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A Review on the Effect of Fly Ash Characteristics and Their Variations on the Synthesis of Fly Ash Based Geopolymer

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Abstract. There are more than four decades since the last 1970s where geopolymers concrete was first introduced and developed to use as a replacement to conventional concrete material which uses cement as a binder. And since the last two decades, geopolymers which utilized fly ash as aluminosilicate source material, i.e. fly ash based geopolymers, have been investigated. Many researchers present how to produce the best fly ash based geopolymer with a various source of constituent material as well as mixing formula to achieve exceptional concrete performance. Although there is a similar trend towards factors affecting the result of fly ash based geopolymer synthesis, there is still remain a wide range in mixture proportion. The considerable variation in fly ash characteristics as source material in the synthesis can very likely be one of the causes of this problem. This paper attempts to identify the effect of source material variation of geopolymer concrete, particularly which use fly ash as source material and focuses on the variation of its characteristics and the effects to properties of concrete. From the reviews it concluded that different sources (and even the same source, but different batch) of fly ash materials will give some different characteristics of the fly ash, where it would affect the synthesis process of the fly ash based geopolymer concretes.

INTRODUCTION

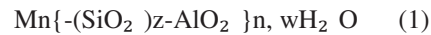
ASTM [1] describes fly ash as the finely divided residue (i.e. a by-product material) that results from the combustion of ground or powdered coal and transported by flue gasses. As a by-product material, fly ash frequently used to replace ordinary Portland cement in the ‘green concrete’, and thus can reduce the CO₂ emission which is one of the causes of global warming. The replacement can go in either partially (generally known as pozzolan cement, fly ash concrete, or high volume fly ash concrete) or entirely (generally named as fly ash based geopolymer, or alkali activated fly ash) of cementitious proportion. Fly ash is also known as pozzolanic material because fly ash contains silica and alumina, which in itself possesses a little or no cementitious value but will (in finely divided form and in the presence of moisture) chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties, as defined by ACI [2]. Nevertheless, some fly ash, especially those generated from lignite and sub-bituminous coal combustion, may possess a varying degree of cementitious value, even without any addition of calcium hydroxide or Portland cement regarding some lime contained in the fly ash.

In term of fly ash based geopolymer, fly ash is one of the main constituents which have an important role in determining the results of the synthesis. As the fly ash generated from the coal combustion, mostly from the power plant industry (which may just focus on electric power generated), the quality and properties of fly ash could differ significantly between plants and even between shipments (in the case of the same plant) [3]. Related to the wide variety of fly ash properties, characterization of fly ash prior to use is substantial, wherein it will determine the level of fly ash reactivity [4], and finally the result of the product, i.e. fresh properties and hardened properties of geopolymers. Furthermore, based on the fact that it is almost impossible to control the nature of fly ash as in cement

production, it is necessary to understand how each of the properties of fly ash will affect the fresh state (e.g. workability, setting time, curing regime, etc.) and hardened behavior (mechanical strength, shrinkage behavior, durability, etc.) of fly ash based geopolymers.

Terminology of Geopolymers

The term of geopolymers (géopolymères in French) was first expressed by Joseph Davidovits to describe an amorphous to semi-crystalline three-dimensional silico-aluminate materials, or in other words, a mineral polymers resulting from geochemistry or geosynthesis process [5]. The proposed terminology for chemical designation of geopolymers was poly(sialate), where “sialate” is an abbreviation for silicon-oxo-aluminate [6]. The empirical formula for this poly(sialate) are as follows:



wherein M is a cation such as potassium, sodium, or calcium, and “n” is the degree of polycondensation, while “z” is 1, 2, 3, and “w” is the amount of binding water.

A polymeric structure of poly(sialate) (Al-O-Si) formed constitutes the main building blocks of geopolymeric structure [7]. Depending on the Si/Al ratios, it can be categorized into three basic forms, which is poly(sialate) for Si/Al=1, poly(sialate-siloxo) for Si/Al=2, and poly(sialate-disiloxo) for Si/Al=3. In industrial application, the geopolymer compounds of the material are either crystalline or non-crystalline (amorphous or glassy structure), where crystalline poly(sialate) and poly(sialate-siloxo) result from the hydrothermal setting condition, and whereas hardening at ambient temperature induces amorphous or glassy structure [6].

The reaction involved in geopolymer synthesis differs from the hydration reaction in Portland cement, wherein the geopolymer synthesis requires an alkaline medium to start the reaction, while in hydration process just involves water to start the reaction. Furthermore, the interesting fact is that during the chemical reaction occurred in the formation of polymer chains, instead of consuming water, the geopolymer matrix will release water [8]. The hardening mechanism or geo-polymerization reaction simultaneously involves the dissolution of Si and Al in the presence of sodium hydroxide (alkaline activator), and then precipitation (or polycondensation) to form aluminosilicate gel phase before hardening to form a solid product [7].

Fly Ash Based Geopolymers Concrete

Because of the structure of geopolymer build from the bond of sialate, basically, all the materials which contain Si and Al, either natural mineral or by-product material, can be used as a constituent in geopolymer to be activated with the presence of alkali solution. Xu and Deventer [9] already investigated 16 natural Al-Si minerals and concluded that all the minerals to some extent soluble in concentrated alkaline solution. While in 1997, Van Jaarsveld, et al. [10], stated that most of the waste materials, included fly ash, contain large amounts of silica and alumina that can be used as a source of aluminosilicate materials for producing geopolymers concrete.

Many researchers have been investigating about the chemistry [5,6,10], the reaction mechanism [6,7,11], the fresh and hardened properties [8,12-14], the microstructure [15-17], and so much more, about this fly ash based geopolymers concrete. Although there are so many researches have been conducted, until now, there is still no clear and standardized guide about the making procedure of fly ash based geopolymer concrete, especially in terms of structural applications.

