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## Review on Current Geopolymer as a Coating Material

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**Abstract:** A world towards the concept of sustainable development and environment with low greenhouse gas emissions, zero waste and low energy consumption is an important endeavor. Geopolymer is an aluminosilicate materials occurred by dissolve it in highly alkaline solution then transform into tridimensional tecto-aluminosilicate materials. As an inorganic material, geopolymer has a potential in fire resistant and protective coating for different surfaces including metal and concrete due to their superior mechanical, chemical and thermal resistance properties. With an additional engineering design, in curing and sintering temperature, Si:Al ratio as well as additives used will improve the geopolymer coating properties. The present paper outlines briefly the potential of geopolymer as a coating material to bring the world towards a better future with a reduced carbon footprint.

**Key words:** geopolymer, coating

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### INTRODUCTION

The environmental concerns about the increasingly evident ecological consequences due to human activities have come to worldwide attention. In the early and mid-1980s, *Our Common Future* popularized the concept of sustainable development (Robinson, 2004; Brundtland, 1987). Researchers and industrialists have searched for ways of making industrial processes more sustainable.

Industrial ecology is the most efficient way to achieve sustainable development (Blisset and Rowson, 2012) by using the by-product generated in particular industrial processes which assimilate in other industrial activities. As an example coal combustion in power plant produced fly ash as a by-product and the by-product is assimilate in concrete industry (Mustafa *et. al.*, 2012). This minimizes the overall material and energy consumption as well as reducing the economic costs and environmental pollution.

Rapid development of a country increasingly the greenhouse gasses since a lot of the development use raw materials that emit carbon dioxide, CO<sub>2</sub> into our atmosphere. For example, in cement industry, the production of one ton Ordinary Portland cement (OPC) requires the burning of large quantities of fuel as well as the decomposition of limestone, resulting in nearly one ton of CO<sub>2</sub> (Kong and Sanjayan, 2008). Cement plants have been reported to emit up to 1.5 billion tons of CO<sub>2</sub> into the atmosphere annually (Malhotra, 2002). Therefore, the search for an alternative binder or new material to achieve the concept of sustainable development as to bring no harm to the environment is an important endeavor.

There are several different group of fire proof material including cementitious materials, intumescent paints, fibrous materials, etc (Temuujin *et. al.*, 2011). Among these materials, cementitious materials as an inorganic material and intumescent sodium silicate based paint are both commonly used. Generally, cementitious materials are durable, wear resistant, inexpensive and do not combust when exposed to fire as its coating is thick and heavy. But as they are made from OPC, they will lose strength and will adversely affected by spalling when exposed to fire.

On the other hand, intumescent sodium silicate based paints can be used as thin coatings as its light, aesthetic and smooth. But they are more expensive and often require extensive surface preparations. It also has poor water resistance, low fire rating and may combine with CO<sub>2</sub> to revert back to its original constituents of silica dioxide, SiO<sub>2</sub> and sodium carbonate, Na<sub>2</sub>CO<sub>3</sub> (Horacek, 2000).



Due to environmental concerns, geopolymer as the green material with many exceptional properties including impressive fire resistance, capacity to encapsulate hazardous waste and inexpensive (Davidovits,

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2008) is in great research to fully utilize its usage which as a coating material. Besides, it can also improve the material or object properties such as corrosion resistance, wear, strength as well as preserving the environment.

#### **Processing of Geopolymer Coating:**

In geopolymer based production of its product, the emission of CO<sub>2</sub> is lesser compared to other material production such as the production of geopolymer industrial structure, railway sleepers (Johnson, 2008) and large concrete columns (Hardjito *et. al.*, 2005). As an inorganic polymer it do not preclude the presence of carbon group. Furthermore it does not pose a threat to the environment throughout their life cycle of production, refinement, application and disposal.

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) plus an ability to immobilize toxic and radioactive materials (Xu *et. al.*, 2005).

