge of Al^{3+} in IV-fold coordination with oxygen. This polymeric model is similar to the formation processes of zeolites and zeolite precursors. The empirical formular of poly(sialates) is shown in equation 2 (Davidovits, 1991):

$$M_n\,[-(SiO_2)_z-AlO_2]_n\,.wH_2O \qquad (2)$$

Where M_n is a cation (the alkaline element), *n* is a degree of polycondensation, w<3 and z is 1, 2 or 3. According to Davidovits (1991) geopolymers are comprised of several fundamental poly(sialates) units as shown in Figure 2.



PS
Poly(sialate)

$$\begin{array}{lccccc} & | & & | & \\ (- & \mathrm{Si} & -\mathrm{O}- & \mathrm{Al} & -\mathrm{O}\,-) \\ & | & & | & \\ & \mathrm{O} & & \mathrm{O} & \\ & | & & | & \end{array}$$

PSS
Poly(sialate-siloxo)

$$\begin{array}{lccccccc} & | & & | & & | & \\ (- & \mathrm{Si} & -\mathrm{O}- & \mathrm{Al} & -\mathrm{O}- & \mathrm{Si} & -\mathrm{O}\,-) \\ & | & & | & & | & \\ & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & \\ & | & & | & & | & \end{array}$$

PSDS
Poly(sialate-disiloxo)

$$\begin{array}{lccccccccc} & | & & | & & | & & | & \\ (- & \mathrm{Si} & -\mathrm{O}- & \mathrm{Al} & -\mathrm{O}- & \mathrm{Si} & -\mathrm{O}- & \mathrm{Si} & -\mathrm{O}\,-) \\ & | & & | & & | & & | & \\ & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & \\ & | & & | & & | & & | & \end{array}$$

Figure 2 Geopolymeric molecular networks.

2.1 Geopolymer cement

Alkali-activated, chemically bonded cement is considered as a special type of cement. Numerous sources of alumina and silica are potentially available to produce this cement. The production of this cement is often based on the utilization of solid wastes and by products such as fly ash and blast furnace slag that may have pozzolanic or latent hydraulic properties. The hydraulic properties of these materials are influenced by their chemical composition, specific surface area and by the type of activation used. Extensive use has been made of glassy slag in the former Soviet Union and Finland. Blast furnace slag is usually granulated and ground to a surface area of 5000 cm^2 g^{-1}, but the mix water is replaced by an equivalent volume of 10 – 30 % NaOH of KOH solution. Other activators such as gypsum ($CaSO_4.2H_2O$) and its soluble anhydrate ($CaSO_4$) can also be used (Glasser, 1995).

It has been mentioned that during the 1980s. Davidovits intensively studied the production of alkali-activated cement by using dexydroxylated kaolinite. The resulting cement which is now known as geopolymer cement or (K-Ca)poly(sialate-siloxo) cement was claimed to have unique properties such as high early strength, low shrinkage, freeze-thaw resistance and acid resistance. The most significant impact of geopolymer cements is its potential to contribute to environmental protection.

A(K-Ca)Poly(silate-siloxo) ((K-CA)-PSS cement, Si:Al = 2) comprises three major compounds, namely :

- Specific aluminosilicate of kaolinite clay species, calcined at 750°C
- Alkali-disilicates (Na_2 or K_2) $(H_2SiO_4)_2$
- Calcium disilicates $Ca(H_3SiO_4)_2$

$$2(Si_2O_5,Al_2O_2)+K_2(H_2SiO_4)_2+Ca(H_2SiO_4)_2 \rightarrow (K_2O,CaO)(8SiO_2,2Al_2O_3,nH_2O) \quad (3)$$

Unlike ordinary Portland cement, geopolymeric cements do not rely on lime and are not dissolved by acidic solutions. Setting of geopolymeric cement takes place through polycondensation of potassium-oligo-(sialate-siloxo) into potassium poly(sialate-siloxo) crosslinked network as shown in Figure 3 (Davidovits 1999).

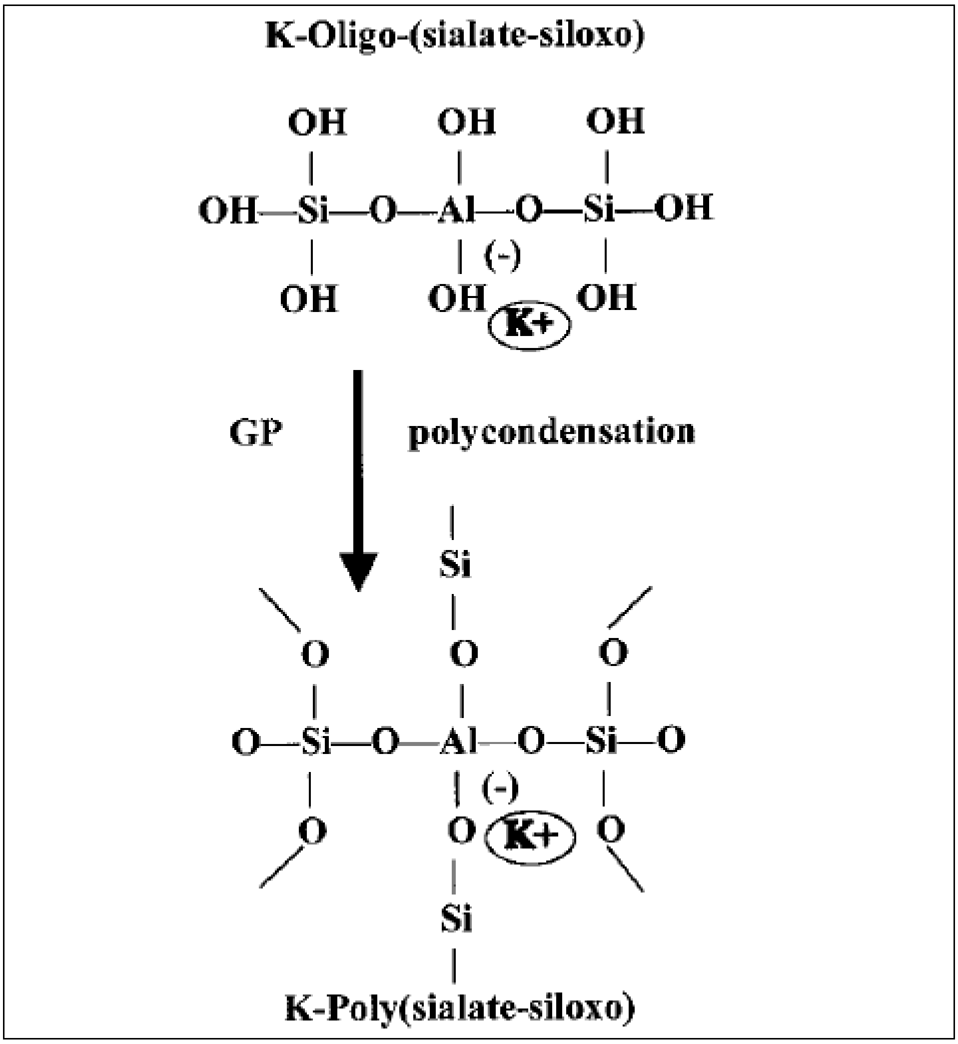


Figure 3 The setting process of potassium poly(sialate-siloxo) geopolymeric cement.
Source: Davidovits (1999)

Structural integrity and reasonable strength of the resulting material are attained in a very short time. In most cases, 20% to 30% of the final compressive strength is developed in the first few hours of setting. The high early strength of geopolymer cement designed particularly for waste containment can be enhanced with the adjunction of microwave preheating devices in order to raise the temperature of the waste up 30-35°C (Davidovits, 1994a).

The ability to absorb toxic chemical wastes such as arsenic, mercury and lead makes geopolymer cement comparable to zeolites. Geopolymer cements immobilize hazardous elemental wastes within the matrix as well as act as binder to convert semi-solid waste into an adhesive solid. The ability of geopolymer cements to provide immobilization systems for toxic wastes is due largely because of their properties such as acid resistance as well as their low permeability (Table 1)(Davidovits, 1994a).

Table 1 Permeability values (cm/s)

Type	Permeability values (cm/s)
Sand	$10^{-1} – 10^{-3}$
Fly ash cement	10^{-6}
Clay	10^{-7}
Geopolymer cement	10^{-7}
Portland cement	10^{-10}
Granite	10^{-10}

Source: Davidovits (1994a)

The technology of geopolymerisation has been applied to produce some cement related products that can be bought commercially (Davidovits 1991, Davidovits 1994a). Despite their superior properties over Portland cement, geopolymer binders have not been widely used mainly because of higher costs. If the cost of production can be reduced, geopolymer cements will eventually meet their applications in many areas such as:

- Massive concrete panels, grouts, and fiber reinforced sheets.
- Building component such as bricks and ceramics tiles.
- Structural surfaces such as floor and storage areas as well as runways.

2.2 The strength of geopolymers

Physical as well as mechanical properties of geopolymers can be tailored by the alteration of the atomic ratio of Si:Al precursors. Geopolymers with low Si:Al (1, 2, 3) initiate a 3D-network that is very rigid which make them suitable for bricks, cements, toxic immobilization and fire protection, while those with Si:Al > 20 provide polymeric character to the geopolymer materials and are suitable for fire or heat resistant composites for aerospace or automobile industries (Davidovits, 1999; Lyon et al., 1997; Xu & van Deventer, 2000; Hermann et al., 1999; Cheng & Chiu, 2003).

Rahier et al. (1996) studies the compressive strength of aluminosilicate inorganic polymers containing sand (quartz) as a filler material with a mean particle size of 240 μm for samples with dimension of 20x30x40 mm. The addition of sand was intended to reduce crack formations as well as to control the porosity. They reported that the compressive strength of their polymer is strongly dependent on the molar ratio of Sil/Mk = k, defined as the stoichiometric ratio of sodium in the silicate solution to aluminium in aluminosilicate materials. The optimum compressive strength is obtained at k = 1, suggesting that this strength was associated with the complete reaction of the aluminium from fly ash with the sodium from the silicate solution.

Rahier's observations, however, are in disagreement with the data reported by Hos, McCormick & Byrne (2002). They reported that the compressive strength of their inorganic polymer synthesised from melt-quenching aluminosilicate ($Al_2O_3.2SiO_2$) pellet increased with decreasing k and achieving maximum strength at k = 0.36. In addition, the maximum compressive strength of their materials was about 360 MPa or 6 times higher than that reported by Rahier et al. (1996). This discrepancy probably originated from the difference of the starting material, as well as the preparation route they used.

One major problem still confronting the strength of geopolymers synthesised from aluminosilicate minerals such as metakaolinite or fly ash is porosity due to air bubbles caused by the evaporation of water during polymerization. It is well known that porosity decreases the strength of ceramics and cementitious materials (Rahier et al., 1996; Zhang & Malhotra, 1998).

Jiang & Guan (1999) studied the effect of pore structure on the strength of high volume fly ash paste. They reported that the relationship between the total porosity and compressive as well as flexural strength is linear. Pores with radii > 100 μm show a great effect on the reduction of the compressive strength. They also reported that the total porosity of the paste increased with increasing fly ash content and water/binder ratio.

The processing and characterisation of geopolymer materials made by using class F FA and formed at elevated temperature were discussed. Long precuring at room temperature before application of heat was beneficial for strength development in all studied materials, as strength comparable to 1 month of curing at elevated temperature can develop in this case only after 24 hours of heat curing. An amorphous alkali aluminosilicate gel was the main product of the reaction in the geopolymeric materials. However, in the case of sodium hydroxide activator in addition to it, (gismondine) zeolites and hydroxysodalite were also present. The type of zeolite present and composition of aluminosilicate gel were based on the curing history. By T.Bakharev.

Palomo et al. have shown that the curing temperature, the curing time, and the type of activator affected the compressive strength, while the solution-to-fly ash ratio was not a relevant parameter. Increase in the curing temperature, increased the compressive strength. It was also found that the type of alkaline activator that contained soluble silicates resulted in a higher reaction rate than when hydroxides were used as the only activator. While van Jaarsveld et al. confirmed the importance of curing at elevated temperature for fly ash-based geopolymeric material, they indicated that curing for a longer period of time at elevated temperature results in weakened microstructure. Barbosa et al. stated that the water content played an important role on the properties of geopolymer binders, besides the chemical composition of the oxides used as activators.

By the shorter setting and hardening time, geopolymers are formed with tightly packed polycrystalline structure to give better mechanical properties than zeolite which have lower density and cage-like crystalline structure. By taking these differences between zeolites and geopolymers into account the following reaction scheme is proposed for the polycondensation process of geopolymerisation from minerals:

$$\text{Al-Si materials (s)} + \text{MOH (aq)} + \text{Na2SiO3 (s or aq)} \quad (4)$$

$$\text{Al-Si materials (s)} + [M_z(AlO_2)_x(SiO_2)_y.nMOH.mH_2O]gel \quad (5)$$

$$\text{Al-Si materials (s)} + [M_a((AlO_2)_a(SiO_2)_b).nMOH.mH_2O]gel \quad (6)$$

In reactions 4 and 5, the amount of Al–Si materials used depends on the particle size, the extent of dissolution of Al–Si materials and the concentration of the alkaline solution. With finer particle sizes (<0.5 μm) and hence higher extent of dissolution, comparatively lower ratios of alumino-silicate powder alkaline solution could be used, as most alumino-silicate particles could then be dissolved as a gel. In most cases, however, alumino-silicate particles cannot be converted totally from the solid phase to the gel phase. Undissolved alumino-silicate solids contained in a geopolymer can behave as reinforcement of the matrix (Palomo et al., 1992). In the present research neither of the 4 minerals dissolved extensively, because their characteristic crystalline peaks could still be detected by XRD after the reaction of geopolymerisation.

2.3 Sol-gel process of geopolymer precursors

As with zeolites, the production of synthetic aluminosilicates has also been studied intensively by using the sol-gel process (Zarsycki, 1998; Sinko & Mezei, 1998; Pozarnsky & McCormick, 1995; Hos, 2000). The sol-gel process is a means of manipulating molecular precursors to form bulk oxide materials. Sol-gel processing of alkoxides has attracted intense interest because it offers non-melt routes to high purity glasses and crystalline ceramics. Controlled hydrolysis-condensation reactions of the molecular precursors give successively: dimers, oilgomers, polymers and a sol(a colloidal suspension of solid particles). In turn, the sol particles join together to form a gel, which is a highly viscous network of metal oxide bonds containing trapped solvent molecules (Gurney & Seymour, 1995).

Sol-gel chemistry of tetra-alkoxy orthosilicates is based on hydrolysis and polycondensation as shown in equation 7 (Hos, 2000).

$$Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH \tag{7}$$

Tetra-ethoxy orthosilicate (TEOS) reacts readily with water at ambient temperatures and produce amorphous gels after several hours. Transparent silica monoliths are obtained after a final calcination and sintering. Tri-alkoxy aluminium compounds hydrolyse in a similar way. Equation 8 shows a reaction to produce amorphous alumina from tri-alkoxy aluminium compounds

$$Al(OR)_3 + 3H_2O \rightarrow Al(OH)_3 + 3ROH \tag{8}$$

Reaction between aluminium tri-isopropoxide, TEOS and water will produce kaolinitic and mullitic precursors.

Theoretically, these geopolymer precursors can be used to produce amorphous aluminosilicates but the formation only works for acidic condition, not basic. As the colloidal particles grow in a basic solution, the high surface charge will cause them to repel each other and therefore inhibit the formation of a gel. This is evidenced by the fact that gels formed from high pH solutions redisperse in water, whereas those from low pH will not, which has been rationalized by the increased solubility of silica at high pH (Hos, 2000).

Sinko & Mezei (1998) used similar preparation processes to produce aluminosilicate ceramic or glass material and reported that up 70%of Al is chemically incorporated in the network. Aluminosilicate ceramics with high Al content are well known for their high chemical, electric and heat resistance and low thermal expansion.

2.4 Microstructural character of geopolymers

Hos, McCormick and Byrne (2002) systematically analysed the microstructure of aluminosilicate inorganic polymer. By using scanning electron microscopy (SEM) they observed the nanoporous microstructure of their materials. According to the authors the nanoporous structure is a result of extensive dissolution of aluminosilicate species that occurs before polycondensation commences and consolidates the shapes of the specimen through a chaotic three-dimensional network of polysodium aluminosilicate. For specimens with low k, the researchers observed up to 40 % unreacted or partly reacted grains of fly ash. The presence of unreacted fly ash in the matrix creates a composite-like microstructure of geopolymers and acts as in-situ reinforcement responsible for high strength materials.

The researchers also reported the formation of needle like-crystals of sodium carbonate on the surface of the specimen as a result of the reaction between the residual sodium silicate with atmospheric CO_2. The formation of sodium carbonate on the surface of geopolymers has also been observed by Barbosa, MacKenzie & Thaumaturgo (2000) as indicated by the band at about 1460 cm^{-1} of FTIR spectra. This suggests that excess sodium is transported by the water to the surface during evaporation to form sodium carbonate.

Alkali-activated cement based on fly ash also exhibits a high density of pores or air bubbles. The material is very porous and the microspheres (originating from fly ash grains) are surrounded by a crust of reaction product. The adherence of the crust to the spheres does not appear to be very strong and the bond between grains is produced through the necks of reaction products. Crack development is evident in the middle of the matrix and is likely to have been initiated from the pore (Palomo, Grutzeck & Blanco, 1999).

3. Fly Ash

Fly ash is a kind of coal ash produced from the combustion process in a coal power plant. Coal ash is a residue of burnt coal which is equivalent to ash in the industrial analysis. Fly ash is a very fine, light dust which is carried off in the stack gases from a boiler unit and collected by mechanical or electrostatic methods. It is derived primarily from rock detritus which collects in the fissures of coal seams, and constitutes 8 to 14 percent of the weight of the coal. The quantity and quality of fly ash produced are a function of several factors. Coal source and method of production are perhaps most influential on the nature of the final product. Anthracitic coal ashes tend to be somewhat higher in carbon content, whereas ignite and western coal ashes have considerably higher calcium oxide contents, all of which can greatly affect the utilization, potential of a fly ash.

Coal ash can be classified as follows depending on a generating place and product type.

1. Fly ash is the finer coal ash powder collected from burning gas by an electrical precipitator. The particle size is approximately 0.001 – 1.00 mm. However, 70-80% of all ash produced in Thailand consist of fly ash.

2. Slag ash is the coarser coal ash power which drops when the combustion gas of a boiler passes through the air preheater or fuel economizer. The production ratio is calculated as 5% of the whole.

3. Bottom ash is the ash that drops and can be collected at the bottom of the boiler. The particle size is approximately 0.50-10.00 mm. The quantity is about 10-20% of the whole amount.

The important compositions of fly ash are Silicon Dioxide (SiO_2), Aluminum Oxide (Al_2O_3), Ferric Oxide(Fe_2O_3), Calcium Oxide (CaO), Magnesium Oxide (MgO), Potassium Dioxide (K_2O), Sulfur Trioxide (SO_3) and C while the three principal constituents are SiO_3 (25 to 60 percent), Al_2O_3 (10 to 30 percent), and Fe_2O_3 (5 to 25 percent) (ACI226.3R,1993). The quantity of each element depends on the source of fly ash. The chemical composition of a fly ash influences its color to a large degree. Fly ashes range in color from cream to dark brown or gray. The cream color is usually produced by a high calcium oxide content and gray to black by increasing quantities of carbon.

Fly ash can be classified into 3 classes according to the ASTM standard (ASTM C618-91); Class N, Class C and Class F. The classification conditions of each class are shown in Table 2 below.

Table 2 Classification of fly ash by ASTM standard.

Properties of fly ash	Classification of fly ash	
	Class F	Class C
$SiO_2 + Al_2O_3 + Fe_2O_3$	70.0	50.0
SO_3, max, %	5.0	5.0
Moisture content, max, %	3.0	3.0
Loss on ignition, max, %	6.0	6.0
Strength activity index, min, percent of control	75.0	75.0

Source: ASTM C618-94a (1995)

MATERIALS AND METHODS

Materials

1. Fly ash : Fly ash was collected from Mae-Moh lignite power plant in Lampang province. The chemical composition of the fly ash, as determined by X-Ray Fluorescence (XRF) analysis (ASTM C311) is as shown in Table 4.
2. Sodium silicate solution, grade B (Na_2O=14.7%, SiO_2=29.4% and water=55.9% by mass.).
3. Sodium Hydroxide (NaOH) in flake from (98% purity).
4. Water : Deionised water.
5. Hobart Mixer.
6. Plastic cylindrical molds (40x80mm).
7. Compressive strength testing machine.
8. Vacuum Filtration Set.
9. Vicat measurement.
10. Glass bowl.
11. Digital scale.
12. Thermometer couple.
13. X-ray Diffractometer.
14. Scanning Electron Microscope.
15. Inductive Coupled Plasma Optical Emission Spectrometer (ICP-OES).
16. Apparatus for use in measurement of length change as specified in ASTM C490-83a.