Nowadays, likely there are two approaches in synthesizing the fly ash to become a polymer material. Davidovits [18] through his patent in 2012 suggests the use of alkali metal silicate only, instead of silicate and hydroxide, but with the addition of blast furnace slag (with a specific surface less than 400 m²/kg), and the fly ash used is ASTM Class F (in which the CaO content is less than 8%). Blast furnace slag will act as basic calcium silicate (having a Ca/Si atomic ratio equal to or greater than 1) that participates in the geopolymeric reaction. In this approach, the fly ash particles would react only on their surface through a different chemical mechanism, namely surface geopolymeric reaction. There are some aspects to be considered when applying this method, such as the production

cost, which in the patent suggests it is better to use potassium silicate (more expensive) instead of sodium silicate. The other aspect is the incorporation of slag in the mixture, which demands better understanding, at least in term of properties of two materials (fly ash and slag) instead of one material (fly ash). It is important to keep in mind that both materials are an industrial by-product, which has a wide variety of properties.

In another hand, the geopolymer synthesis starts by dissolving the fly ashes in order to get the individual reactive elements of silica and alumina from the surfaces of the particles followed by the polymerization of active surface groups and soluble species to form a gel before resulting hardened geopolymer structure [15]. The dissolving process starts when the fly ash mixed with alkali metal hydroxide, either sodium or potassium hydroxide. Since the reagent used to dissolve and to activate fly ash is an alkaline based liquid, therefore some researchers used the term alkali-activated fly ash. Palomo et al. [4,19] described two different models of alkali activated material based on two different conditions of the starting situation. The first model is based on Si and Ca compound in the source material, while the second model based on Si and Al compound.

As mentioned previously, the second reactant to be considered in geopolymer synthesis is an alkaline metal solution, which has a role as an activator to start the reaction. The most common alkaline metal solution used in geopolymer is sodium or potassium hydroxide, and in some cases, the addition of soluble silicates such as sodium or potassium silicate can boost the reaction at higher rates [19]. The effect of different type of alkali metal activator (i.e. sodium and potassium hydroxide and sodium and potassium silicate) on the properties of fly ash based geopolymer was studied comprehensively by Van Jaarsveld and Van Deventer [20]. They concluded that the type of alkali metal cation present in the hydroxide solution will affect every stage in the synthesis of fly ash based geopolymer. The choice of type of alkali metal cation is strongly related to the properties of fly ash used in the synthesis as well as the final objective in terms of application. Rattanasak and Chindaprasirt [16] also studied the influence of alkali solution particularly NaOH on the synthesis of fly ash based geopolymer. They investigate the leaching capability of aluminum and silicon ion from the surface of fly ash particle by sodium hydroxide at different alkali concentration and different leaching time. The results showed that sufficient time of leaching (approximately 5-10 minutes) with certain concentration would optimize the gel formation.

Contrary to the fly ash, which is a by-product material, alkali metal solution used in the synthesis is a kind of industrial product that can be easily arranged to produce consistent properties. Depart from that fact; it is not an exaggeration to say that a good understanding of the influence of each characteristic of fly ash become essential because different properties of fly ash will lead to different properties of the geopolymer final products. Therefore, the rest of this review will give emphasize more on the variation properties of fly ash and its effect on geopolymer synthesis and finally the properties of geopolymer products.

FLY ASH: CHARACTERISTICS AND CLASSIFICATION

As we already know that fly ash is a by-product material derived from the combustion of pulverized coal, therefore, the properties of fly ash is strongly depending on the characteristics of the source material, which is coal, and also the combustion process, as well as the cooling process. Owing to the rapid cooling of the material, fly ash are composed about 50-90% of the mineral matter in the form of glassy particles [21]. Additionally, the rapid cooling in the post-combustion zone also results in the formation of spherical and amorphous particles [22]. Generally, there are at least 3 major characterizations of fly ash, i.e. chemical composition, physical properties, and mineralogical composition.

For the classification system of fly ash, there are various standards that each has a requirement that must be met before the fly ash could be used as a mixture of concrete. In line with the many variations of fly ash, there is difference name of classification for different standards. The name of the fly ash classification is given due to the differences both in term of its chemical composition and physical properties. The mostly used method to determine the chemical composition of fly ash is by using X-Ray fluorescence (XRF) technique, while the physical properties of fly ash are determined mostly by its particle size distribution and specific surface area. In some cases, X-ray diffraction is also used for researching the crystalline phases in fly ashes or in another word the mineralogical behavior. Actually, it is important to know the phase composition in fly ash for the reason that the amorphous

composition is one of the reactive compounds that can be effectively synthesis to become geopolymer product as demonstrated in the experiments performed by Temuujin et al [23].

Variations in Chemical Composition

ASTM C618 [1] is one of the most used benchmarks for fly ash characterization and classification, which divided fly ash into 2 classes, i.e. class F which normally produced from burning anthracite or bituminous coal, and class C which normally produced from lignite or sub-bituminous coal. From the chemical composition requirements, ASTM prescribes the total composition of silicon oxide (SiO_2) plus alumina oxide (Al_2O_3) plus iron oxide (Fe_2O_3) are minimum 70% (by weight) for class F fly ash and 50% (by weight) for class C fly ash.

One of the other standards that also classify the fly ash is Canadian Standard, CAN/CSA-A3000-03 [24]. This standard divides fly ash into 3 categories, where calcium oxide as one of the chemical composition of fly ash becomes the major differentiator. Fly ash with the calcium compound below 8% (by weight) classified as F type, whereas those with the calcium compound in the range of 8-20% (by weight) belong to type CI, and when it is above 20% (by weight), the fly ash categorized as type CH.

