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THESIS

THE EFFECT OF PRE-DISSOLUTION TIME TO GEOPOLYMER PROPERTIES

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Geopolymerization is the reaction between rich silica (Si) and alumina (Al) base materials and highly alkaline solution. The result from this reaction is a new material with cement-like workability and engineering properties. This paper presents the effect of pre-dissolution time on geopolymer properties by investigating the dissolution of Al, Si and Ca ions using ICP-OES method. The study was conducted by using class C and class F fly ash as the base materials, dissolved by 4 M of NaOH and varied in pre-dissolution times between 5 - 180 min. Na_2SiO_3 was then added to produce geopolymer.

The results showed that the effect of pre-dissolution time on the dissolution of ions that Si, Al and Ca increased to a maximum values at pre-dissolution time of 30 min for both classes of fly ash. After that, the concentration decreased. For Al, the dissolution continued until end of experiment for class F fly ash. For compressive strength, there was no difference on strength prepared by class F fly ash when increased pre-dissolution times while increase pre-dissolution time decreased strength for geopolymer prepared by class C fly ash. It was found that initial and final setting times increase as the pre-dissolution time increase for both materials. Geopolymer prepared by class C fly ash faster setting than class F geopolymer. For the microstructure analysis, geopolymer was a composite material which consisted of matrix, surrounded by non-reacted fly ash. This hardening led to compressive strength of geopolymer. The high amount of Al and Si dissolution increased the density of matrix. The XRD results indicated that geopolymer showed the same basic features mostly attributable to reacting fly ash. For instance, peaks due to haematite (F), quartz (Q) and mullite (M) were all regularly observed.

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Rattanakorn Na Wittayanan

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LIST OF ABBREVIATIONS

Al = Aluminium
ASTM = American Standard Testing Method
Ca = Calcium
CaO = Calcium Oxide
cm = Centimeter
conc = Concentration
F = haemitite
FA = Fly ash
FA/C = Class C fly ash
FA/F = Class F fly ash
ICP-OES = Inductive Coupled Plasma Optical Emission Spectrometer
ksc = Kilogram per square centimeter
M = Molarity
min = Minute
mm = Millimeter
NaOH = Sodium Hydroxide
Na_2SiO_3 = Sodium Silicate
Q = Quartz
SEM-EDX = Scanning Electron Microscope and Energy Dispersive X-Ray microscope
Si = Silica
Sol = Solution
Wt = Weigth
XRD = X-ray Diffractometer

THE EFFECT OF PRE-DISSOLUTION TIME TO GEOPOLYMER PROPERTIES

INTRODUCTION

Geopolymer is inorganic polymeric material, first introduced by Joseph Davidovits in late 1970s. Geopolymer is attractive because excellent mechanical properties and durability can be achieved (Palomo *et al.*, 1992, Davidovits, 1988). Thermal stability and resistance to acid attack are excellent (T. Bakharev). Furthermore, due to low Ca content, geopolymer-based materials are much more resistant to acid attack than Portland cement based materials (T. Bakharev, 2005). Due to these properties, the applications of geopolymer range within the fields of new ceramics, cements, matrices for hazardous waste stabilization, fire-resistant materials. (Davidovits, 1991; van Jaarsveld *et al.*, 1997, 1999; Kriven *et al.*, 2004).

Geopolymer is formed by the alkali silicate activation of alumino-silicate materials. Fly ash, slag, rice husk ash and kaolinite are commonly used as the source materials due to high Si and Al. The alkaline liquids are, therefore, from soluble alkali metals that are usually Sodium (Na) or Potassium (K) based. The most common alkaline liquid used in geopolymerization is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate.

The synthesis of geopolymer takes place by dissolution and polycondensation phases. The dissolution starts immediately when source materials contact with high alkaline solution. The OH^- ions in the system are responsible for the breakdown of Si-O-Si and Al–O–Al bonds. With increasing dissolution, a part of the material will be destroyed at the surface and produce surface pores. Products of the dissolution reaction are three-dimensional pyramid units of Si^{4+} and Al^{3+} which creates four-arms coordinates with oxygen. The negatively charged and tetrahedrally coordinated Al atoms inside the network are charge-balanced by alkali metal cations (Na^+, K^+ and Ca^{++}) coming from the activating solution. Finally, polycondensation takes place to form a three-dimensional aluminosilicate framework and range from amorphous to semi-crystalline structures, in which the undissolved solid particles are bonded and the whole system hardens in a final durable structure. Finally, the production of a highly polymerized material leads to the high mechanical strength.

The mechanism controlling the chemical reaction is initially associated to a dissolution process and affects the engineering properties as well as microstructure of geopolymer. The aim of this study is to investigate the effect of class F and class C fly ash on pre-dissolution time to dissolution of Al, Si and Ca ions, regarding the engineering properties and the microstructure.

OBJECTIVES

This research was carried out with the following objectives:

1. To find the effect of pre-dissolution time on dissolution ions from starting materials.

2. To find the effect of pre-dissolution time on setting time, strength and microstructure.

3. To compare the pre-dissolution time relations from class F and class C fly ash.

Scope of work

The aim of this study is to discuss the effect of pre-dissolution time on dissolution of Al, Si and Ca ions, geopolymer properties and microstructure.

In the study, two classes of fly ash (class F and class C) obtained from Mae Moh power plant were used as starting materials. Sodium Hydroxide (NaOH) of 4M was served as leachant and as an alkaline solution when mixed together with Sodium Silicate (Na_2SiO_3) in order to produce geopolymer.

Throughout this experiment, a total of 8 mixes were investigated by keeping quantities of all starting materials constant at a ratio of 1.5 FA/Sol and 1 of Na_2SiO_3/ NaOH ratio by weight varied the pre-dissolution times in range as follows: 5, 30, 90 and 180 min.

LITERATURE REVIEW

1. Coal ash

Coal ash is generated from the burning of pulverized coal in a boiler. As a product of burning process in electric plant, the particles are left to cool down and are defined as coal ash.

1.1 Classification of coal ash

1.1.1 Bottom ash (clinker ash) is the dropping ash that can be collected at the bottom of the boiler. The particle size is approximately 0.50 – 10 mm.

1.1.2 Cinder ash is the coarser coal ash powders which drop when the combustion gas of a boiler passes through the air pre-heater or fuel economizer.

1.1.3 Fly ash is the finer coal ash powders collected from burning gas by an electrical precipitator. The particle size is approximately 0.001 – 1.0 mm. The particles of this ash are spherical.

2. Fly ash

Fly ash is known as waste by-product from the electric power plant and which is produced in gradually higher quantities each year. It was classified as pozzalan which is not cementitious in itself until it is in contact with water and free lime or CaO, which is in fly ash will react with water and transform into $Ca(OH)_2$ and lead to cementitious properties. Later, $Ca(OH)_2$ interacts with SiO_2 and Al_2O_3, forming Calcium Silicate Hydrate (CSH) and Calcium Aluminate Hydrate (CAH) components and hydrogranet is produced at later step.

2.1 Fly ash properties

2.1.1 Physical properties

Fly ash consists of fine, powdery particles that are mostly in spherical, irregular shape**,** generally ranging from 1µm – 100 µm. The carbonaceous material in fly ash is composed of angular particles. The particle size distribution of most bituminous coal fly ash is generally similar to that of silt (less than a 0.075 mm or No. 200 sieve). Although subbituminous coal fly ash is also silt-sized, they are generally slightly coarser than bituminous coal fly ash. The specific gravity of fly ash usually ranges from 2.1 to 3.0, while its specific surface area (measured by the Blaine air permeability method) may range from 170 to 1000 m^2/kg. The color of fly ash can vary from tan to gray to black, depending on the amount of unburned carbon in the ash. The lighter the color, the lower the carbon content. Lignite or subbituminous fly ash is usually light tan to buff in color, indicating relatively low amounts of carbon, as well as the presence of some lime or calcium. Bituminous fly ash is usually some shade of gray, with the lighter shades of gray generally indicating a higher quality of ash.

2.2.2 Chemical properties

The chemical properties of fly ash are influenced to a great extent by those of the coal burned and the techniques used for handling and storage. There are basically four types, or ranks, of coal, each of which varies in terms of its heating value, chemical composition, ash content, and geological origin. The four types, or ranks, of coal are anthracite, bituminous, subbituminous and lignite. In addition to being handled in a dry, conditioned, or wet form, fly ash is also sometimes classified according to the type of coal from which the ash was derived.

The principal components of bituminous coal fly ash are silica, alumina, iron oxide, and calcium, with varying amounts of carbon, as measured by the loss on ignition (LOI). Lignite and subbituminous coal fly ash is characterized by higher concentrations of calcium and magnesium oxide and reduced percentages of silica and iron oxide, as well as lower carbon content, compared with bituminous coal fly ash. Very little anthracite coal is burned in utility boilers, so there are only small amounts. When comparing the normal range of the chemical constituents of bituminous coal fly ash with those of lignite coal fly ash and subbituminous coal fly ash, it has been proved that lignite and subbituminous coal fly ash has a higher calcium oxide content and lower loss on ignition than fly ash from bituminous coals. Lignite and subbituminous coal fly ash may has a higher concentration of sulfate compounds than bituminous coal fly ash.

Chemical composition of fly ash consists mostly of silicon dioxide (SiO_2), which is present in two forms: amorphous, which is rounded and smooth, and crystalline, which is sharp, pointed and hazardous; aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3). Fly ash is generally highly heterogeneous, consisting of a mixture of glassy particles with various identifiable crystalline phases such as quartz (Q), mullite (M) and various iron oxides.

Two classes of fly ash were classified by ASTM C 618; class C and F. Their properties depend on the nature of coal and the combustion process. Class F is mostly produced from bituminous coals which have low concentration of calcium compounds. Subbituminous coals have higher concentration of calcium carbonate ($CaCO_3$), thus, produced fly ash class C. To classify these two classes of fly ash, the chemical requirements in Table 1 should be followed:

Table 1 Chemical requirements for fly ash classification.

Chemical requirements for fly Ash classification	Class of fly ash	
	Class F	Class C
Silicon dioxide (SiO_2) plus aluminum oxide (Al_2O_3) plus iron oxide (Fe_2O_3), min, %	70	50
Sulfur trioxide (SO_3), max, %	5	5
Moisture Content, max, %	3	3
Loss on ignition, max, %	6	6

2.2 Fly ash from Mae Moh power plant

Mae Moh power plant is located in Mae Moh district, Lampang province in the northern part of Thailand. This Electricity Generating Authority (EGAT) produces 3 million tons per year. Burning Lignite in the temperature of around 900-1,100°C finally produce grey to grey - black to brown smooth spherical shape whose diameter is 1-150μm. According to ASTM C618, this fly ash can be classified as class F fly ash which mostly has the sum range of SiO_3, Al_2O_3 and Fe_2O_3 of 72 – 80% and contains CaO component in the range of 7 – 12% (Chai, 2007), the maximum of SO_3 at 4% and the maximum of free CaO at 2% (EGAT, 1998). Average chemical compositions of fly ash at Mae Moh electric power plant are shown in Table 2 and 3

Table 2 Chemical compositions of lignite fly ash from Mae Moh power plant (1985 – 2001).

Year	Chemical Composition (%)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	LOI
2528	12.0	5.9	17.3	39.5	4.6	2.0	0.8	11.5	6.3
2533	37.8	20.5	14.2	17.4	3.3	0.9	2.1	3.9	0.8
2535	40.3	24.0	15.0	11.2	2.8	1.0	2.6	3.1	0.5
2540	41.5	28.1	12.3	10.0	1.2	0.6	3.3	2.0	0.8
2544	39.9	18.2	13.6	17.2	2.4	1.3	2.7	1.5	0.1

Source: Prinya (2003)

Table 3 Chemical properties of lignite fly ash from Mae Moh power plant (1991).

Month	Chemical Composition (%)								Total	
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Acid	Base
Jan	46.96	26.4	12.04	7.79	2.08	1.83	0.64	2.25	73.36	24.38
Feb	50.7	24.54	12.11	6.87	1.01	1.97	0.34	2.26	75.24	22.30
Mar	44.4	22.61	14.27	9.91	1.49	2.01	0.52	3.8	67.01	28.20
Apr	42.87	22.88	16.12	9.8	1.72	2.06	0.50	3.54	65.75	30.20
May	-	-	-	-	-	-	-	-	-	-
Jun	40.35	22.94	14.34	12.41	2.63	2.47	1.07	3.52	63.29	22.92
Jul	40.63	23.7	16.2	11.1	2.6	2.34	0.83	3.6	64.33	33.07
Aug	39.56	20.47	14.65	15.01	3.09	2.14	1.14	3.94	60.3	36.03
Sep	38.22	21.23	15.15	14.24	3.16	2.13	1.37	4.85	59.45	36.05
Oct	37.77	22.3	14.38	14.34	3.27	2.42	1.09	4.43	60.07	35.50
Nov	41.8	22.04	12.61	13.46	3.05	2.32	0.92	3.8	63.84	32.36
Dec	43.96	24.95	13.71	9.37	2.34	2.66	0.73	2.26	68.93	28.81
Avg	42.47	23.1	14.14	11.3	2.40	2.21	0.83	3.48	65.57	29.98

Source: Narumit (1995)

2.3 The application of fly ash

2.3.1 Replacing Portland cement

Fly ash is well known and interestingly used as a mixture in concrete mix or in replacement of Portland cement which contains high oxide such as SiO_2, Al_2O_3 and CaO that produces Calcium Silicate Hydrate and Calcium Aluminate Hydrate which, in turn, produces cementitious products. The use of fly ash as a partial replacement for Portland cement is generally limited to class F fly ash because of its low calcium content. It can replace up to 30% by mass of Portland cement, and can be added to increase the concrete final strength, its chemical resistance and durability.

Lane and Best (1982) explained the advantage of using fly ash in concrete as:

1. Improve the workability
2. Reduce unit water content
3. Increase long term strength
4. Reduce heat of hydration
5. Improve water tightness
6. Improve resistance against chemical attack
7. Reduce drying shrinkage
8. Produce less creep

2.3.2 Soil Stabilization

To improve unfavorable soil properties, fly ash was used as the base material to produce cementitious compound that binds the soil particles and thereby achieves the desired stabilization. It has been already proven to be a self-cementing additive for promoting soil stabilization and compressive strength in a wide array of soil, including clay soil, by mixing with Portland cement or cement by-products.