Methods

1. Chemical preparation for testing

1.1 To determine the oxide compound of fly ash by using XRF analysis, known as X-Ray Fluorescence.

1.2 To determine the physical properties of fly ash namely pH, moisture content, volatile solids, and fixed solids after burning at 550°C in accordance with the procedure described in the Standard Method.

1.3 A sodium hydroxide solution was prepared by dissolving sodium hydroxide pellets in water. The degree of purity of the pellets was 98% and was taken into account to modify the quantities. Distilled water was used to dissolve the pellets to avoid affecting the solution by tap water contaminations.

Table 3 Result of the chemical analysis of Mae Moh fly ash by X-Ray Florescence spectrometer

Chemical composition of Fly ash	Class C fly ash %	Class F fly ash %
SiO_2	30.23	35.30
Al_2O_3	17.24	21.50
Fe_2O_3	14.86	14.20
CaO	25.59	18.70
MgO	2.18	3.00
Na_2O	2.30	2.50
K_2O	2.31	2.00
LOI	0.40	0.40

Table 4 Proportional of NaOH

NaOH concentration (M)	98% purity (g/L)	100% purity (g/L)
2	80	81.60
4	160	163.20
6	240	244.80
8	320	326.40
10	400	408.00

2. Dissolution ion procedure

2.1 Prepare all samples for dissolution ion process by varying NaOH : FA ratio which were 0.21, 0.33, 0.50, 0.75, and 1.17 by weight.

2.2 The procedures for dissolution of silica, alumina, and calcium from fly ash are as follows:

- Place sodium silicate solution and fly ash into the mixer and mixed for 5 minutes.
- The prepared mix was placed in vacuum filtered set by using a 0.45µm membrane paper as filter.
- Using pump to increase the ability of sample filtrated through a membrane.
- Finally, the filtrated sample was analyzed to determine quantities of dissolution ions from fly ash by using Inductive Coupled Plasma Optical Emission Spectrometer (ICP-OES).

Table 5 Detail of proportions for dissolution ion from fly ash

Mix No.	Designation	Fly Ash (gram)	NaOH (gram)	Water (gram)	NaOH : FA Ratio
1	Class C - FA-1	282	60.4	150	0.21
2	Class C - FA-2	181	60.4	150	0.33
3	Class C - FA-3	121	60.4	150	0.50
4	Class C - FA-4	81	60.4	150	0.75
5	Class C - FA-5	52	60.4	150	1.17
6	Class F - FB-1	282	60.4	150	0.21
7	Class F - FB-2	181	60.4	150	0.33
8	Class F - FB-3	121	60.4	150	0.50
9	Class F - FB-4	81	60.4	150	0.75
10	Class F - FB-5	52	60.4	150	1.17

2.3 The dissolution liquid from previous samples were mixed with sodium silicate. After that, each samples was observed for its characteristics, such as physical change and any formation of geopolymer.

Figure 4 Vacuum Filtration Set

Figure 5 ICP-OES testing

ICP-OES is an analytical method used to determine elemental composition in the sub-ppm range. In the ICP-OES instrument, an ICP source dissociates the sample into its constituent atoms or ions and excites them so that they emit light of a characteristic wavelength. Many elements can be screened per single sample run of less than one minute and the samples can be analyzed in a variety of aqueous or organic matrices. The detection limit of the instrument is < 1 ppm. Solid sample must be dissolved or digested to run on ICP. 4-5 mL of the sample is required for a good run, smaller samples can be diluted to this volume if necessary. A minimum of three standard solution is needed for calibration, for all elements of interest. These standards should have a concentration near the expected concentration for the sample.

3. Mixing Geopolymer

3.1 Prepare the solution of sodium hydroxide and fly ash by varying the NaOH:FA ratios as the same as dissolution ion procedures. Then, prepare sodium silicate solution which had the same weight percent of sodium hydroxide.

3.2 Geopolymer mixing procedures are as follows :

- Place the solution of NaOH and Fly ash into the Hobart mixer.
- Mixed for 5 minutes.
- Add the sodium silicate solution and mix for 5 minutes.
- Place geopolymer in cylinder mold. The cylinder mold had the diameter of 4 cm. and the height of 8 cm. Then, keep the mold for 24 hours and remold.
- Finally, wrap by plastic film and keep all samples in zip-lock bag to prevent the evaporation of water from exposed sample and keep at room temperature.

Table 6 Detail of mix proportions for geopolymer

Mix No.	Designation	Solution		Fly ash (% by weight)	Solution: FA Ratio
		NaOH (% by weight)	Na_2SiO_3 (% by weight)		
1	Class C - FA-1	30	30	30	0.43
2	Class C - FA-2	40	40	40	0.67
3	Class C - FA-3	50	50	50	1.00
4	Class C - FA-4	60	60	60	1.50
5	Class C - FA-5	70	70	70	2.33
6	Class F - FB-1	30	30	30	0.43
7	Class F - FB-2	40	40	40	0.67
8	Class F - FB-3	50	50	50	1.00
9	Class F - FB-4	60	60	60	1.50
10	Class F - FB-5	70	70	70	2.33

4. Compressive strength

Compression tests were conducted to investigate the ultimate strength of fly ash-based geopolymers with class C and class F fly ash. The compressive tests were conducted after ageing the specimen at 1, 3, 7, 14 and 28 days. These tests were performed using a Wykeham Farrance 50 ton compression test machine with a loading rate of 0.33 mm/minute. The test specimens were cylindrical in shape, 8.00 cm in length and 4.00 cm in diameter and hence the length to diameter ratio (2:1) fulfils the standard requirement for compression test ASTM C773. Each measurement was conducted on 3 samples.

5. Microstructural Characterisation

5.1 Scanning electron microscopy (SEM)

SEM was performed to investigate the microstructures of pastes (including porosity and crack formation) and the paste-aggregate interface in the matrix of the samples. The SEM imaging was conducted on a Philips XL-30 using secondary as well as backscattered electron detectors. The microscope was coupled with an Oxford Instrument energy dispersive X-ray spectrometer (EDX) for elemental analysis. Analysis of EDX spectra was performed using Inca-Analyzer software.

Microstructural analysis was performed on polished as well as on fractured specimens. Sample preparation for SEM investigation was as follows. The samples were cut to a size of 2.00 to 4.00 mm in height and 10 to 25 mm in diameter. Samples were polished to a 1 um finish using diamond paste. The samples were then cleaned to remove any polishing residue using an ultrasonic bath. The samples were oven dried at about 60°C for at least 1 hour. Following drying the samples were gold coated for imaging and carbon coated for EDX work. Samples were mounted on the SEM samples stage with conductive, double-side carbon tape.

5.2 X-ray diffraction (XRD)

X-ray diffraction (XRD) measurements were performed for phase analysis of the starting materials and to investigate the crystallinity of the resulting geopolymers. Random powder samples of fly ash were prepared by lightly pressing powder samples into aluminium holders. Samples from the resulting geopolymers were prepared either in a powder form or by cutting 0.5 mm thick slices of specimen and mounting in aluminium holders.

Diffraction patterns were acquired on a Siemens D500 Bragg-Brentano Diffractometer. Operating conditions were 40 kV and 30 mA, Cu-K wavelengths : 1.54060 and 1.54439 A. In collecting data sets, the 2θ step size was 0.02˚, the counting time per step was 1.2 s, and the 2θ range between 10 – 70. The software MDI-Jade (version 5) for peak identification and automated search and match was used to analyze the results of diffraction patterns.

Figure 6 X-ray diffractometer for chemical analysis

RESULTS AND DICUSSION

1. Dissolution ions

1.1 Dissolution ion from 2 classes of fly ash

The result of experiment showed that concentration of alkali solution, known as NaOH, influence geopolymer formation. The dissolution of alumina, silica, and calcium began, when alumino-silicate materials were mixed in alkali solution. Subsequent reactions of the species resulted in the formation of geopolymer and the reduction of concentration of dissolution species and further dissolution. Figures 7 show the concentrations of silica, alumina and calcium ions dissolution from class C fly ash and class F fly ash particles using NaOH concentration of 15, 20, 25, 30 and 35 percent by weight. It was found that the amount of NaOH solution affected the dissolution of fly ash. This higher NaOH : FA ratio increased the amount of dissolution silica from fly ash. However, when NaOH : FA ratio was increased over 0.75, the amount of dissolution silica was reduced. The reason for this result was silica could not be dissolution when the solution had high viscosity. The range of NaOH : FA ratios between 0.21-0.50 of class F fly ash produced more silica ion than class C fly ash. On the contrary, The ratio of NaOH : FA over 0.5, silica of class C fly ash was dissolution more than class F fly ash.

When the amount of dissolution alumina was considered, the results showed that NaOH : FA ratio was increased. The dissolution of alumina from class F fly ash was higher than class C fly ash for all mixes, especially at the ratio of NaOH : FA = 0.75. In addition, both classes of fly ash produced highest silica and alumina at the NaOH : FA ratio of 0.75 using 4M of NaOH concentration.

Furthermore, the amount of calcium was also observed for this testing. It was found that increase in NaOH :FA ratio resulted in decrease in the dissolution of calcium. However, the amount of calcium in class C fly ash dissolution leached out more than class F fly ash. It could probably be due to higher CaO compound of class C fly ash.

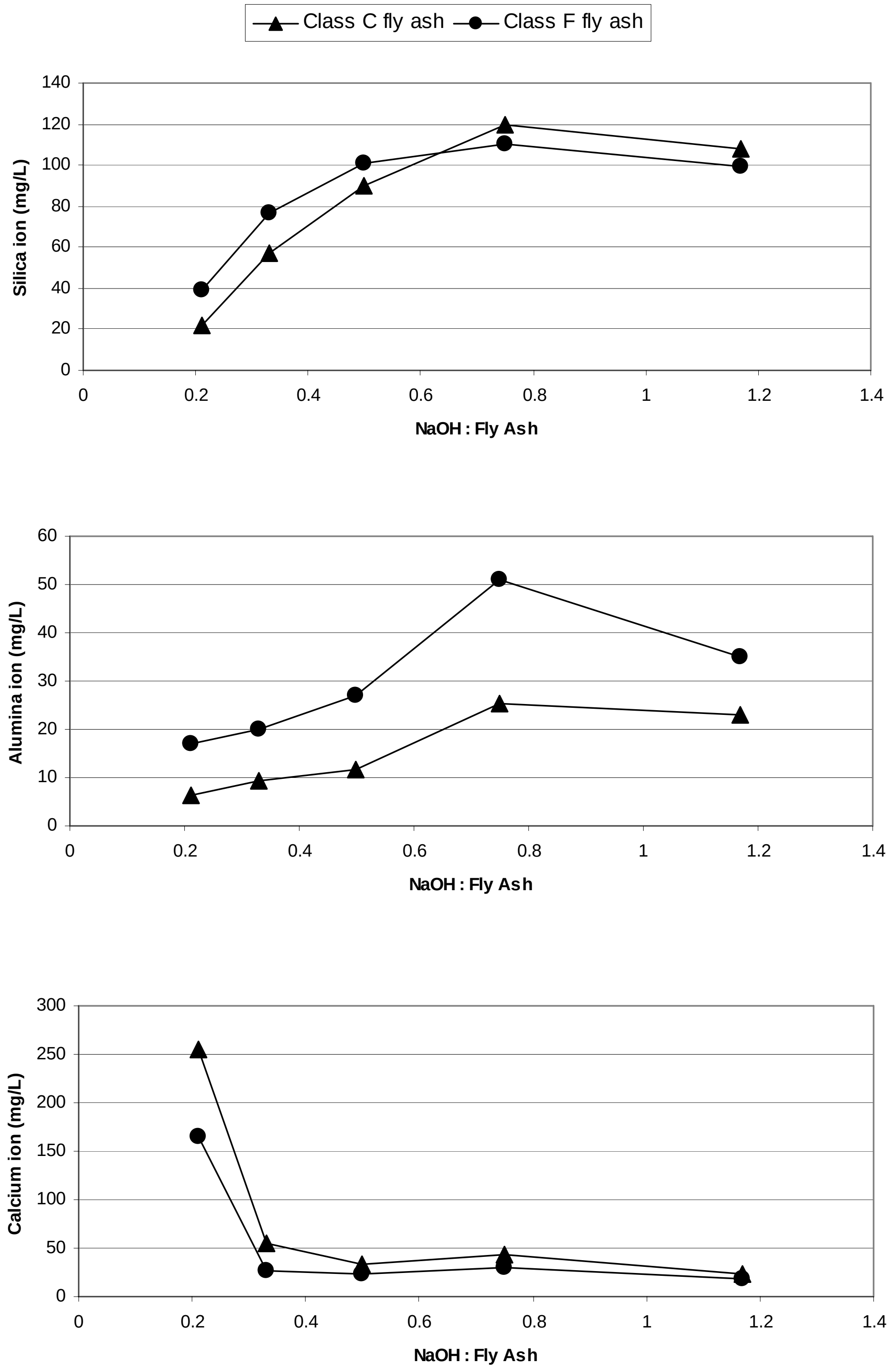
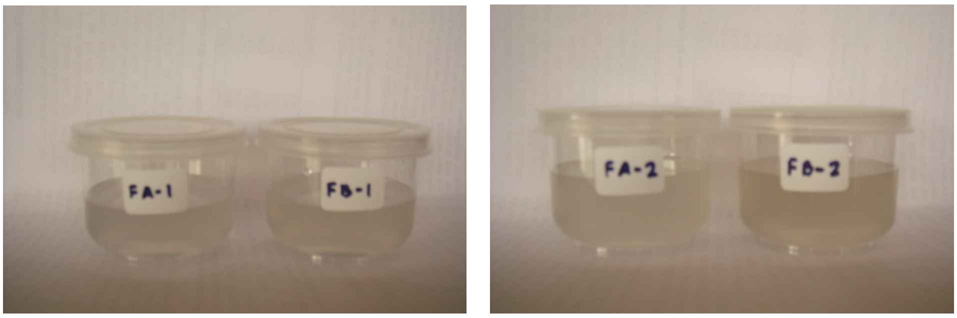


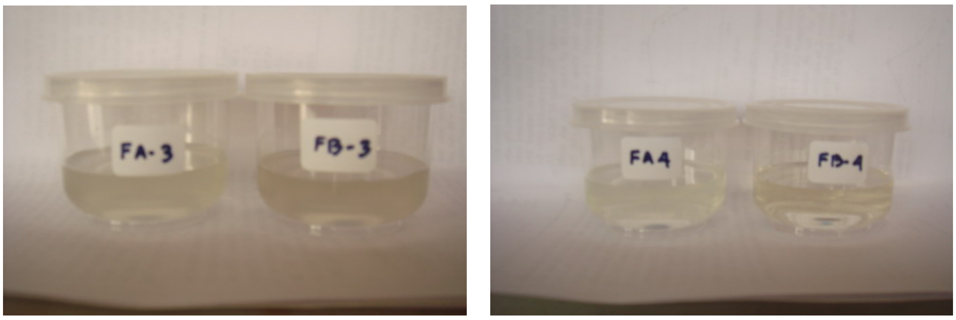
Figure 7 The silica, alumina and calcium ions dissolution from fly ash

1.2 Dissolution liquid mixed with sodium silicate

When the sodium silicate was added in the dissolution liquid from previous experiment, which was obtained from the dissolution process of fly ash by using NaOH, there was no formation as shown in Figure 8, the result of dissolution liquid mixed with sodium silicate. This showed that the main factors for the formation of geopolymer were sodium silicate, sodium hydroxide, and mineral ions in fly ash as the initial substances. Moreover, the precipitation of fly ash was helpfully for the formation of geopolymer. These samples were also tested for turbidity by Turbidity meter, 2100AN, Hach in Laboratory of Environmental Engineering. The result of turbidly shown 99.9 as in the result when testing the deionised water in all of samples.



(1) NaOH : FA ratio of 0.21 (2) NaOH : FA ratio of 0.33



(3) NaOH : FA ratio of 0.50 (4) NaOH : FA ratio of 0.75

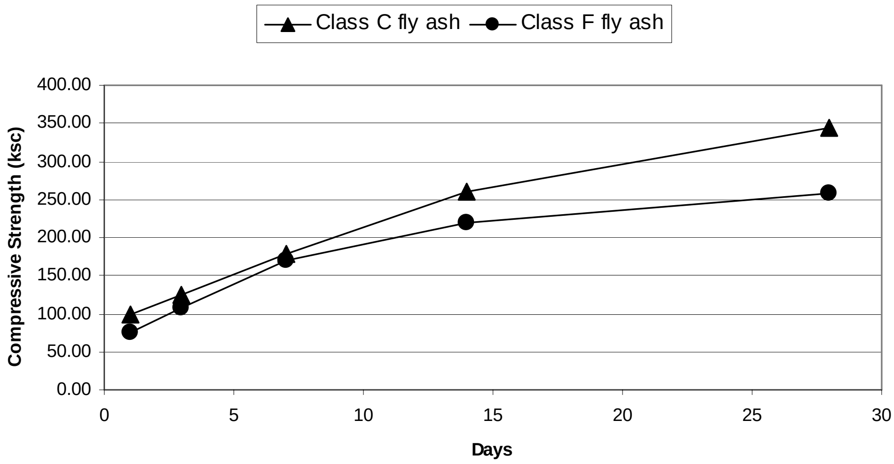
Figure 8 The result of dissolution liquid mixed with sodium silicate

2. Compressive strength

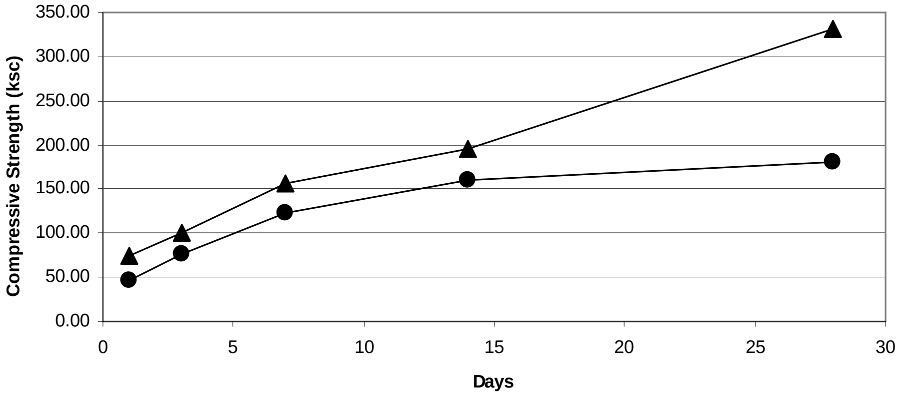
2.1 Compressive strength development of geopolymer

The compressive strength of the 1, 3, 7, 14 and 28 days geopolymer cylinders were tested. There were 3 cylinders for each proportion. The compressive strength test of geopolymer cylinders for each sample was performed in accordance with ASTM C39/C39M-99 Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens. The effect of replacement percentage of sodium hydroxide on compressive strength of geopolymer was summarized and shown in Figure 9 and 10. These figures show the compressive strength development of geopolymer mixed from class C fly ash and class F fly ash with the ratio of Sol : FA at 0.43, 0.67, 1.00, 1.50 and 2.33.