The type of fly ashes used by some researchers is plotted in Figure 1 where it shows the relationship of two classification systems i.e. ASTM and CSA. The CSA standard classifies the fly ash according to the CaO contents, while ASTM standardly classifies according to the total contents of SiO_2 , Al_2O_3 , and Fe_2O_3 . It also can be derived that CSA type F and type CI fly ash is similar to the ASTM class F, while CSA type CH is similar to the ASTM class C fly ash.

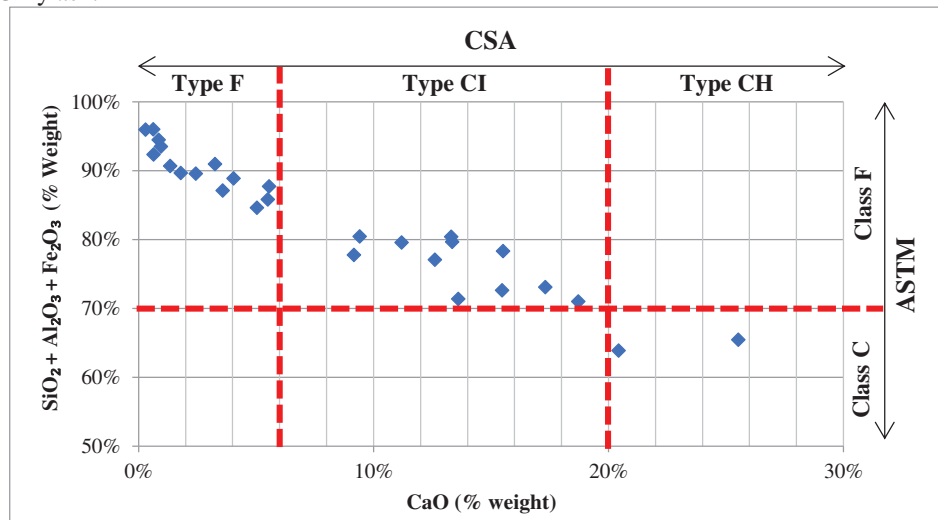


FIGURE 1. Classification of fly ash (according to ASTM and CSA) used in some geopolymer researches. Calcium Compound

Related to the use of fly ash as a source material in the geopolymer synthesis, Gourley [25] stated that low calcium fly ash or ASTM Class F fly ash is preferred than high calcium or ASTM Class C fly ash because the presence of calcium in high amount may interfere the polymerization process and alter the microstructure. However, the reality is we cannot choose which type of fly ash we want to use because it depends on the availability of fly ash source in each area. And also for the reason of economical aspect, it will not efficient for transporting fly ash from far place to be utilized. On the other hand, this term of high calcium fly ash based geopolymer is similar with the slag based geopolymer, where it has been reported that CSH gel can be formed within the geopolymeric binder and this CSH gel is responsible for the strength increase [26].

Besides the advantage of increasing the strength, the calcium content could interfere the setting time of geopolymeric binders [27], which result in faster setting time. Nicholson et al. also confirmed that high calcium fly ash based geopolymer has fast setting time, and therefore they added the additive, i.e. borate in the mixture to

compensate the fast setting time. Furthermore, when Hardjito et al. worked with low calcium fly ash, they said that the fresh fly ash based geopolymer concrete is easily handled up to 120 minutes without any sign of setting [8]. But vice versa, when worked with ASTM class C fly ash, the fast even flash setting time occurred, and therefore they used borax as an addition in the mixture to prolong the setting time [14,28]. Additionally, the development in strength was also indicated by the utilized of fly ash which has significant calcium content [3].

Silica and Alumina Compound

Silica is the most amount of oxide contained in fly ash, and as a source material of geopolymer where silica is the main constituent of the structural skeleton of the reaction product, silica content (especially the reactive one) is the most important factor in the alkaline activation of the ashes [4]. Additionally, since the main reaction product of geopolymeric synthesis is an aluminosilicate gel, it means that high reactive silica content involves the formation of a high amount of alkaline aluminosilicate gel and consequently a high mechanical strength is developed in the resulting material.

Alumina content in fly ash is as important as silica because the main product of the geopolymer is polymeric chain consisting of silica and alumina which share the oxygen ion. Apparently, from most studies that have been conducted, the role of silica and alumina in geopolymer synthesis cannot be separated. The role of silica and alumina oxide is usually expressed as Si/Al ratio, where it is believed that increasing in that ratio will increase the compressive strength of geopolymer product [29].

Figure 2 shows that different sources or batches of fly ash produce the different chemical compound, especially silica, alumina, and calcium oxides. It also shows that Si/Al ratio in various fly ashes different, between one and the others with the trend of Si/Al around 2. This difference, where lead to difference behavior of geopolymer synthesis, is one of the important factors when dealing with fly ash based geopolymer. Unfortunately, the effect of Si/Al ratio on the behavior of fly ash based geopolymer is still not clear, where difference fly ash will give difference result regarding Si/Al ratio. For example, one study [30] shows that increase in Si/Al will decrease both setting time and compressive strength. The other study [31] shows that increase in Si/Al ratio in a mixture will increase the compressive strength. Other studies [14,32] show that fly ash Si/Al ratio did not show a correlation with setting time and compressive strength for five difference source of fly ashes.

