

Effects of Na: Al and water: solid ratios on the mechanical properties of fly ash based geopolymer

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[Abstract]. Every segment industry infrastructure like onshore/offshore setup, power generation and water management is part of a complex system which involves large investment. Unfortunately, these infrastructures easily susceptible to be attacked by corrosion, resulting in hundreds of millions of dollars in losses. Conventionally, steel is protected by anticorrosive chromate coatings. But these coatings contain carcinogenic hexavalent chromium compound which may cause to environment and health related issues. To reduce those impacts, conventional coatings are replaced by water-based alternatives and inorganic coatings. Geopolymer as a green inorganic material with superior properties is in great research to be explored as a new coating material. The present paper outlines briefly the potential of geopolymer as a coating material through the mechanical performance test of adhesion and flexural strength. Scanning electron microscopy (SEM) was used to examine the morphology of geopolymer and unreacted fly ash matrix. The test was conducted by varying two aspects of Na: Al and water: solid ratios. The findings show both the alkali and water content plays a significant role in geopolymerization. The increase in water content at low Na/Al ratio causes dilution of activator thus resulted in decreased of adhesion and flexural strength.

1. Introduction

Estimates of the annual cost of corrosion around the world lead to a huge number. In any case, corrosion represents a tremendous economic loss and much can be done to reduce it. Corrosion of bridges is a major problem as they age and require replacement, which costs billions. A large chemical company spent more than \$400,000 per year for corrosion maintenance in its sulfuric acid plants. The petroleum industry spends a million dollars per day to protect underground pipelines [1].

In order to maintain the durability of systems, coatings are applied on metal surface. There are several types of coatings that available in the market such as organic coatings, metallic coatings, zinc coatings and ceramic coatings, in which, different coatings serve for different application [2]. When the coatings itself is subjected into certain failure or damage, consequently it will cause a serious corrosion issue occurs. Basically, there is a gradual formation of defect such as the presence of void or a pore inside the coatings, which may cause detachment occurred. Later, it will followed by the penetration of the corrosive species likes chlorine ions that promote adhesion loss and indirectly attacks the underlying metal. Thus, in order to solve that such issue, a major operation process is required which caused big economic losses [3] - [6].

There are several types of coatings that have been used as surface protection materials such as acrylic, polyurethane, epoxy, etc. However, these coatings usually cover the material surface by



physical absorption. In fact, to achieve an excellent protection, coatings should be coated the surface by both physical and chemical absorption. On top of that, most of the available coating materials in the market nowadays are being derived from the compound that is not only harmful to the humans but also to the environment. The content of volatile organic compounds (VOCs) in coatings may lead into serious health related issues such as asthma, bronchitis and sometimes skin and lung cancer [7]. Meanwhile, it may also affect to the depletion of the ozone layer and greenhouse effect.

Geopolymers have been materialized as a potentially new inorganic material with interesting properties such as high compressive strength, good thermal stability, high flexural strength and good fire resistance. Geopolymers are synthetic green polymeric materials prepared by the chemical interaction of raw aluminosilicates obtained from power plants such as coal fly ash, mineral clays (metakaolin), and slag from metallurgy, with an aqueous alkaline solution of hydroxide and/or silicate as reaction process accelerators resulted in the development of solid, insoluble binding material [8] - [9]. Chemically geopolymers are tetrahedrally cross linked alumino silicates with Si^{+4} and Al^{+4} units and the structure is charge stabilized by alkali cation. The content of Si and Al will much influence the chemistry of geopolymers [10]. Geopolymers chemistry is synonymous to zeolite with the exceptions that geopolymers are amorphous and the unreacted starting material is also intact with geopolymer gel.