2.3.3 Geopolymer

Fly ash was used as raw material because of its high content of Si and Al that once attacked with high alkaline solution, new bridge structures were formed and resulted in geopolymer. This material possesses high early strength, low shrinkage, freeze-thaw, resistance, sulfate resistance, corrosion resistance, acid resistance and fire resistance.

3. Geopolymer

3.1 General

Geopolymer can be defined as “amorphous analogues of natural zeolitic-materials, synthesized by polymerising a variety of alkaline silicates with silico-aluminates” (Davidovits, 1994). A geopolymer consists of “a polymeric silicon-oxygen-aluminium framework with alternating silicon and aluminium tetrahedral joined together in three directions by sharing all the oxygen atoms” (Davidovits, 1994).

Davidovits (1988, 1994) proposed that an alkaline liquid could be used to react with the silicon (Si) and the aluminum (Al) in geological source materials or in by-product materials such as fly ash and rice husk ash. Since this chemical reaction provides binders and produces inorganic polymeric materials, he created the term “geopolymer” in 1978 to present these binders and classify this new geo-synthesis.

Geopolymer is categorized as “inorganic polymer” whose repeat-units use chemical elements other than carbon. They are synthetic minerals belonging to the same family of alumino-silicates as zeolites, hence the chemical composition is similar to natural zeolitic materials. Unlike zeolites, however, they are essentially amorphous polymers as seen in their microstructures (Davidovits, 1994).

3.2 The constitution of geopolymer

Geopolymer consists of two main materials, namely “source materials” and “alkaline liquids”.

3.2.1 Source materials

The source materials for geopolymer based on alumina-silicate should be rich in silicon (Si) and aluminium (Al). These could be natural minerals such as kaolinite, clays, etc. Alternatively, by-product materials such as fly ash, silica fume, slag, rice-husk ash, red mud and etc could be used as source materials.

3.2.2 Alkaline liquids

The aluminium (Al), used as source material for geopolymer, is four-coordinated and this alone gives a negative charge. Electric neutrality in the matrix can be hence balanced with the presence of cations such as Na^+ and K^+.

The alkaline liquids are, therefore, from soluble alkali metals that are usually Sodium (Na) or Potassium (K) based. The most common alkaline liquid used in polymerization is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate.

3.3 The polymerization process

"The polymerization process involves a substantially fast chemical reaction under alkaline condition on Si-Al minerals that result in a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds" (Davidovits, 1994). The reaction of alumino-silicate materials in a strong alkaline environment results, firstly, in a breakdown of Si–O–Si bonds. Secondly, a new phase of the reaction takes place. A dominant process of this phase is for Al atoms to penetrate into the original Si–O–Si structure.

Alumino-silicate gels (zeolite precursors) are mostly formed in this phase. Their composition can be represented by the formula

$$M_n[-(Si\text{-}O)_z\text{-}Al\text{-}O]_n \; wH_2O$$

Where z is 1, 2 or 3; M was an alkali cation, such as potassium (K) or sodium (Na), and n was the degree of polymerization (as seen in the formula).Secondary H_2O may be formed during these (poly-condensation) reactions. Amorphous (gel-like) or partially amorphous or crystalline substances may originate depending on the character of starting raw materials and on the conditions of the reaction.

The solid matter has been concentrated in the process of alkali activation, which mostly generates crystalline zeolite-type products.

3.4 The formation of geopolymer

Davidovits (2002) reported that geopolymer was an indefinite-shape aluminosilicate material which derived from the components of amorphous and semi-crystalline materials. The source material of geopolymer was a compound substance which consisted of silica and alumina. When mixed with alkali solution, it caused reaction at normal or high temperature which results in formation with good compressive strength. Like a reaction of cement paste, this reaction produced heat. It was a condensation type of polymerization which can be divided into 2 main steps (Davidovits, 1999).

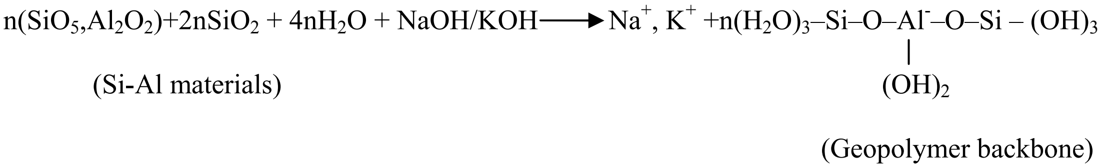
3.4.1 Dissolution

The source materials (pozzolan materials), when mixed with high-alkali liquid, will cause dissolution of various components. Aluminium (Al) and silicon (Si) dissolved in high amount because they were the main components in source materials. Increased dissolution, a part of the material will be destroyed at the surface and produced surface pores that facilitate easy reaction of the liquid.

3.4.2 Chain reaction

Products of the dissolution reaction were three-dimensional pyramid units of Si^{4+} and Al^{3+} which created four-arm coordinates with oxygen. These units were distributed as polymeric chain structure. At the initial phase, there were high-Al meta-stable units. With increasing reaction, they change into high-Si units. Thus, the main structure consists of one, two, three, and four three-dimensional pyramid units: polysialate (PS); polysialate siloxo (PSS); and polysialate disiloxo (PSDS), respectively. The amount of SiO_4 increased from one to three units. With increasing reaction, the bonds of polymeric chain also increased and condensed which causes a structure with high compressive strength.

The chain reaction of geopolymer is very complicated and cannot be extensively explained. However, Hue *et al*. (2000) proposed that silica (Si) and alumina (Al) compounds, when mixed with hydroxide alkali liquid and water, caused a main reaction that results in polysialate units which have positive charge of alkali liquid. These cause a balance as in Equations 2. The polysialate units lead to further reaction with hydroxide alkali liquid and produce a bond of polymeric chain.

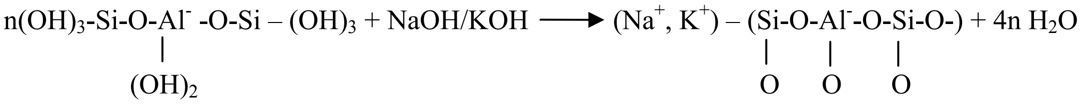


$$\mathrm{n(SiO_5,Al_2O_2)+2nSiO_2+4nH_2O+NaOH/KOH \longrightarrow Na^+, K^+ + n(H_2O)_3{-}Si{-}O{-}\underset{\underset{(OH)_2}{|}}{Al^-}{-}O{-}Si-(OH)_3}$$

(Si-Al materials)

(Geopolymer backbone)

Equation 1



$$\mathrm{n(OH)_3\text{-}Si\text{-}O\text{-}\underset{\underset{(OH)_2}{|}}{Al^-}\text{-}O\text{-}Si-(OH)_3 + NaOH/KOH \longrightarrow (Na^+, K^+) - (\underset{\underset{O}{|}}{Si}\text{-}O\text{-}\underset{\underset{O}{|}}{Al^-}\text{-}O\text{-}\underset{\underset{O}{|}}{Si}\text{-}O\text{-}) + 4n\ H_2O}$$

Equation 2

3.5 Properties of geopolymer

Previous studies have reported that geopolymer possess high early strength, low shrinkage, freeze-thaw resistance, sulfate resistance, corrosion resistance, acid resistance, fire resistance and no dangerous alkali-aggregate reaction.

3.5.1 High compressive strength

Based on laboratory tests, Davidovits (1988) reported that geopolymer cement can harden rapidly at room temperature and gain the compressive strength in the range of 20 MPa after only 4 hours at 20°C and about 70 - 100 MPa after 28 days.

Comrie *et al.* (1988) conducted tests on geopolymer mortars and reported that most of the 28day strength was gained during the first 2 days of curing.

3.5.2 Heat and fire resistant

Geopolymeric cement was superior to Portland cement in terms of heat and fire resistance, as the Portland cement experienced a rapid deterioration in compressive strength at 300°C whereas the geopolymeric cements were stable up to 600°C (Davidovits, 1988, 1994).

3.5.3 Low shrinkage

It has also been shown that compared to Portland cement, geopolymeric cement showed higher expansion in water, but had extremely low shrinkage in air. Davidovits reported that this was an important property of geopolymeric cement.

3.5.4 Resistant to strong alkali and acid corrosion

The presence of alkalis in the normal Portland cement or concrete could generate dangerous Alkali-Aggregate-Reaction. However the geopolymeric system is safe from that phenomenon even with higher alkali content.

As demonstrated by Davidovits (1994), based on ASTM C 227 bar expansion test, geopolymer cements with much higher alkali content compared to Portland cement did not generate any dangerous alkali-aggregate reaction where the Portland cement did.

Geopolymer cement was also acid-resistant, unlike the Portland cement, because geopolymer cements did not rely on lime and were not dissolved by acidic solutions. As shown by the tests of exposing the specimens in 5% of sulfuric acid and chloric acid, geopolymer cements were relatively stable with the weight lose in the range of 5 - 8% while the Portland based cements were destroyed and the calcium alumina cement lost the weight about 30 - 60% (Davidovits, 1994). Some recently published papers (T. Bakharev, 2005; Song *et al.*, 2005) also reported the results of the tests on acid resistance of geopolymer and geopolymer concrete. However, Bakharev and Song *et al.* had also observed that there was degradation in the compressive strength of test specimens after acid exposure and the rate of degradation depended on the period of exposure.

3.6 Application of geoploymer materials

Due to various properties of geopolymer material, which are similar to concrete and Portland cement, it is utilized in several applications. For example, due to its low water permeability, geopolymer can be used for a surface closure or a bottom liner of solid waste landfill, construction of irrigation dams, a liner of water canals, a structure of dams or for a structure in mining industry such as floor of pathway, building or store. Because of its high alkalinity, geopolymer is also used for collecting heavy metals like arsenic, lead, copper manganese, mercury or other metals. Geopolymer can be used to prevent dissolution of toxic waste which contains heavy metals by nearly 100% (van Jaarsveld *et al.*, 1997) or to collect toxic waste from asbestos and radioactive waste (Davidovits *et al.*, 2002). From its composition of heat-resistant and fire-resistant fiber, geopolymer is also used to produce heat-resistant wall panels, ceramic and artistic products, depending on its chemical component of source and activate materials. Davidovits suggested that a molar with ratio of Si to Al at approximately 2 is suitable for producing cement and concrete.

3.6.1 Greenhouse gas (CO_2) emission of geopolymer

In 2002, Davidovits compared the emission of greenhouse gas (CO_2) from the production of Portland cement with that of geopolymer cement. He found that in the production of Portland cement, the source material (calcium carbonate) was prepared by burning to cause calcinations. The burning of source materials to produce 1 ton of cement will emit 0.55 ton of CO_2 gas. Also, the burning process used carbon fuel that emitted 0.4 ton of CO_2 gas. In other words, the production of 1 ton of Portland cement emitted 1 ton of CO_2. On the other hand, the production of geopolymer, calcanite, a by product from furnace was burned to cause calcinations at 800°C. One ton of the product emitted about 0.184 ton of CO_2 from the burning process that used carbon fuel. When comparing the production of 1 ton of Portland cement with geopolymer cement, it was found that the production of geopolymer cement emits less CO_2 than that of Portland cement by about 5-6 times.

At present, the production of Portland cement is the main source of CO_2 emission into the atmosphere and it tends to increase constantly. Hence, geopolymer technology is not only useful for construction work, but is also environmental friendly. It can reduce carbon dioxide from the production of Portland cement by about 80%. It also recycles wastes to lower overhead and add value to the materials.

3.7 Related research

The mixing of other materials in Portland cement to increase certain properties and to lower its use or production has been going on for many decades. Mostly, fly ash is commonly used because it has similar chemical property to Portland cement. For example, fly ash is used in fresh concrete work in which the increased volume of paste is found. Fly ash will penetrate between total masses. The circular shape of fly ash helped decrease friction between total mass and paste (Ravina, 1980). Santisuk (1994) found that mortar which used fly ash in place of Portland cement required less water while providing similar workability. Burachat and Phichai (1994) revealed that fly ash which had a feature of pozzolan materials that can replaced cement in concrete work and provided longer formation period of fly ash-based mortar than normal mortar. Fine fly ash tended to provide fast formation while coarse fly ash tended to delay formation (Kriwood *et al*., 2001). Prinya (2006) revealed that increasing amount of SO_3 in fly ash can increase formation period. Chakaphan *et al.* (2005) revealed that besides fly ash, there were also other materials that can be used as starting materials, such as rice husk. Chittakon (2000) revealed that water sediment from Bang Khen Water Supply Plant can be activated to possess pozzolan properties by burning at a high temperature of 650 - 1000°C, in which it yielded high pozzolan index. When mixed with mortar it showed good compressive strength (Thanes *et al*., 2003).

In addition, there were also studies about using materials with pozzolan like property as binders in place of Portland cement. It began when a kind of material was found in Ukraine and was called soil-cement.

Davidovits (1976) had tested chemical composition of this material and found that it mainly consisted of silica and alumina. He named this material “geopolymer” which gained increasing attention from extensive studies.

Davidovits *et al.* (1999) had explained that chemical composition of geopolymer materials was similar to that of zeolite but with indefinite small structure. When activated with high-alkali liquid, silica and alumina components in the material acted as binder and turned into geopolymer paste. This geopolymer paste had good compressive strength and can be used extensively.

Palamo *et al.* (1999) studied the use of fly ash as polymer and found that factors that affected its compressive strength were curing temperature and type of high-alkali activating materials used. Moreover, other materials were also studied with fly ash, such as mixing kaolin burning at the temperature of 500 - 600°C with fly ash to burned kaolin ratio of 86:14 by mass. It was found that the mixture yielded good compressive strength (van Jaarsdveld *et al.*, 2002).

van Jaarsveld *et al.* (2002) studied a production of geopolymer from kaolin which consisted of silica and alumina. The study revealed that burning temperature of kaolin depended on burning duration which should be between 500 - 600°C. The production of geopolymer from fly ash mixed with kaolin at a ratio of 86:14 yielded good compressive strength. However, the mixture which contained kaolin burned at other temperature yielded low compressive strength. Hence, more research in this aspect is needed.