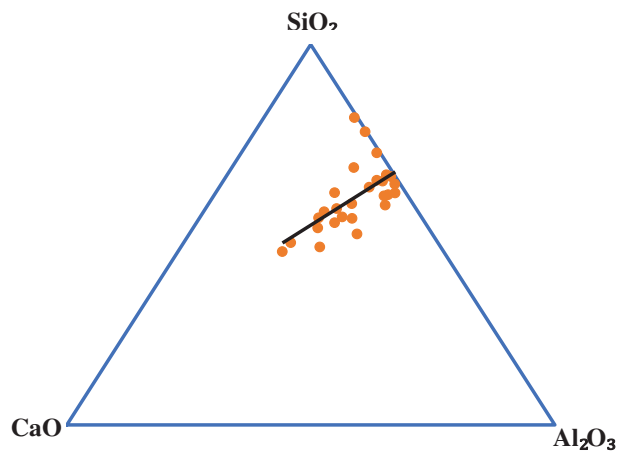


FIGURE 2. Ternary diagram of silica, alumina, and calcium content in fly ash.

Fe₂O₃ , MgO, SO₃ , Compounds and LOI

The other countable chemical compound in fly ash is ferrite oxide, which in some cases it determines the color of the fly ash. Besides affecting the appearance of fly ash, the maximum content of ferrite oxide in fly ash has been confirmed for maximum specific gravity value of fly ashes [21]. There is just a few research was reported related to the effect of Fe₂O₃ in fly ash based geopolymer synthesis. In chemical term, Jimenez and Palomo [4] stated that the role of iron oxide in the geopolymer synthesis is still unclear and hypothetically did not form a part of main

products and consequently did not contribute to the mechanical strength. In line with the last statement, based on the data reviewed from two studies [31,32] which each used five different sources of fly ash, showed there is no correlation between iron oxide contained in the fly ash with the compressive strength. One interesting experiment conducted (although did not use fly ash) by Choi and Lee [33], which used mine tailing and melting slag as aluminosilicate source material and an addition of iron oxide into the geopolymer mixture to study its effect. The result showed that the addition of iron oxide could inhibit the geopolymerization reaction.

MgO content in fly ash is being spelled out in fairly small amount and just some standard (e.g. Indian Standard [34] and Russian Standard [35]) give a limitation of maximum 5% by weight. As one of the earth alkalis (besides CaO), MgO is also producing the hydroxide ion in geopolymer reaction [36]. In addition, MgO is also considered to have a contribution in high pH value, which has significant effect on the setting time of fly ash based geopolymer concrete [14].

SO₃ or sulfur trioxide also prescribed by almost all standards for fly ash classification including [37]. ASTM [1] and CSA [24] limit the SO₃ content to maximum 5%, while Australian Standard [38] gives the limit to maximum 3%. The limitation was set to anticipate the expansion of conventional concrete containing fly ash because the reaction of SO₃ will produce expansion product namely ettringite at early stages and mono sulphoaluminate at later ages [21]. However, in term of fly ash based geopolymer, there is still no research focusing on the effect of SO₃ in the synthesis. Although, based on its behavior in conventional concrete, SO₃ has some possibilities in affecting the properties of fly ash based geopolymer concrete (e.g. setting time due to the formation of ettringite).

LOI or loss on ignition is generally used to describe or to quantify the total content of unburned coal residues. The terms LOI and content of carbon are also often used interchangeably [21]. The most detrimental effect of high LOI is higher water demand and consequently reduces compressive strength, when considering conventional concrete. Finally, a higher LOI will lead to a lower final compressive strength as well as a higher porosity of prepared geopolymers [39]. There are variations to the limitation of LOI given by various standards; however, ASTM [1] prescribes the limitation of maximum 6% by weight related the LOI contents.

Variations in Physical Properties

For the physical properties, the ASTM C618 [1] requirements are almost the same for both classes of fly ash, which one of them is the amount retained when wet-sieved on 45µm (No.325) sieve is limited to maximum 34% (by weight). Beside fineness requirements, there are also strength activity index, water requirement, soundness, and uniformity requirements prescribed by ASTM. While CAN/CSA-A3000-03 [24] prescribes physical requirements such as the limitation of SO₃ to maximum 5% for all types, LOI maximum 8% for type F and 6% for type CI and CH, fineness of maximum 34% (by weight) retained when sieved on 45µm (No.325) sieve, and limitation of expansion to maximum 0.8%.

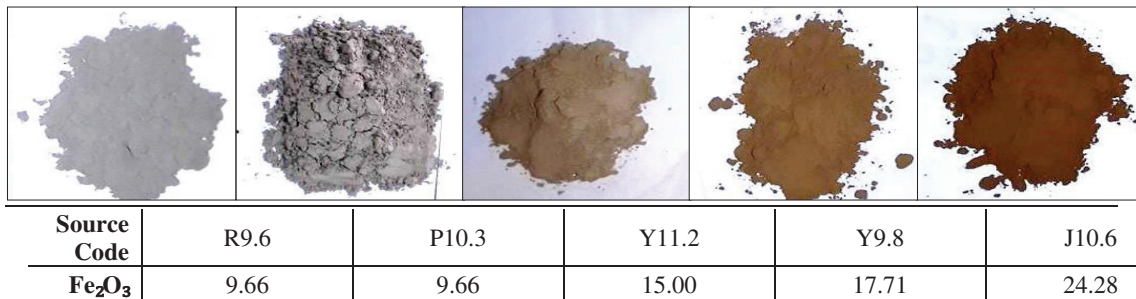


FIGURE 3. The color of fly ash which obtained from five different sources with each Fe₂ O₃ contents [14].

The physical properties of fly ash also include the visual properties especially color, which in many cases the color of fly ash is determined by the content of iron oxide as mentioned earlier, and carbon content [21]. Moreover, the carbon percentage, ranging from 0.5 to 10 or 12% in certain cases, is responsible for the black or gray

appearance of some concretes. Figure 3 confirms above statement regarding the correlation between amounts of iron oxide and the color of fly ash.

On the other hand, the morphology and composition of fly ash particles which depend on the heating and cooling processes can be observed by using SEM [22]. Moreover, in a detail examination of fly ash particles, the iron oxide exhibits various texture both on the surface and internal. Figure 4 is an example of SEM image of fly ash that shows the various sizes and shapes of spherical particles and the presence of lumps and dust in some sample.