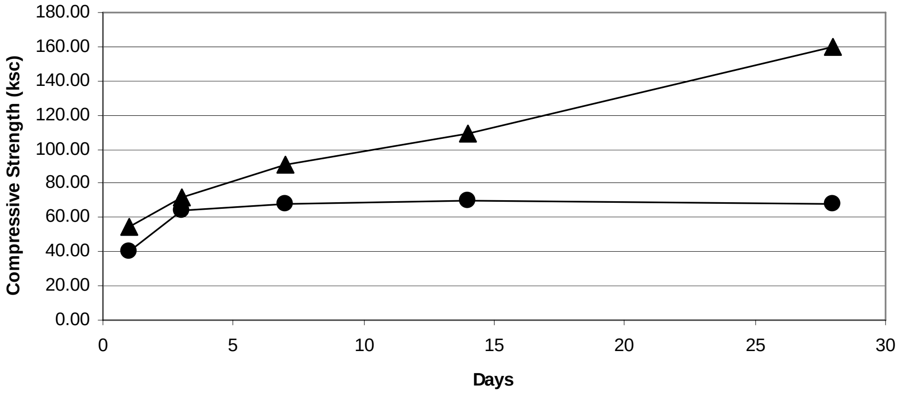
From the obtained data, the compressive strength of geopolymer could be increased as the age of geopolymer increased. Geopolymer which obtained from class C fly ash was slightly higher than class F fly ash. As seen from Figure 9, the tendency of development in compressive strength at age between 1 and 14 days for both types of class C fly ash and class F fly ash gradually increased. However, the development in compressive strength for class F fly ash based geopolymer was more or less the same at after 14 days. The compressive strength at the ages of 14 and 28 days were 219 ksc and 258 ksc, respectively for class F fly ash based geopolymer. For class C fly ash based geopolymer, the development of compressive strength between 14 and 28 days was 85 ksc. From this result, it was found that the development of compressive strength in geopolymer of class C fly ash was higher than class F fly ash.



Sol : FA = 0.43

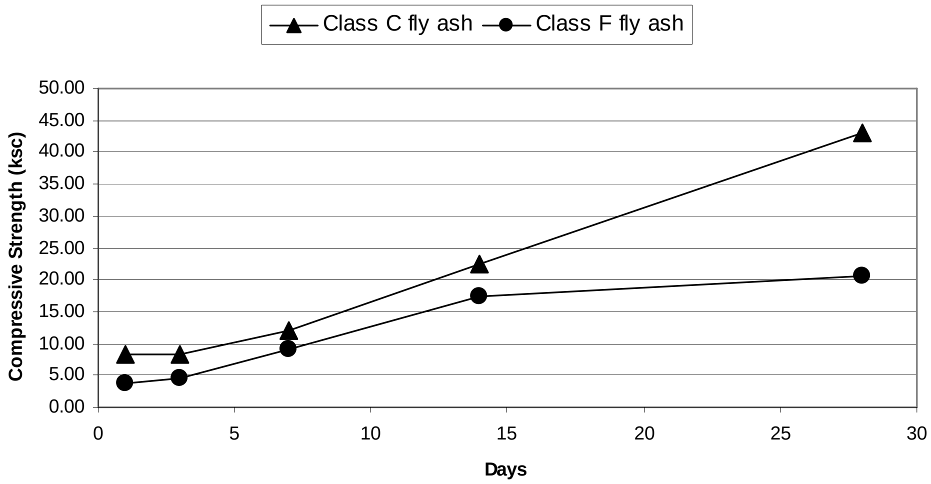


Sol : FA = 0.67

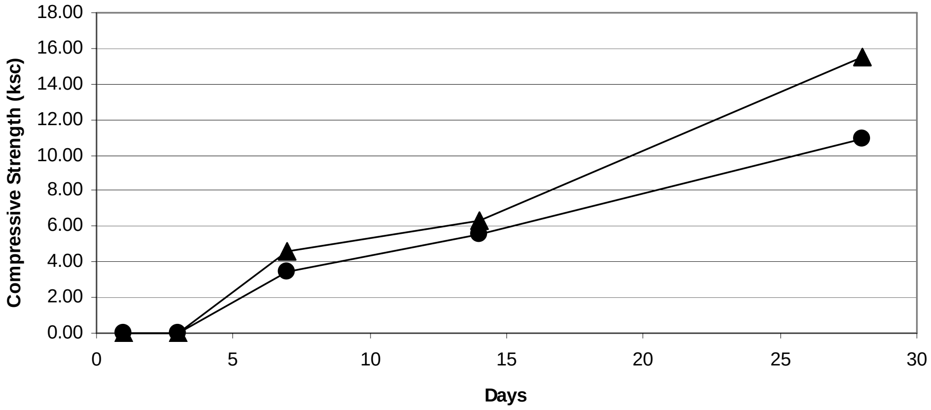


Sol : FA = 1.00

Figure 9 The compressive strength development of geopolymer



Sol : FA = 1.50



Sol : FA = 2.33

Figure 10 The compressive strength development of geopolymer mixed with class C and Class F fly ash with Sol : FA ratio 1.50 and 2.33 respectively.

2.2 Comparison of compressive strength of geopolymer mixed with 2 classes of fly ash.

The compressive strength at 28 days decreased with the increase in the proportion of NaOH : FA ratio. The compressive strength of geopolymer containing class C fly ash was higher than that of geopolymer containing class F fly ash. It could be especially observed that the compressive strength of class C fly ash was 344 ksc compared to 258 ksc of class F fly ash with Sol : FA = 0.43. However, when the Sol : FA ratio was increased to 2.33, the compressive strength of class C fly ash was 43 ksc which was significantly higher than class F fly ash mix of 21 ksc. Figure 16 presented the results of compressive strength at 28 days.

The increase of NaOH content in the aqueous phase of the geopolymeric system has as a result the direct increase of the dissolution rate of Si and Si-Al phases of fly ash improving the effectiveness of the geopolymerisation process. Increased Si and Al content in the aqueous phase of geopolymeric systems are essential for the initiation of the formation of oilgomeric precursors and therefore, of the polycondensation that is the most important process of strength development in geopolymeric materials.

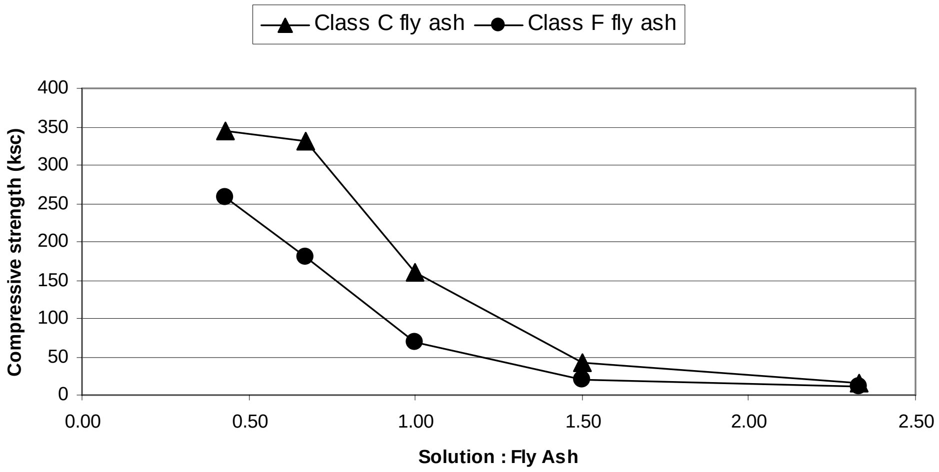


Figure 11 The compressive strength of geopolymer mixed with class C fly ash and class F fly ash at 28 days

As it is mentioned, the compressive strength of geopolymers is related to the degree of polymerization, which is strongly related to the degree of polymerization, which is strongly affected by the soluble silicate and aluminate of the geopolymeric system. In general, the higher the degree of polymerization in the geopolymeric structures, the higher the obtained compressive strength.

As far as calcium is concerned, the CaO content of the source material appears to strengthen the geopolymer by forming amorphously structured Ca-Al-Si gel (Yip and Van Deventer, 2001). Various studies (Xu and Van Deventer, 2000a; Yip et al., 2005) have found that calcium has a positive effect on the compressive strength of geopolymeric binders. When the CaO content is high, the microstructural porosity decreases and the resulting formation of amorphous structure Ca-Al-Si gel strengthens the final product (Van Jaarsveld et al., 1998; Xu and Van Deventer, 2002b). Phair and Van Deventer (2001), support that strength development by calcium is more likely to be achieved through enhancing silicate and polysialate network formation and hardening throughout the matrix. Minarikova and Skvara (2005), have also proven that the presence of calcium ions in the geopolymer matrix improves the resistance of fly ash-based geopolymers during leaching.

Dombrowski et al. (2007) assessed the influence of calcium and its dosage on structure formation and property development. With prolonged reaction time and increased calcium content, fly ash based geopolymers showed increased reaction degree and thus acquired higher strength. According to Lee (2002), the amount of calcium presenting a geopolymeric reacting system, regardless of its initial source, is important in determining the nature of the alumino-silicate gel formed, which presumably controls the macroscopic strength of a geopolymeric product. Van Deventer et al. (2007) proved that the amount of calcium present in a waste used during geopolymerisation affects the process by providing extra nucleation sites for precipitation of dissolved species.

The influence of calcium content on the performance of fly ash geopolymeric binders has been also determined by Buchwald et al. (2005). Addition of high amounts of calcium hydroxide to fly ash based geopolymers improves early strength, whereas addition of small amounts of calcium improves strength at later stages. For fly ash based geopolymer binder, an exchange of about 10% of the aluminosilicates material with calcium hydroxide seem to be favoured.

Yip (2004) stated that the form of added Ca^{2+} plays a significant role in determining the physical properties of the final geopolymer. The effect of calcium on the final reaction product can be determined by the level of dissolved silicate in the activating solution through pH control. If the solid raw material is deficient in calcium, $CaCO_3$ and CaO can be introduced in the form of an aqueous suspension to improve the physical and mechanical properties of geopolymers (Yip et al., 2005).

3. Setting time of geopolymer

Setting time testing was performed for determining the workability of geopolymer setting time. The results showed that when the ratio of solution to fly ash (Sol:FA) increased, the setting time of geopolymer was also increased. Moreover, the setting time of class C fly ash was shorter than class F fly ash because class C fly ash has higher CaO compound as shown in Figure 12. At the Sol : FA ratio of 0.43, fresh geopolymer which is obtained by two types of fly ash, has high viscosity and the setting time also became shorter. The setting times of geopolymer were 30 minutes and 75 minutes for class C fly ash and class F fly ash, respectively. On the other hand, when the Sol : FA ratio was increased to 2.33, geopolymer was low in viscosity and took a longer time for setting. In this case, the setting time of geopolymer mixed with fly ash type C and class F fly ash were 1540 minutes and 2035 minutes, respectively.

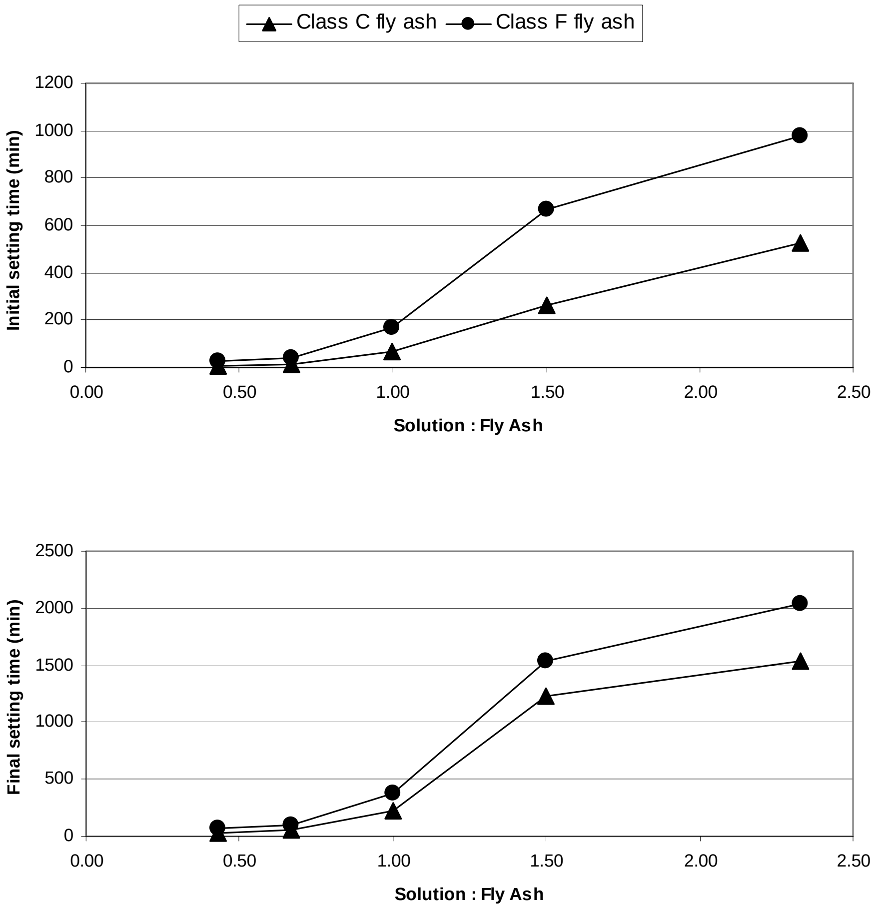
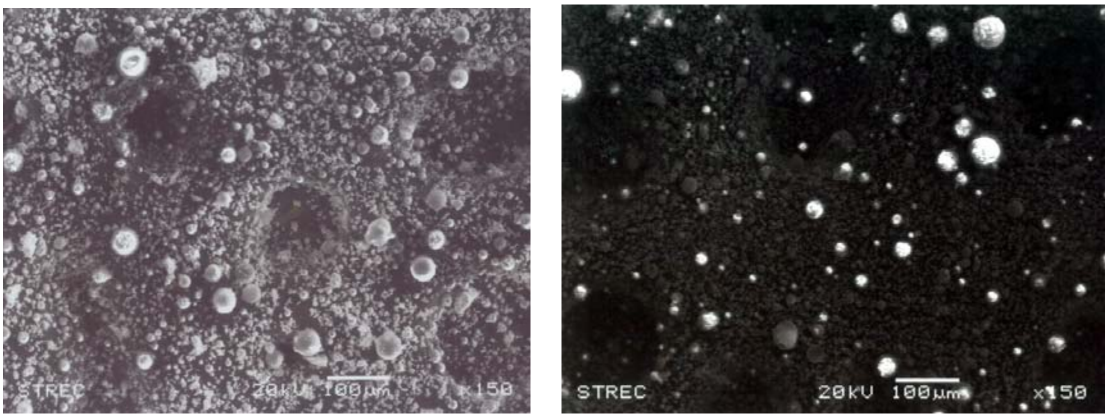


Figure 12 Initial and final setting time of geopolymers

4. Microstructure of fly ash – based geopolymer

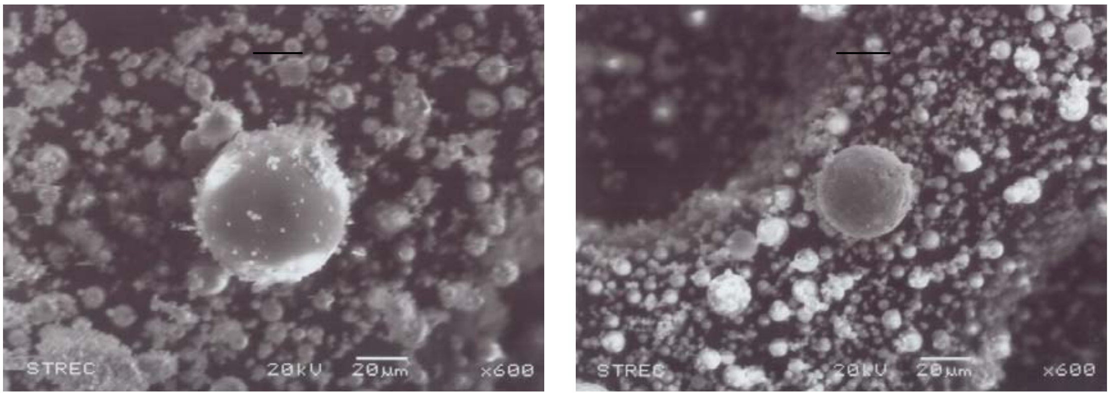
4.1 Scanning electron microscopy of 2 classes of fly ash

The scanning electro n microscopy (SEM) of fly ash based geopolymer containing class C fly ash and class F fly ash was illustrated as shown in Figure 13 and 14. This fly ash consists of a series of spherical vitreous particles of different size (diameters ranging from 200 to 10 um). Whilst usually hollow, some of these spheres may contain other particles of a smaller size in their interiors.



(I) (II)

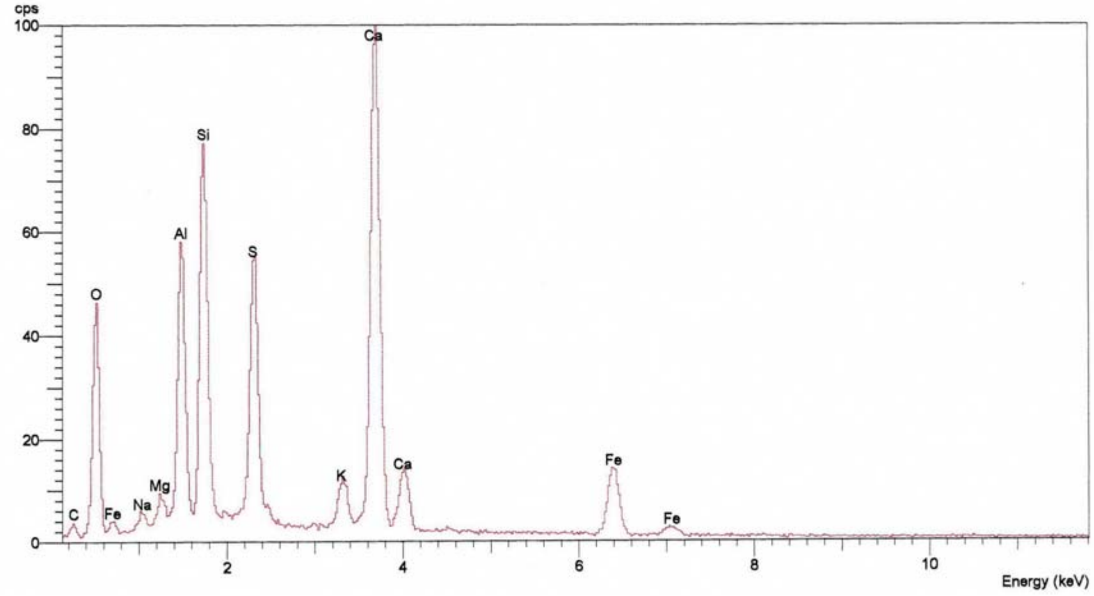
Figure 13 SEM micrographs of class C (I) & class F (II) fly ash with amplify 150x



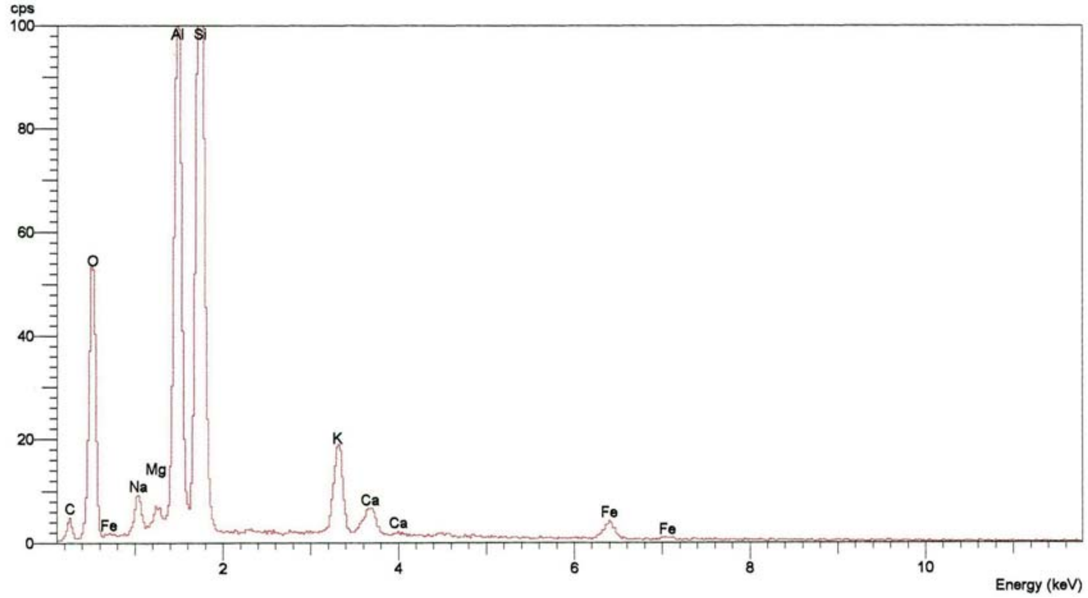
(I) (II)

Figure 14 SEM micrographs of class C (I) & class F (II) fly ash with amplify 600x

Figure 15, shows the SEM-EDX micrographs of the particle of class C fly ash and class F fly ash. The particle of class C fly ash has an oxide component of silica and alumina lower than the particle of class F fly ash, but the particle of class C fly ash has calcium higher than class F fly ash. The fly ash component by SEM-EDX method has the same result from the X-ray Diffractometer (XRD) method.



