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Reviews on Fly Ash based Geopolymer Materials for Protective Coating Field Implementations

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Abstract: Geopolymer is an environmentally cementitious binder that does not require the presence of ordinary Portland cement (OPC). Geopolymer has good advantages include high early strength, low shrinkage, fire resistance and good in chemical resistance. Fly ash, metakaolin, and furnace slag are by-products produced by industry that have been used as raw materials for preparation of geopolymer coating. This geopolymer coating offers an innovative and sustainable solution for maintaining infrastructure and also provides superior thermal, chemical and mechanical performance. The results for geopolymer material for coating implementation showed that it can prevent from corrosion, heat and abrasion resistant. Geopolymer coating material is also high in adhesion strength between existing structures that suitable used for coating field application.

Key words: Fly ash, Metakaolin, Coating, Geopolymer

INTRODUCTION

Geopolymer is one of the green materials that exhibit many exceptional properties such as high compressive strength, low shrinkage, acid and fire resistant (Temuujin *et al.*, 2012). Geopolymer known as inorganic polymer or alkali-activated binder (Davidovits, 1994; Duxson *et al.*, 2007) has gained worldwide interests and its high anticorrosion makes it a novel coating material. Geopolymers are amorphous to semi crystalline three-dimensional silica-aluminate materials. Geopolymer are prepared by activating aluminosilicate sources such as fly ash, furnace slag or metakaolin with alkaline liquid (sodium hydroxide and/or sodium silicate) and curing at a moderate temperature (Temuujin *et al.*, 2012). Geopolymerization process occurred by synthesizing aluminosilicate source materials with alkaline activator liquid to form hydrated product. The materials of geopolymer are a source material from solid phase and liquid phase. Fly ash geopolymers are being used in structural applications such as large concrete column (Hardjito *et al*., 2005). It also has the potential to be manufactured into fire resistant panel (Cheng *et al*., 2003) or as fire resistant coatings on metal (Krivenko *et al.,* 2008). Fly ash based compositions with a molar ratio of Si:Al = 3.5 exhibit strong adhesion to steel substrates and has promising fire resistant characteristics (Temuujin *et al*., 2010). Besides, Davidovits (1994) noted that by increasing the Si:Al ratio, the fire and heat resistant characteristics can be improved. Chemical analysis of fly ash shows silicon axide (SiO2), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3), titanium oxide (TiO_2), etc. as its major constituents.

Thus, the chemical composition of fly ash indicates its coating potential (Davidovits, 1994). For successful long term performance, the coating material itself should be durable, bond well to parent surface and be compatible with parent surface in terms of expansion or contraction during temperature changes (Balaguru, 1998). As a way to produce the metal coatings can withstand high temperature is by the presence of a porous heat insulating layer, designing the coating to release a fire protective atmosphere and also inducing endothermic process that lower the surface temperature (Temuujin *et al*., 2012). According to research study Kong *et al*., (2008) the main mass loss occurred before 130°C and 11% mass loss upon fly ash geopolymer heating. In the meantime, Rickard *et al*. (2010) detected up to 10% mass loss from fly ash geopolymer and it occurred before 200°C and started to stabilize at temperature around 500°C . Cheng and Chiu (2003) fabricate a granulated blast furnace slag based geopolymer for fire resistant application. The geopolymer panel made was exposed to 1100 ^{0}C flame, with the measured reverse-side temperature reaching less than 350 ^{0}C after 35 min. This research showed that geopolymer based material has the ability to withstand fire at high temperature thus allowing it to be made as the coating material purpose of altering its chemical composition in the reaction system.

MATERIALS AND METHOD

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Raw Materials:

Class F fly ash used as aluminosilicate source to produce geopolymer coating material by using various geopolymer compositions sodium hydroxide added to sodium aluminate or sodium silicate solutions. The ratio Si:Al was varied from 1 to 3.5 as way to maintain the molar Na:Al = 1 of all compositions. Table 1 shows the summarized of mix design formulation prepared by Temuujin *et al*. (2010).

Table 1: Mix design of coating composition using different alkaline activator. (Temuujin *et al*., 2010)

Samples	Fly ash, mass %	Sodium aluminate, mass %	Sodium silicate, D-A53, mass %	Sodium silicate, N42, mass %	Sodium hydroxide, pellet, mass %	Deionized water, mass %
FA1	54.03	31.40	-	-	1.52	13.02
FA2	67.57	-	1.06	-	5.86	25.50
FA3	56.92	-	-	26.67	1.80	14.60
FA3.5a	52.84	-	-	36.72	0.20	10.23
FA3.5b	55.38	-	-	38.45	0.20	5.95
FA3.5c	58.09	-	-	40.37	0.20	1.30

Based on research work by Hardjito and Rangan (2005) the ratio of pozzolanic materials/alkaline activator and Na_2SiO_3/NaOH used was 2.5, 3.0 and 3.5 for all mixtures. This ratio produced the highest compressive strength. Alkaline activator solutions were prepared by the dissolution of sodium hydroxide in one liter of distilled water in a volumetric flask to obtain a 12 M concentration. Alkaline activator, which consisted of the combination of NaOH and Na_2SiO_3, was prepared just before it was to be mixed with the fly ash. Table 2 shows the mix proportion design of geopolymer paste material (Mustafa *et al*., 2012).