Hardjito *et al.* (2002) studied activating materials by activating fly ash from coal-burning power plant with alkali silicate and alkali hydroxide. They found that the higher concentration of the liquid, the better the compressive strength. The ratio of activating materials Na_2SiO_3/NaOH also had effect on the strength.

Swanepoel *et al.* (2002) studied a production of geopolymer from fly ash mixed with materials which contain silica and alumina, i.e. kaolin activated with high-alkali liquid which contained Na_2SiO_3, NaOH and water. The mixture was cured in the oven to accelerate the reaction at the temperature of 40, 50, 60 and 70°C for different duration (6, 24, 48 and 72 hours). It was found that the most suitable condition, with the temperature of 60°C for 48 hours yielded the highest compressive strength of 8 MPa after 28 days.

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W. Wang and T.W. Cheng (2003) studied geopolymer produced from fly ash with high-alkali activator, i.e. sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH) liquid for specific feature of fire resistance. It was found that geopolymer produced from fly ash hardened at room temperature within 9.5 hours. However, the geopolymer produced from fly ash would harden within 1 hour after mixing by curing in an oven at a temperature of 60 - 70°C to accelerate polymerization. After testing for compressive strength and fire-resistance at the age of 2 days, it was found that the geopolymer yielded compressive strength of 64 MPa. The process of reaction and development of compressive strength continued for 7 days. After that, the reaction obviously decreased. In other words, the reaction and development of compressive strength of geopolymer material is not significant. For a test of fire resistance at 1100°C at the front surface of 10 mm-thick sample material for 30 min, a temperature of 440 - 470°C could be measured from the back side of the sample. It is obvious that geopolymer material was strong and fire-resistant. It, therefore, was a potential material to be developed as construction material in the future.

Hardjito *et al.* (2004) studied the use of fly ash which contained silica (Si) and alumina (Al), resulted from coal-burning in electric plant, to produce geopolymer material with good compressive strength, as when using Portland cement. The geopolymer material was produced by mixing fly ash with activator at a temperature of 60 - 90°C. To accelerate reaction, alkali silicate and alkali hydroxide were used. It was found from the study that compressive strength depended on various factors like sodium hydroxide solution. The higher the concentration, the better the compressive strength. Increasing ratio of Na_2SiO_3/NaOH also affected the resulting compressive strength, temperature used in accelerating reaction and curing duration.

T. Bakharev (2005) studied acid resistance of geopolymer material produced from selective-size class F fly ash. High-alkali liquid sodium silicate, sodium hydroxide and potassium hydroxide were used to activate silicon and alumina ions in the material to create polymerization. Major factors studied were suitable weight, compressive strength, change of micro structure, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM). It was found from the study that geopolymer material mixed with selective-size fly ash had more acid resistance than geopolymer produced from ordinary cement (OPC).

U. Rattanasak, W. Chalee and P. Chindaprasirt (2006) studied the leaching of SiO_2 and Al_2O_3 from fly ash. Fly ash/NaOH at the ratio of 3:1 by weight was used and varied with NaOH concentrations of 5M, 10M and 15M in the leaching times of 5, 10, 20 and 30 min. Na_2SiO_3 was added to enhance the formation of geopolymer. In addition, the strength of geopolymer mortar was also tested by adding sand to the mixture at the ratio of sand/fly ash at 2 by weight. The results revealed that the solubility of fly ash depended on the concentration of NaOH and the leaching time. From the leaching test, Si and Al reached the highest concentration in 10 min of leaching for 10M of NaOH. This result induced the highest compressive strength up to 65 MPa and was comparable to the highest strength mortar.

P. Chindaprasirt, T. Chareerat and V. Sirivatnanon (2007) studied geopolymer production with good performance from selective-size fly ash. They found that the finer the fly ash, the higher ability of expansion. Compressive strength also increased with the fineness of fly ash.

Criado *et al.* (2007) found that the concentration of silica in activating liquid and storing temperature had certain effect on reaction in geopolymer which can be seen in the development of compressive strength. This corresponds to the study of Lee and van Devanter (2003) who found that when the concentration of silicate (SiO_2) liquid increased, geopolymer yielded significant increase of compressive strength.

In Thailand, research about geopolymer started in late 2004. Thanatkit and Prinya (2005) tried to produce geopolymer from fly ash obtained from Mae Moh power plant. They began their initial study by synthesizing geopolymer from selective size of Mae Moh fly ash. They found increasing compressive strength in geopolymer when the concentration of sodium hydroxide liquid increased and with significant fineness level of fly ash. Moreover, there are several articles in academic publications, several presentations in the conference at the First National Conference on Concrete and Geopolymer in 2005 and the First International Conference on Concrete and Geopolymer. For example, the study of Anuchat (2005) produced geopolymer from fly ash mixed with kaolin burning at the temperature of 600°C for 2 hours and used the ratio of NaO_2+SiO_3 liquid per NaOH at 0.67 - 1.0 by weight. Fly ash can be replaced with burning kaolin at the maximum of 30% by weight. If the replacement increased, the compressive strength decreased. Songpiriyakij (2005) studied the effect of mixing temperature and storing temperature on compressive strength and found that the mixing and storing at room temperature yielded low compressive strength in the initial phase. However, the compressive strength increased in a period of 28 days, higher than the sample kept at high temperature. Kamhangritirong (2006) found that when the concentration of sodium hydroxide increased, the formation period decreased while compressive strength increased significantly.

MATERIALS AND METHODS

Materials

1. In this study, two different types of fly ash were used and both of them were obtained from Mae Moh electric plant. Chemical compositions and loss on ignition (LOI) are given in Table 4

Table 4 Result of the chemical compositions of Mae Moh fly ash by X-ray florescence spectrometer (ASTM C 311)

Oxide	Class F	Class C
SiO_2	35.30	30.23
Al_2O_3	21.50	15.24
Fe_2O_3	14.20	13.86
SO_3	4.75	4.49
CaO	18.70	25.59
MgO	3.00	2.18
Na_2O	2.50	2.30
K_2O	2.00	2.31
LOI	0.40	0.40

2. Sodium silicate solution (Na_2O=14.7%, SiO_2=29.4% and water 55.9% by mass)
3. Concentration of Sodium Hydroxide (NaOH) 4 M (98% purity)
4. Conc. Acetone
5. Deionised water
6. Cement concrete mixer
7. Mould cylinders 1.5x3 inches
8. Vacuum filtration set (including vacuum pump and filter holder)

9. Membrane filter size 0.45 µ
10. Shaker
11. Digital scale, 30 kg capacity with accuracy of 0.01 kg
12. Compressive strength testing machine (Vice versa machine)
13. Vicat apparatus
14. X-ray diffractometer
15. Scanning electron microscope
16. Energy dispersive X-ray fluorescence spectrometer
17. Inductively coupled plasma atomic emission spectrometer (ICP-OES)
18. Computer
19. Vernier caliper

Figure 1 Filter holder

Methods

In this study, 2 different types of fly ash (class F and class C) were used as starting materials with fly ash to solution at a ratio (FA/Sol) of 1.5 and Sodium Silicate to Sodium Hydroxide at a ratio (Na_2SiO_3/NaOH) of 1 by weight. Totally 8 mixes were investigated. The mix proportion was prepared with 2000g of fly ash, 666.67g of NaOH and 666.67g of Na_2SiO_3. Pre-dissolution times investigated in this study were 5, 30, 90 and 180 min. This research consisted of 3 parts according to the following tests:

Specimens prepared by class F fly ash

1. Dissolution test

1.1 Preparation of specimens

1.1.1 Class F fly ash and Sodium Hydroxide (NaOH) were mixed and varied in different pre-dissolution times (5, 30, 90 and 180 min).

1.1.2 The paste was extracted by vacuum filter set and filtered by membrane filter.

1.1.3 The specimens were neutralized for quantitative determination by adding acetone (conc.) until the acidity value changed to pH 2.

1.2 Quantitative Determination

In this study, Inductively-coupled plasma equipped with optical emission spectroscopy (ICP-OES) was used to determine Si, Al and Ca contents in the solution.

2. Geopolymerized hardening observation

Specimens in this procedure were prepared by the same procedures as in 1.1.1 to 1.1.2. To enhance the formation of geopolymer, Sodium Silicate (Na_2SiO_3) was added for another 3 min and investigated for setting and hardening.

3. Fly ash-based geopolymer

3.1 Preparation for fly ash-based geopolymer specimens

3.1.1 Class F fly ash and Sodium Hydroxide (NaOH) were mixed in varied pre-dissolution times 5, 30, 90 and 180 min.

3.1.2 Sodium Silicate (Na_2SiO_3) was then added and followed by a further 3 min of mixing.

3.1.3 The specimens were poured into 1.5x3 inches cylindrical moulds and left to cool down for 24 hours.

3.1.4 The specimens were removed and wrapped with plastic sheets to prevent moisture loss.

3.2 Testing fly ash-based geopolymer

3.2.1 Engineering properties

3.2.1.1 Setting time of geopolymer paste was tested in accordance with ASTM C 191.

3.2.1.2 Compressive strength of prepared specimens was tested at the age of 1, 3, 7, 14 and 28 days in accordance with ASTM C 618 by using mold size cylinder of 1.5x3 inches.

3.2.1.3 Microstructure Analysis

3.2.1.3.1 X-ray diffraction (XRD) method was used to characterize the atomic-scale structure of an existing mineral in fly ash-based geopolymer at the age of 28 days.

3.2.1.3.2 Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Microscope (EDX) techniques were used to produce an image of the sample surface by scanning and for elemental analyses of the specimens. The specimens here were the fragment from compressive test at the age of 28 days.

Specimens prepared by class C fly ash

Specimens prepared by class C fly ash were tested repeating the same procedures as class F fly ash.

RESULTS AND DISCUSSIONS

1. Dissolution test

The specimens were prepared into liquid phase and analyzed by ICP-OES technique. The test results are shown in Figs 2 and 3. Graphs were plotted between the concentrations of Al, Si and Ca contents against pre-dissolution times (5 – 180 min).

The examination of specimens prepared by class F fly ash is shown in Fig. 2. Si content reached the highest amount at 30 min as well as Ca, contrary to Al which reached the highest amount at 180 min. The results indicated that the concentration of these three ions showed the same trend until 30 min. For pre-dissolution time of 30 to 90 min, Si and Ca ion dissolution amounts decreased. From 90 to 180 min, small amount of Ca ion can be detected. For Si ion, there was no difference of dissolution amount from pre-dissolution time of 90 min. However, for Al ion, the highest amount of dissolution was detected. Therefore, it can be implied that the highest dissolution amounts of Ca and Si ions can be detected at 30 min pre-dissolution time. On the other hand, for Al ion, the highest dissolution amount can be detected at 180 min.

Fig.3 shows that the highest dissolution amount of Si, Ca and Al ions prepared by class C fly ash were achieved at pre-dissolution time of 30 min. Later (30 to 180 min), the dissolution amount of all ions decreased continuously. It can be concluded that using longer pre-dissolution times seem to have no effect on dissolution of the ions from class C fly ash.

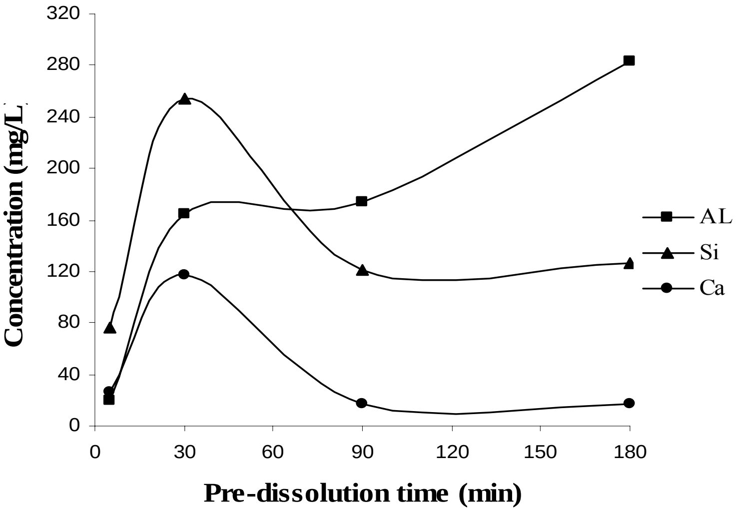


Figure 2 Dissolution contents of Al, Si and Ca from class F fly ash in different pre-dissolution times

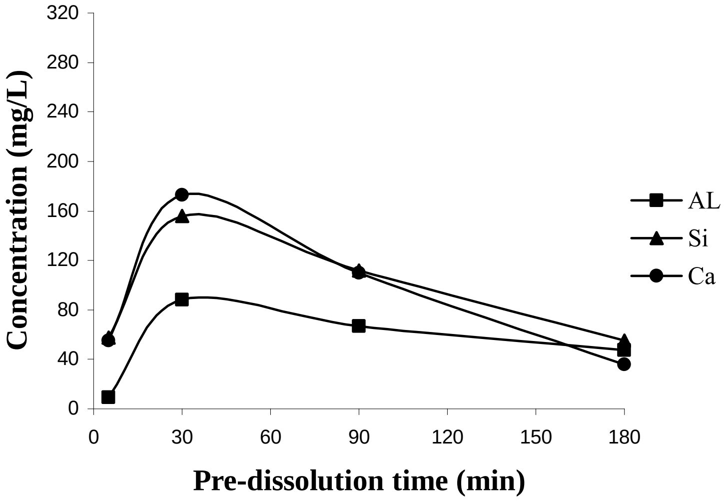


Figure 3 Dissolution contents of Al, Si and Ca from class C fly ash in different pre-dissolution times

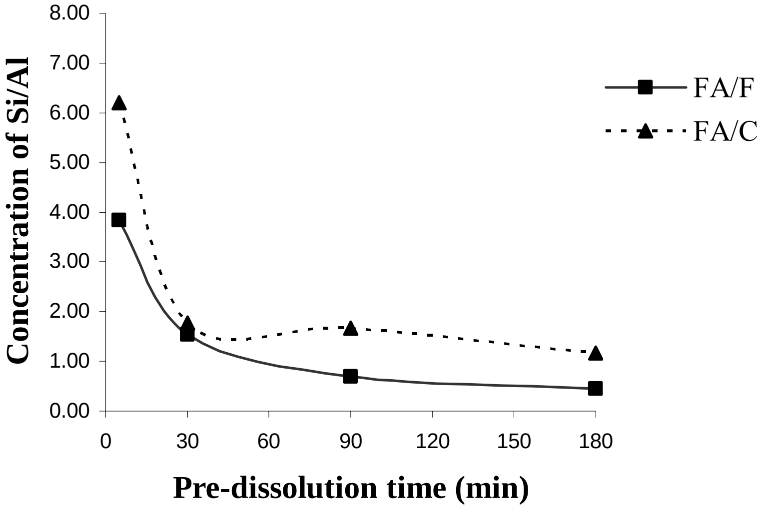


Figure 4 Dissolution contents of Si/Al from class F and class C fly ash in different pre-dissolution times

Fig. 4 shows the ratio concentration of Si/Al at different pre-dissolution times. As shown, increased pre-dissolution time decreased Si/Al concentration in both materials. Class C showed higher dissolution concentration compared with class F fly ash.