(I)



(II)

Figure 15 SEM-EDX micrographs of class C fly ash (I) and class F fly ash (II)

4.2 Scanning electron microscopy of geopolymer

Geopolymer samples were also examined under a Scanning Electron Microscope machine. Samples were selected from mixtures by NaOH : FA ratio 0.21, 0.33, 0.50, 0.75 and 1.17. Figure 16 shows the SEM micrograph of a specimen from NaOH : FA ratio 0.21. The picture reveals the sample consisted of a paste with a combination of porous and dense areas. At the top left side of the picture, a more compacted area is visible. Arrow 1 indicates a non-reacted fly ash grain, 2 shows a micro crack. The crack can have occurred at the time of cutting. This mixture incorporated NaOH : FA ratio 0.21 and yielded 344 ksc. compressive strength after 28 days.

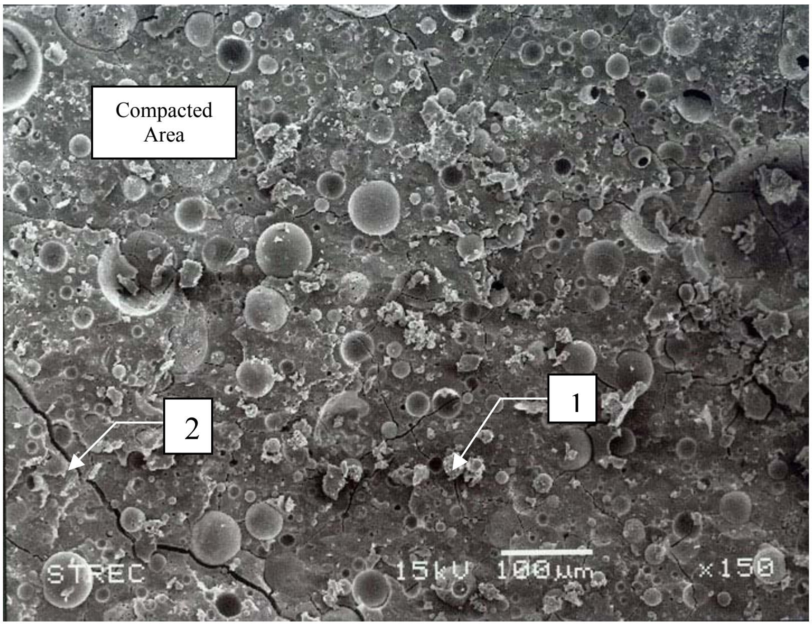
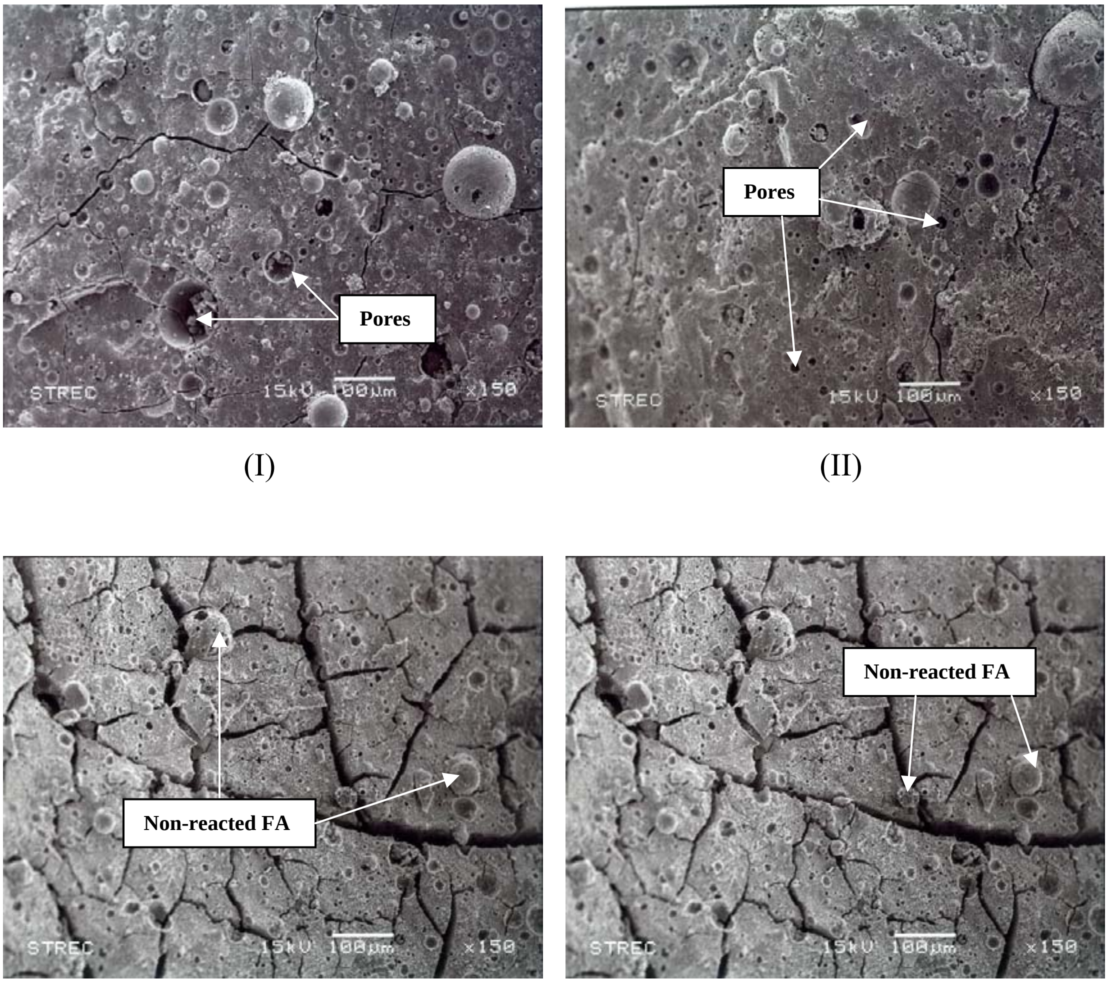


Figure 16 SEM micrographs of class C fly ash-based geopolymer with NaOH : FA ratio 0.21 at 28 days

Figure 17 shows SEM micrographs of class C fly ash-based geopolymer with NaOH : FA ratio 0.33, 0.50, 0.75 and 1.17 respectively. A combination of porous and well-compacted areas is also notable.



(I) (II)

(III) (IV)

Figure 17 SEM micrographs of class C fly ash-based geopolymer with NaOH : FA ratio 0.33, 0.50, 0.75 and 1.17 at 28 days respectively

While the change in microstructure appeared most dramatic between NaOH : FA ratios of 0.21 and 0.33, there was a general trend of decreasing presence of fly ash particles as NaOH : FA increased. This was as expected. Also, the proportion of hemispherical “pores” appeared to increase steadily. The pores are thought to be what is left of fly ash particles after the dissolving by sodium hydroxide has run its course.

Specimens with NaOH : FA > 0.50 exhibited a microstructure comprising large pores, loosely structured matrix and non-reacted material, corresponding to low mechanical strength. Geopolymer with NaOH : FA ratio < 0.5 are categorized by a largely homogeneous binder containing non-reacted particles and some smaller isolated pores of a few microns in size.

The fly ash-based geopolymer gel is comprised of aluminosilicate particulates, which are connected and forming nano-channels and pores, as has been reported elsewhere. The substrate of mixtures of geopolymer containing class C fly ash and class F fly ash was varied. When the mixtures of geopolymer containing class F fly ash were considered, it could be noticed that this class of geopolymer presented high porosity and low-density microstructure whereas the NaOH : Class F fly ash ration was increased. These results could be illustrated in Figure 18. The SEM picture was taken from mix with the same ratio of NaOH : FA in class C fly ash.

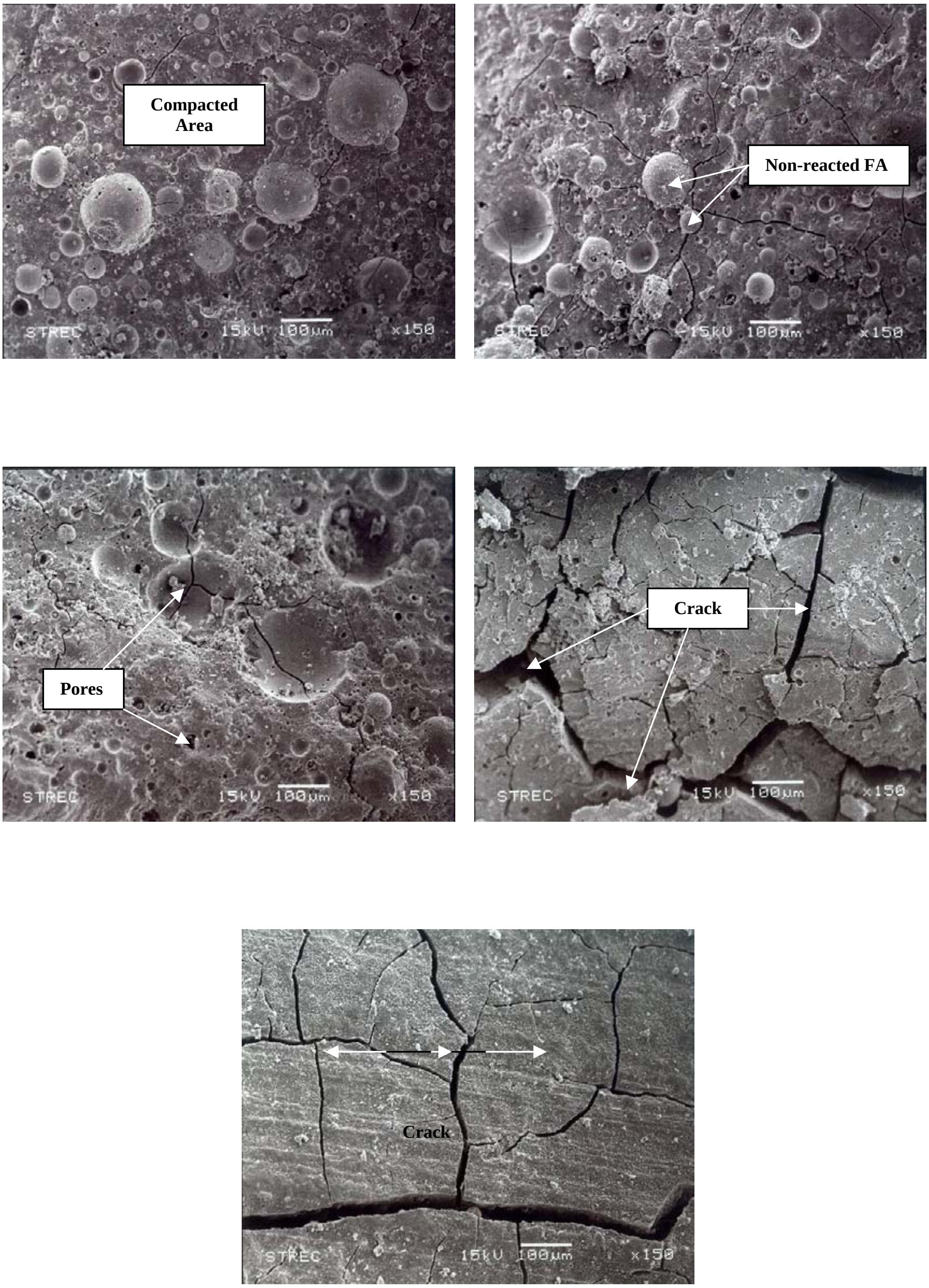


Figure 18 SEM micrographs of class F fly ash-based geopolymer at 28 days

Geopolymers are known to contain on amount of non-reacted solid aluminosilicate source. Fly ash is confirmed by the plate-shaped voids observed in the SEM micrographs. These voids are produced during the polishing process as the soft, like fly ash particles remaining non-reacted are torn from binder phase. However, there is no definitive and accurate method for quantitatively determining the amount of unreacted material variations between specimens and would therefore be expected to have correspondingly varying effects on their mechanical properties. Fly ash is weak and will be expected to act as a point defect in the structure, locally intensifying the stress in the binder and precipitating failure.

Therefore, improvement in micro-structural homogeneity provides a strong reasoning for the increase in mechanical properties at lower NaOH : FA ratio, but there is nothing directly observable in SEM micro-graphs that can explain what is responsible for the decrease in strength. Theoretically, Si-O-Si linkages are stronger than Si-O-Al and Al-O-Al bonds, meaning that the strength of geopolymers should decrease with NaOH : FA ratio since the density of Si-O-Si bonds increases.

The change in pore volume distributions of fly ash-based geopolymers can be observed to shift into many pores as the NaOH : FA ratio increases. However, the pore size distribution of the specimen with NaOH : FA ratio of 1.17 is observed to be large, which can be explained by the large volume of pores in combination with some level of crystallinity in alkali-activated specimens. The nominal densities of geopolymers with varying NaOH : FA ratios are also presented in Figure 19. The density of geopolymers is seen to decrease from 2.22 to 1.56 g/cm^3 and 1.93 to 1.44 g/cm^3 in class C fly ash and F respectively. The decrease in nominal density of geopolymers observed with increasing NaOH : FA ratio results from the lower proportion of solid components due to addition of silicon to the activating solution. This provides an activating solution of lower density, and so mixing a given amount of this solution with a particular amount of fly ash will give a product of lower nominal density.

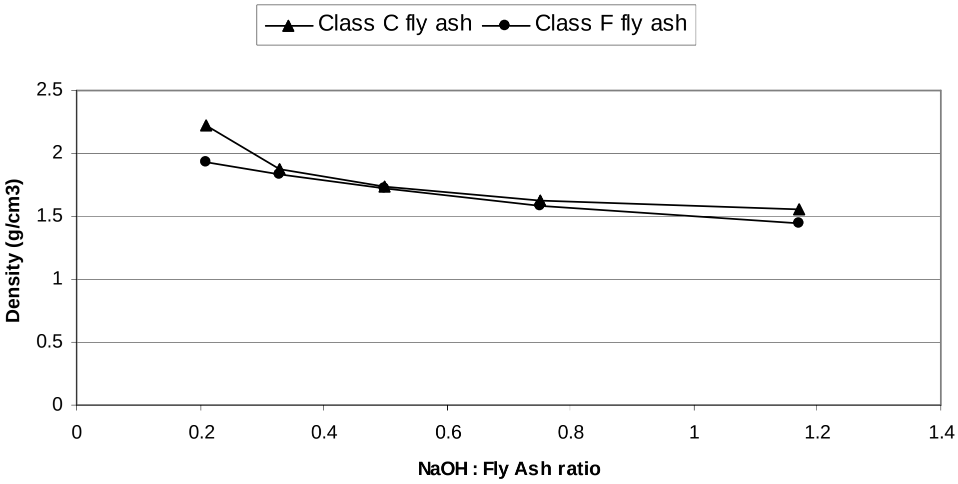


Figure 19 Density of geopolymers

4.3 X-ray diffraction (XRD)

The X-ray diffractograms of fly ash-based geopolymers are shown Figure 20. Although fly ash is an essentially vitreous material, it also contains a series of minority crystalline phases such as quartz (SiO_2, JCPDS 05-0492), mullite ($3Al_2O_3.2SiO_2$, JCPDS 15-0776) and magnetite (Fe_3O_4, JCPDS 19-0629). The diffraction pattern changed appreciably after the activation of the original fly ash with the different Sol:FA ratio. It has to be highlighted that the shift in the position of the halo attributed to the vitreous phase in the initial ash to slightly higher angular values (25-40°). This effect indicates the formation of an alkaline aluminosilicate gel. The crystalline phases (quartz, mullite and magnetite) detected in the initial material remained apparently unaltered with activation. Other zeolite-type crystalline phases also appeared after activation, which varied depending on the nature of the activating solution used and proportional.

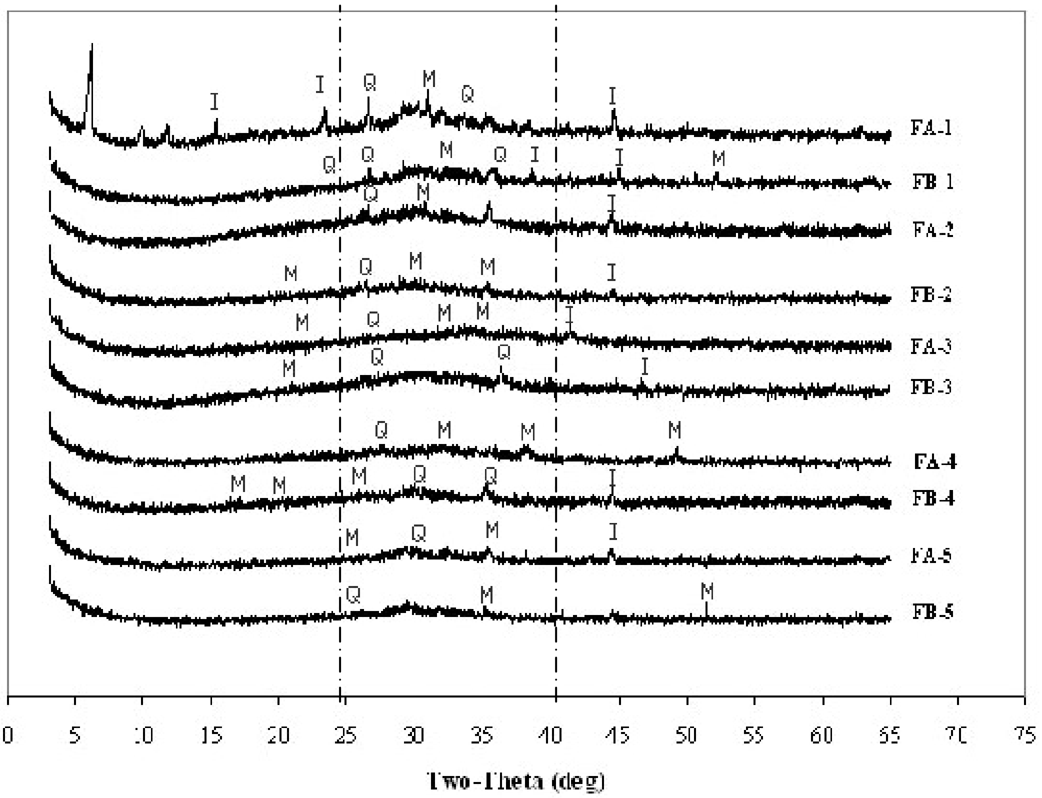


Figure 20 X-ray diffractograms of fly ash-based geopolymers at 28 days

In fly ash, there is a shoulder at the diffraction angles (2θ) ranging from 20° to 30°. This shoulder is associated with the amorphous aluminosilicate phases in fly ash. Activation of fly ash with alkali-silicate solution results in the shift of amorphous shoulder to 25° to 40° (Phair et al., 2001), which has been identified as the characteristic diffraction patterns of geopolymers. Lower Sol : FA ratio is also believed to induce the formation of crystalline phases in fly ash-based geopolymers. These changes can be explained by the fact that zeolites are metastable and may undergo successive transformation into one or several more stable phases. Species with a very open structure convert to closed structure zeolites that eventually form analcime (the most stable and densest of common zeolites).

All fly ash-based geopolymeric matrices produced on X-ray diffractogram with the same basic features mostly attributable to reacting fly ash. For instance, peaks due to haematite, quartz and mullite were all regularly observed, as was the hump due to amorphous silica in the diffractogram. The exact value for the maximum of this hump is largely controlled by the degree of polycondensation, or the M_2O : SiO_2 ratio (Rahier et al., 1997), which was confirmed by the slight shift observed in the peak with variable NaOH/FA ratio, which altered the degree of polycondensation. There was a general trend for all humps to shift the hump maximum from around 30° to 40° 2θ with increasing NaOH : FA ratio.