Table 2: Mix proportion design of geopolymer paste material (Mustafa *et. al*., 2012)

Mixture of geopolymer	Mass Ratios (2.5)	Mass Ratios (3.0)	Mass Ratios (3.5)
Ratio of fly ash/alkaline activator	2.5	3.0	3.5
Ratio Na_2SiO_3/NaOH	2.5	3.0	3.5
Mass of fly ash (g)	1210	1270	1310
Mass of NaOH (g)	137.8	105.5	83.3
Mass of Na_2SiO_3 (g)	344.4	316.4	291.7

Metakaolin (MK) was prepared by calcining the kaolin at temperature 750 °C for 24 hours (Temuujin *et. al*., 2009). The optimal geopolymer type composition for Si:Al ratio was 2.5 and Na:Al = 1 was selected from Temuujin *et al*., (2010) previous work as a good result to implement. The water and cement weight ratio influences the properties of the coatings. The three different water:cement compositions were prepared to study the influences of the ratio. Table 3 summarizes the composition of metakaolin geopolymer coating mixtures (Temuujin *et. al*., 2009).

Table 3: Composition of metakaolin geopolymer coating mixtures (Temuujin *et. al*., 2009)

Samples	Sodium silicate, wt%	Metakaolin, wt%	Sodium hydroxide pallet, wt%	Water, wt%
MK 1	70.24	28.43	0.89	0.42
MK 2	67.64	27.38	0.86	4.09
MK 3	64.56	26.13	0.82	8.47

According to Zhang *et al*. (2010) the combination of granulated blast furnace slag (GBFS) with MK also can be used as raw material to prepare geopolymer coating paste. The mixing was prepared by using sodium hydroxide and distilled water as alkaline activator. The volume stability and the large shrinkage development was modifying and controlled using magnesium oxide (MgO) expansion agent with polypropylene fiber. Combination of this material with alkaline activator to form slurry geopolymer was used as protective coating material especially on the marine concrete application.

Methods:

Fly ash geopolymer coating was prepared by mixing alumino-silicate with the alkaline activator solution by modifying the dissolution of sodium hydroxide in one liter of distilled water in a volumetric flask to obtain a 12 M concentration of NaOH. The geopolymer paste was coated by dipping to the ceramic plates as substrates (Mustafa *et. al*., 2013).

For preparation of MK and combination of MK with GBFS geopolymer coating, Temuujin *et al*. (2009) and Zhang *et al*. (2010) used mild steel plates and stainless steel coated to the geopolymer mixture using dipping coating method. The MK geopolymer mixture was prepared with plates dimensions of 5 x 6 cm. The Si:Al composition for geopolymer prepared from fly ash and MK were 2.5 and 3.5 respectively. While Cheng and Chiu, (2003) mentioned for SiO_2/Al_2O_3 ratio in the range of 3.16-3.46. The ratio of fly ash/alkaline activator to Na_2SiO_3/NaOH use Mustafa *et al*. (2012) was 2.5. Both research using either fly ash or MK was cured at 70 °C for 24 hours after dip coating to substrates. Varied thickness of coating is between 0.2 to 0.5 mm.

RESULTS AND DISCUSSION

The flexural strength of fly ash geopolymer coating samples were measured using mechanical testing with Automatic Max (Instron, 5569 USA) after sintering on temperature 1500 °C tested at day 7 shows the highest strength of 40 MPa (Mustafa *et al*., 2013).

High adhesion strength of coating using MK for fire resistant results showed the performance more than 3.5 MPa using Elcometer 106 equipment. For a coating to be retained and to perform its function, adhesion to the substrate must tolerate mechanical stress, thermal stress, elastoplastic distortions and environment or process fluid displacement. Fly ash coated onto mild steel showed adhesive strength of 2.7 MPa while for stainless steel results 0.25 MPa (Temuujin *et al*., 2009). Figure 1 shows the adhesion between mild steel and stainless steel which exhibit higher adhesion coating on mild steel compared with stainless steel (Temuujin *et al*., 2009). Yong *et al*. (2007) suggested that the growth of synthetic geopolymeric gel is more rapid when placed on an iron substrate due to chemical bonding while the presence of Cr in stainless steel inhibit the growth of geopolymeric and weak bonding was observed.