Early research on the alkali activation works dating back to 1908, when Kuhl *et al* patented their first formulation called slag cement by mixing the blast furnace slag (BFS) with alkaline components [11]. Later on, in 1930-1950, work by Prudon *et al* was conducted in a lab scale project to fabricate cement from steel slag and alkalis. Based on the findings, the idea and technology were adopted in 1950 to commercialize the materials in Belgium. Noticeably, the idea was implemented in the construction buildings at that period [12]. Glukhovskii from Russia had developed building materials using alkali activation of low calcium aluminosilicate precursor by calling the material as soil cement and soil silicates [13]. The term of 'geopolymer' was initially introduced by Davidovits in 1970s for alkali activated metakaolin. The term of geopolymer was used by him as to resemblances the geopolymers with organic thermoset resins [14]. The findings from Davidovits' work become a direction for researchers to develop new material for building structure. A hybrid concrete as called Pyrament with high early strength was commercialized in 1980-1990 in North America [15].

The application of fly ash in geopolymer based was first reported in 1990s by Wastiels *et al*. The binder was prepared for the work by chemical reaction of alkaline solution with blast furnace slag and fly ash [16]. A superior properties of geopolymer such as controlled setting time, low water permeability, resist to corrosion, heat and fire attack make it a new potential material that can be used as a coating. Temuujin *et al* has proven thin coatings from geopolymer had shown a good resistance towards the heat and fire. High adhesion strength of $>3.5\text{MPa}$ was obtained from the work and good thermal stability as only 5-8% mass loss was recorded during heating from 50-800°C [17]. It was found that different parameters significantly influenced the performances of geopolymer coatings, including chemical composition, water content, and particle sizes of the precursors [30]-[32]. Besides, the ratio of Na: Al, Si:Al and water: solid plays a significant role towards geopolymer properties. In another study by Temuujin *et al* reported the adhesion strength of geopolymer coating was much affected by Si: Al and water: solid ratio. Noticeable, an increasing in strength was directly proportional with increasing of Si: Al and water: solid ratio [18].

Reflected to the available knowledge in literature, current research was conducted on the fly ash based geopolymers as to expend more the mechanical properties especially in adhesion strength and flexural strength. In order to find the optimum performance of geopolymers, there were two parameters that are chosen to be tested on synthesization of geopolymers. The effect of Na: Al and water: solid ratios were tested in the current study. The results were comparatively reported.

2. Experimental section

2.1 Raw materials

Coal fly ash was procured from Malaysia power plant. To minimize the variation in the particle size distribution, and to spate larger particles, the fly ash was sieved through a 45 μ m sieve using a vibratory sieve shaker (AS200 Basic, RETSCH, Germany). Sodium hydroxide (99%) was procured from Merck Millipore, Malaysia. Hydroxide solution was prepared individually by dissolving NaOH pellets in demineralized water, according to the Na: Al and water: solid ratio. The solution was stored in air tight Pyrex container to prevent changes in the composition of the solution due to contamination. A carbon steel plate with the dimension of (3 x 50 x 127 mm) was used for adhesion testing. Prior to adhesion testing, the plate was gone for surface finishing using abrasive paper at specific grade. Then, the plate was degreased with acetone and finally washed with distilled water to remove all the impurities on the plate surface.

2.2 Geopolymer synthesis process

Fly ash was mixed with an alkali activator solution of NaOH using an overhead mechanical stirrer at a stirring speed of 1000 rpm for 5 minutes. Prior to adhesion and flexural testing, samples were cured in an oven at 60°C. The ratios of water: solid and Na: Al were varied to find a better and stable geopolymers property. The Si: Al ratio of 1.78 was the actual composition of fly ash, whereas the Na: Al ratio was altered by use of alkalis of different concentrations.

Twelve different geopolymers formulations were produced with varying Na: Al molar ratio (0.60, 0.80, 1.00 and 1.20) and water to solid ratios of 0.30, 0.33, and 0.36. The samples were nominated using a general formula Na/Al_xW/S_y where x and y represents the ratio values as shown in table 1.

Table 1. Mix design of fly ash based geopolymers coatings.