Particle size distribution may be defined as the quantification of particles in term of their size and it is one of the physical properties of fly ash that most strongly affects their reactivity [4]. The fineness of the fly ashes is commonly measured by sieve analysis, which can be performed using the dry or wet method. Generally, there are two approaches in determining the fineness of the fly ash [4]. The first one is the total amount of particles with a similar or lower size than $45\mu\text{m}$ expressed as weight percentage. The second one is the specific surface area of the overall particles, in the same amount (e.g. 1kg) of fly ash. The greater the surface area indicates higher fineness.

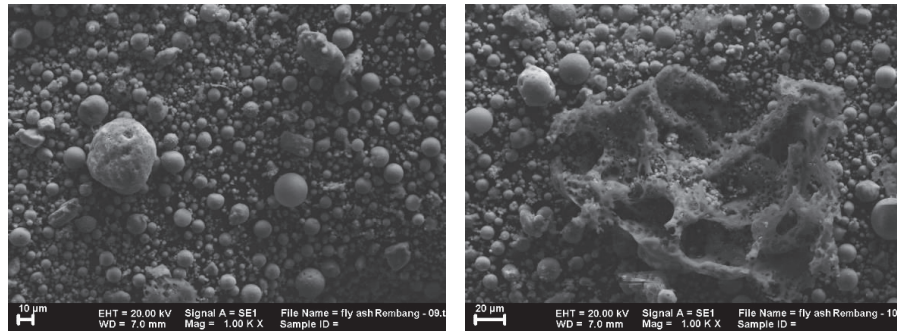


FIGURE 4. SEM images of fly ash from PLTU Rembang (R9.6) [14].

Because of the geopolymer synthesis starts with the leaching of silica and aluminum on the surface of fly ash prior to condensation, it makes sense if the greater surface area will propose the greater amount of silica and aluminum to be leached which will result in higher rate of geopolymerization. Gunasekara et al. [40] proved that the higher the surface area and the greater the number of particles smaller than $20\mu\text{m}$, the better the gel formation. An experiment conducted by Chindaprasirt et al. [41] also confirmed that the finer the particle size of fly ash, the higher the compressive strength of fly ash based geopolymer. Moreover, a study conducted by Antoni, et al. [14] indicates that fly ash with finer particle tends to have accelerated initial setting time.

GEPOLYMER BEHAVIOURS TOWARD FLY ASH VARIATIONS

As in conventional concrete, fly ash based geopolymer concrete also goes through the fresh state before entering the hardened state. Both states were strongly affected by a variety of material parameters including water content, thermal history, particle size, and degree of crystallinity or amorphicity [15]. Antoni et al. divide the factors that could affect the fresh and hardened state behaviors of fly ash based geopolymers into internal factor and external factor [14,32]. Physical and chemical properties of fly ash are kinds of internal factors, while mix design and mixing procedure including the peripherals of alkaline solution grouped as external factors. Moreover, separate work was done by Antoni et al. presents an interesting fact that even when the fly ashes were obtained from the same source, their characteristics not necessarily the same [3]. It is also worth to keep in mind that fly ash is by-product material, so its characteristics more or less derived from the properties of pulverized coal chemistry, which naturally vary, and the combustion condition in the furnace [42].

Fresh State Behaviors

Fresh state properties of fly ash based geopolymer concrete can be derived from some aspects mainly workability of the concrete and both initial and final setting time of the concrete. Additionally, the curing regime in a fresh state of fly ash based geopolymer concrete also plays an important role in determining its hardened

properties. Moreover, treatment of fresh state mixture, i.e. mixing sequence and procedure, seems to affect the synthesis mechanism and finally the mechanical properties of hardened geopolymers.

Similar to conventional concrete, the workability of a mixture is strongly affected by water content. In fly ash based geopolymer concrete, the amount of water content usually defined by water to solid (fly ash) ratio or in some study expressed as H_2O to Na_2O ratio. It also has been shown to affect the workability of a mixture for both low calcium [43] and high calcium [17] fly ash based geopolymer concretes. This trend of water content affecting on the workability and later on compressive strength is the same with the conventional Portland cement concrete, where the chemical reaction involved is hydration process [44]. Furthermore, from the review of some previous studies, it seems that variation in chemical composition of the fly ash has less effect on the workability, with the exclusion of flash setting problems. On the other hand, the workability (measured by flow) of fly ash based geopolymers increased with an increase in fly ash fineness [41]. However, it is important to be noted that particle shape has a dominant influence on the workability. Therefore, the shape of the fly ash, which naturally spherical, need to be maintained. Additionally, the workability of fly ash based geopolymer concrete is more depended on the composition of the alkaline reagents, both hydroxide and silicate solution [45].

Setting time generally can be said as one of the most important parameters of the fly ash based geopolymer concretes, because besides there is a need of handling time before placing and compacting, it also determines the properties of the hardened state. As mentioned above, setting time behavior is mostly depending on the chemical compound of fly ash particularly the content of CaO [14,15]. Contrary to the chemical reaction occurred in geopolymerization, where heating is needed to initiate the reaction, fly ash based geopolymers which contain some amount of CaO (e.g. above 8%) does not need any heat to start the hydration reaction, instead of producing some degree of heat, that later may initiate geopolymerization.

Van Jaarsveld et al. [15] states that dissolution of Si and Al (which will determine the rate of reaction and later the setting time) from various fly ashes appears to be unaffected by the particle size of fly ash. On the opposite, Chindaprasirt et al. [41] showed that setting time of fly ash based geopolymer affected by the particle size of fly ash. This contrary statement may be due to a different type of fly ash used, where the earlier used fly ash with CaO content below 10%, while the latter used fly ash with CaO content more than 10%. One more thing to be considered, the work was done by Van Jaarsveld used five different sources of fly ash with different physical and chemical characteristics, while Chindaprasirt used the same source and even one batch of fly ash, where the chemical characteristics can be said the same.