Mineral polymer is manifest in nature itself in great abundance. 55% of the volume of Earth's crust is composed of sialate-siloxo, Si-O-Al-O-Si-O and sialates, Si-O-Al-O. The process is based on the ability of the aluminium ion, Al<sup>3+</sup> to induce the crystallographic and chemical changes in a silica backbone. These mineral polymers (Davidovits, 1976; Davidovits, 1982) which result from geochemistry or geosynthesis (Davidovits 1988) are latter called geopolymer in 1978 (Davidovits, 1979).

Since 1972, Davidovits, J., showed that the naturally occurring alumino-silicate materials with ceramic like properties such as kaolinite are produced and transformed at low temperature into tridimensional tecto-aluminosilicates in a very short time. This geochemistry rules the synthesis of zeolites and molecular sieves (Barrer, 1957). The process yields nanocomposites (amorphous to semi-crystalline three-dimensional silico-aluminate materials).

Geopolymerization process takes place when reactive aluminosilicate materials with less or no calcium oxide, CaO component (such as metakaolin, fly ash) is rapidly dissolved in highly alkaline solutions, in the presence of alkali hydroxide (sodium/potassium hydroxide, NaOH/KOH) and silicate solution (sodium/potassium silicate, Na<sub>2</sub>SiO<sub>3</sub>/K<sub>2</sub>SiO<sub>3</sub>) to form free tetrahedral units, SiO<sub>4</sub> and AlO<sub>4</sub> in the solution. With the development of reaction, water is gradually split out and these tetrahedral units are alternatively linked to polymeric precursors (-SiO<sub>4</sub>-AlO<sub>4</sub>-, or -SiO<sub>4</sub>-AlO<sub>4</sub>-SiO<sub>4</sub>-, or -SiO<sub>4</sub>-AlO<sub>4</sub>-SiO<sub>4</sub>-SiO<sub>4</sub>-) by sharing oxygen atoms forming amorphous geopolymeric products with a three-dimensional network structure (Zhang *et. al.*, 2009). The geopolymer are then cure at room temperature. The cation (potassium ions, K<sup>+</sup> or sodium ions, Na<sup>+</sup>) present in the framework cavities, balance the negative charge (Davidovits, 1994; Duxson *et. al.*, 2007).

There have been several attempts on formation mechanism has been made since the invention of geopolymers. However, Davidovits believed that the synthesis of geopolymer consist of three steps (Li and Ding, 2001). The first step is dissolution of alumino-silicate under strong alkali solution which includes 8 pathways. In thermodynamic, different pathway can create different ion clusters that directly determine the final properties of geopolymers. Thus, it is very important to understand the actual pathway in order to gain insight into the mechanism of geopolymerization process. The second step is reorientation of free ion cluster and followed by polycondensation process. Up until now, these studies are not done yet. This is because the forming rate of geopolymer is very rapid. As a result, these three steps take place almost at the same time which makes the kinetics of these steps inter-dependent.

According to Geopolymer Chemistry and Applications book (Davidovits, 2011), geopolymerization process with metakaolin, MK-750 involves 3 phases. The first phase is alkaline depolymerization of the poly(siloxo) layer of kaolinite. While the second phase involve the formation of the ortho-sialate (OH)<sub>3</sub>-Si-O-Al-(OH)<sub>3</sub> molecule followed by polymerization (polycondensation) into higher oligomers and polymers.

The geopolymer reaction with NaOH or KOH is as follow. First step is the alkalination and formation of tetravalent Al in the side group sialate -Si-O-Al-(OH)<sub>3</sub>-Na<sup>+</sup>. Then, the alkaline dissolution starts with the attachment of the base hydroxide, OH<sup>-</sup> to the silicon atom, which is able to extend its valence sphere to the penta-covalent state. The subsequent course of the reaction can be explained by the cleavage of the siloxane oxygen in Si-O-Si through the transfer of the electron from Si to O, formation of the intermediate silanol, Si-OH on the one hand, and basic siloxo, Si-O on the other hand.