Sample Id	Abbreviation	Si:Al	Na:Al	Water: solid
Na/Al _{0.60} W/S _{0.30}	AD1	1.78	0.60	0.30
Na/Al _{0.60} W/S _{0.33}	AD2	1.78	0.60	0.33
Na/Al _{0.60} W/S _{0.36}	AD3	1.78	0.60	0.36
Na/Al _{0.80} W/S _{0.30}	AD4	1.78	0.80	0.30
Na/Al _{0.80} W/S _{0.33}	AD5	1.78	0.80	0.33
Na/Al _{0.80} W/S _{0.36}	AD6	1.78	0.80	0.36
Na/Al _{1.00} W/S _{0.30}	AD7	1.78	1.00	0.30
Na/Al _{1.00} W/S _{0.33}	AD8	1.78	1.00	0.33
Na/Al _{1.00} W/S _{0.36}	AD9	1.78	1.00	0.36
Na/Al _{1.20} W/S _{0.30}	AD10	1.78	1.20	0.30
Na/Al _{1.20} W/S _{0.33}	AD11	1.78	1.20	0.33
Na/Al _{1.20} W/S _{0.36}	AD12	1.78	1.20	0.36

2.3 Adhesion strength testing

Prior to adhesion testing, a carbon steel plate was gone for surface finishing using abrasive paper at specific grade. The plate was degreased with acetone and washed with distilled water to remove all the impurities on the plate surface. The adhesion strength of the coating material was determined using pull-off adhesion tester called Elcometer 108 following the ASTM D-4541 [19]. This adhesion tester employs a pull-off method to determine the force required to pull an area of coatings from the steel substrate. Before application, the surface of the Dolly (2mm) was abraded with an abrasive paper and was fixed to the coating surface using epoxy adhesive (Araldite regular, Belgium) and isothermally cured at 60°C for 24 h in an electric oven. The sides of the dolly were cut around to minimize the effect of the surrounding coatings. The dolly was carefully pulled off by Elcometer 108, and the adhesion strength was documented for 3 days cured samples. The detached surfaces were examined for any adhesion failure. If the coating was completely removed with dolly, the test was considered 100% valid. Only 100% valid test was considered in this study.

2.4 Flexural strength testing

Flexural strength measurement was conducted on specimens (3.2 mm x 12.7 mm x 125 mm) using a three-point bending flexural test on an Instron Universal Testing Machine, following ASTM standard D790 B [20]. The purpose of this test is to determine the flexural properties of geopolymers utilizing a three-point loading system to apply a load to a simply supported specimen.

3. Result and Discussion

3.1 Adhesion strength analysis

Figure 1 shows the adhesion strength analysis of cured geopolymers samples coated on steel plate for 3 days. There was a gradual increase in adhesion strength with increasing in Na:Al ratio from 0.60 to 1.20 with the value varied in the range of 1.80 – 4.00 MPa.

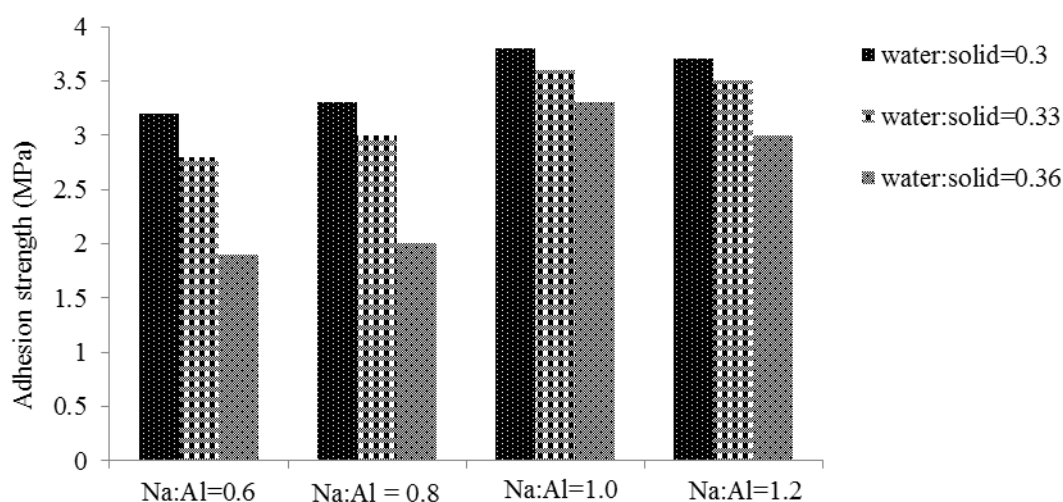


Figure 1. Adhesion strength of geopolymers at different Na: Al and water: solid ratios