CONCLUSION AND RECOMMENDATION

Conclusion

1. Class F fly ash contained higher amount of silica and alumina than class C fly ash. Regarding the higher amount of silica and alumina, the amount of dissolution of silica and alumina from class F fly ash was higher than class C fly ash. Moreover, it could be noticed that the ratio of NaOH : FA = 1 : 1.33 was an optimum ratio which could produce more dissolution of silica and alumina from both classes of fly ash.

2. Calcium ion was more dissolution from class C fly ash than class F fly ash because class C fly ash contained higher CaO compound. If the amount of fly ash was reduced, the dissolution of calcium ion was also reduced.

3. When the sodium silicate was added in the dissolution liquid, which was obtained from the dissolution process of fly ash by using NaOH, it had no formation. This showed that the main factors for the formation of geopolymer were sodium silicate, sodium hydroxide, and mineral ions in fly ash as the initial substances. Moreover, the precipitation of fly ash was helpfull for the formation of geopolymer.

4. Sodium hydroxide content in the synthesis of geopolymers was found to affect significantly their compressive strength. It is in the aqueous phase that the geopolymeric system acts on the dissolution process, as well as on the bonding that the solid particles in the final structure. The compressive strength of geopolymer was reduced with the increase in Sol : FA. The setting time of geopolymer was also longer. The compressive strengths of geopolymer at 28 days with the 0.43 of Sol : FA ratio were 344 ksc. and 258 ksc. for class C fly ash and class F fly ash, respectively.

5. Calcium oxide has the effect on the setting time of fly ash-based geopolymer. Increasing the ratio of NaOH : FA, the setting time of geopolymer was also increased. Class C fly ash-based geopolymer has setting time shorter than class F fly ash-based geopolymer.

6. The XRD investigation on fly ash-based geopolymers revealed that this material consist of amorphous aluminosilicate and crystalline zeolite. SEM observations revealed the morphology of geopolymer matrix (amorphous aluminosilicate) in conjunction with grains of unreacted fly ash, pores and cracks.

7. The microstructure of geopolymer mixed with class C fly ash and class F fly ash produced low-density but high porous geopolymer with an increase of Sol : FA ratio.

Recommendation

1. Different class, batch, source and properties of fly ashes should be considered. Fly ash is effective in enhancing the compressive strength and reducing the requirements of alkaline solution. Three features have been noted in this thesis, its finer particles, higher surface area and higher content of aluminium to form Si-O-Al bonds in the resultant Geopolymer binder, since Al is liberated from Geopolymer gel resulting in the destruction of Si-O-Al bonds. In other words, there could be a relationship between the Si:Al ratio of the resultant geopolymer.

2. The inclusion of calcium from fly ash into geopolymer precursors in order to produce geopolymer cements deserves an in-depth study. This is expected to create calcium-aluminosilicate, which can act as a binding phase in geopolymeric systems. It is still not clear whether this binding phase will create stronger bonds in geopolymer matrix.

3. Investigate the reaction kinetics in order to enable identification of the optimum parameters, such as desired content of the most important oxides in starting material, aging period, phase identification and final properties acquired.

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APPENDIX

Appendix Table 1 Mixed design of fly ash-based geopolymer

Mix No.	Designation	NaOH (gram)	Na_2SiO_3 (gram)	Fly ash (gram)	Solution : FA Ratio
1	Type C-FA-1	750	750	3500	30 : 70
2	Type C-FA-2	1000	1000	3000	40 : 60
3	Type C-FA-3	1250	1250	2500	50 : 50
4	Type C-FA-4	1500	1500	2000	60 : 40
5	Type C-FA-5	1750	1750	1500	70 : 30
6	Type F-FB-1	750	750	3500	30 : 70
7	Type F-FB-2	1000	1000	3000	40 : 60
8	Type F-FB-3	1250	1250	2500	50 : 50
9	Type F-FB-4	1500	1500	2000	60 : 40
10	Type F-FB-5	1750	1750	1500	70 : 30

Appendix Table 2 Result of dissolution ions test

NaOH : Fly Ash Ratio	Dissolution Silica ion (mg/L)		Dissolution Alumina ion (mg/L)		Dissolution Calcium ion (mg/L)	
	Class C Fly ash	Class F Fly ash	Class C Fly ash	Class F Fly ash	Class C Fly ash	Class F Fly ash
0.21	21.57	39.12	6.44	17.11	254.80	165.00
0.33	57.47	76.28	9.27	19.85	54.96	26.82
0.50	90.12	100.80	11.65	26.94	32.71	23.35
0.75	119.30	110.40	25.49	50.94	43.05	29.53
1.17	107.60	99.36	22.99	34.98	23.21	19.08

Appendix Table 3 Result of compressive strength testing for geopolymer mixed with class C fly ash and Sol : FA ratio of 0.43

Age (days)	Sample No.	Height (cm.)	Dia. (cm.)	Weight (kg.)	Area (cm^2)	Load (kg.)	Compressive strength (ksc)	Average (ksc)
	1	8.04	4.30	224.30	14.53	1425	98.09	
1	2	8.02	4.30	225.70	14.53	1525	104.97	99.03
	3	8.00	4.43	230.60	15.42	1450	94.04	
	1	8.00	4.32	223.10	14.66	1800	122.76	
3	2	7.83	4.30	221.90	14.53	1825	125.62	125.24
	3	8.13	4.30	225.50	14.53	1850	127.34	
	1	8.00	4.34	230.30	14.80	2675	180.75	
7	2	7.02	4.34	230.90	14.80	2625	177.37	179.03
	3	8.02	4.30	222.70	14.53	2600	178.97	
	1	8.00	4.30	375.00	14.53	3750	258.12	
14	2	8.00	4.30	375.00	14.53	3750	258.12	259.27
	3	8.00	4.30	38.00	14.53	3800	261.57	
	1	8.00	4.30	228.30	14.53	5000	344.17	
28	2	8.00	4.30	229.50	14.53	5000	344.17	344.17
	3	8.00	4.30	232.20	14.53	5000	344.17	

Appendix Table 4 Result of compressive strength testing for geopolymer mixed with class F fly ash and Sol : FA ratio of 0.43

Age (days)	Sample No.	Height (cm.)	Dia. (cm.)	Weight (kg.)	Area (cm^2)	Load (kg.)	Compressive strength (ksc)	Average (ksc)
	1	8.10	4.30	224.10	14.53	1200	82.60	
1	2	7.94	4.30	222.10	14.53	1100	75.72	75.72
	3	8.10	4.30	225.50	14.53	1000	68.83	
	1	8.03	4.30	223.00	14.53	1475	101.53	
3	2	8.00	4.34	229.10	14.80	1550	104.73	106.61
	3	7.92	4.30	221.10	14.53	1650	113.57	
	1	7.92	4.30	222.50	14.53	2450	168.64	
7	2	8.20	4.30	227.30	14.53	2500	172.08	169.88
	3	7.90	4.34	226.00	14.80	2500	168.93	
	1	7.90	4.30	221.20	14.53	3125	215.10	
14	2	8.00	4.30	224.30	14.53	3200	220.27	219.69
	3	8.00	4.30	224.80	14.53	3250	223.71	
	1	8.00	4.30	225.60	14.53	3725	256.40	
28	2	8.00	4.30	226.30	14.53	3800	261.57	258.12
	3	8.00	4.30	224.20	14.53	3725	256.40	

Appendix Table 5 Result of compressive strength testing for geopolymer mixed with class C fly ash and Sol : FA ratio of 0.67

Age (days)	Sample No.	Height (cm.)	Dia. (cm.)	Weight (kg.)	Area (cm^2)	Load (kg.)	Compressive strength (ksc)	Average (ksc)
1	1	7.52	4.42	219.60	15.35	1000	65.15	74.05
	2	7.54	4.32	217.80	14.66	1075	73.31	
	3	7.44	4.36	216.20	14.94	1250	83.69	
3	1	7.62	4.42	218.30	15.35	1500	97.72	101.36
	2	7.62	4.42	217.80	15.35	1550	100.98	
	3	7.72	4.43	218.60	15.42	1625	105.39	
7	1	7.63	4.44	214.50	15.49	2400	154.95	156.97
	2	7.90	4.42	223.80	15.35	2500	162.87	
	3	7.83	4.42	221.10	15.35	2350	153.09	
14	1	7.80	4.43	221.10	15.42	3000	194.56	195.10
	2	7.63	4.43	218.20	15.42	2900	188.07	
	3	7.70	4.43	219.60	15.42	3125	202.66	
28	1	7.80	4.30	219.40	14.53	4700	323.52	311.47
	2	8.00	4.30	221.30	14.53	4500	309.75	
	3	7.80	4.30	218.40	14.53	4375	301.15	

Appendix Table 6 Result of compressive strength testing for geopolymer mixed with class F fly ash and Sol : FA ratio of 0.67

Age (days)	Sample No.	Height (cm.)	Dia. (cm.)	Weight (kg.)	Area (cm^2)	Load (kg.)	Compressive strength (ksc)	Average (ksc)
	1	7.60	4.40	218.40	15.21	750	49.31	
1	2	7.42	4.34	213.10	14.80	700	47.30	47.27
	3	7.54	4.36	216.00	14.94	675	45.19	
	1	7.74	4.44	219.40	15.49	1050	67.79	
3	2	7.92	4.44	218.90	15.49	1200	77.47	76.65
	3	7.63	4.42	216.70	15.35	1300	84.69	
	1	7.82	4.42	221.00	15.35	1825	118.89	
7	2	7.84	4.42	222.30	15.35	1875	122.15	123.78
	3	7.75	4.42	221.80	15.35	2000	130.29	
	1	7.62	4.43	215.10	15.42	2500	162.13	
14	2	7.63	4.43	213.40	15.42	2450	158.89	159.97
	3	7.63	4.43	217.40	15.42	2450	158.89	
	1	7.62	4.30	213.20	14.53	2700	185.85	
28	2	7.63	4.30	211.40	14.53	2550	175.52	180.11
	3	7.63	4.30	213.80	14.53	2600	178.97	

Appendix Table 7 Result of compressive strength testing for geopolymer mixed with class C fly ash and Sol : FA ratio of 1.00

Age (days)	Sample No.	Height (cm.)	Dia. (cm.)	Weight (kg.)	Area (cm^2)	Load (kg.)	Compressive strength (ksc)	Average (ksc)
1	1	7.74	4.30	204.40	14.53	775	53.35	54.55
	2	7.44	4.32	204.60	14.66	825	56.26	
	3	7.54	4.34	206.30	14.80	800	54.06	
3	1	7.80	4.30	197.30	14.53	950	65.39	71.64
	2	7.72	4.42	207.30	15.35	1200	78.18	
	3	7.80	4.43	203.10	15.42	1100	71.34	
7	1	7.72	4.42	206.60	15.35	1250	81.43	90.53
	2	7.72	4.42	206.00	15.35	1525	99.35	
	3	7.71	4.43	206.20	15.42	1400	90.79	
14	1	8.00	4.43	208.80	15.42	1800	116.73	109.00
	2	8.00	4.43	182.50	15.42	1650	107.01	
	3	8.00	4.30	181.20	14.53	1500	103.25	
28	1	8.00	4.30	184.30	14.53	2400	165.20	159.46
	2	8.00	4.30	185.60	14.53	2200	151.43	
	3	8.00	4.30	184.80	14.53	2350	161.76	

Appendix Table 8 Result of compressive strength testing for geopolymer mixed with class F fly ash and Sol : FA ratio of 1.00

Age (days)	Sample No.	Height (cm.)	Dia. (cm.)	Weight (kg.)	Area (cm^2)	Load (kg.)	Compressive strength (ksc)	Average (ksc)
1	1	7.54	4.34	199.50	14.80	650	43.92	40.54
	2	7.64	4.34	206.60	14.80	550	37.16	
	3	7.70	4.34	206.80	14.80	600	40.54	
3	1	7.50	4.42	200.00	15.35	900	58.63	64.06
	2	7.82	4.42	206.90	15.35	1050	68.40	
	3	7.60	4.42	201.20	15.35	1000	65.15	
7	1	7.84	4.36	211.00	14.94	1000	66.95	68.25
	2	7.92	4.43	210.20	15.42	1100	71.34	
	3	7.74	4.43	201.80	15.42	1025	66.47	
14	1	7.72	4.43	205.80	15.42	1100	71.34	70.36
	2	7.72	4.42	204.30	15.35	1075	70.03	
	3	7.82	4.43	200.20	15.42	1075	69.72	
28	1	7.90	4.30	203.10	14.53	1000	68.83	68.26
	2	7.90	4.30	204.20	14.53	1025	70.55	
	3	7.90	4.30	203.50	14.53	950	65.39	

Appendix Table 9 Result of compressive strength testing for geopolymer mixed with class C fly ash and Sol : FA ratio of 1.50

Age (days)	Sample No.	Height (cm.)	Dia. (cm.)	Weight (kg.)	Area (cm^2)	Load (kg.)	Compressive strength (ksc)	Average (ksc)
1	1	7.90	4.30	195.30	14.53	100	6.88	8.28
	2	7.84	4.22	194.50	13.99	125	8.93	
	3	7.70	4.20	184.30	13.86	125	9.02	
3	1	7.84	4.42	197.70	15.35	150	9.77	8.25
	2	7.81	4.43	196.40	15.42	125	8.11	
	3	8.02	4.30	189.90	14.53	100	6.88	
7	1	7.92	4.30	185.00	14.53	200	13.77	12.00
	2	7.72	4.30	183.00	14.53	125	8.60	
	3	7.83	4.32	190.60	14.66	200	13.64	
14	1	7.81	4.30	184.70	14.53	325	22.37	22.37
	2	7.81	4.30	191.80	14.53	300	20.65	
	3	7.83	4.30	182.40	14.53	350	24.09	
28	1	7.83	4.30	180.20	14.53	550	37.86	43.02
	2	7.82	4.30	181.40	14.53	600	41.30	
	3	7.84	4.30	186.40	14.53	725	49.90	

Appendix Table 10 Result of compressive strength testing for geopolymer mixed with class F fly ash and Sol : FA ratio of 1.50

Age (days)	Sample No.	Height (cm.)	Dia. (cm.)	Weight (kg.)	Area (cm^2)	Load (kg.)	Compressive strength (ksc)	Average (ksc)
1	1	7.60	4.20	182.10	13.86	50	3.61	3.61
	2	7.84	4.20	188.00	13.86	75	5.41	
	3	7.44	4.20	180.70	13.86	25	1.80	
3	1	7.30	4.44	179.70	15.49	70	4.52	4.64
	2	7.64	4.43	189.70	15.42	75	4.86	
	3	7.82	4.43	198.20	15.42	70	4.54	
7	1	8.03	4.30	188.60	14.53	125	8.60	9.18
	2	7.62	4.30	180.30	14.53	150	10.32	
	3	7.94	4.30	188.80	14.53	125	8.60	
14	1	7.81	4.43	185.90	15.42	250	16.21	17.45
	2	7.82	4.30	182.40	14.53	250	17.21	
	3	7.82	4.30	181.90	14.53	275	18.93	
28	1	7.71	4.30	180.20	14.53	300	20.65	20.65
	2	7.72	4.30	181.30	14.53	300	20.65	
	3	7.72	4.30	179.40	14.53	300	20.65	

Appendix Table 11 Result of compressive strength testing for geopolymer mixed with class C fly ash and Sol : FA ratio of 2.33

Age (days)	Sample No.	Height (cm.)	Dia. (cm.)	Weight (kg.)	Area (cm^2)	Load (kg.)	Compressive strength (ksc)	Average (ksc)
1	1	8.20	4.20	175.20	13.86	0	0.00	0.00
	2	8.20	4.20	174.30	13.86	0	0.00	
	3	8.20	4.20	176.20	13.86	0	0.00	
3	1	8.20	4.20	174.30	13.86	0	0.00	0.00
	2	8.20	4.20	172.10	13.86	0	0.00	
	3	8.20	4.20	172.60	13.86	0	0.00	
7	1	8.20	4.20	174.30	13.86	75	5.41	4.81
	2	8.20	4.20	172.40	13.86	50	3.61	
	3	8.20	4.20	173.40	13.86	75	5.41	
14	1	8.20	4.20	172.50	13.86	75	5.41	6.61
	2	8.20	4.20	172.80	13.86	100	7.22	
	3	8.20	4.20	173.20	13.86	100	7.22	
28	1	8.20	4.20	172.30	13.86	225	16.23	15.63
	2	8.20	4.20	173.60	13.86	200	14.43	
	3	8.20	4.20	173.40	13.86	225	16.23	

Appendix Table 12 Result of compressive strength testing for geopolymer mixed with class F fly ash and Sol : FA ratio of 2.33

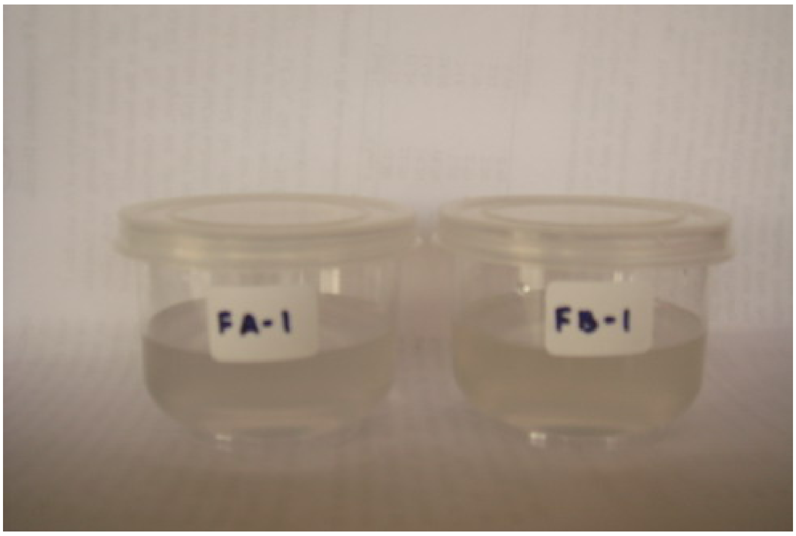
Age (days)	Sample No.	Height (cm.)	Dia. (cm.)	Weight (kg.)	Area (cm^2)	Load (kg.)	Compressive strength (ksc)	Average (ksc)
	1	8.20	4.20	170.40	13.86	0	0.00	
1	2	8.20	4.20	171.20	13.86	0	0.00	0.00
	3	8.20	4.20	170.30	13.86	0	0.00	
	1	8.20	4.20	170.40	13.86	0	0.00	
3	2	8.20	4.20	172.50	13.86	0	0.00	0.00
	3	8.20	4.20	174.20	13.86	0	0.00	
	1	8.20	4.20	175.60	13.86	50	3.61	
7	2	8.20	4.20	173.40	13.86	50	3.61	3.61
	3	8.20	4.20	170.30	13.86	50	3.61	
	1	8.20	4.20	172.10	13.86	75	5.41	
14	2	8.20	4.20	174.20	13.86	75	5.41	5.41
	3	8.20	4.20	170.30	13.86	75	5.41	
	1	8.20	4.20	172.30	13.86	125	9.02	
28	2	8.20	4.20	170.00	13.86	150	10.82	10.22
	3	8.20	4.20	171.30	13.86	150	10.82	

Appendix Figure 1 Hobart mixer.

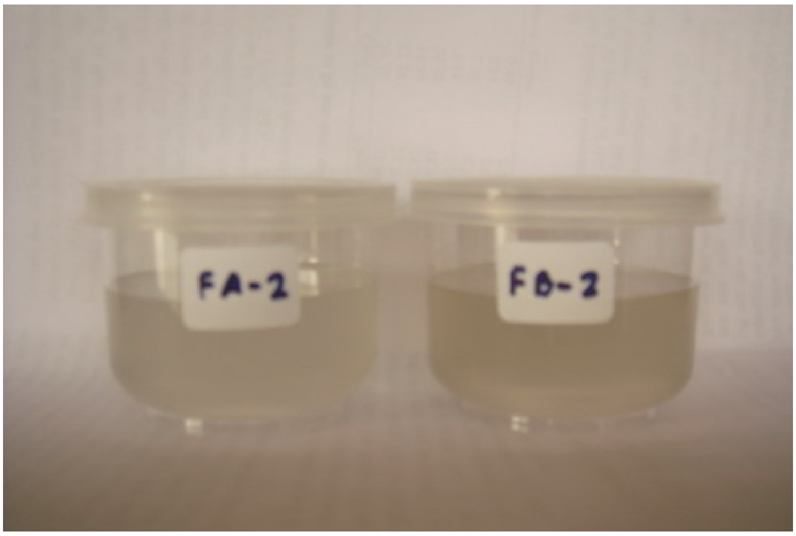
Appendix Figure 2 Specimen of fly ash – based geopolymer.