Fig 5 shows the comparison between class F and class C fly ash in ability of dissolution of Al, Si and Ca ions at each pre-dissolution time. In case of Si and Al, class F fly ash showed better dissolution ability than those from class C fly ash. It maybe due to the fact that class F fly ash contained higher SiO_2 and Al_2O_3 content compared with class C fly ash. On the other hand, class C fly ash was able to dissolve in Ca content better than those of class F fly ash. This maybe also be due to the fact that class C fly ash contained higher CaO content than class F fly ash. From the results, it can be concluded that the dissolution is strongly dependent on the composition of fly ash.

In alkaline attack of starting ashes, Al–O bonds are more readily broken than Si–O bonds (Xiao and Lasaga). Thus, it is expected to dissolve Al higher than Si in the early stage. According to the profiles in Figs. 2 and 3, in early stage (0-30 min), both materials provided higher silica dissolution than alumina. This is in agreement with the experimental observation from W.K.W. Lee (2002), who investigated the dissolution of Al, Si and Ca ions from fly ash using NaOH and suggested that these results maybe due partly to the secondary precipitation which might involve more in Al. For Ca, increasing pre-dissolution times after 30 min provided no clear effect on calcium (Ca) concentration.

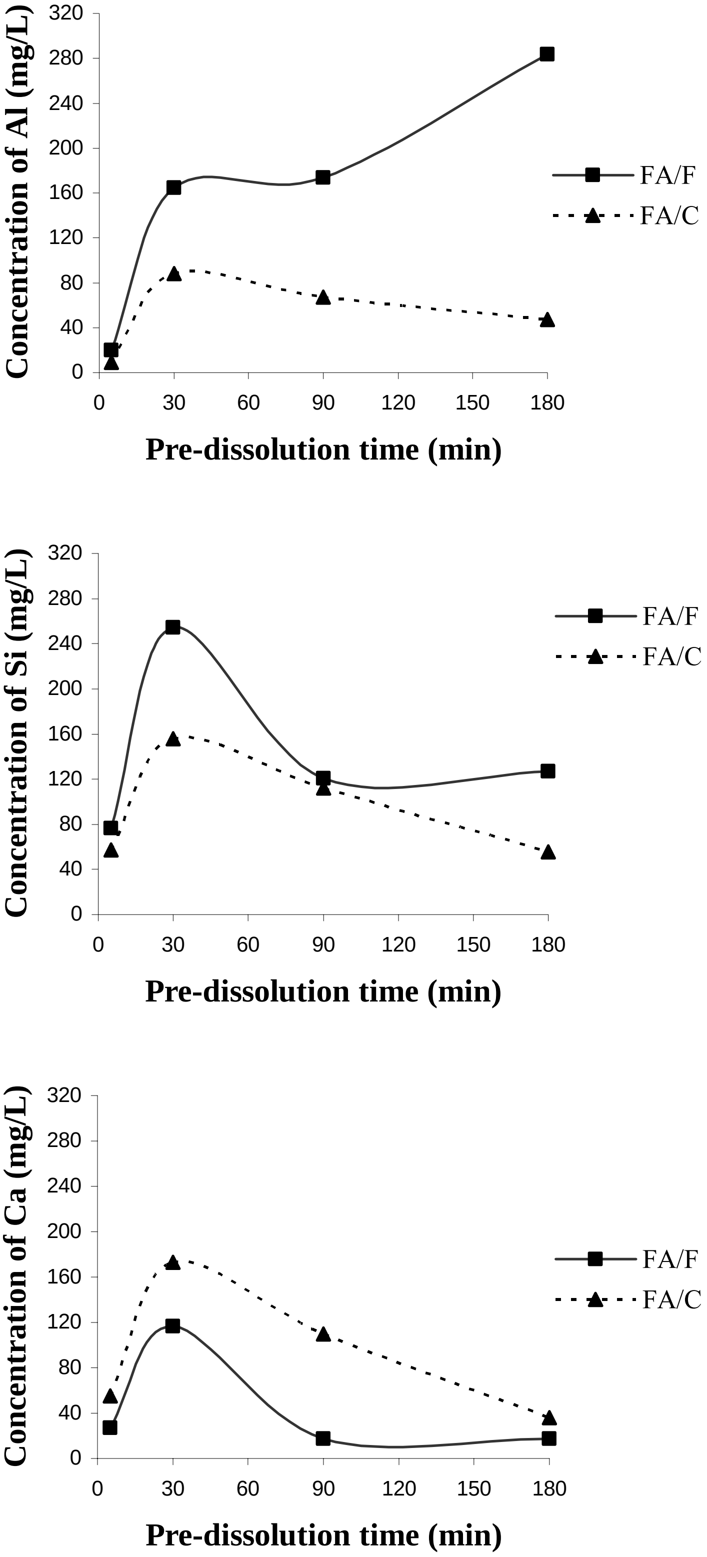


Figure 5 Concentrations of Al, Si and Ca ions prepared by class F and class C fly ash at different pre dissolution times

2. Setting time measurements

Setting time analysis was performed using a Vicat needle as described in ASTM C191. The values of penetration distances were determined every 5 min after the paste has been made. The test results of initial and final setting time are shown in Table 5.

Table 5 Setting time of geopolymer paste.

Pre-dissolution times	class F fly ash		class C fly ash	
	Initial setting time (min)	Final setting time (min)	Initial setting time (min)	Final setting time (min)
5	42.2	100	21.7	60
30	142	315	65	190
90	284	545	130	300
180	480	785	440	615

Figs. 6 and 7 show the effect of pre-dissolution times on initial and final setting times, respectively, for geopolymer prepared by class F and class C fly ash. It can be seen that initial and final setting times increased with the pre-dissolution time. In addition, class C fly ash appeared to set faster than that containing class F fly ash. The results can be explained by the dissolution of Si/Al concentration, Figs. 8 and 9 show the Si/Al concentration against initial and final setting times, respectively. As shown, increased Si/Al concentration caused faster setting time. This is due to Al and Si dissolving from starting materials readily to form geopolymer after Na_2SiO_3 was added to complete geopolymerization.

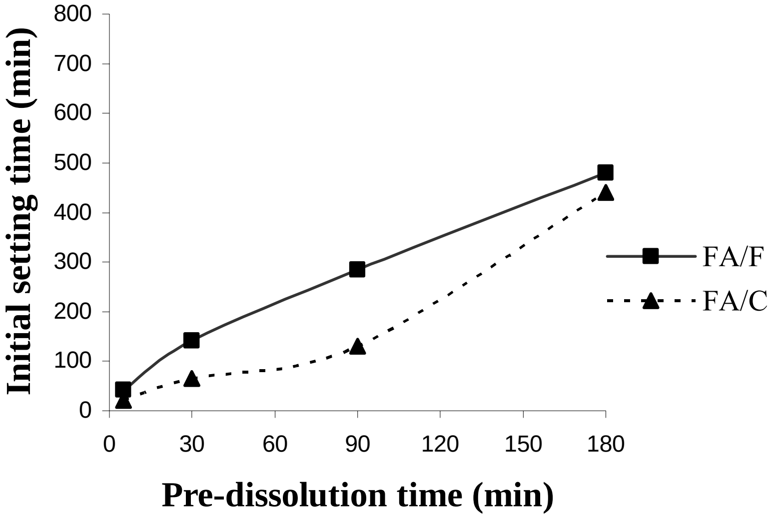


Figure 6 Initial setting time of geopolymer at different pre-dissolution times

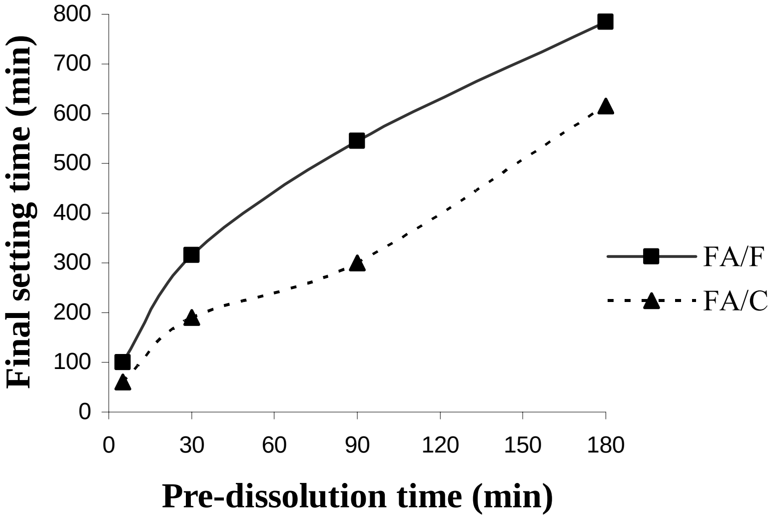


Figure 7 Final setting time of geopolymer at different pre-dissolution times

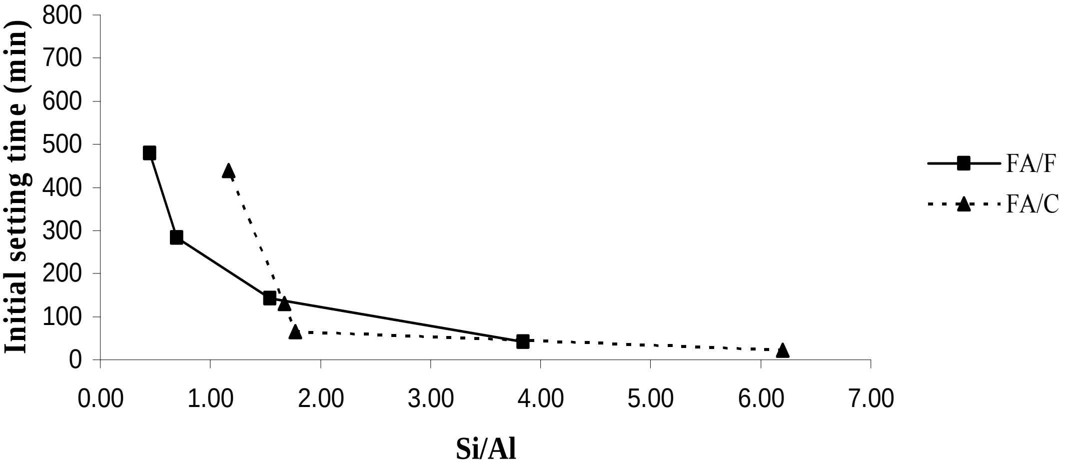


Figure 8 Si/Al concentration against initial setting time

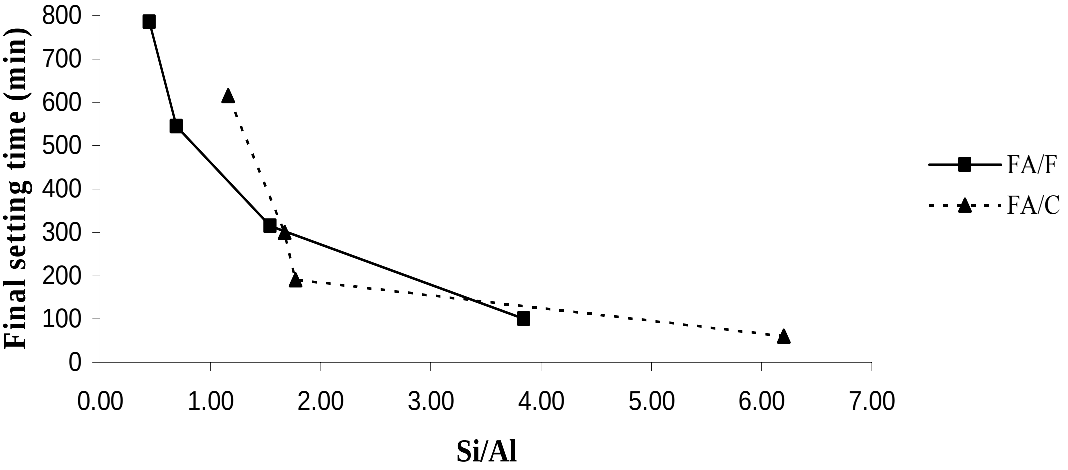


Figure 9 Si/Al concentration against final setting time

3. Compressive strength test

Fig 10 shows compressive strength of geopolymer produced from class F fly ash. As shown, the compressive strength achieved maximum value of 180 ksc at pre-dissolution time of 180 min at the age of 28 days. At this time, compressive strength profile was found to exhibit a higher development rate at 7 to 28 days, compared with other times.

Fig.11 shows the effect of pre-dissolution times to compressive strength of geopolymer produced from class C fly ash. As shown, the compressive strength achieved maximum value of 220 ksc at pre-dissolution time of 5 min at the age of 28 days.