Curing regime varies due to the wide variety of fly ash characteristics use in the synthesis, where temperature and duration of curing are the most common parameters to describe the regime. Some researches which utilize low calcium fly ash [44,46] indicates that the reaction of geopolymerization would not start without elevated temperature curing and did not harden for at least one day. On the other side, a work conducted by Somna et al. [47] shows that curing in the room temperature is possible when utilizing the high calcium fly ash with a high concentration of alkaline activator. However, the compressive strength achieved is slightly low, with only 20-23 MPa, at the age of 28 days.

Duration of curing, particularly at the elevated temperature, was proven to have an impact on the mechanical properties of hardened fly ash based geopolymers [8]. However, curing over 24 hours at elevated temperature shows less impact. Such impact of curing duration at elevated temperature seems to be not affected by difference chemical characteristics of fly ash, especially the CaO content, as shown by Li et al. [48].

Finally, from the above discussion, it can be seen that curing regime affects the setting time, while setting time itself affects the workability of fresh fly ash based geopolymer concretes. All the three parameters used to describe the fresh state behaviors seem to be affected by both chemical and physical characteristics of fly ash as main constituents. Regarding the importance of setting time, one of the rapid methods that can be used to evaluate whether the fly ash will encounter flash setting time is pH measurement [18].

Hardened State Behaviors

Compressive strength is the most used benchmark to determine the hardened state of concrete especially in term of mechanical strength. In fly ash based geopolymer, the compressive strength of the binder depends on the strength of the geopolymer gel, i.e. aluminosilicate gel. Experimental works conducted by Jaarsveld et al. [15] and Antoni, et al. [3] show that higher content of calcium compound in the fly ash will result in higher compressive strength. Additionally, both works also show that compressive strength of fly ash based geopolymer is influenced by the physical properties of fly ash, e.g. specific surface area and particle size distribution. A work has been done by Gunasekara et al. which utilizing five difference sources of fly ash with difference characteristics, particularly in term of particle size, also shows the same trend. The finer the particle of fly ash, the higher the compressive strength of fly ash based geopolymers. Other work conducted by Chindaprasirt et al. [41] confirmed the effect of particle size on the compressive strength while using chemically the same characteristics of fly ash. The higher compressive strength for finer particle size, in most cases, is due to more area available to be leaching and then activating for later development of geopolymer gel which contributing to compressive strength. The trend of particle size effect on compressive strength of fly ash based geopolymer from some researches can be seen in Figure 5.

Compressive strength in fly ash based geopolymer normally does not show a significant development along with the age because the chemical reaction of the geopolymer gel is due to the substantially fast polymerization process [43]. However, in some cases where high calcium fly ash is used in the geopolymers synthesis, it shows some development in compressive strength along with the age [32]. This interesting fact is may be due to the calcium content in the fly ash reacts with dissolved silicate and aluminate species and forms hydrate product, either CSH or CAH. There is still not clear about the exact mechanism, whether the geopolymerization reaction and hydration reaction goes contiguously or overlapping each other or in other ways.

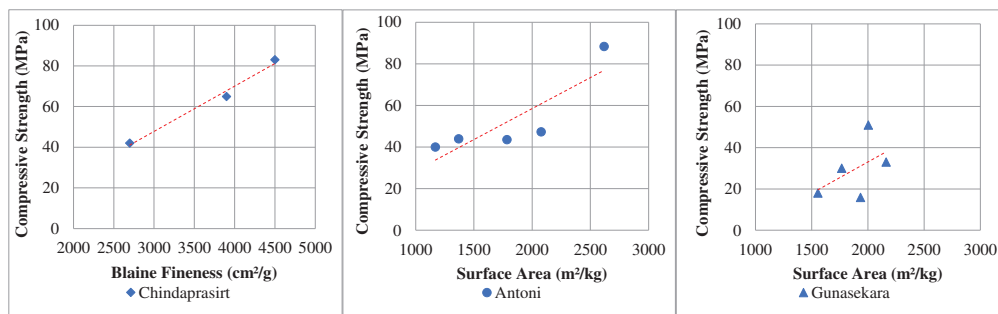


FIGURE 5. Effect of particle size (expressed as fineness and surface area) on the compressive strength [45,40,32].

The other hardened state behavior of fly ash based geopolymers is splitting or tensile strength. A study conducted by Chindaprasirt et al. [13] indicates that splitting tensile strength of high calcium fly ash based geopolymer concrete is related to the compressive strength, as in the conventional concrete. It shows higher strength than the strengths calculated using standard design codes. Modulus elasticity of high calcium fly ash based geopolymer is also studied, where the results show the same trend as conventional concrete. Additionally, the bond strength between high calcium fly ash based geopolymer concrete and rebar were significantly higher. Djwantoro et al. [8] also investigating some others hardened state behaviors of low calcium fly ash based geopolymer concrete including modulus of elasticity, Poisson's ratio, the stress-strain relation in compression, and indirect tensile strength. The results are slightly different from conventional concrete in term of values but still gave the same trend.

CONCLUSIONS AND RECOMMENDATIONS

From the reviews above, it is obvious that different sources (and even the same source) of fly ash materials will give different characteristics of the fly ash, where lately will give a different effect on the synthesis of fly ash based geopolymer concretes. Finally, each source or even each batch of the fly ash will lead to different results both in fresh and hardened state of the fly ash based geopolymer concretes. Some points that can be emphasized based on the above reviews are:

1. Both chemical compounds and physical as well as mineralogical properties of the fly ash significantly influences

the sintering process of geopolymer and finally affecting both fresh and hardened state behavior of fly ash based geopolymers.