Appendix Figure 3 Dissolution test of fly ash with NaOH.

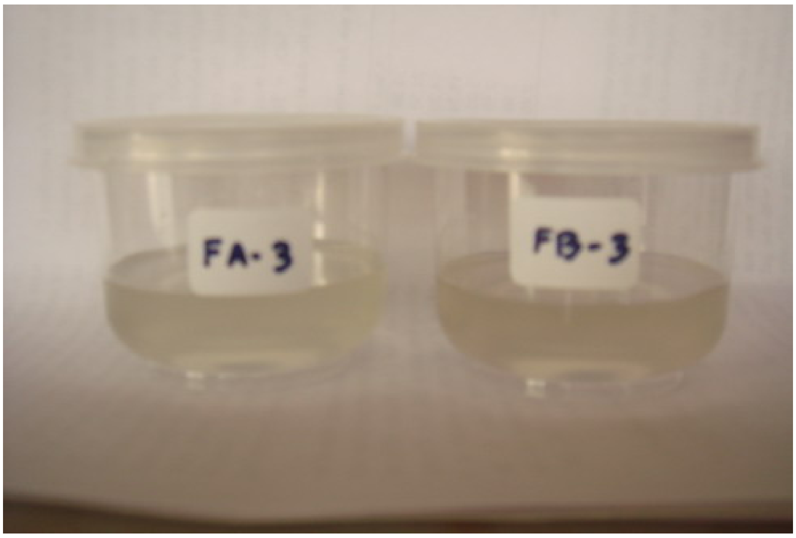
Appendix Figure 4 Example of dissolution liquid.



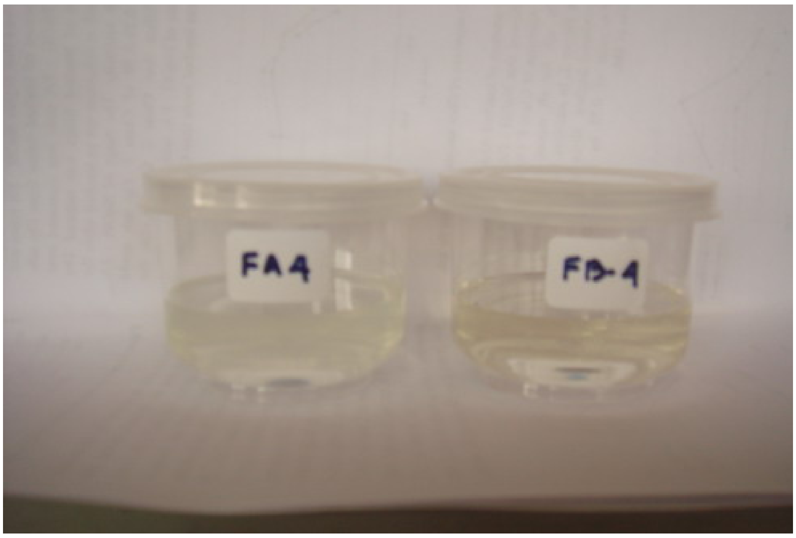
Appendix Figure 5 Result of dissolution liquid (70% FA) mixed with sodium silicate.



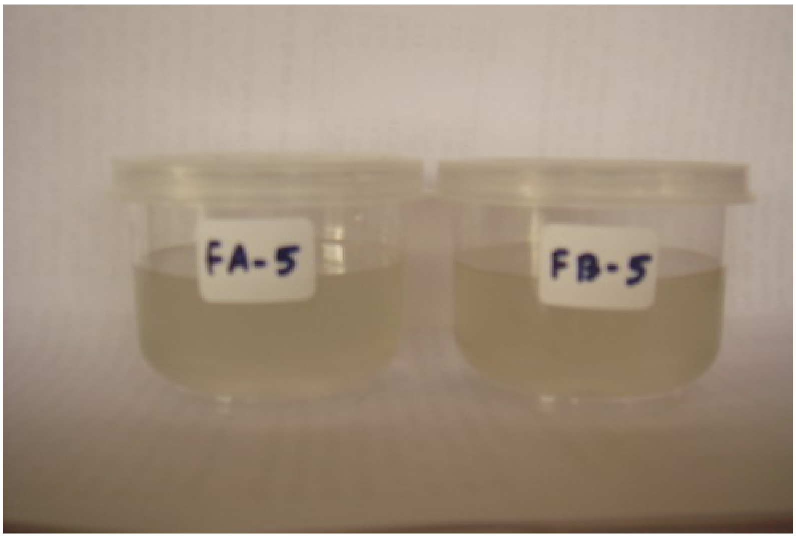
Appendix Figure 6 Result of dissolution liquid (60% FA) mixed with sodium silicate.



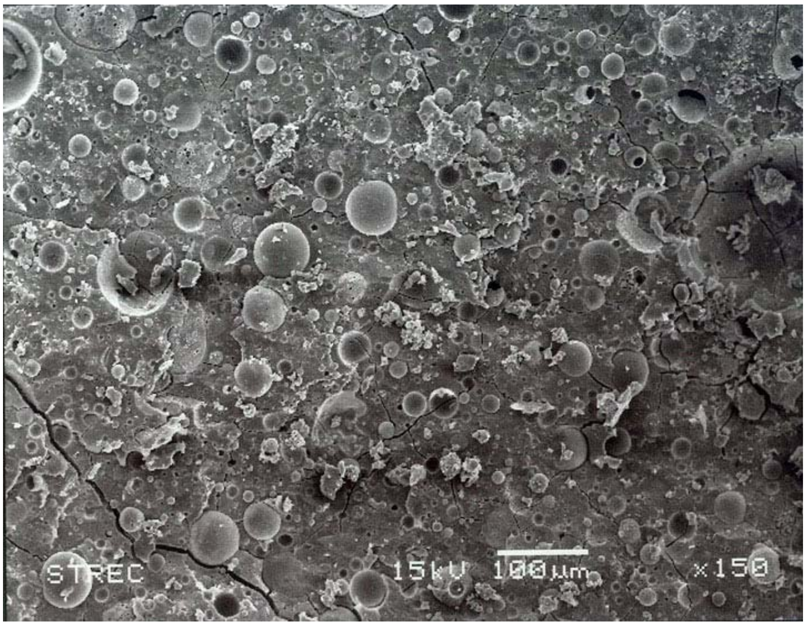
Appendix Figure 7 Result of dissolution liquid (50% FA) mixed with sodium silicate.



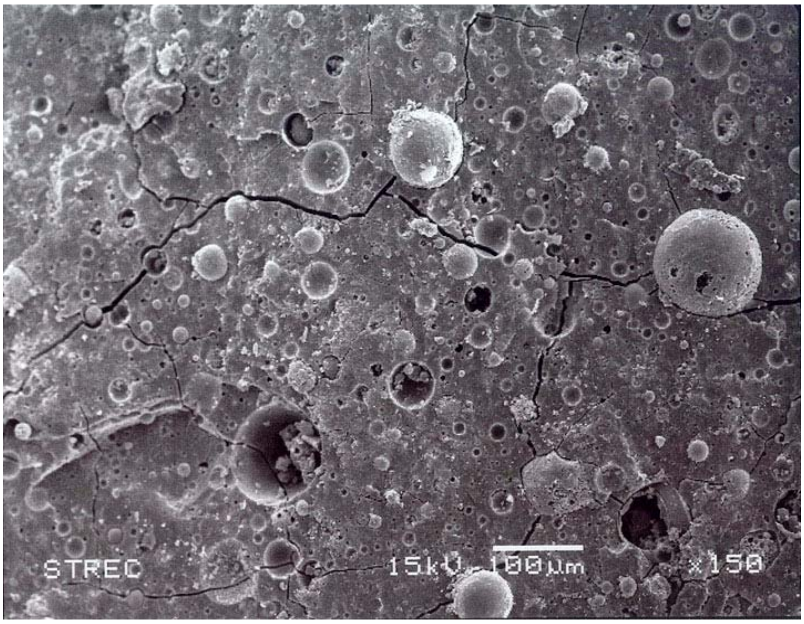
Appendix Figure 8 Result of dissolution liquid (40% FA) mixed with sodium silicate.



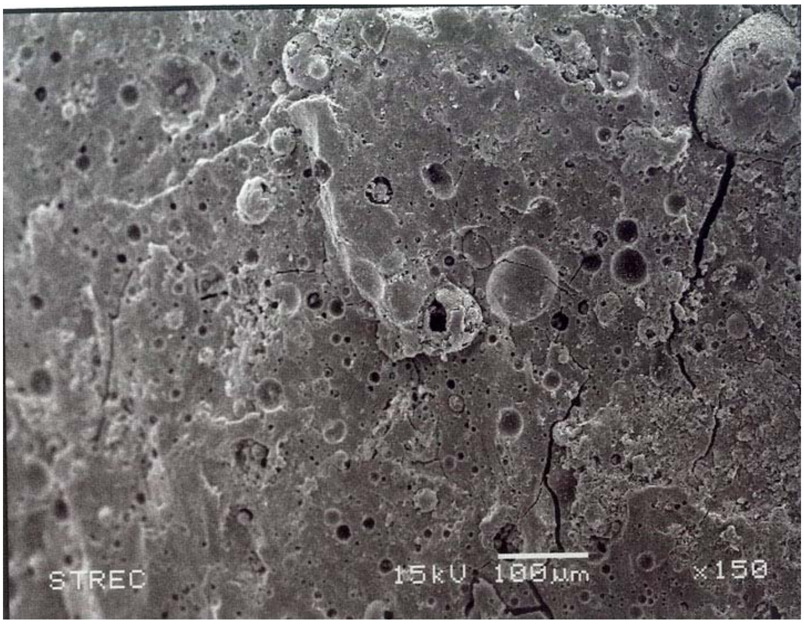
Appendix Figure 9 Result of dissolution liquid (30% FA) mixed with sodium silicate.



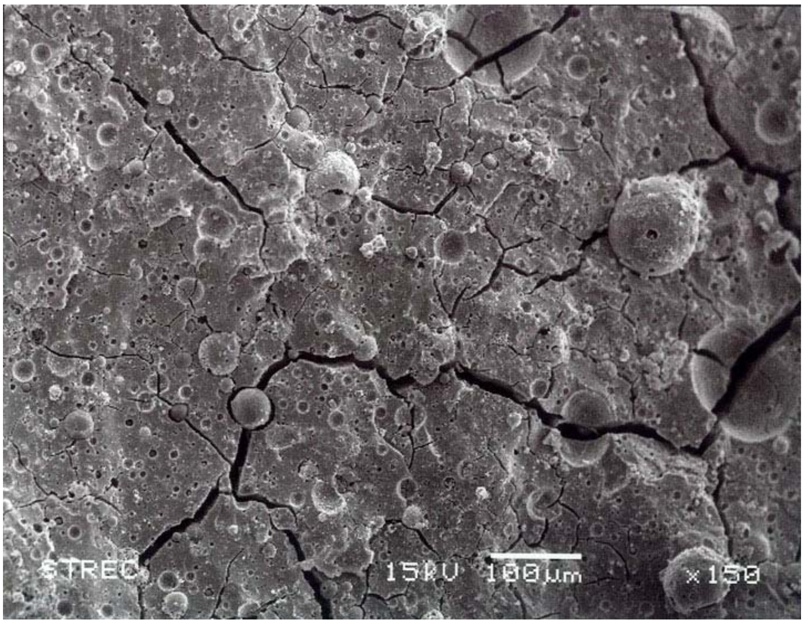
Appendix Figure 10 SEM micrographs of geopolymers with NaOH : FA class C ratio 0.21



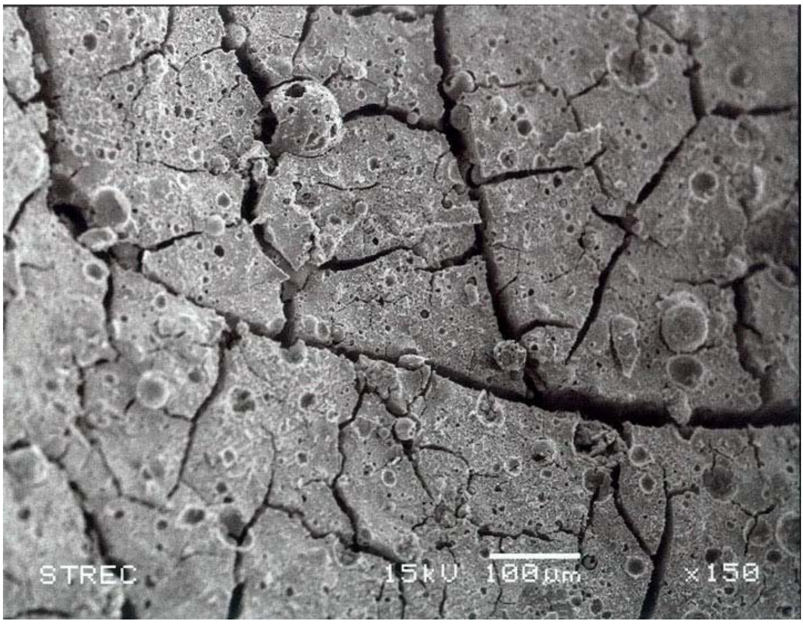
Appendix Figure 11 SEM micrographs of geopolymers with NaOH : FA class C ratio 0.33



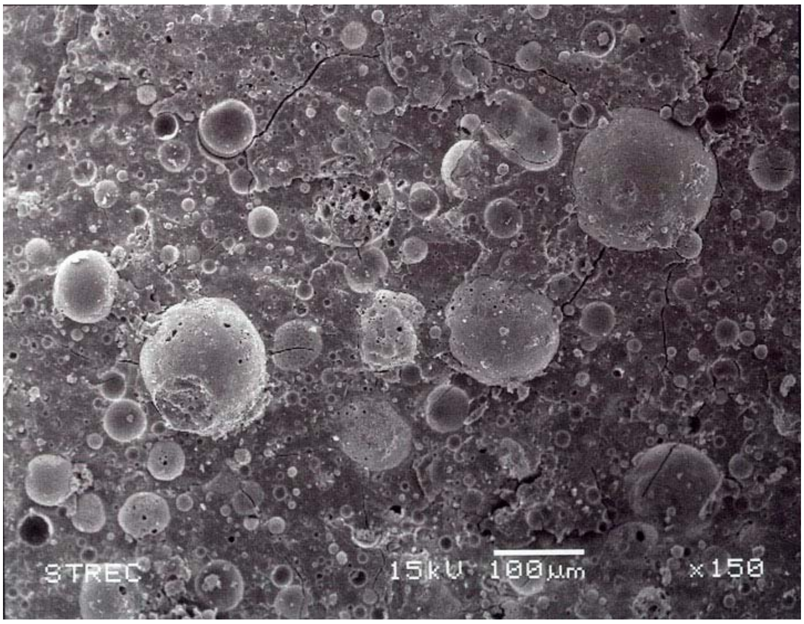
Appendix Figure 12 SEM micrographs of geopolymers with NaOH : FA class C ratio 0.50



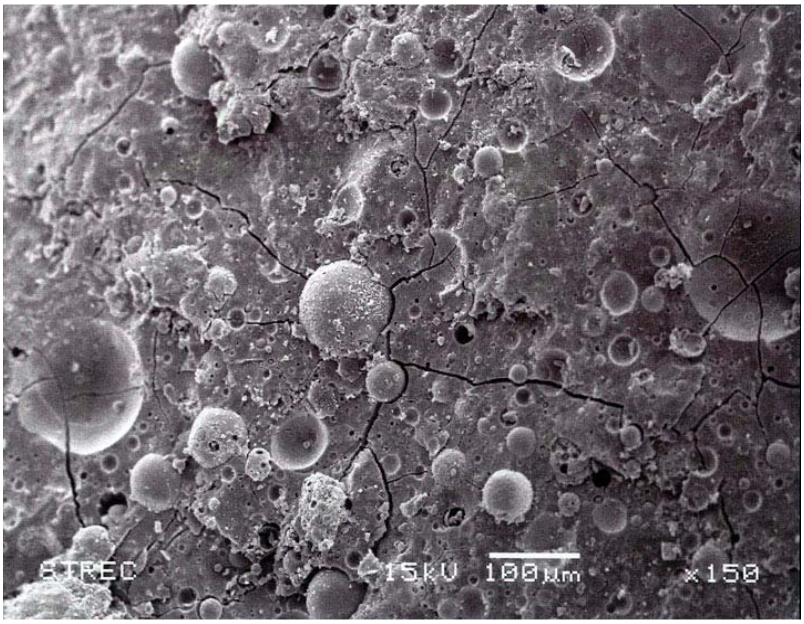
Appendix Figure 13 SEM micrographs of geopolymers with NaOH : FA class C ratio 0.75



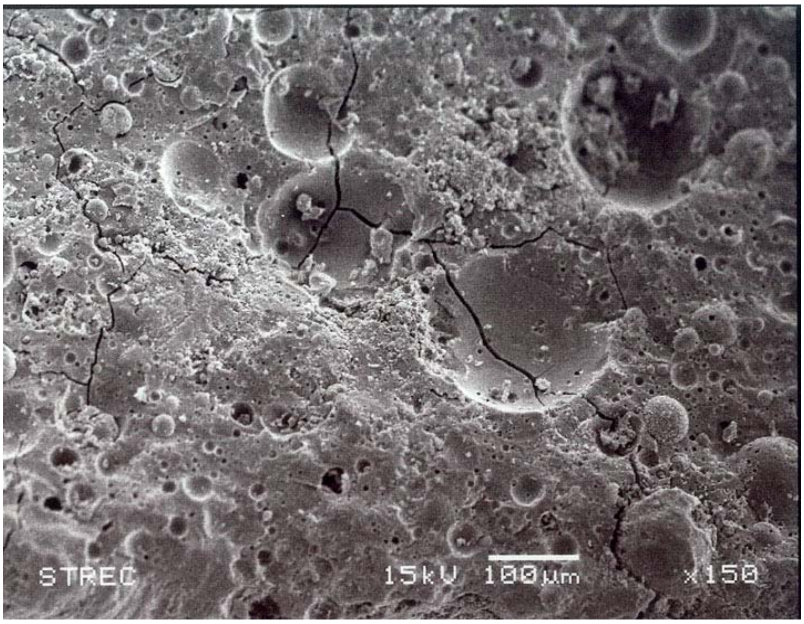
Appendix Figure 14 SEM micrographs of geopolymers with NaOH : FA class C ratio 1.17



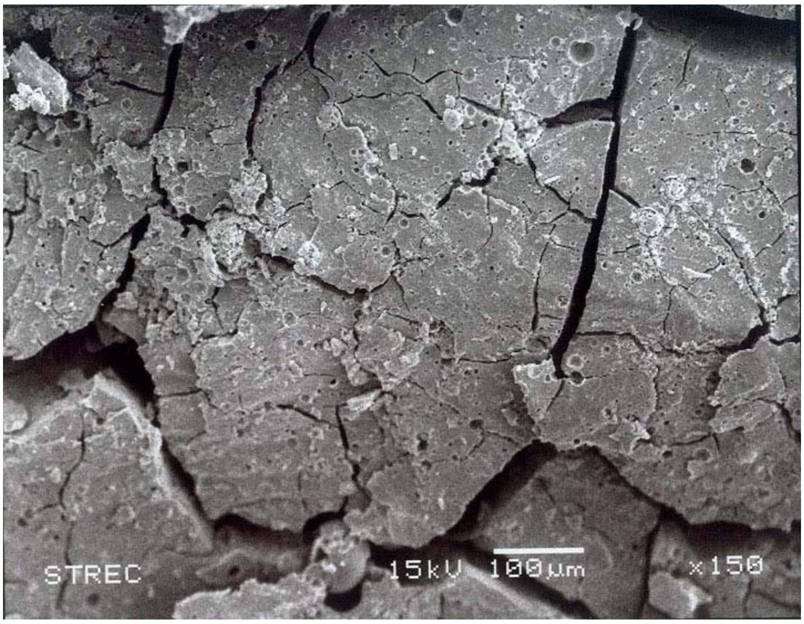
Appendix Figure 15 SEM micrographs of geopolymers with NaOH : FA class F ratio 0.21