Next step involve further formation of Si-OH groups and isolation of the ortho-sialate molecule, the primary unit in geopolymerization. Follow by the reaction of the basic Si-O with the Na<sup>+</sup> and formation of Si-O-Na terminal bond. Then, the condensation between ortho-sialate molecules, reactive groups Si-ONa and aluminium hydroxyl OH-Al, with production of NaOH, creation of cyclo-tri-sialate structure takes place, whereby the alkali NaOH is liberated and reacts again and further polycondensation into Na-poly(sialate) nepheline framework.

In the presence of waterglass (soluble Na-polysiloxonate) one gets condensation between di-siloxonate and ortho-sialate-molecules, reactive groups Si-ONa, Si-OH and aluminium hydroxyl OH-Al-, creation of ortho-sialate-disiloxo cyclic structure, whereby the alkali NaOH is liberated and reacts again. Finally, further

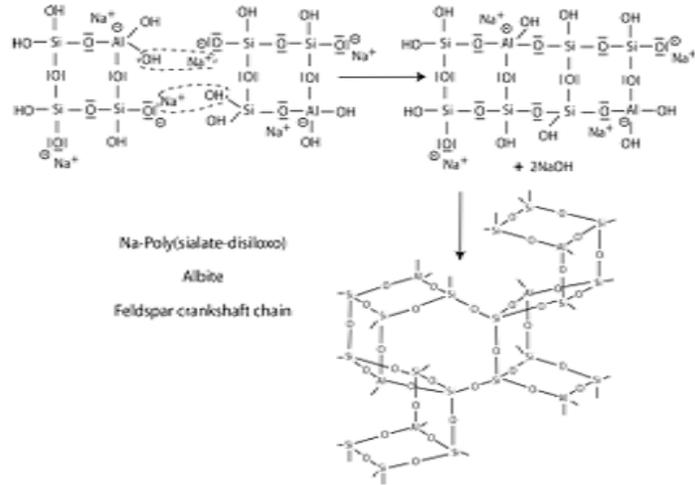
polycondensation into Na-poly(sialate-disiloxo) albite framework with its typical feldspar crankshaft chain structure takes place as shown in the Figure 1 above.

For chemical designation of geopolymers based on silico-aluminates, the term poly(sialate) that is an abbreviation for silico-oxo-aluminate has been proposed. Poly(sialates) are chain and ring polymers with  $Si^{4+}$  and  $Al^{3+}$  in 4-fold coordination with oxygen and their general formula is

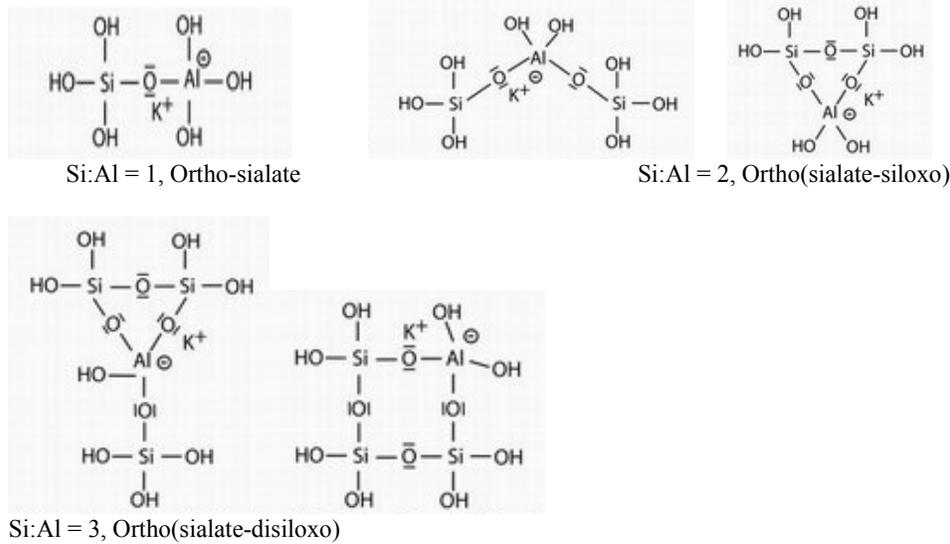


Where

- M = monovalent cation such as  $K^+$  or  $Na^+$
- n = degree of polycondensation
- z = 1,2,3 or  $\gg 3$



**Fig. 1:** Polycondensation into Na-poly (sialate-disiloxo).



**Fig. 2:** Geopolymer Oligomer Molecules.

Chains and rings are formed and cross-linked together always through a sialate, Si-O-Al-O bridge. The amorphous to semi-crystalline three dimensional silico-aluminate structures are illustrated in Figure 2.