From these results, it is interesting to note that despite the highest concentrations of Al and Si detected (at 30 min dissolution), the compressive strength did not seem to show the highest strength in this experiment. The results also agree with previous studied done by J.S.J van Deventer (1999), who tested dissolution of Al and Si from fly ash and suggested that the compressive strength which developed after geopolymerization was not dependent only on Si and Al but also strongly dependent on the chemical properties of starting materials. The final setting time of geopolymer paste prepared with both classes of fly ash was increased due to prolonging the pre-dissolution times which could be a reason for the early-age strength of geopolymer which yielded the highest strength at pre-dissolution time of 5 min.

Figs. 12 and 13 show the compressive strength of the specimens prepared by both classes of fly ash at the age of 7 and 28 days. The strength development could be observed from the specimens prepared by class F fly ash at the pre-dissolution time of 180 min. It was found that the increase of pre-dissolution time increased strength development in class F fly ash. This trend was not found in geopolymer prepared by class C fly ash.

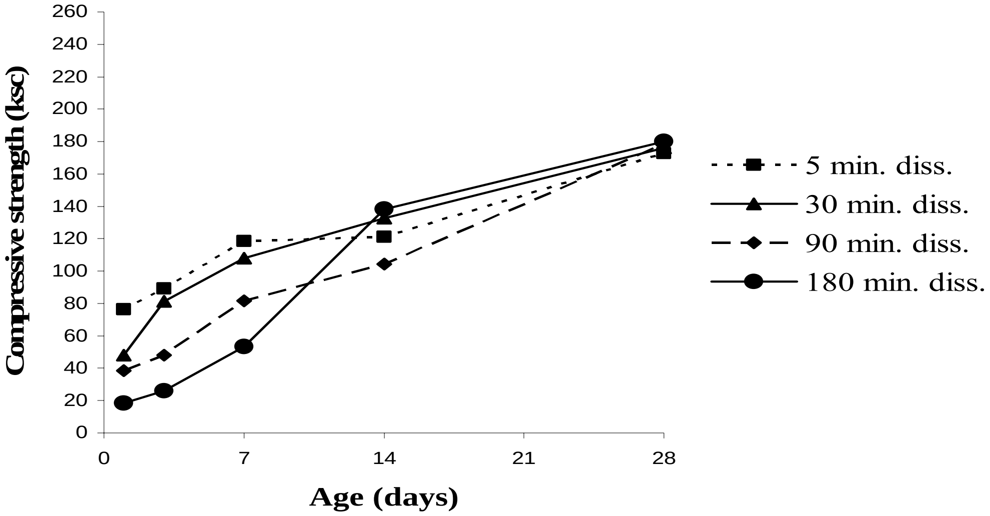


Figure 10 Compressive strength of class F fly ash geopolymer at various pre-dissolution times

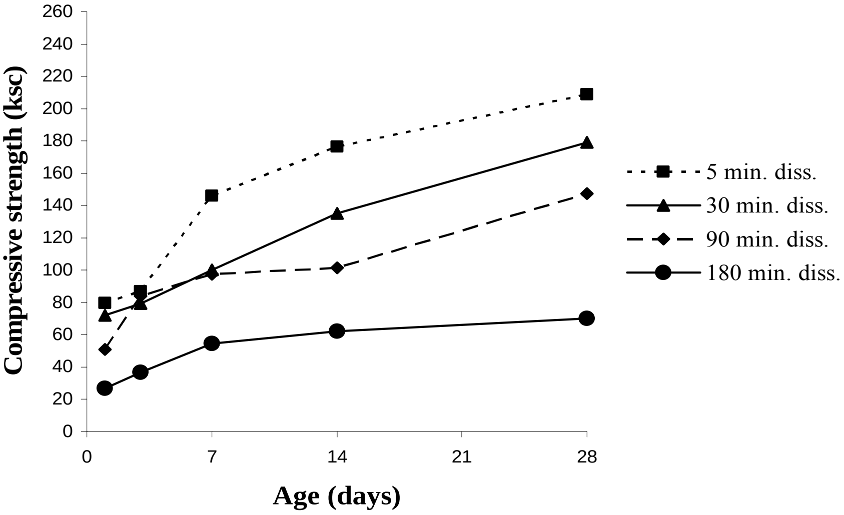


Figure 11 Compressive strength of class C fly ash geopolymer at various pre-dissolution times

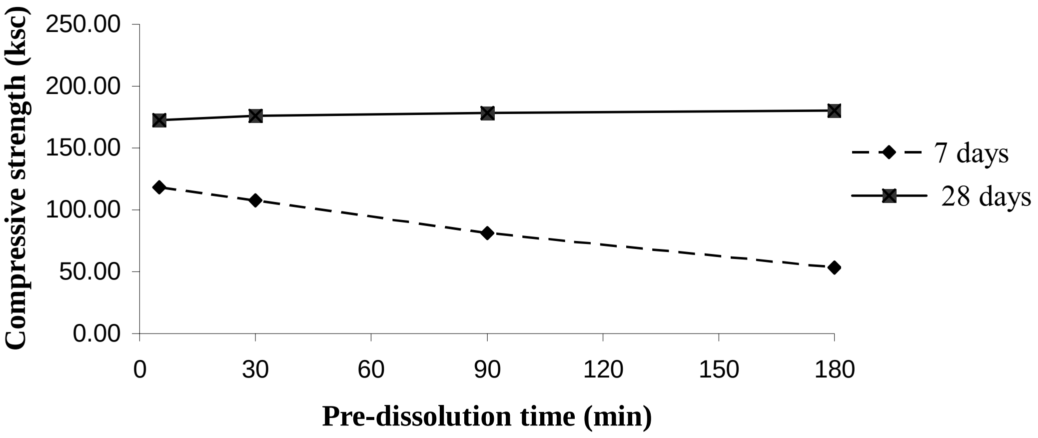


Figure 12 Strength development of class F fly ash geopolymer

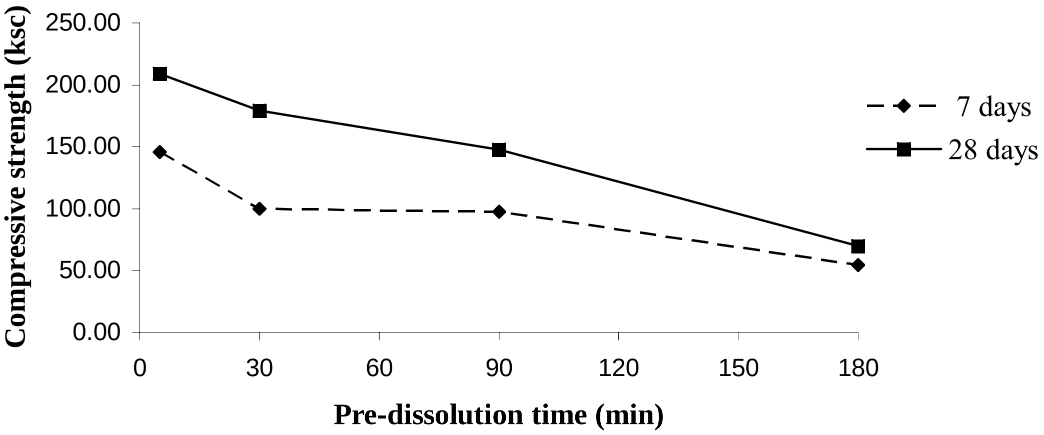


Figure 13 Strength development of class C fly ash geopolymer

Fig. 14 shows the compressive strength of specimens prepared by class F and class C fly ash at the age of 28 days at different pre-dissolution times. As shown, the compressive strength of class F fly ash geopolymer slightly increased with pre-dissolution time. For class C fly ash geopolymer, the increase of pre-dissolution time seemed to weaken the structures.

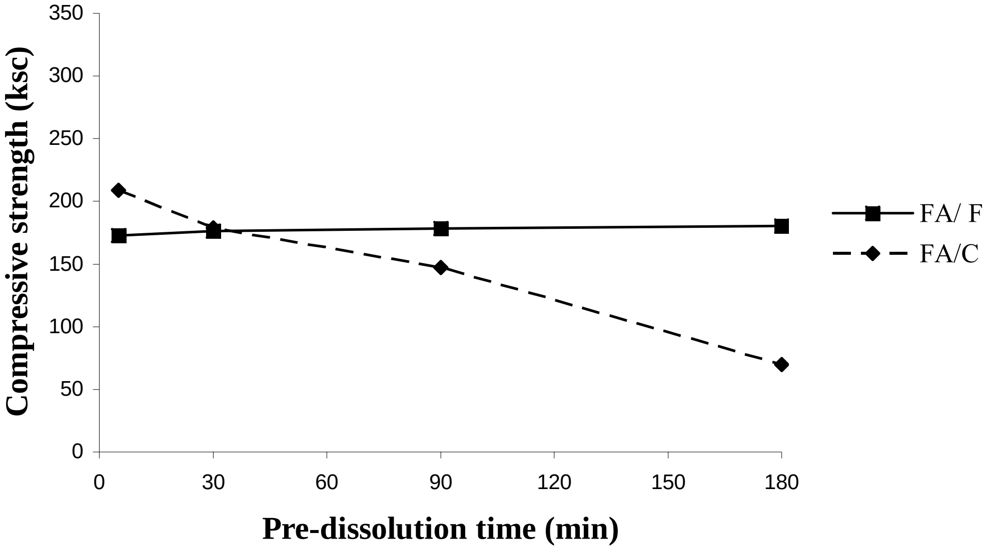


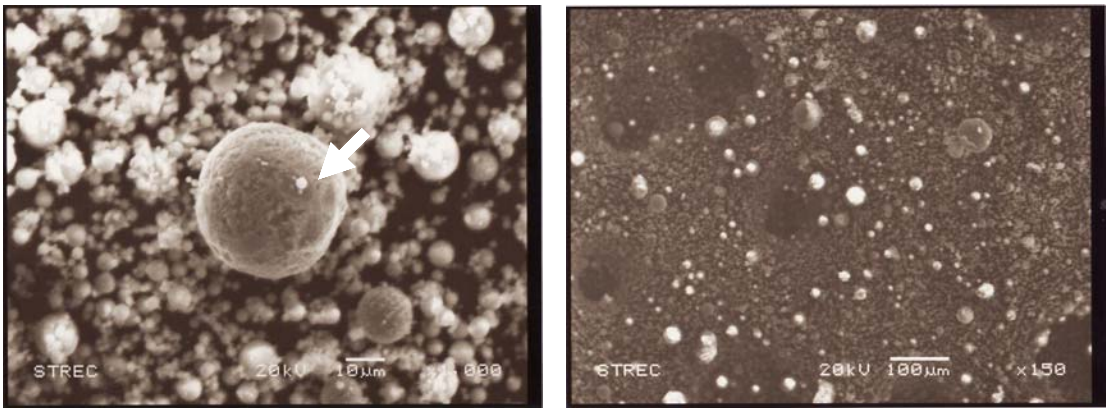
Figure 14 Comparison of compressive strength at 28 days between class F and class C fly ash at different pre-dissolution times

4. Mineralogical and microstructure characterization

4.1 SEM-EDX

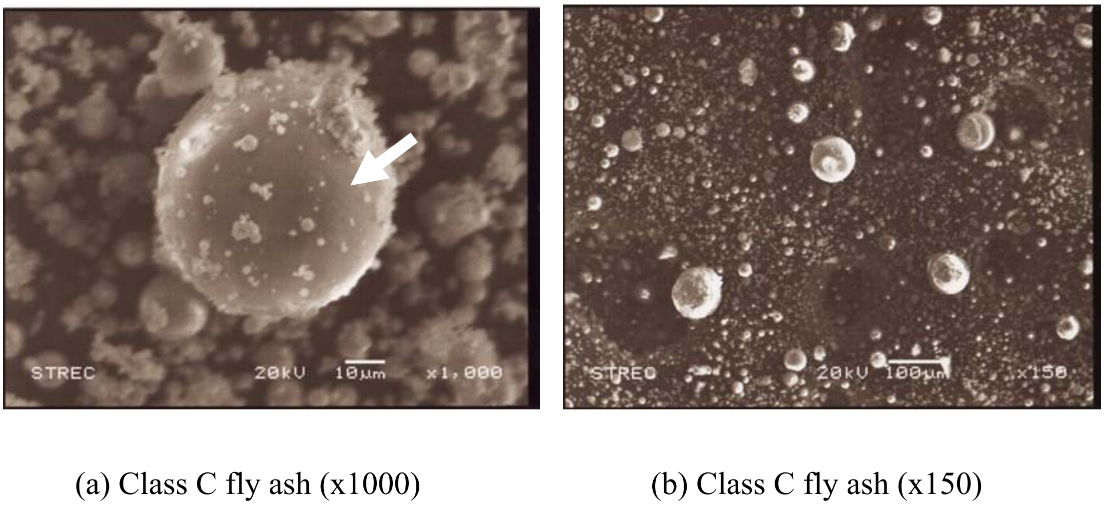
Scanning electron microscopy-energy dispersive x-ray (SEM-EDX) analysis was conducted in order to get a better understanding of fly ash as starting material as well as fly ash-based geopolymer.

Figs. 15 and 16 show the SEM micrographs of class F and class C fly ash at x1000 and x150 magnification. As shown, the majority of particles are spherical shape of different sizes but with a regular smooth texture. The principal composition of fly ash was silicate (Si) and alumina (Al). The corresponding result from EDX in Figs. 17 and 18 confirmed the relatively high content of Al and Si. Some existence of solid deposits or small crystal on fly ash surface can be detected. This is shown clearly on Fig. 16(a). As J.G.S van Jaarsveld *et al*. (2003) had stated that particle size is one of the factors which greatly affects both initial mix and final properties of geopolymer.