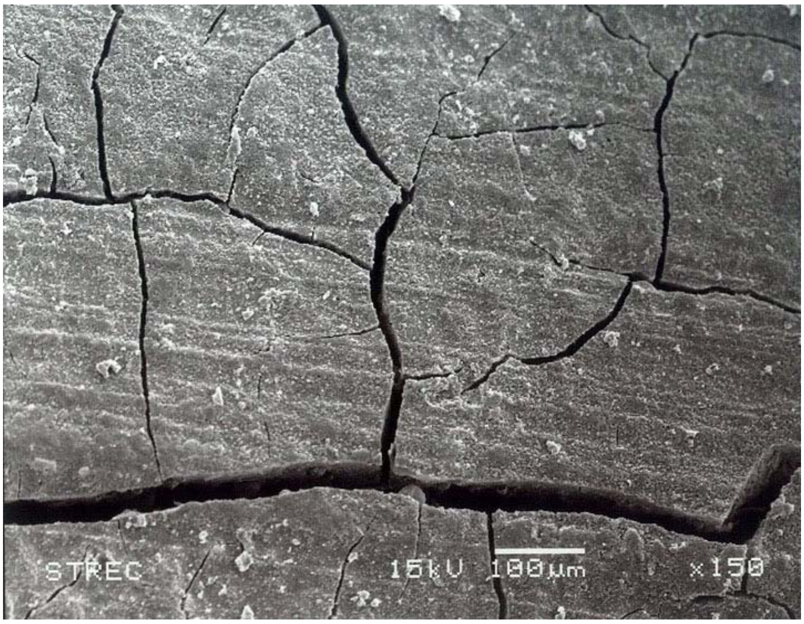
Appendix Figure 16 SEM micrographs of geopolymers with NaOH : FA class F ratio 0.33



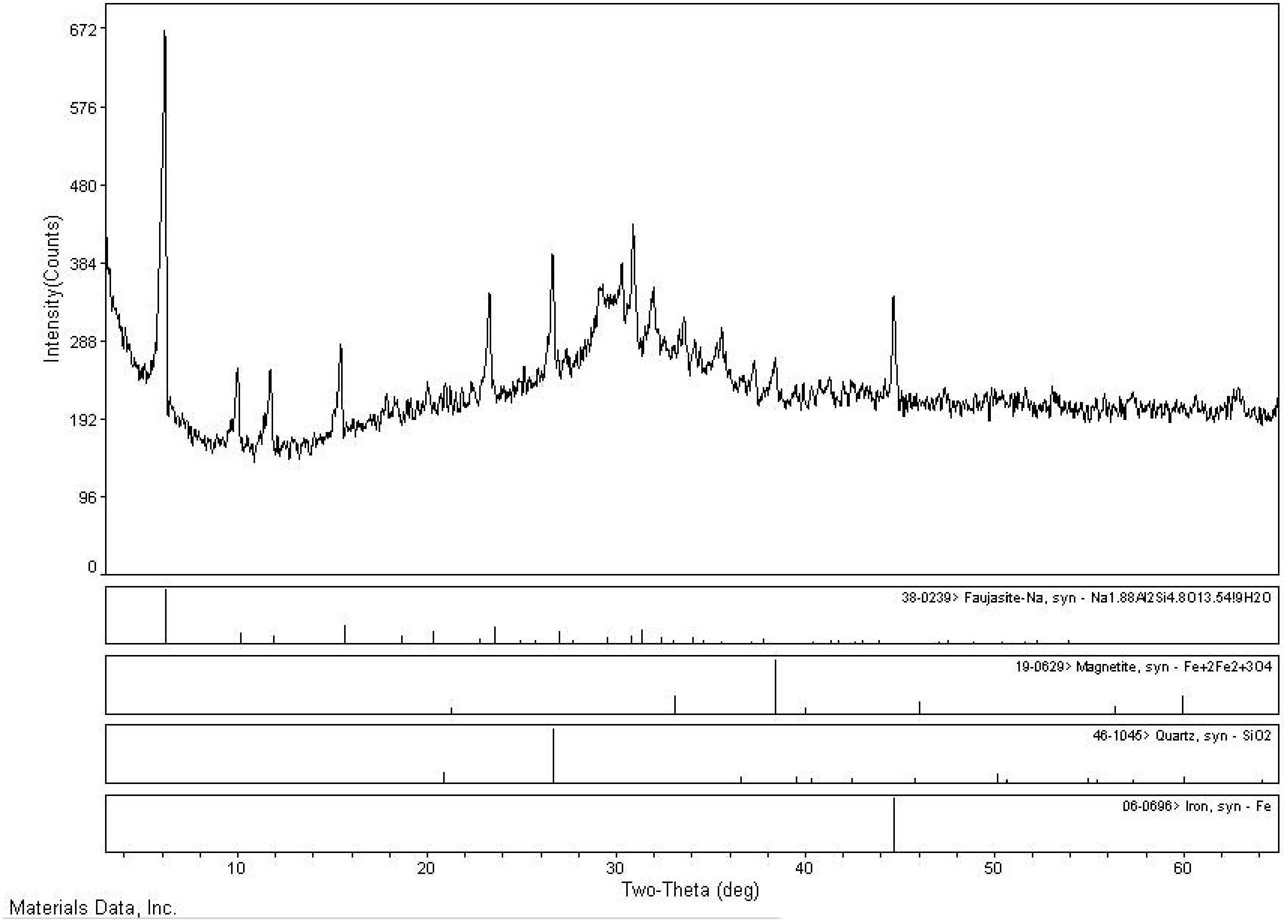
Appendix Figure 17 SEM micrographs of geopolymers with NaOH : FA class F ratio 0.50



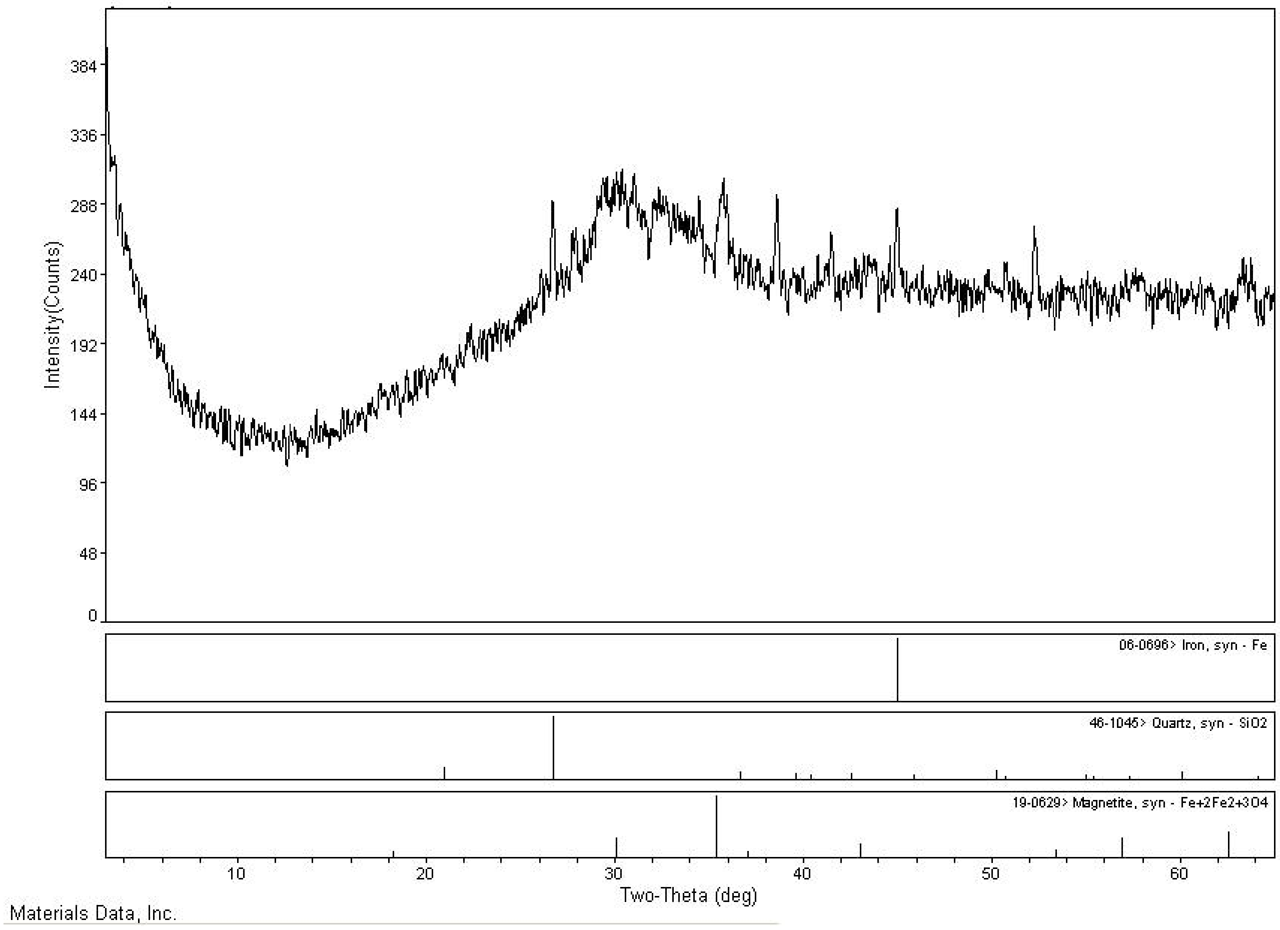
Appendix Figure 18 SEM micrographs of geopolymers with NaOH : FA class F ratio 0.75



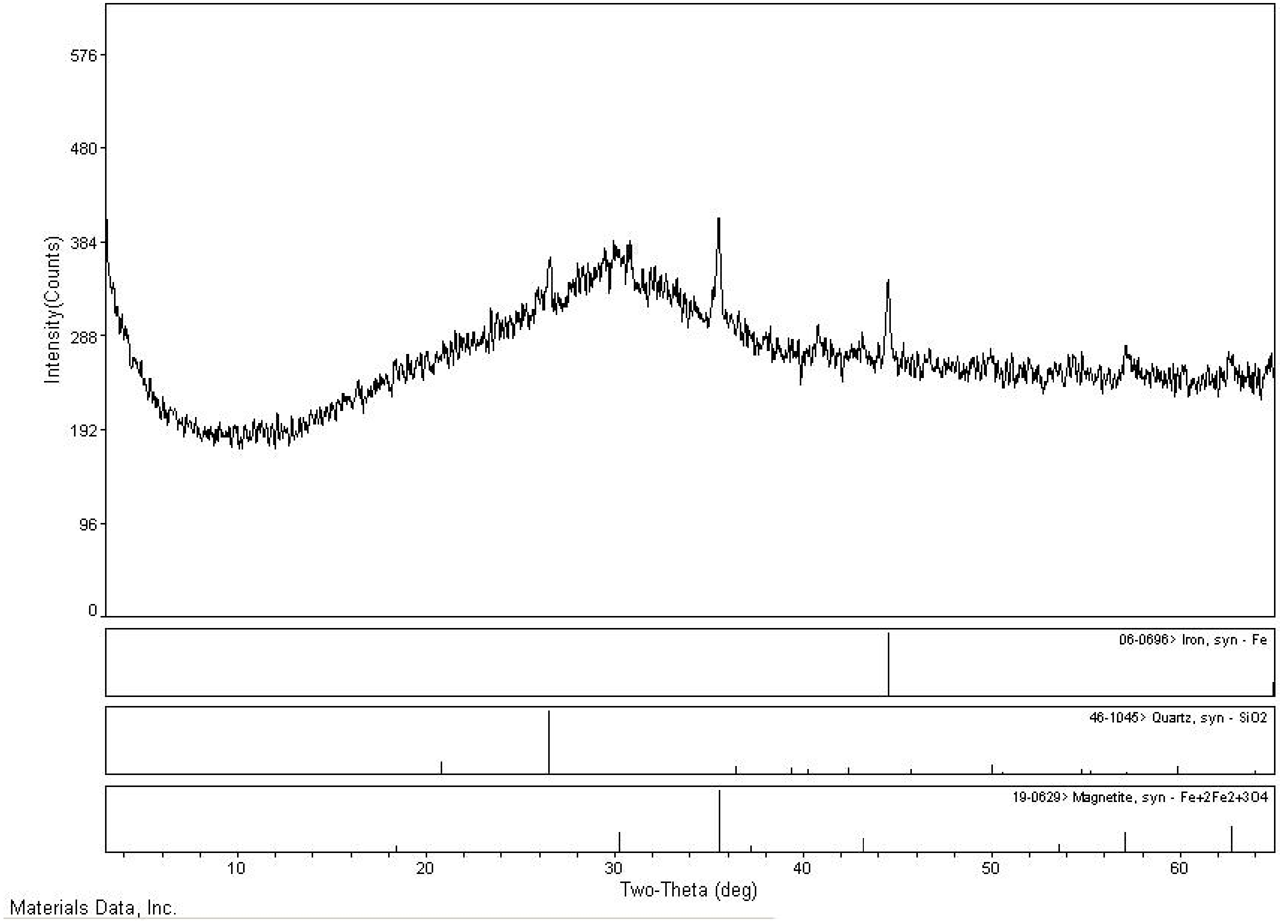
Appendix Figure 19 SEM micrographs of geopolymers with NaOH : FA class F ratio 1.17



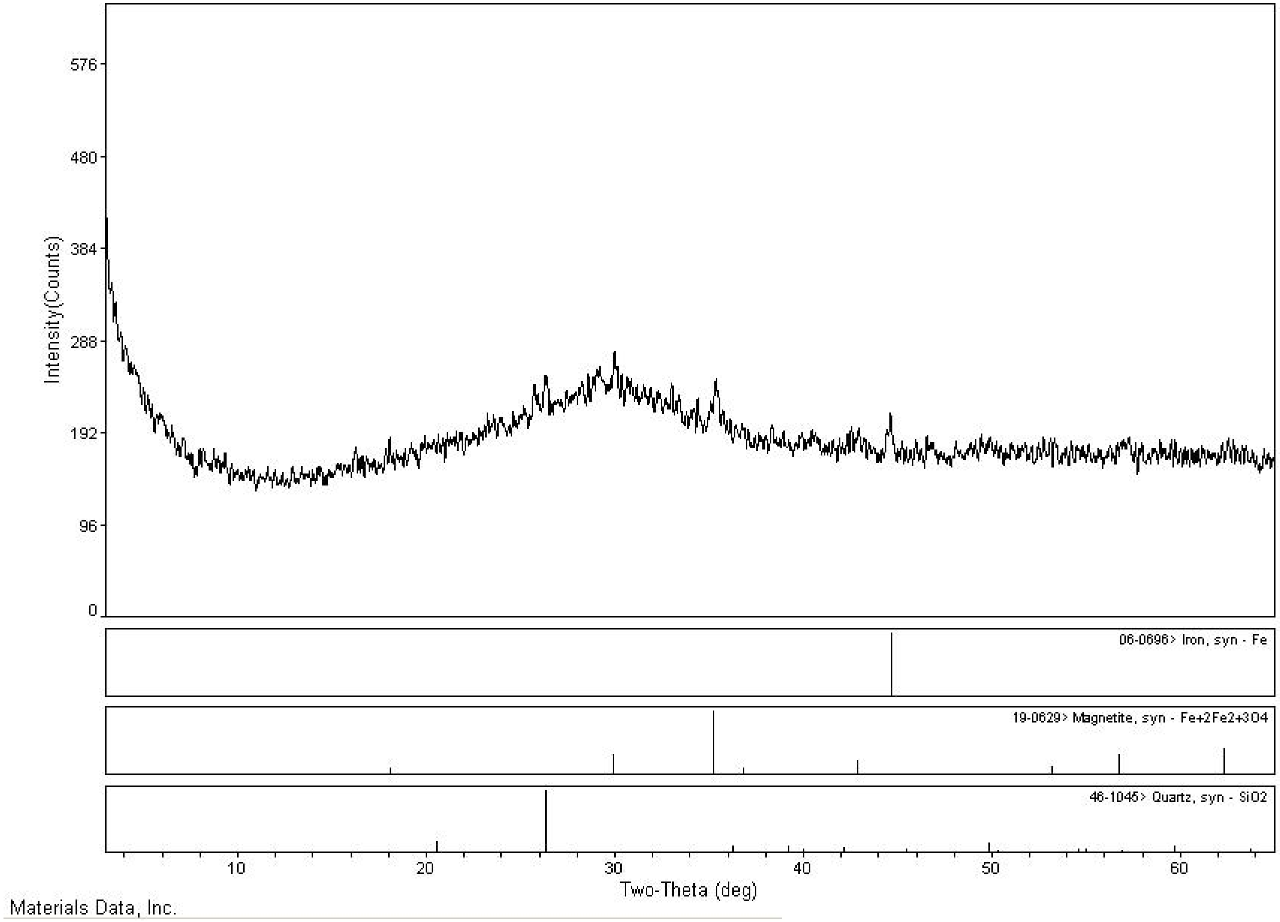
Appendix Figure 20 X-ray diffractograms of class C fly ash-based geopolymer with Sol : FA ratio 0.43



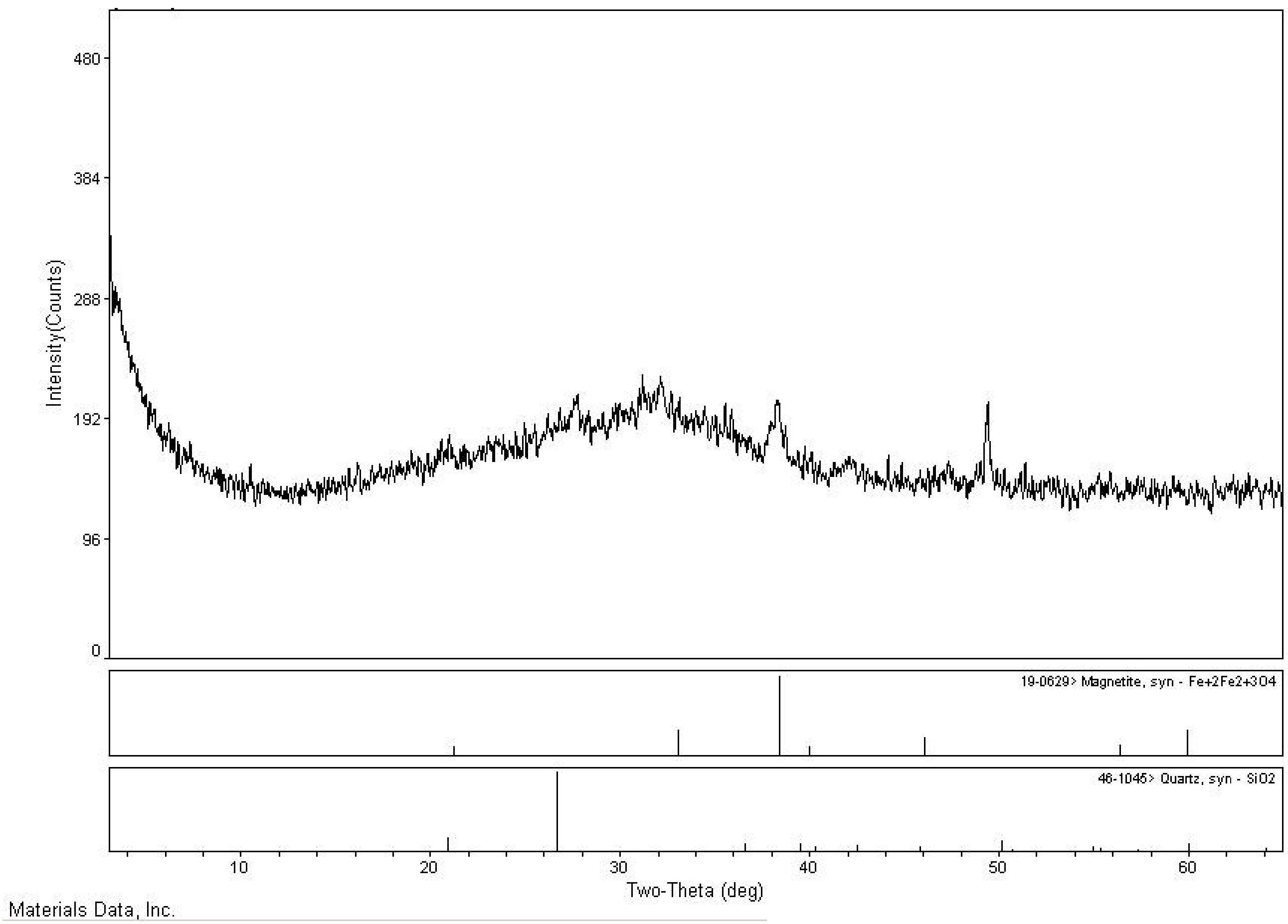
Appendix Figure 21 X-ray diffractograms of class F fly ash-based geopolymer with Sol : FA ratio 0.43