2. Utilization of low calcium fly ash e.g. ASTM class F or CSA type F in geopolymer synthesis seems to have fewer problems compared to high calcium fly ash. The most problem when work with high calcium fly ash is setting time of the geopolymer synthesis too fast and tends to flash setting in some cases.
3. Regardless of the problems, the use of high calcium fly ash in geopolymer concretes can give higher compressive strength and also shows some strength development along with the age. It can happen because the reaction involved is not only the polymerization but also the hydration reaction. However, this mechanism is still not clear and needs further research.
4. Physical properties along with chemical compounds of fly ash seem to be related each other in determining the final products. Therefore it cannot be separate when considering the effect of each characteristic towards the behavior of fly ash based geopolymers.
5. As by-product material, the characteristics and properties of the fly ash cannot be controlled, therefore it is necessary to do material testing prior to utilize as a geopolymer source material. But the problem is comprehensive material testing can be expensive and not necessarily can be done in all situations. A well-developed rapid indicator will give an opportunity and more preferable to use.

REFERENCES

1. ASTM C618-03, "Standard specification for coal fly ash and raw or calcined natural pozzolona for use in concrete," West Conshohocken, PA, (2003).
2. A. 116R-00, "Cement and Concrete Terminology," (2000).
3. Antoni, J. Satria, A. Sugiarto, and D. Hardjito, "Effect of Variability of Fly Ash Obtained from the Same Source on the Characteristics of Geopolymer," *MATEC Web of Conferences* (97)01026, (2017).
4. A. Fernández-Jiménez and A. Palomo, "Characterisation of fly ashes. Potential reactivity as alkaline cements," *Fuel*, vol. 82, no. 18, pp. 2259–2265, (2003).
5. J. Davidovits, *Geopolymer Chemistry & Application*. Morrisville: Institute Geopolymere, (2015).
6. J. Davidovits, "Geopolymers: Inorganic Polymeric New Materials," *J. Therm. Anal.*, vol. 37, no. 8, pp. 1633–1656, (1991).
7. D. Khale and R. Chaudhary, "Mechanism of geopolymerization and factors influencing its development: A review," *J. Mater. Sci.*, vol. 42, no. 3, pp. 729–746, (2007).
8. D. Hardjito and B. V. Rangan, "Development and properties of low-calcium fly ash-based geopolymer concrete," *Res. Rep. GC*, p. 94, (2005).
9. H. Xu and J. S. J. Van Deventer, "The geopolymerisation of alumino-silicate minerals," *Int. J. Miner. Process.*, vol. 59, no. 3, pp. 247–266, (2000).
10. J. G. S. Van Jaarsveld, J. S. J. Van Deventer, and L. Lorenzen, "Potential use of geopolymeric materials to immobilize toxic metals: Part I. Theory and applications," *Miner. Eng.*, vol. 10, no. 7, pp. 659–669, (1997).
11. J. L. Provis, G. C. Lukey, and J. S. J. Van Deventer, "Do geopolymers actually contain nanocrystalline zeolites? a reexamination of existing results," *Chem. Mater.*, vol. 17, no. 12, pp. 3075–3085, (2005).
12. N. A. Lloyd and B. V. Rangan, "Geopolymer Concrete with Fly Ash," *Second Int. Conf. Sustain. Constr. Mater. Technol.*, vol. 3, no. January, pp. 1493–1504, (2010).
13. P. Topark-ngarm, P. Chindaprasirt, and V. Sata, "Setting Time, Strength, and Bond of High-Calcium Fly Ash Geopolymer Concrete," *J. Mater. Civ. Eng.*, vol. 27, no. 2011, pp. 1–7, (2014).
14. Antoni, S. Wibiarta Wijaya, and D. Hardjito, "Factors Affecting the Setting Time of Fly Ash - Based Geopolymer," *Mater. Sci. Forum*, vol. 841, pp. 90–97, (2016).
15. J. G. S. Van Jaarsveld, J. S. J. Van Deventer, and G. C. Lukey, "The characterisation of source materials in fly ash-based geopolymers," *Mater. Lett.*, vol. 57, no. 7, pp. 1272–1280, (2003).
16. U. Rattanasak and P. Chindaprasirt, "Influence of NaOH solution on the synthesis of fly ash geopolymer," *Miner. Eng.*, vol. 22, no. 12, pp. 1073–1078, (2009).
17. X. Li, X. Ma, S. Zhang, and E. Zheng, "Mechanical properties and microstructure of class C fly ash-based geopolymer paste and mortar," *Materials (Basel)*, vol. 6, no. 4, pp. 1485–1495, (2013).
18. J. Davidovits, R. Davidovits, and M. Davidovits, "Geopolymer Cement Based on Fly Ash and Harmless to Use," (2012).