Noticeable, the effect of water: solid ratio plays a significant role in adhesion strength of geopolymers. The adhesion strength of all geopolymers decreased with the increasing of water: solid ratio. There are several factors that affect the adhesion of geopolymer to metal surface include the type of raw aluminosilicate material, its mineralogical composition, particle size, geopolymer formulation, test matrix design and nature of metal substrate. The presence of water will function as a reactant in geopolymerization process. High volume of water in the system will caused the activator become more diluted, thus resulting in decreasing of adhesion strength [21].

On the other side of the effect of Na: Al ratio to the adhesion strength, surprisingly the strength was increased with the increasing of ratio. The highest adhesion strength was obtained at 4.0 MPa and 3.5 MPa when the ratio of Na: Al are at 1.0 and 1.2 respectively. While, the lowest adhesion strength were recorded for Na: Al = 0.6 and 0.8 because of the weakness of alkali and lesser dissolution rate of fly ash. The process of geopolymerization started with the dissolution of fly ash, whereby the dissolution rate is dependent to the alkali content [22]. When the amount of Na^+ cations is increased, the more aluminium will leach out from the fly ash, thus the formation of geopolymers will be more [23]. By definition, geopolymers has negatively charged aluminum that was stabilized by metal cations, therefore at least one mole of Na^+ cation was needed for the formation of stable geopolymers. This explanation is in agreement with the strength of systems at Na: Al =1.0 and 1.2. Surprisingly,

inconsistent behavior of the system with Na: Al =1.2 can be related to the unreacted sodium hydroxide [24] – [25].

3.2 Flexural strength analysis

The flexural strength of geopolymers samples was shown in Figure 2. It can be seen that, the effects of Na: Al and water: solid ratios have significantly influenced the strength properties. Highest flexural strength of 6.7 MPa and 6.3 MPa were obtained when Na: Al ratio = 1.0 and 1.2 respectively. Both systems achieved almost 50% increment in strength as compared to the 0.6 and 0.8 Na: Al ratios. This could be explained by the large amount of Al was leached out from the fly ash, resulted in more stable geopolymers. As a result, higher flexural strength was recorded [26]. A similar finding was observed in the study by Nur Ain *et al* [27], in which formation of homogeneous and denser geopolymers structure was obtained by increasing the concentration of sodium hydroxide.

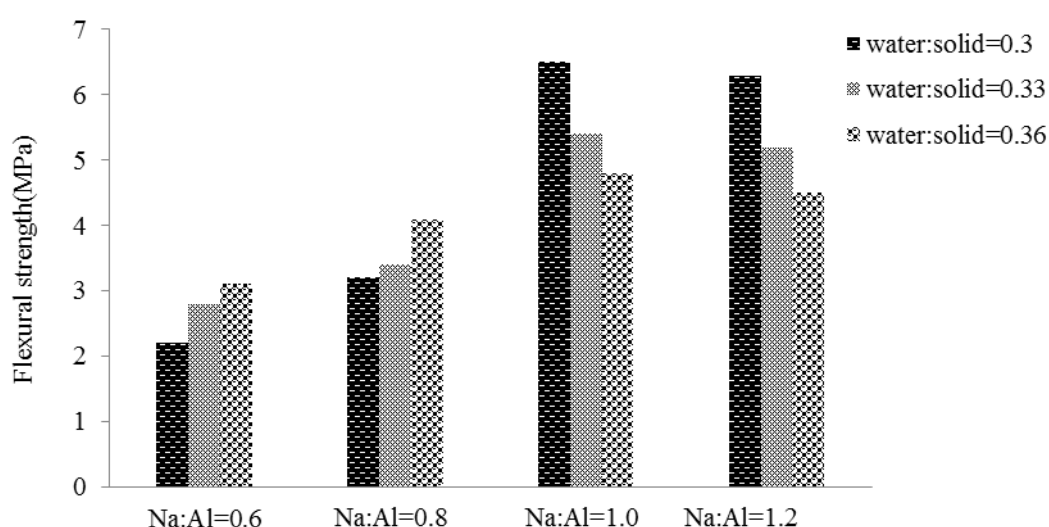


Figure 2. Flexural strength of geopolymers at different Na: Al and water: solid ratios