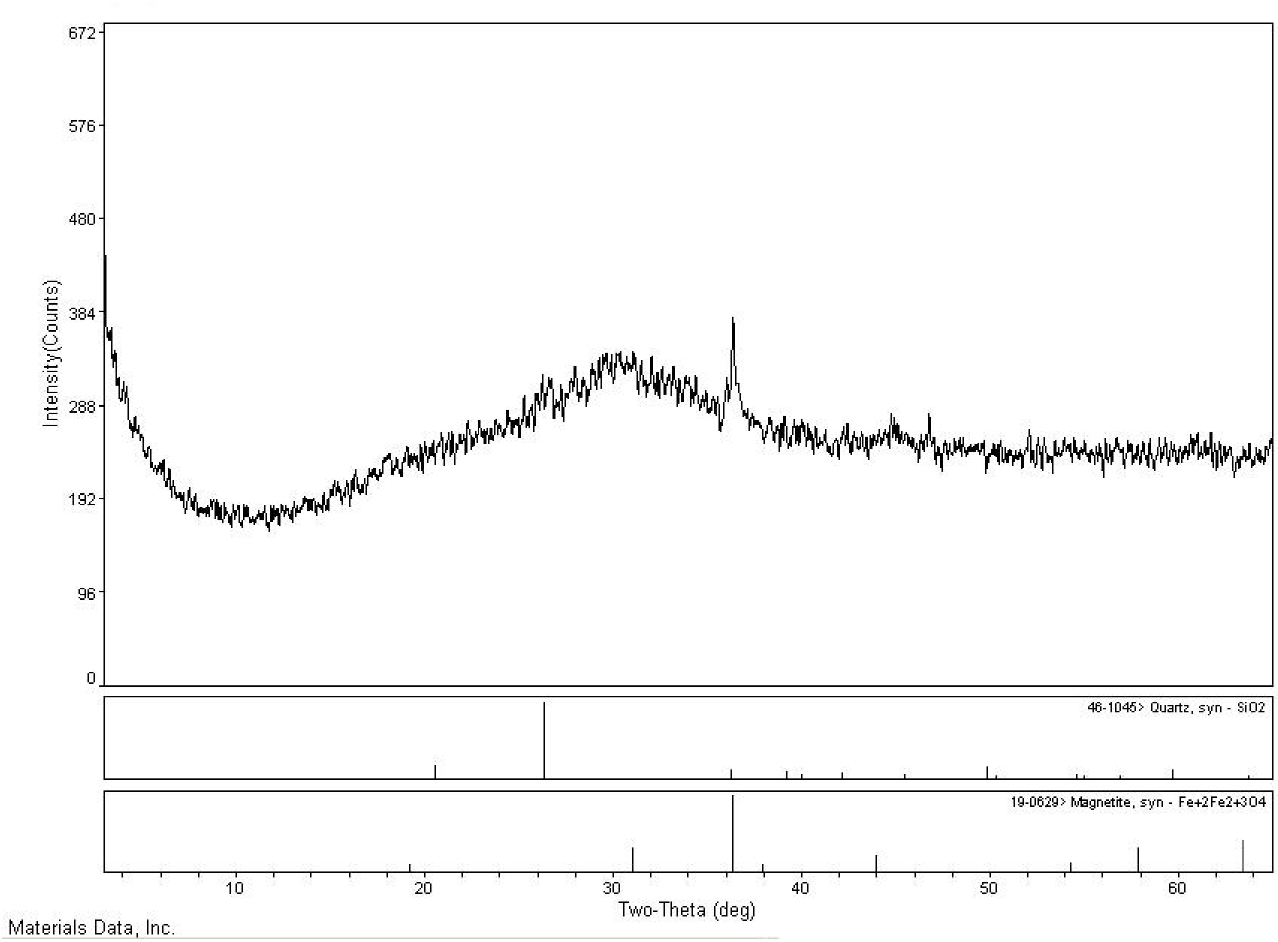
Appendix Figure 22 X-ray diffractograms of class C fly ash-based geopolymer with Sol : FA ratio 0.67



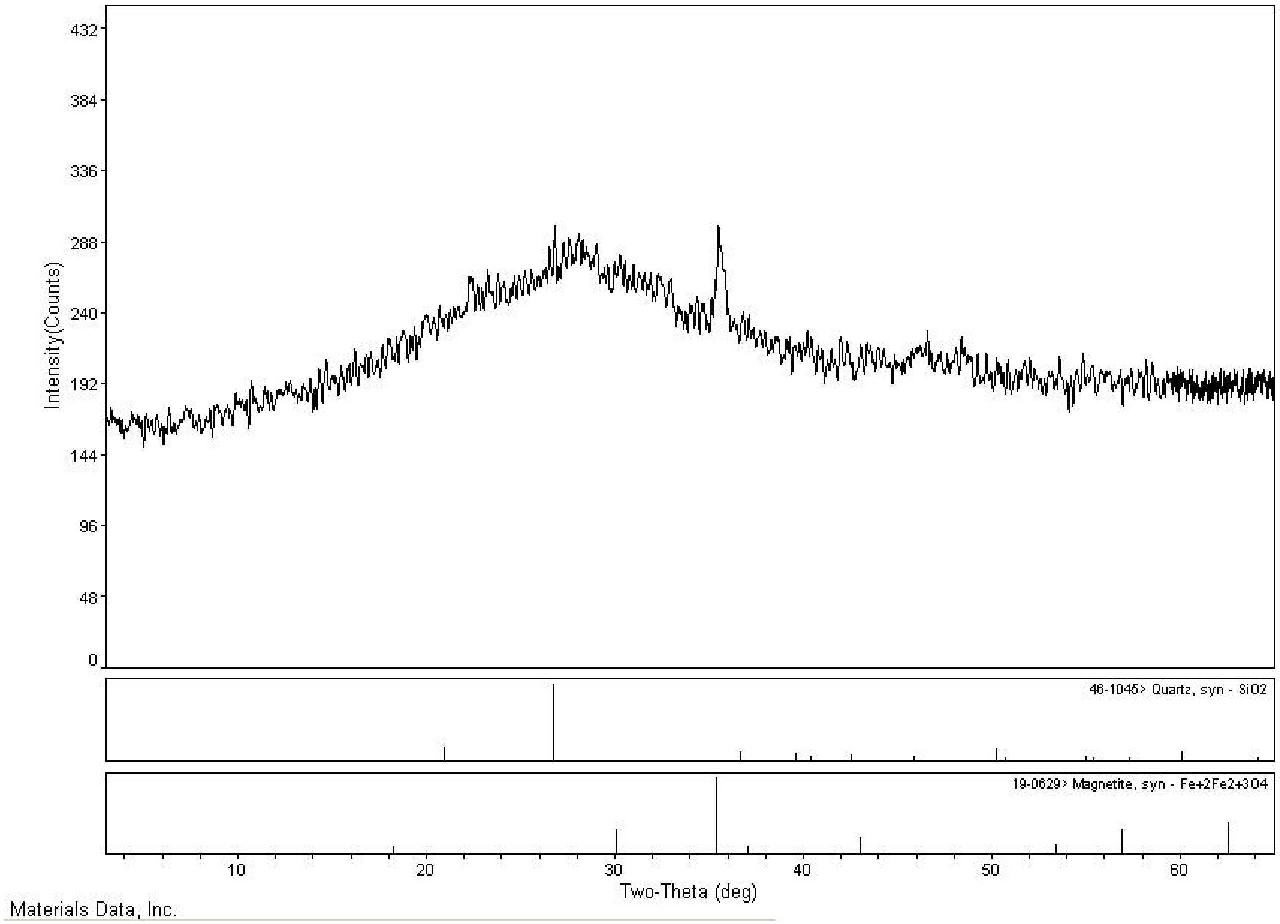
Appendix Figure 23 X-ray diffractograms of class F fly ash-based geopolymer with Sol : FA ratio 0.67



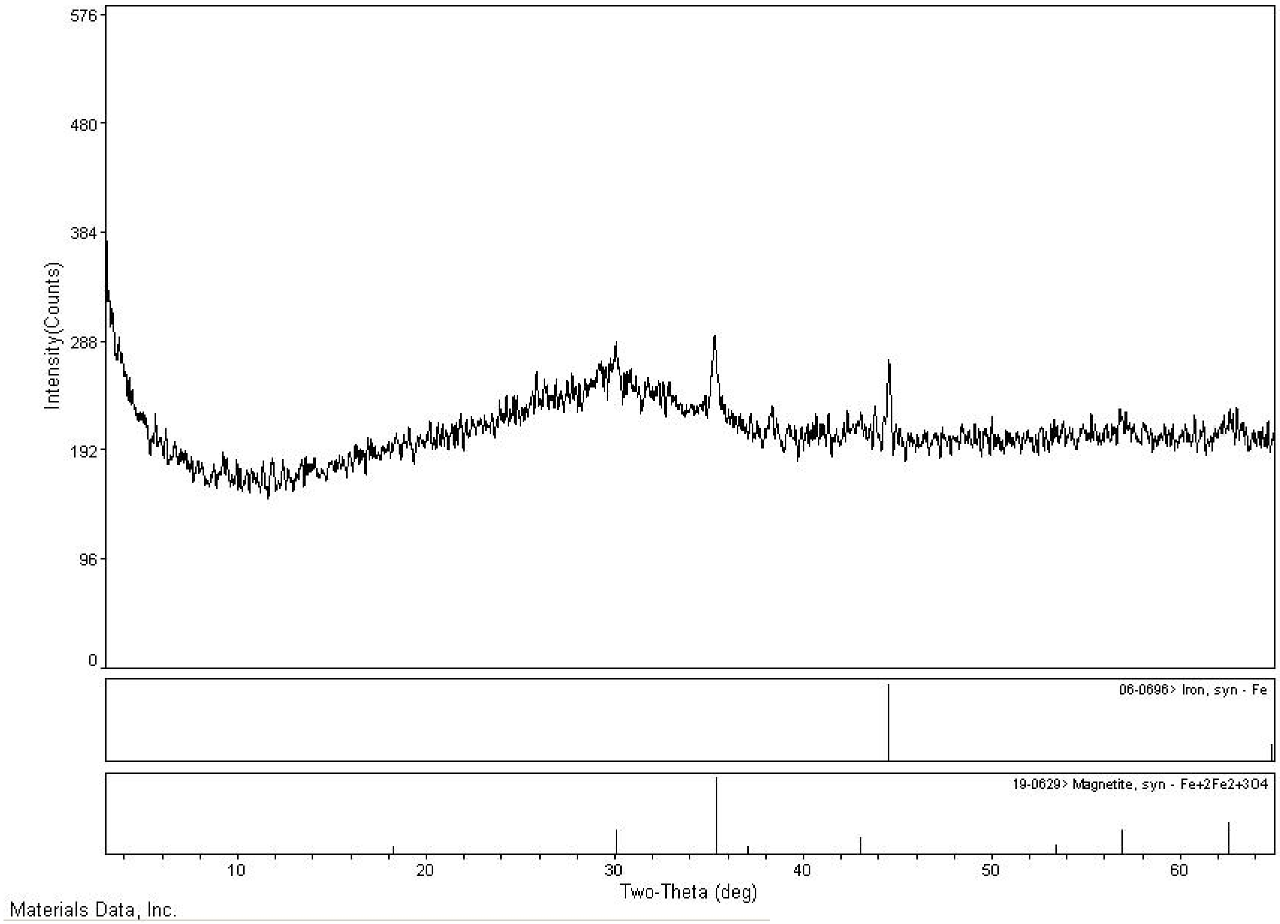
Appendix Figure 24 X-ray diffractograms of class C fly ash-based geopolymer with Sol : FA ratio 1.00



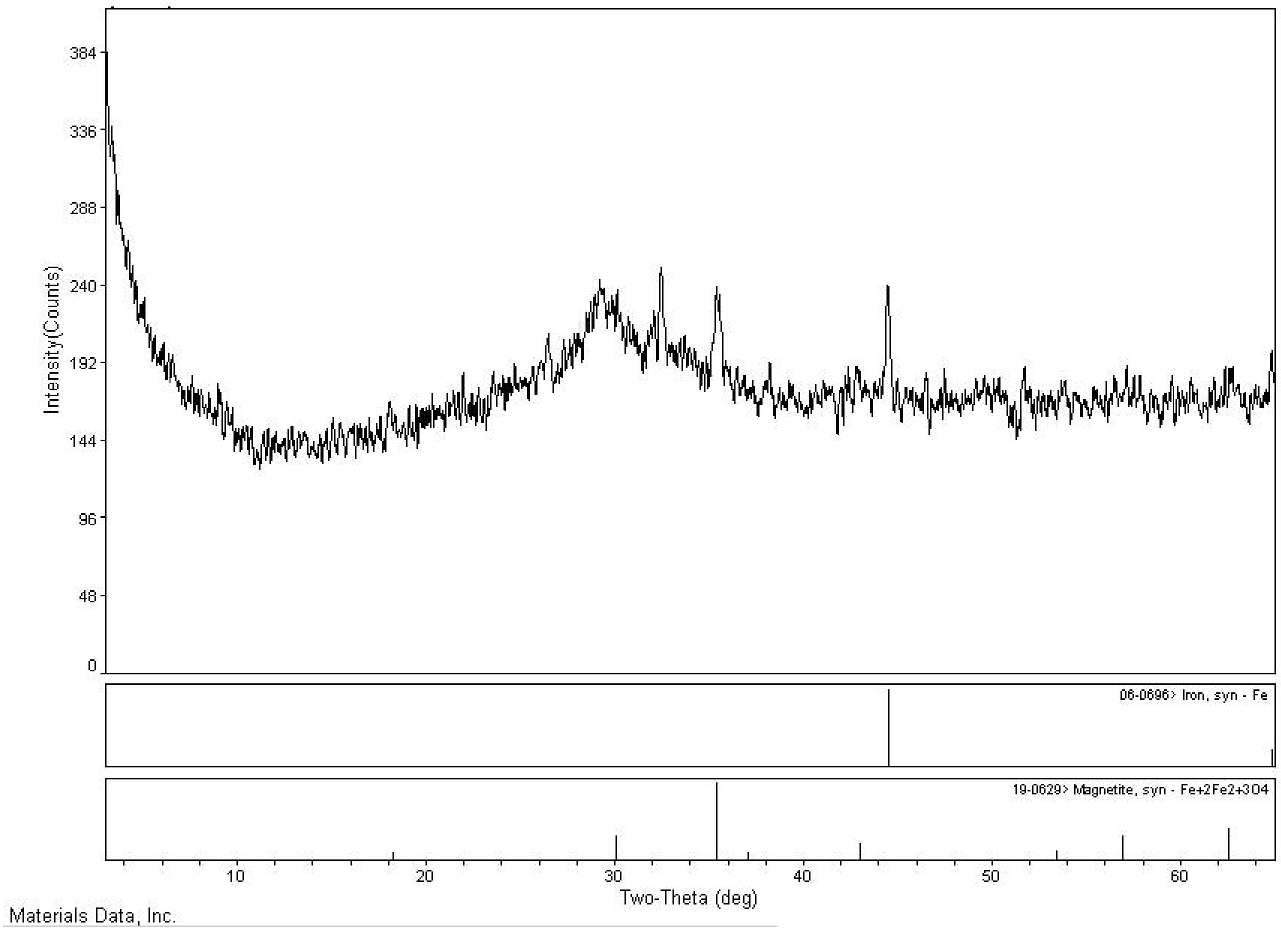
Appendix Figure 25 X-ray diffractograms of class F fly ash-based geopolymer with Sol : FA ratio 1.00



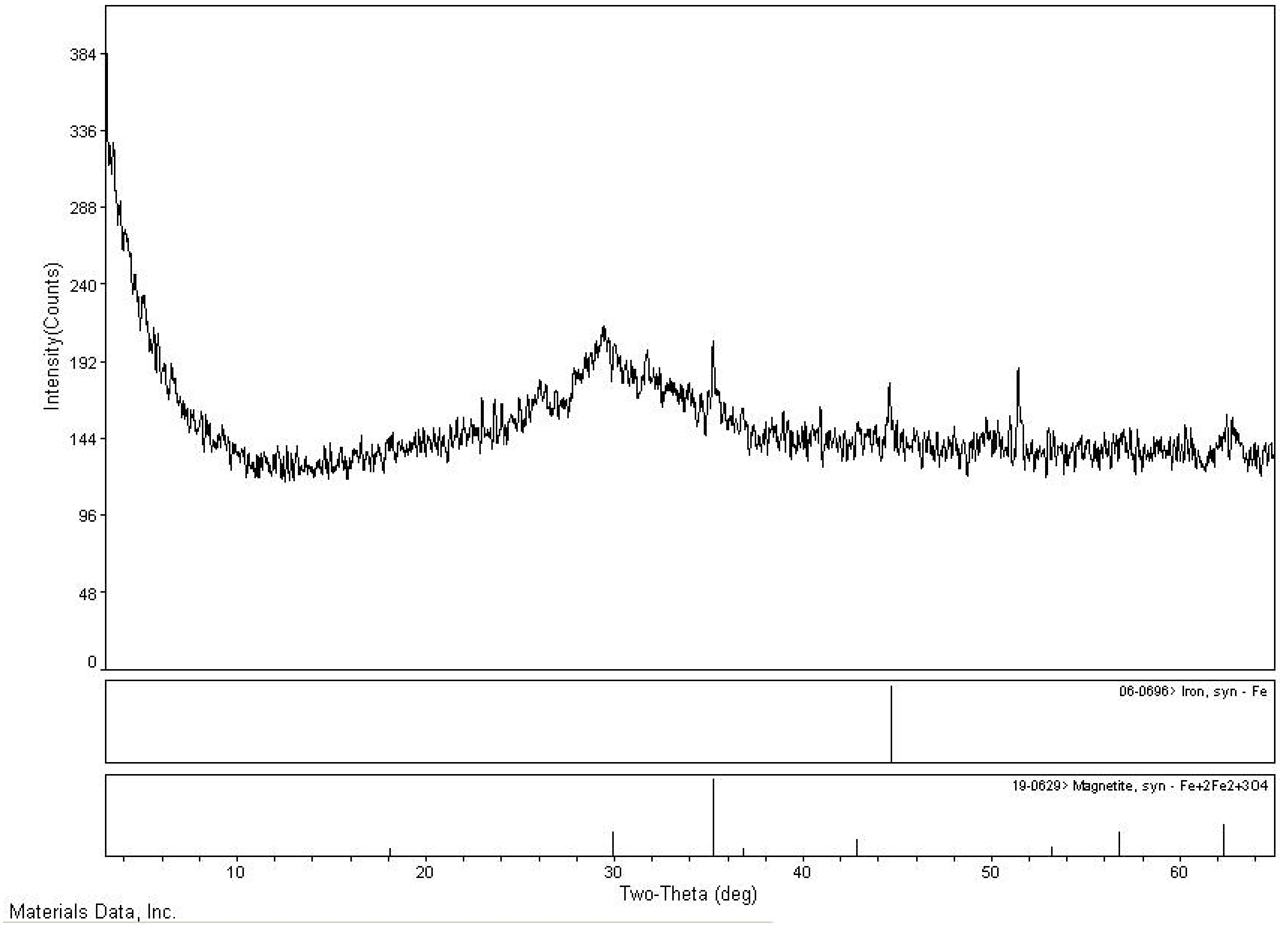
Appendix Figure 26 X-ray diffractograms of class C fly ash-based geopolymer with Sol : FA ratio 1.50



Appendix Figure 27 X-ray diffractograms of class F fly ash-based geopolymer with Sol : FA ratio 1.50



Appendix Figure 28 X-ray diffractograms of class C fly ash-based geopolymer with Sol : FA ratio 2.33



Appendix Figure 29 X-ray diffractograms of class F fly ash-based geopolymer with Sol : FA ratio 2.33

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