19. A. Palomo, M. W. Grutzeck, and M. T. Blanco, "Alkali-activated fly ashes: A cement for the future," *Cem. Concr. Res.*, vol. 29, no. 8, pp. 1323–1329, (1999).
20. J. G. S. Van Jaarsveld and J. S. J. Van Deventer, "Effect of the Alkali Metal Activator on the Properties of Fly Ash Based Geopolymers," *Ind. Eng. Chem. Res.* 38, pp. 3932–3941, (1999).
21. K. Wesche, *Fly ash in concrete: properties and performance*. (2004).
22. B. G. Kutchko and A. G. Kim, "Fly ash characterization by SEM-EDS," *Fuel*, vol. 85, no. 17–18, pp. 2537–2544, (2006).
23. J. Temuujin, A. Van Riessen, and R. Williams, "Influence of calcium compounds on the mechanical properties of fly ash geopolymer pastes," *J. Hazard. Mater.*, vol. 167, no. 1–3, pp. 82–88, (2009).
24. CAN/CSA-A3001-03, "Cementitious Materials for Use in Concrete," Toronto, (2003).
25. J. T. Gourley, "Geopolymers; opportunities for environmentally friendly construction materials," Material 2003 Conference: Adaptive materials for modern society, Sydney, Institute of Materials Engineering Australia, (2003).
26. C. K. Yip, G. C. Lukey, and J. S. J. Van Deventer, "The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation," *Cem. Concr. Res.*, vol. 35, no. 9, pp. 1688–1697, (2005).
27. W. K. W. Lee and J. S. J. Van Deventer, "The effect of ionic contaminants on the early-age properties of alkali-activated fly ash-based cements," *Cem. Concr. Res.*, vol. 32, no. 4, pp. 577–584, (2002).
28. Antoni, S. W. Wijaya, J. Satria, A. Sugiarto, and D. Hardjito, "The Use of Borax in Deterring Flash Setting of High Calcium Fly Ash Based Geopolymer," *Mater. Sci. Forum*, vol. 857, pp. 416–420, (2016).
29. P. Kamhangrittirong, P. Suwanvitaya, and P. Chindaprasirt, "Synthesis and Properties of High Calcium Fly Ash Based Geopolymer for Concrete Applications," in *36th Conference on Our World in Concrete & Structures*, (2011), p. 9.
30. P. Chindaprasirt, P. De Silva, K. Sagoe-Crentsil, and S. Hanjitsuwan, "Effect of SiO₂ and Al₂O₃ on the setting and hardening of high calcium fly ash-based geopolymer systems," *J. Mater. Sci.*, vol. 47, no. 12, pp. 4876–4883, (2012).
31. C. Gunasekara, D. W. Law, and S. Setunge, "Effect of Composition of Fly Ash On Compressive Strength of Fly Ash Based Geopolymer Mortar," in *23rd Australasian Conference on the Mechanics of Structures and Materials (ACMSM23)*, (2014), vol. 3, no. 1, pp. 168–177.
32. Antoni, S. W. Wijaya, and D. Hardjito, "Compressive Strength of Geopolymer using Fly Ash from Various Sources," vol. 841, no. 1, pp. 0–5, (2016).
33. Su-Cheol Choi and Woo-Keun Lee, "Effect of Fe₂O₃ on the Physical Property of Geopolymer Paste," *Adv. Mater. Res.*, vol. 586, pp. 126–129, (2012).
34. Bureau of Indian Standard(BIS), "IS 3812:2003 Pulverized Fuel Ash-Specification," (2003).
35. ГОСТ25818-91, "Thermal plant fly-ashes for concretes. Specifications."
36. H. J. H. Brouwers and R. J. Van Eijk, "Chemical Reaction of Fly Ash," pp. 11–16, (2003).
37. R. P. Kelly, "Parallels and Nonconformities in Worldwide Fly Ash Classification : The Need for a Robust, Universal Classification System for Fly Ash," (2015).
38. A. 3582.1-1998, "Supplementary cementitious materials for use with portland and blended cement - Fly ash."
39. J. Škvarla, M. Sisol, J. Botula, M. Kolesárová, and I. Krinická, "The potential use of fly ash with a high content of unburned carbon in geopolymers," *Acta Geodyn. Geomater.*, vol. 8, no. 2, pp. 123–132, (2011).
40. C. Gunasekara, D. W. Law, S. Setunge, and J. G. Sanjayan, "Zeta potential, gel formation and compressive strength of low calcium fly ash geopolymers," *Constr. Build. Mater.*, vol. 95, pp. 592–599, (2015).
41. P. Chindaprasirt and T. Chareerat, "High-strength geopolymer using fine high-calcium fly ash," *J. Mater. Civ. Eng.*, vol. 23, no. March, pp. 264–270, (2011).
42. R. S. Kalyoncu, "COAL COMBUSTION BY-PRODUCTS Coal Combustion By-Products and Western Coal Mines : A Technical Interactive Forum," in *Coal Combustion By-Products and Western Coal Mines : A Technical Interactive Forum*, (2002), pp. 13–24.
43. D. Hardjito, S. E. Wallah, D. M. J. Sumajouw, and B. V Rangan, "Factors Influencing the Compressive Strength of Fly Ash Based Geopolymer Concrete," *Civ. Eng. Dimens.*, vol. 6, no. 2, pp. 88–93, (2004).
44. D. Hardjito, C. C. Cheak, and C. H. Lee Ing, "Strength and Setting Times of Low Calcium Fly Ash-based Geopolymer Mortar," *Mod. Appl. Sci.*, vol. 2, no. 4, pp. 3–11, (2008).
45. P. Chindaprasirt, T. Chareerat, and V. Sirivivatnanon, "Workability and strength of coarse high calcium fly ash geopolymer," *Cem. Concr. Compos.*, vol. 29, no. 3, pp. 224–229, (2007).

46. Sindhunata, J. S. J. Van Deventer, G. C. Lukey, and H. Xu, "Effect of curing temperature and silicate concentration on fly-ash-based geopolymerization," *Ind. Eng. Chem. Res.*, vol. 45, no. 10, pp. 3559–3568, 2006.
47. K. Somna, C. Jaturapitakkul, P. Kajitvichyanukul, and P. Chindaprasirt, "NaOH-activated ground fly ash geopolymer cured at ambient temperature," *Fuel*, vol. 90, no. 6, pp. 2118–2124, (2011).
48. X. Li, Z. Wang, and Z. Jiao, "Influence of curing on the strength development of calcium-containing geopolymer mortar," *Materials (Basel)*, vol. 6, no. 11, pp. 5069–5076, (2013).