Geopolymer is form through geochemical processes of geomolecules during genesis can be classified into two major groups which is pure inorganic and organic containing synthetic analogues of naturally-occurring macromolecules. As we know, geopolymer is proposed as pure inorganic materials but it could be extend to include geomaterials with organic content. The ancient Egyptians used straw and riverine mud containing organics (e.g humic materials) to manufacture construction components of remarkable strength and durability.

Roman concretes also contained mud as a binding agent. Therefore, it should be note the existence of crosslink between inorganic and organic species during geopolymerization (Kim *et. al.*, 2006; Davidovits, 1993).

The materials of geopolymer are a source material from solid phase and liquid phase. From solid phase the material itself should be high percentage of silicon, Si and aluminium, Al. This material can act as geopolymer precursor if it can dissolve in an alkaline solution and geopolymerize. Metakaolin (Kamseu *et. al.*, 2010) produced by calcinations of kaolin at 750°C and fly ash (Wan Mastura *et. al.*, 2013) which contain 40-60% of SiO<sub>2</sub> and 20-30% of Al<sub>2</sub>O<sub>3</sub> is produced by burning pulverized coal are both use for the production of geopolymers. 16 natural Al-Si minerals have been studied by Xu and van Deventer (Xu and van Deventer, 2000) as the potential source for the production of geopolymers.

Geopolymeric material show significant potential for utilization in a number of areas, essentially as a replacement for OPC and also as a relatively inexpensive yet heat resistant ceramic material (Provis *et. al.*, 2006). Other potential applications of geopolymers include stabilization/immobilization of hazardous wastes, surface capping and stabilization of waste dumps, construction of low permeability base liner in landfills, water control structures, and construction of heap leach pads.

In the mining sector, geopolymerisation due to fast setting and high early strength of the paste may be considered in back-fill or cut-and-fill operations (Van Jaarsveld *et. al.*, 2000; Komnitsas *et. al.*, 2007). Geopolymers can even find applications as biomaterials. They have previously been considered for implant applications, where they have shown to be bioactive with low tendency of ion leakage (Jamstorp *et. al.*, 2010; Oudadesse *et. al.*, 2007; Catauro *et. al.*, 2010).

Besides, there are a lot of by-products produced by industry today in huge quantities in every country including mining, metallurgical, municipal, construction and demolition that can also be utilize as a feedstock for geopolymers, such as fly ash, blast furnace slag, bauxite residues and mine tailing. As an inorganic polymer based on synthetic aluminosilicate (Davidovits, 1993) materials, geopolymer has a potential in fire resistant and protective coating for different surfaces including metal (Temuujin *et. al.*, 2010) due to their superior mechanical, chemical and thermal resistance properties (Yong *et. al.*, 2007).

Uncoated material or object does not have a coating applied or covered to the surface of the object. It is generally not as smooth as coated material or object, more porous and tends to have lower fire resistance, corrosion resistance and wettability compare to coat material or object. The uncoated material or object is exposed directly to the harsh condition without any protection, e.g: fire, scratch, corrosion and bad weather. Once the material or object is damaged (crack or corrode) it would be costly to repair thus shortens the service life of the material or object.

However, coated materials or object is covered with a layer of coating material. This coating material protects the material or object from exposed to the harsh condition. Thus, extend the life of the material or object. In National University of Malaysia, Che Haron *et. al.* (2011) found that the 35<sup>0</sup>-diamond-shaped insert with simple grooves of coated carbide tools were superior to the uncoated carbide tools and their flank wear grew smoothly. This research showed that coated material or object is better in its properties compared to uncoated material or object.