(a) Class F fly ash (x1000) (b) Class F fly ash (x150)

Figure 15 SEM micrographs of class F fly ash



(a) Class C fly ash (x1000) (b) Class C fly ash (x150)

Figure 16 SEM micrographs of class C fly ash

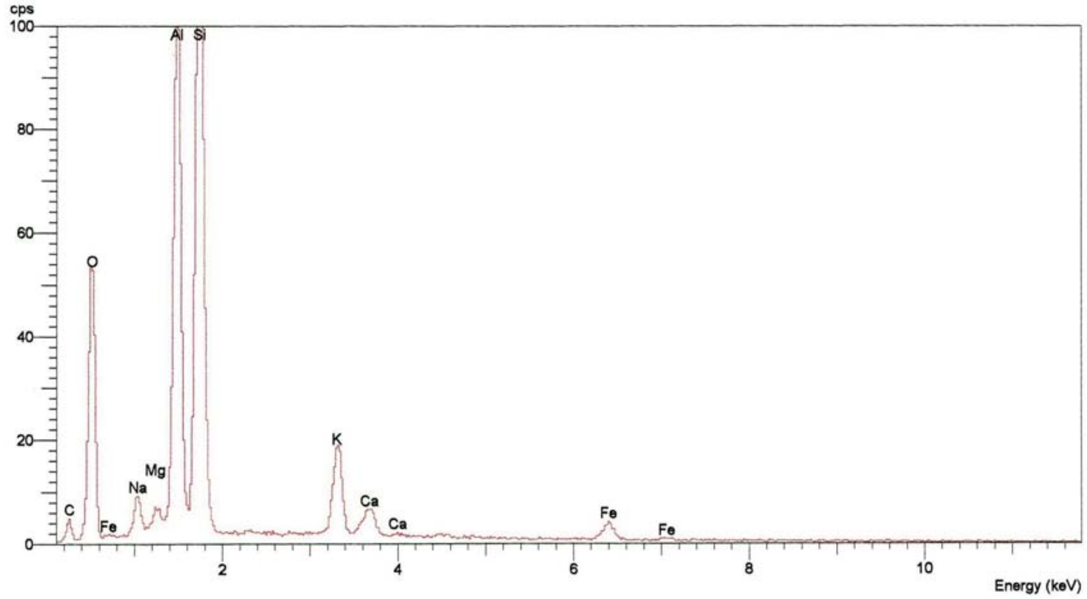


Figure 17 SEM - EDS micrograph of class F fly ash

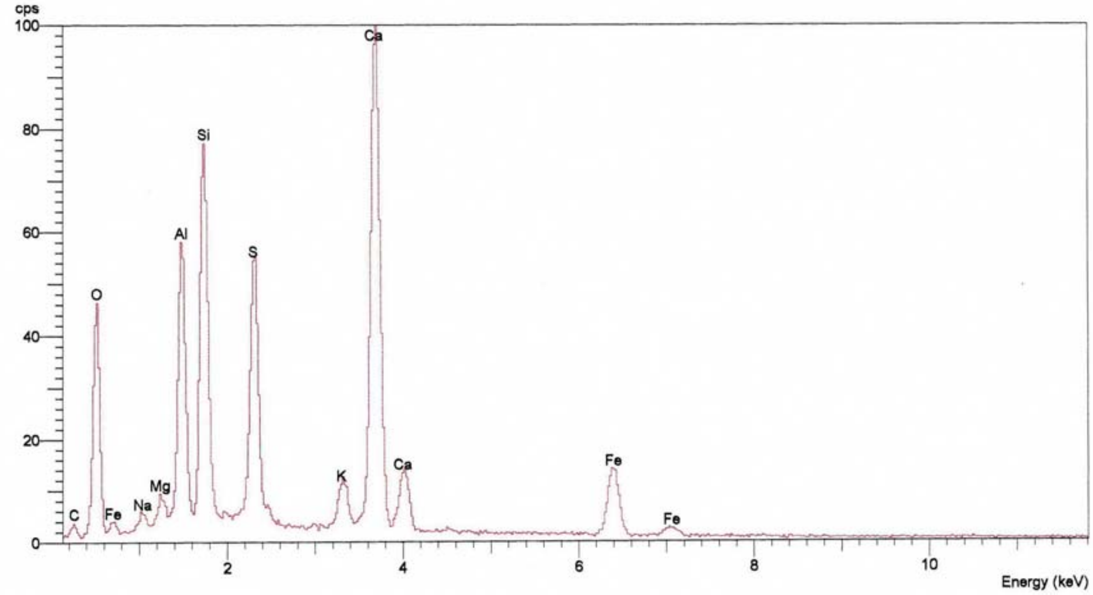
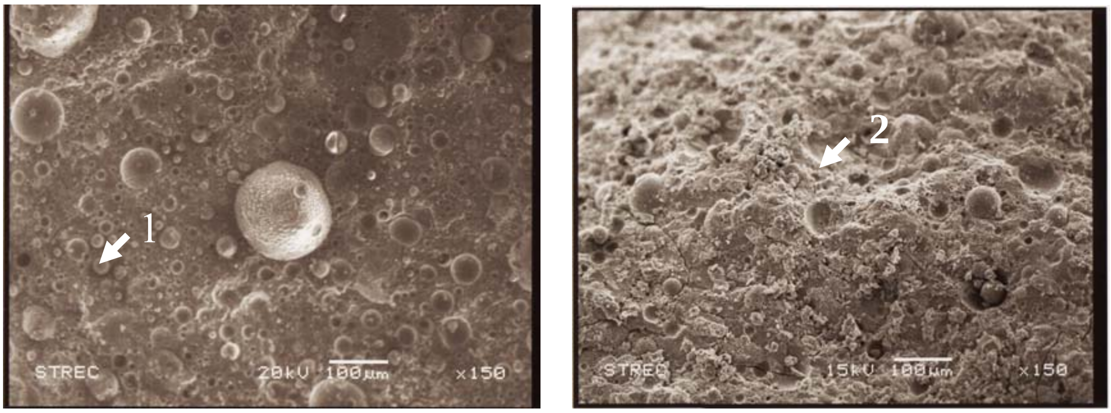
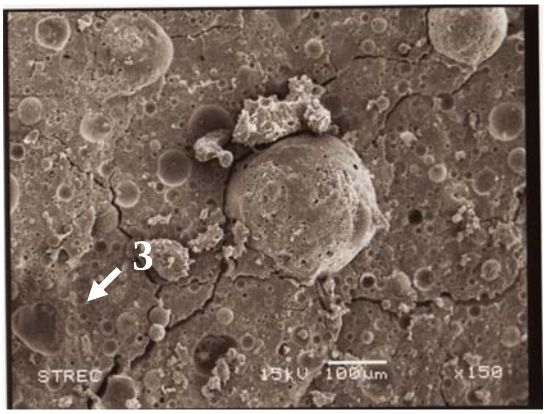


Figure 18 SEM - EDS micrograph of class C fly ash

Fig. 19 shows geopolymer synthesis from class F fly ash at pre-dissolution time of 5, 30 and 180 min. As shown, fly ash-based geopolymer was a composite material that contained dense packing of particles of starting material, surrounded by geopolymer matrix and pores. Voids were also clearly visible. Cracks can be detected only from the pre-dissolution time of 180 min. These cracks were running in the binding matrix but not passed through fly ash and grain-matrix interface either. The evidence of large pores was also seen due to entrapped air. A significant difference in the appearance of the matrix-forming phase was observed in Fig. 19(b). It showed dense matrix and small amount of non-reacted fly ash in geopolymer. More voids can be detected. This matrix was the consequence of polycondensation attained from the Al and Si from the dissolution phase. It can be explained by the dissolution test which also yielded the highest amount of Al and Si.



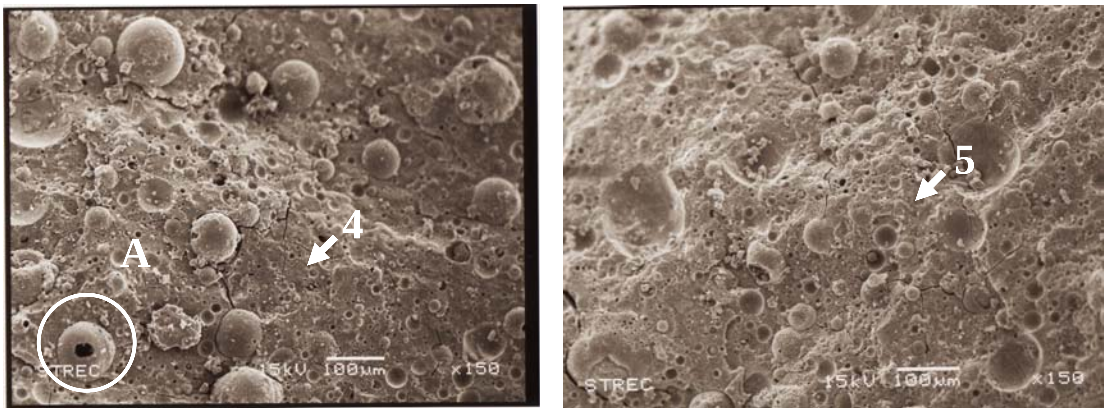
(a) Pre-dissolution time at 5 min (b) Pre-dissolution time at 30 min



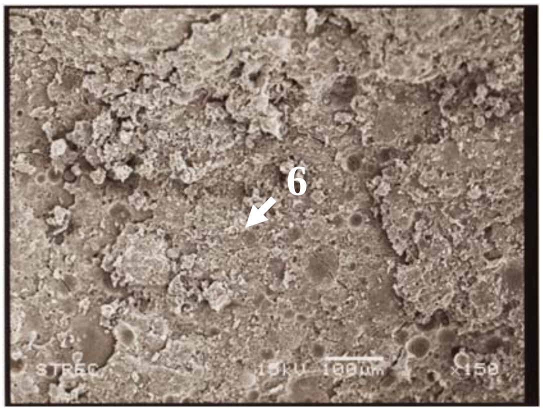
(C) Pre-dissolution time at 180 min

Figure 19 SEM photographs of geopolymer synthesis from class F fly ash

Fig.20 shows geopolymer synthesis from class C fly ash at the pre-dissolution time of 5, 30 and 180 min. As shown, the ones yielding highest and lowest strength were 5 and 180 min, respectively. The SEM micrograph showed that the structure was dense, with non-reacted fly ash the same as that corresponding to geopolymer prepared with class F, while only loose structure precipitation can be detected from specimens using 180 min. This is compatible with the compressive strength results which yielded the highest and lowest strength which were attained at pre-dissolution of 5 and 180 min, respectively. As shown in point A, Fig. 20(a), it confirmed that the alkaline dissolution dissolved part of the surface of fly ash.



(a) Pre-dissolution time at 5 min (b) Pre-dissolution time at 30 min



(C) Pre-dissolution time at 180 min

Figure 20 SEM photographs of geopolymer synthesis from class C fly ash

EDX analysis has been performed to determine mineralogical characteristics of fly ash-based geopolymer. The results of EDX analyses (Table 6) of points 1 to 6 (Figs. 19 and 20) showed that it was mainly alumino-silicates with a small amount of Na component contained in geopolymer. Si concentration showed constant value in all points and different from Al. It can be explained that Si species not only come from the dissolution from the particle but also from the soluble alkaline silicate while Al species only dissolved from the starting material under high alkaline solution. Mg is very low in every point the as same as Fe and Na.

Table 6 EDX microanalysis on specific points of samples (% of atomic).

Point	Al	Si	Ca	Fe	Mg	Na
1	4.15	12.01	12.00	1.81	0.25	3.81
2	6.87	15.19	3.83	0.72	0.15	2.21
3	12.34	14.45	12.00	1.44	0.97	3.20
4	8.39	14.70	3.67	2.18	1.21	2.29
5	5.73	14.50	2.53	1.53	1.23	1.13
6	9.26	14.36	3.93	1.44	0.75	3.20

4.2 XRD

Mineralogical characterization was carried out by XRD. Scans were performed from 3 to 65° 2θ at 0.02° 2θ steps. The results in Figs 21 and 22 showed all fly ash based geopolymer produced an X-ray diffractogram with the same basic features mostly attributable to reacting fly ash. For instance, peaks due to haematite (F), quartz (Q) and mullite (M) were all regularly observed. The board hump registered in both classes of specimens were from $2\theta = 20^{o} - 35^{o}$. A hump in this region was the characteristic of amorphous silica. This indicated that there may be some non-reacted fly ash which remained in geopolymer.

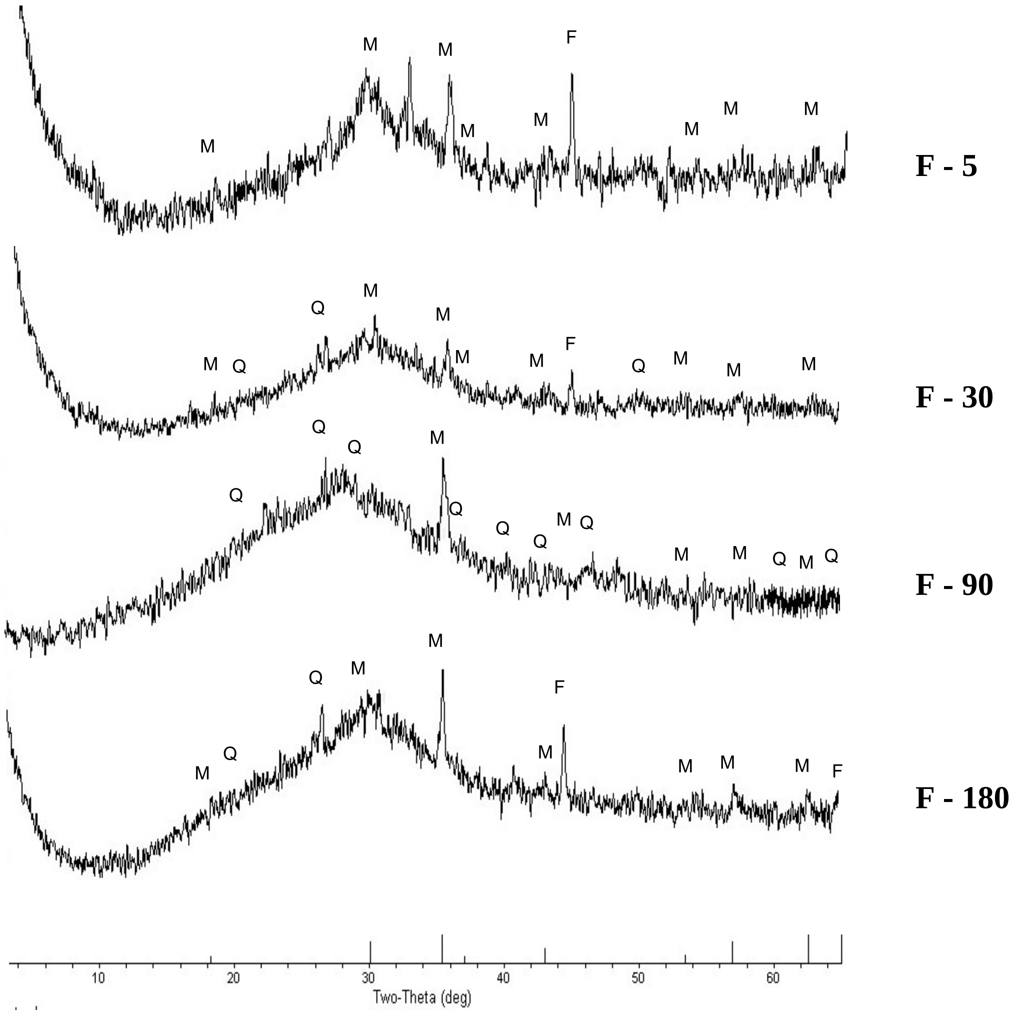


Figure 21 XRD - pattern of fly ash based geopolymer prepared by class F fly ash: Q= quartz, M= mullite and F = hematite