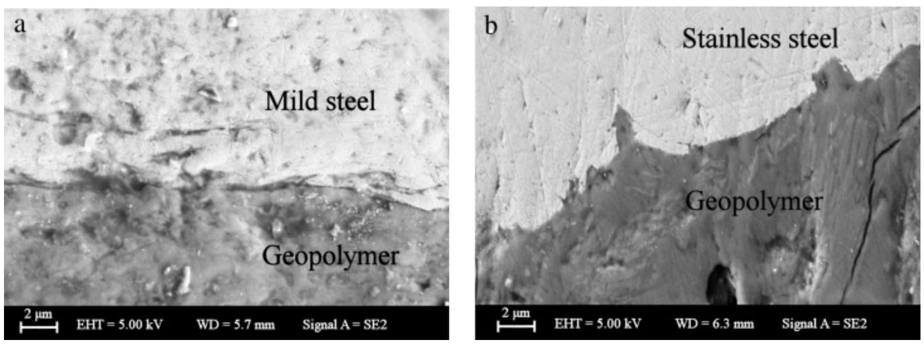

Fig. 1: Adhesion strength interface of geopolymer with steel (Temuujin *et al*., 2009)

The interface bond strength of coating is evaluated by pull-out method. The increasing of power level applied to the coating substrate will increased the strength to maximum value of 34.5MPa. Maximum operating power level exhibited a detrimental effect on the interface strength. The melting fraction and velocity of the particles increased will effects better splashing and mechanical interlocking of molten particles on the substrate surface leading to high adhesion strength (Satapathy *et al*., 2009)

Temuujin *et al*. (2009) mentioned the thermal expansion of geopolymer samples was measured with heating these geopolymer compositions to 1000 °C by gas torch for 30 minutes resulted in formation of sodium aluminosilicate or nepheline. Thermal expansion measurements of the Si:Al = 2.5 composition revealed expansion of up to 6% at 800 °C, while for Si:Al = 1 and Si:Al = 2 compositions up to 4% shrinkage was observed. It showed no crack formation with high structural integrity.

Figure 2 reviewing SEM micrograph of the fly ash shows a composite of an amorphous glassy phase and residual fly ash (Temuujin *et al*., 2010). The compositions exhibited shrinkage with temperature increase up to 820 °C. The metal substrates expand after heated while geopolymer shrink creating of the coating and loss of adhesion. Formation of cracks during heating due to heat flow directly to metal substrate caused loss of strength.

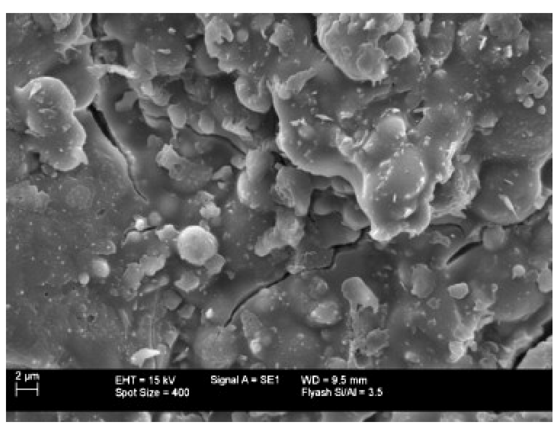

Fig. 2: SEM micrograph of geopolymer fly ash after heating at 820 °C (Temuujin *et al*., 2010)

Mustafa *et al*., (2012) shows in figure 3 the SEM microstructure fly ash particles appear sever damaged while in the high temperature sintering (1500 °C) Fly ash particles shows fine particle with interacted with the alkaline liquids. It is suggest that the coating represents a mixture of semi-reacted amorphous glassy phase and fly ash microspheres (Temuujin *et al*., 2011).

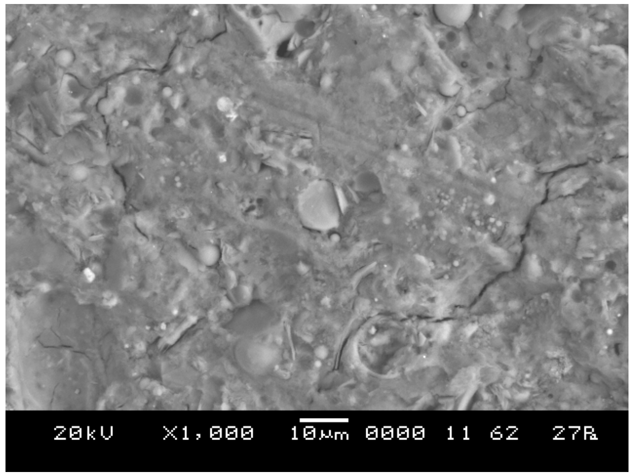

Fig. 3: SEM microstructure of geopolymer fly ash at 1500 °C (Mustafa *et al*., 2012)

Conclusion:

This paper summarized the suitability of geopolymer materials used for coating applications including fire resistance and capacity to encapsulate hazardous waste. Besides, geopolymer coating exhibits excellent properties which offer sustainable solution and environmental friendly for extending the service life of infrastructure and maintenance cost.

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