3.3 Scanning Electron Microscopy (SEM) analysis

SEM images of geopolymer of AD 1 and AD 8 were chosen as to observe the effect of Na: Al and water: solid ratio on morphological of samples. Figure 3 shows there were two types of fly ash particles found in the geopolymer, i.e. unreacted and reacted particles. Larger particles remained unreacted in AD 1(Figure 3(a)) might be due to the low water content and less alkalinity. Meanwhile, reacted particles was observed at AD 8 as shown in Figure 3(b). Higher water content and high alkali in system might caused to the morphology obtained which directly contributed to the high strength of adhesion and flexural. This can be supported by EDS analysis as shown in Table 2, in which the amount of Al was increased in AD 8 system indicating more Al was leached out from the fly ash.

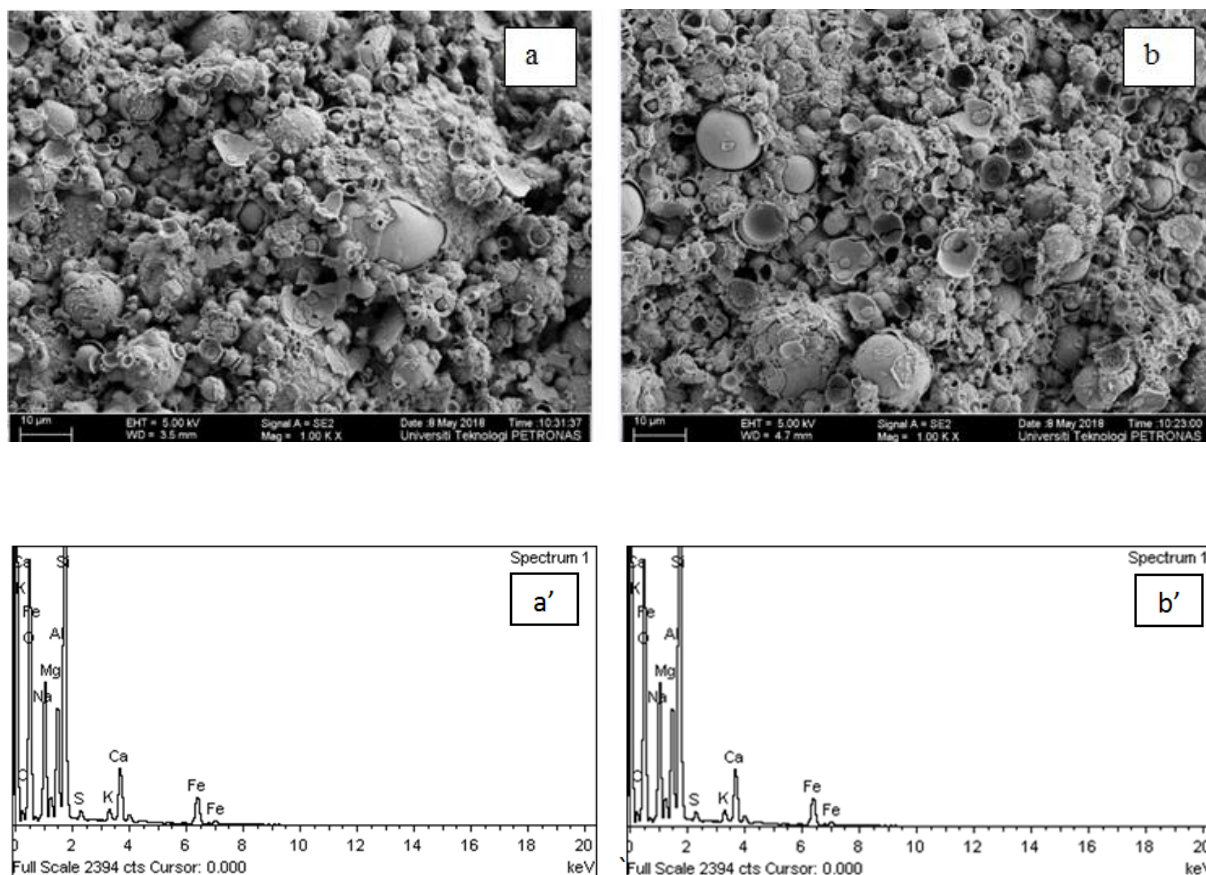


Figure 3. SEM image and EDX analysis of geopolymer of AD 1(a, a') and AD 8(b, b')

Table 2. EDX of AD1 and AD 8

Elements	Weight %	
	AD 1	AD 8
O K	50	51.75
Na K	25.4	22.64
Al K	9.61	18.77
Si K	4.36	3.4
K K	1.02	0.44
Ca K	4.48	2.21
Fe K	4.89	0.79

3.4 Fourier Transform Infra-red (FTIR) analysis