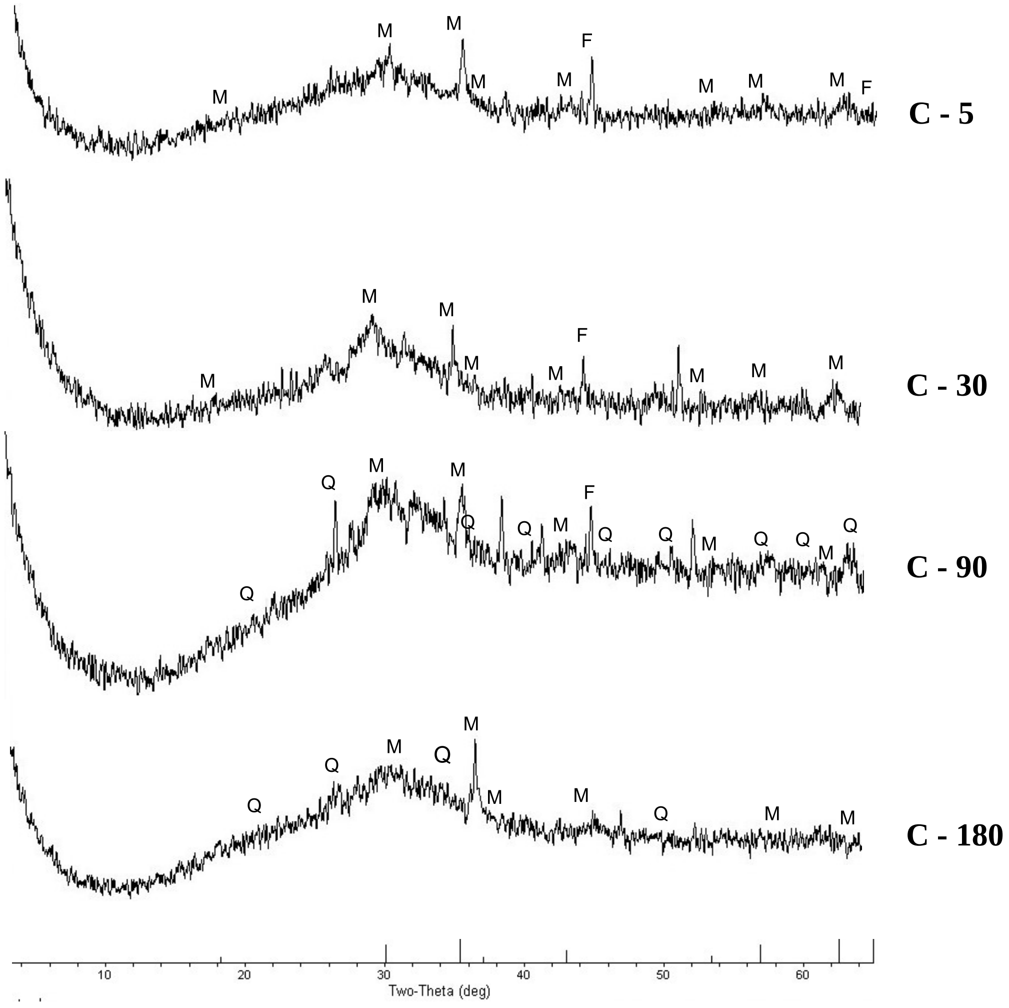


Figure 22 XRD - pattern of fly ash based geopolymer prepared by class C fly ash: Q= quartz, M= mullite and F = hemitite

5. Geopolymerized hardening

Geopolymer is an amorphous semi-crystalline material with three dimensional polymeric chain and ring of polymer with Si^{4+} and Al^{3+} structures. Geopolymerization consisted of dissolution condensation phases. To confirm this procedure, specimens that contain Si, Al and Ca elemental compositions were prepared and filtered from the paste mixture of fly ash and NaOH at different pre-dissolution times (5, 30, 90 and 180 min). To complete the geopolymerization, Na_2SiO_3 was then added.

From results of the test, no change was observed after mixing all substances. After 4 hours, only turbidity of the mixture from specimens prepared with Class F fly ash was observed to be increased. The most obvious was change of turbidity from class F fly ash at the period of 5 min. No setting was observed in all specimens. It can be concluded that geopolymer production also needs several other factors to make the whole system harden in a final structure. Further study about this reaction is needed in the future.

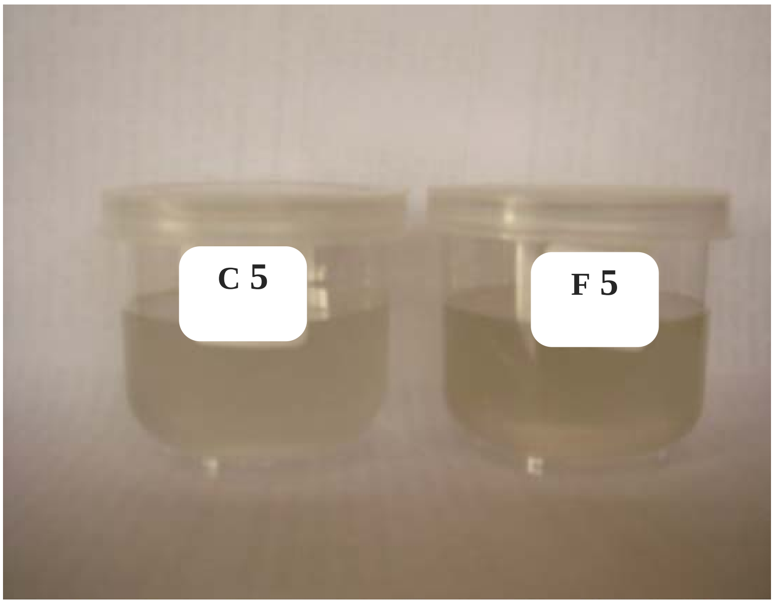


Figure 23 Change of substance after 4 hours for class F and class C fly ash at pre-dissolution at 5 min

CONCLUSION AND RECOMMENDATIONS

Conclusion

It was found from the study about effect of pre-dissolution time on dissolution of Al, Si and Ca ions from fly ash, on mechanical properties which consisted of compressive strength, setting time, and on microstructure of geopolymer prepared by using 2 types of fly ash (Class C and Class F) that

1. Si, Al and Ca increased to a maximum values at pre-dissolution time of 30 min for both classes of fly ash. After that, the concentration decreased. For Al, the dissolution continued until end of experiment for class F fly ash.

2. Pre-dissolution time has different effect on strength, depending on type of fly ash. Class F geopolymer yielded minimal difference in at 28 - days strength. For class C geopolymer, increase pre-dissolution time showed significant decrease in strength. In this study, no relationship was found between dissolution ions concentration and strength.

3. Increased pre-dissolution time increased setting time in both classes of geopolymer. Class C fly ash geopolymer showed faster setting time than class F fly ash geopolymer.

4. Geopolymer was a composite material which consisted of the matrix, surrounded by non-reacted fly ash. This hardening leads to compressive strength of geopolymer. The XRD results indicated that geopolymer showed the same basic features mostly attributable to reacting fly ash. For instance, haematite (F), quartz (Q) and mullite (M) were all regularly observed in all specimens.

Recommendations

1. Recommend topics for further study as following:

1.1 Study about higher Sodium Hydroxide (NaOH) morality should be discussed.

1.2 Study about other ratio of FA/solution should be discussed.

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APPENDICES

Appendix A

Results of compressive strength

Appendix Table A1 Compressive strength of geopolymer prepared by class F fly ash at pre-dissolution time of 5 min

Pre-dissolution time (min)	Age (days)	Sample No.	Height (cm)	Diameter (cm)	Weight (g)	Area (cm^2)	P (kg)	Stress (kg/cm^2)	
5 min	1	1	7.60	4.40	218.40	15.21	1075	70.70	76.31
		2	7.42	4.34	213.10	14.79	1325	89.57	
		3	7.54	4.36	216.00	14.93	1025	68.65	
	3	1	7.74	4.44	219.40	15.48	1325	85.58	89.07
		2	7.92	4.44	218.90	15.48	1450	93.65	
		3	7.63	4.42	216.70	15.34	1350	87.98	
	7	1	7.82	4.42	221.00	15.34	1825	118.94	118.40
		2	7.84	4.42	222.30	15.34	1875	122.20	
		3	7.75	4.42	221.80	15.34	1750	114.05	
	14	1	7.62	4.43	215.10	15.41	1700	110.29	121.11
		2	7.63	4.43	213.40	15.41	2200	142.73	
		3	7.63	4.43	217.40	15.41	1700	110.29	
	28	1	7.73	4.31	220.00	14.59	2500	171.35	172.79
		2	7.67	4.31	218.20	14.59	2450	167.93	
		3	7.69	4.32	218.70	14.66	2625	179.09	

Appendix Table A2 Compressive strength of geopolymer prepared by class F fly ash at pre-dissolution time of 30 min

Pre-dissolution time (min)	Age (days)	Sample No.	Height (cm)	Diameter (cm)	Weight (g)	Area (cm^2)	P (kg)	Stress (kg/cm^2)	
30 min	1	1	7.72	4.2	209.1	13.85	700	50.53	47.98
		2	7.92	4.26	215.2	14.25	650	45.60	
		3	7.74	4.24	214.3	14.12	675	47.81	
	3	1	7.83	4.31	206.8	14.59	1150	78.82	81.41
		2	7.82	4.31	208.5	14.59	1125	77.11	
		3	7.7	4.33	211.6	14.73	1300	88.28	
	7	1	7.58	4.32	207.8	14.66	1500	102.34	107.85
		2	7.62	4.33	205.9	14.73	1600	108.66	
		3	7.65	4.32	208.2	14.66	1650	112.57	
	14	1	7.56	4.35	206.6	14.86	1975	132.89	132.75
		2	7.68	4.36	216.8	14.93	1950	130.61	
		3	7.58	4.32	205.9	14.66	1975	134.74	
	28	1	7.41	4.41	204.5	15.27	2675	175.13	176.19
		2	7.38	4.38	202.8	15.07	2650	175.88	
		3	7.41	4.4	203.7	15.21	2700	177.57	

Appendix Table A3 Compressive strength of geopolymer prepared by class F fly ash at pre-dissolution time of 90 min

Pre-dissolution time	Age	Sample	Height	Diameter	Weight	Area	P	Stress	
(min)	(days)	No.	(cm)	(cm)	(g)	(cm^2)	(kg)	(kg/cm^2)	
90 min	1	1	7.74	4.20	209.30	13.85	500	36.09	38.50
		2	7.74	4.20	208.30	13.85	500	36.09	
		3	7.72	4.20	209.60	13.85	600	43.31	
	3	1	7.60	4.43	219.00	15.41	750	48.66	48.06
		2	7.92	4.30	212.40	14.52	700	48.20	
		3	7.83	4.34	217.30	14.79	700	47.32	
	7	1	7.65	4.30	218.30	14.52	1100	75.75	81.49
		2	7.43	4.30	209.40	14.52	1200	82.63	
		3	7.50	4.30	210.10	14.52	1250	86.08	
	14	1	7.74	4.30	219.40	14.52	1600	110.18	104.32
		2	7.58	4.44	207.40	15.48	1525	98.49	
		3	7.62	4.42	208.30	15.34	1600	104.28	
	28	1	7.45	4.30	211.40	14.52	2550	175.60	178.46
		2	7.55	4.30	213.60	14.52	2625	180.76	
		3	7.50	4.30	209.70	14.52	2600	179.04	

Appendix Table A4 Compressive strength of geopolymer prepared by class F fly ash at pre-dissolution time of 180 min

Pre-dissolution time	Age	Sample	Height	Diameter	Weight	Area	P	Stress	
(min)	(days)	No.	(cm)	(cm)	(g)	(cm^2)	(kg)	(kg/cm^2)	
180 min	1	1	7.54	4.36	216.60	14.93	275	18.42	18.53
		2	7.74	4.34	223.20	14.79	275	18.59	
		3	7.74	4.34	220.20	14.79	275	18.59	
	3	1	7.70	4.43	218.40	15.41	425	27.57	25.95
		2	7.73	4.43	221.50	15.41	400	25.95	
		3	7.53	4.43	214.20	15.41	375	24.33	
	7	1	7.74	4.32	219.60	14.66	750	51.17	53.44
		2	7.68	4.32	216.90	14.66	850	57.99	
		3	7.72	4.32	222.10	14.66	750	51.17	
	14	1	7.80	4.30	223.70	14.52	2000	137.72	138.30
		2	7.74	4.30	215.70	14.52	2025	139.44	
		3	7.68	4.30	217.00	14.52	2000	137.72	
	28	1	7.42	4.30	218.70	14.52	2600	179.04	180.19
		2	7.33	4.30	216.40	14.52	2650	182.48	
		3	7.23	4.30	217.80	14.52	2600	179.04	

Appendix Table A5 Compressive strength of geopolymer prepared by class C fly ash at pre-dissolution time of 5 min