An infrared spectrum of geopolymer is presented in Figure 4. The spectra are consisted of different peaks, and to better define the position and shape of these peaks the spectra are divided into Figure 4(a) and (b) representing wave number region of 4000-850 cm^{-1} and 850-450 cm^{-1} , respectively. In Figure 5 (a), the peaks at 3451 cm^{-1} and 1631 cm^{-1} are assigned to the asymmetric stretching and bending vibrations of O-H groups, respectively. Peak at 1091 cm^{-1} originated due the Si-O-Si

asymmetric stretching vibrations [28]. The presence of peaks due to hydroxyl group can be linked with presence of water in the raw material and KBr. Besides, it also represents the presence of silanol functional group (Si-O-H) [29].

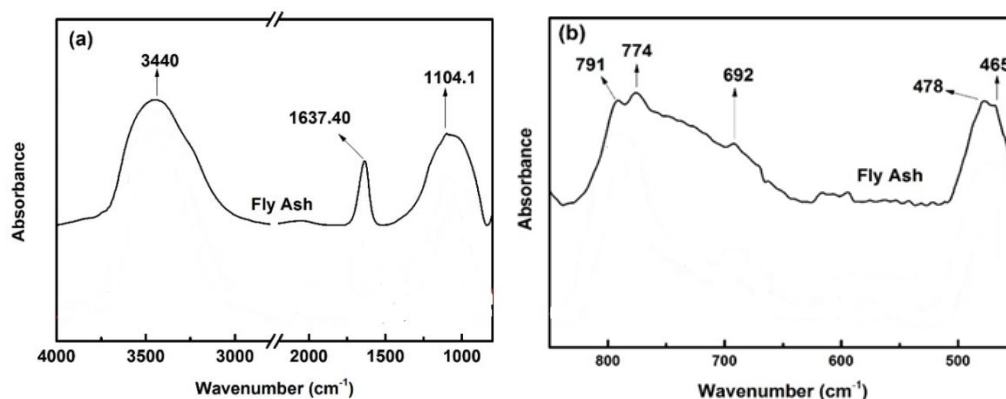


Figure 4. FTiR spectra of fly ash (a) 4000-900 cm^{-1} (b) 900-400 cm^{-1}

4. Conclusion

In this study, fly ash based geopolymers with different Na/Al and water /solid ratios were successfully prepared and synthesized. The samples were then examined under adhesion and flexural analysis. Adhesion strength was much affected with the Na: Al ratio where, there was an increment in adhesion strength up to 4.0 MPA when the ratio increased from 0.60 to 1.20. A similar trend was also observed for flexural strength analysis, in which the strength was much affected by Na: Al ratio. Almost 50% of the increment in flexural strength was obtained by increasing Na: Al ratio to 1.0 and 1.2.

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