Pre-dissolution time	Age	Sample	Height	Diameter	Wt.	Area	P	Stress	
(min)	(days)	No.	(cm)	(cm)	(g)	(cm^2)	(kg)	(kg/cm^2)	
5 min	1	1	7.52	4.42	219.60	15.34	1250	81.43	79.48
		2	7.54	4.32	217.80	14.66	1075	73.31	
		3	7.44	4.36	216.20	14.93	1250	83.69	
	3	1	7.62	4.42	218.30	15.34	1350	87.98	86.76
		2	7.62	4.42	217.80	15.34	1300	84.72	
		3	7.72	4.43	218.60	15.41	1350	87.59	
	7	1	7.8	4.43	221.10	15.41	2200	142.73	145.98
		2	7.63	4.43	218.20	15.41	2250	145.98	
		3	7.7	4.43	219.60	15.41	2300	149.22	
	14	1	7.63	4.44	214.50	15.48	2700	174.38	176.53
		2	7.9	4.42	223.80	15.34	2700	175.97	
		3	7.83	4.42	221.10	15.34	2750	179.22	
	28	1	7.64	4.31	219.20	14.59	3050	209.05	208.90
		2	7.66	4.33	217.20	14.73	3100	210.52	
		3	7.71	4.33	218.10	14.73	3050	207.13	

Appendix Table A6 Compressive strength of geopolymer prepared by class C fly ash at pre-dissolution time of 30 min

Pre-dissolution time (min)	Age (days)	Sample No.	Height (cm)	Diameter (cm)	Wt. (g)	Area (cm^2)	P (kg)	Stress (kg/cm^2)	
30 min	1	1	7.90	4.20	211.80	13.85	1125	81.20	71.95
		2	8.06	4.20	215.60	13.85	875	63.16	
		3	8.00	4.22	210.30	13.99	1000	71.50	
	3	1	8.02	4.30	213.40	14.52	1175	80.91	79.16
		2	7.90	4.35	215.80	14.86	1175	79.06	
		3	7.83	4.44	215.40	15.48	1200	77.50	
	7	1	7.42	4.41	212.30	15.27	1550	101.48	100.00
		2	7.61	4.36	208.90	14.93	1450	97.12	
		3	7.54	4.34	210.10	14.79	1500	101.40	
	14	1	7.58	4.32	212.80	14.66	2000	136.45	135.02
		2	7.74	4.37	221.80	15.00	2025	135.01	
		3	7.80	4.42	220.10	15.34	2050	133.60	
	28	1	7.52	4.31	215.60	14.59	2600	178.21	179.06
		2	7.59	4.35	217.80	14.86	2800	188.40	
		3	7.62	4.32	213.70	14.66	2500	170.56	

Appendix Table A7 Compressive strength of geopolymer prepared by class C fly ash at pre-dissolution time of 90 min

Pre-dissolution time (min)	Age (days)	Sample No.	Height (cm)	Diameter (cm)	Wt. (g)	Area (cm^2)	P (kg)	Stress (kg/cm^2)	
90 min	1	1	7.80	4.44	217.80	15.48	775	50.05	50.80
		2	7.66	4.20	206.90	13.85	750	54.13	
		3	7.80	4.30	219.10	14.52	700	48.20	
	3	1	7.84	4.34	219.00	14.79	1250	84.50	83.90
		2	7.83	4.34	220.10	14.79	1250	84.50	
		3	7.84	4.43	225.70	15.41	1275	82.72	
	7	1	7.63	4.31	213.60	14.59	1400	95.96	97.47
		2	7.65	4.32	214.00	14.66	1400	95.51	
		3	7.52	4.35	216.10	14.86	1500	100.93	
	14	1	7.66	4.34	213.10	14.79	1500	101.40	101.40
		2	7.72	4.34	213.20	14.79	1500	101.40	
		3	7.60	4.34	212.80	14.79	1500	101.40	
	28	1	7.63	4.32	209.40	14.66	2200	150.09	147.48
		2	7.60	4.31	205.00	14.59	2125	145.65	
		3	7.62	4.32	204.30	14.66	2150	146.68	

Appendix Table A8 Compressive strength of geopolymer prepared by class C fly ash at pre-dissolution time of 180 min

Pre-dissolution time	Age	Sample	Height	Diameter	Wt.	Area	P	Stress	
(min)	(days)	No.	(cm)	(cm)	(g)	(cm^2)	(kg)	(kg/cm^2)	
180 min	1	1	7.80	4.21	215.60	13.92	375	26.94	26.69
		2	7.80	4.24	215.60	14.12	375	26.56	
		3	7.80	4.24	215.60	14.12	375	26.56	
	3	1	7.63	4.30	207.50	14.52	550	37.87	36.73
		2	7.90	4.30	215.60	14.52	550	37.87	
		3	7.80	4.30	212.30	14.52	500	34.43	
	7	1	7.80	4.30	219.90	14.52	800	55.09	54.51
		2	7.62	4.30	209.60	14.52	750	51.65	
		3	7.78	4.30	217.70	14.52	825	56.81	
	14	1	7.78	4.43	218.00	15.41	950	61.63	62.18
		2	7.82	4.43	220.10	15.41	950	61.63	
		3	7.70	4.43	216.00	15.41	975	63.26	
	28	1	7.56	4.30	217.80	14.52	1000	68.86	70.01
		2	7.44	4.30	219.60	14.52	1000	68.86	
		3	7.51	4.30	216.50	14.52	1050	72.30	

Appendix B

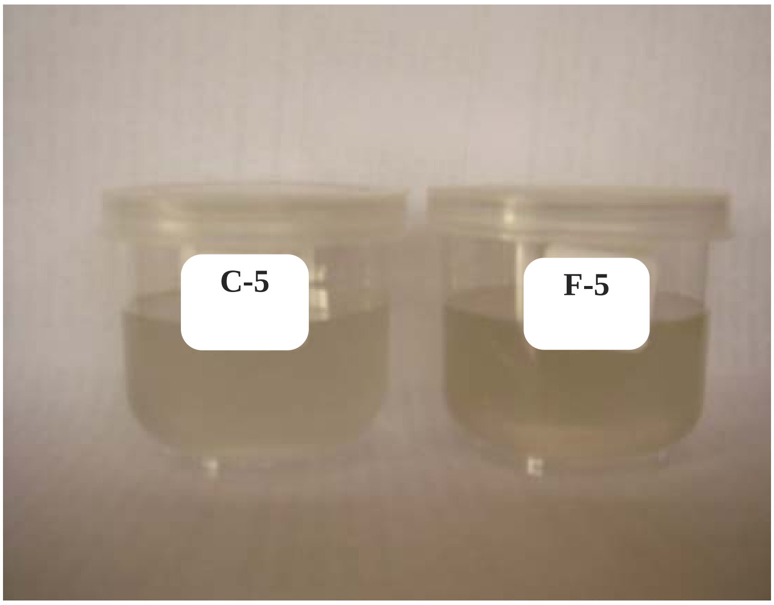
Results of dissolution test

Appendix Table B1 Quantitative determination of geopolymer paste prepared by class F and class C fly ash at different pre-dissolution times

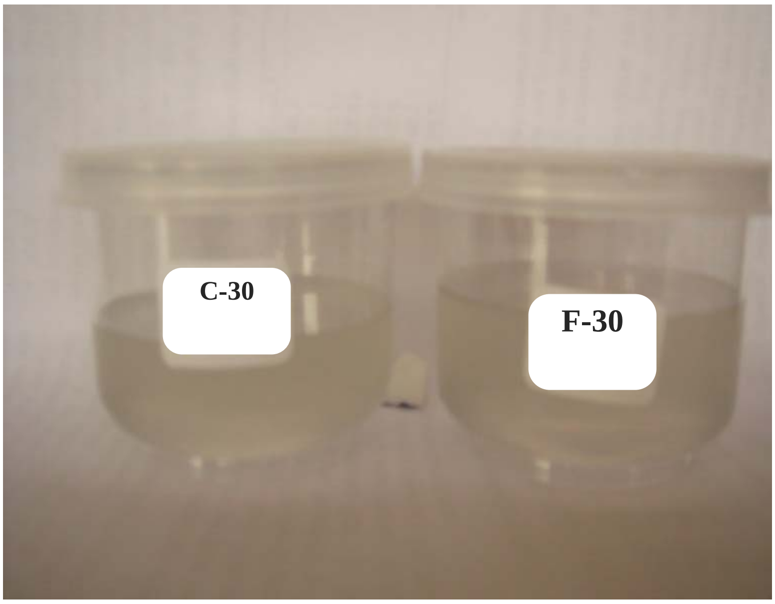
Type of fly ash	Pre-dissolution time	Elemental Composition		
		Al	Si	Ca
	(min)	(mg/L)	(mg/L)	(mg/L)
Class F	5	19.85	76.28	26.82
	30	164.70	254.20	116.90
	90	173.50	120.50	17.65
	180	283.60	126.80	17.19
Class C	5	9.27	57.47	54.96
	30	87.99	156.00	173.00
	90	66.93	112.00	109.80
	180	47.48	55.35	35.93

Appendix C

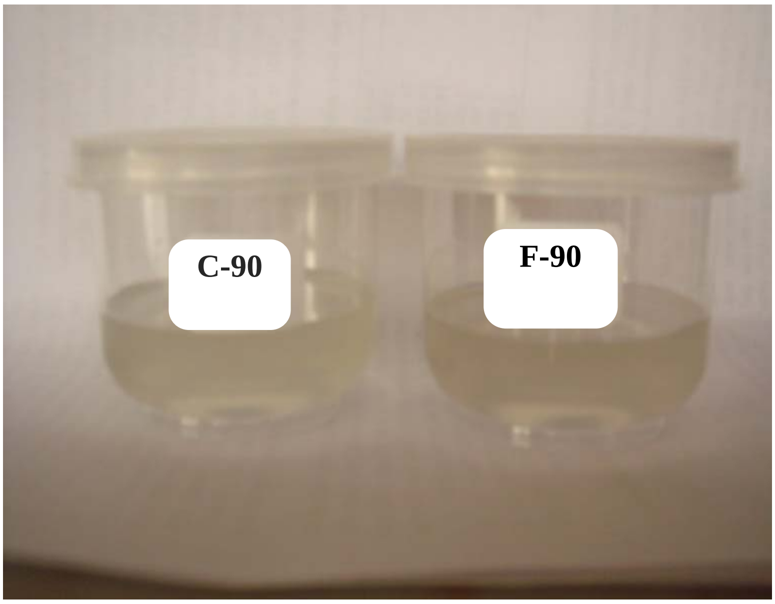
Photos of geopolymerized hardening



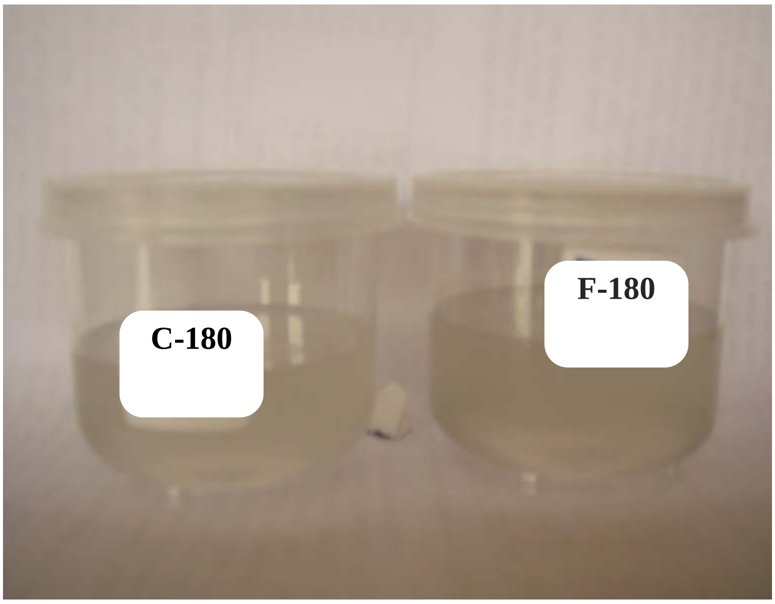
Appendix Figure C1 Change of substance after 4 hours for class F and class C fly ash at pre-dissolution of 5 min



Appendix Figure C2 Change of substance after 4 hours for class F and class C fly ash at pre-dissolution of 30 min



Appendix Figure C3 Change of substance after 4 hours for class F and class C fly ash at pre-dissolution of 90 min



Appendix Figure C4 Change of substance after 4 hours for class F and class C fly ash at pre-dissolution of 180 min

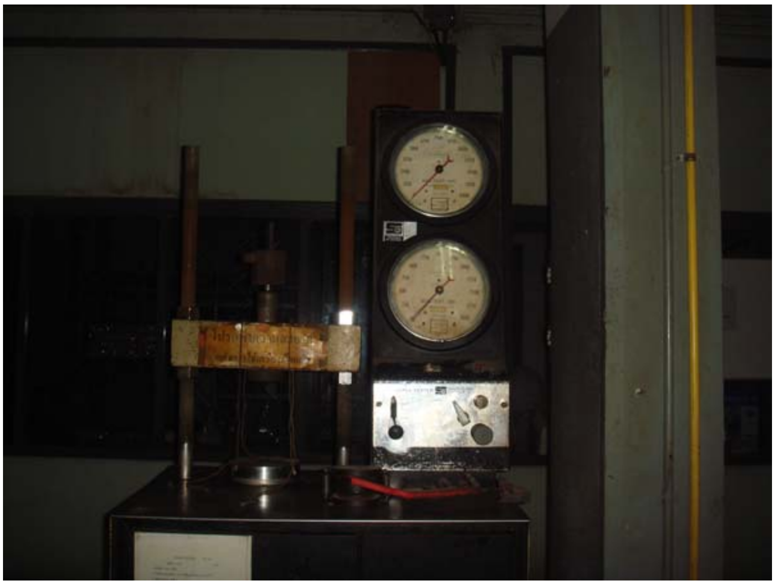
Appendix D

Photos of the equipment

Appendix Figure D1 Filter pumper

Appendix Figure D2 Filter set and membrane filter

Appendix Figure D3 Concrete mixer



Appendix Figure D4 Compressive strength machine (Vice Versa)

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