Basically, coating is applied to the surface of an object or substrate to improve surface properties of the substrate, such as appearance, adhesion, wettability, corrosion resistance, wear resistance, scratch and also its thermal resistance. Application of the coating also allows the lifespan of existing infrastructure or product to be lengthened as well as reducing the maintenance cost.

Balaguru *et al.* (2008) showed that the used of coating create a graffiti resistant surface by curing the matrix of coating materials to a glassy texture and hence an organic paints do not adhere to the coated surface. These coating used to prevent bad appearances or images of people vandalism while reducing the cost to clean up the graffiti painted.

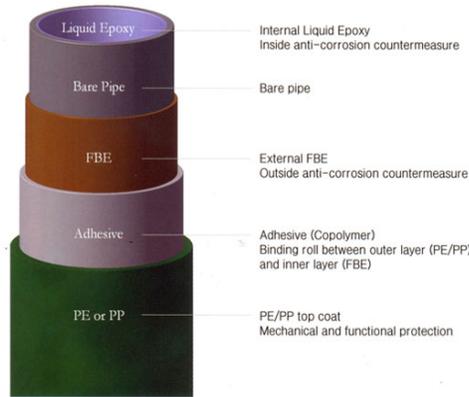
Coating can extend the service life of all polymer structure by improving the surface properties of surface substrate such as ceramic and glass-ceramic coatings used in modern gas turbine (Han *et. al.*, 2011), carbon composite materials with silicon carbide coating in electrolysis (Zhang *et. al.*, 2011), as well as silica coating applied on polished ferrous (Le-Maguer *et. al.*, ). These coating are applied to protect various hot zone components from oxidation, hot corrosive, thermal and thermo-mechanical degradation and thus extend these materials while maintaining or improving its mechanical and physical properties.

In other cases, in particular in marine concrete, the coating applied inhibits the intrusion of corrosive ions. Thus, improve the anticorrosion properties of the marine concrete (Zhang *et. al.*, 2010) while maintaining the concrete properties.

While in Centre of Sustainable Resource Processing, CSR conference, Rickard showed that geopolymers are one possible solution to improve fire protection of an infrastructures and it is more economical since the raw materials for geopolymers used are made from waste product (Rickard and van Riessen, 2008). This unique properties can be applied in coating as it protect the material or object coated as well as used of geopolymer, an inorganic material will lead towards sustainable environment. Figures below show an example of product with and without coating with different material.



**Fig. 3:** Before (a) and after (b) coated with fluoropolymers in protection from seizing, galling, friction and corrosion.



**Fig. 4:** Different type of coating material used.

There are several types of coatings that have been tried as surface protection materials such as acrylic, polyurethane, epoxy, etc (Rodrigues *et. al.*, 2000; Almusallam *et. al.*, 2003; Medeiros and Helene, 2009) . However, these organic coating usually covers on the material surface by physical absorption that makes it caduceus. For a good coating application, the coating material need to be coat on the substrate by both physical and chemical adsorption or bonding which will improve the material protection (Balaguru *et. al.*, 2008).

In order to improve the adhesion of coating material to substrate, the use of an inorganic coating has been proposed to substitute an organic coating. It is well known that geopolymer is an inorganic polymer or alkali activated binders (Duxson *et. al.*, 2007; Davidovits, 1994) has gained worldwide interests and its high anticorrosion makes it a novel coating material. The coating formulation of geopolymer utilizes by-products that would otherwise be disposed of in landfills at a growing cost and liability. Use of the by-product creates the opportunity for carbon offset credits to further enhance profitability.

The geopolymer coating has valuable uses in municipal water systems, industrial applications, transportation projects and petrochemical plants. The coating also offers an innovative, sustainable solution for maintaining infrastructure in a manner that enhances public image and safety while reducing greenhouse emissions.

Geopolymerization process occurred by synthesizing pozzolanic compounds or aluminosilicate source materials such as fly ash, blast furnace slag, bauxite residues, and mine tailing with alkaline activator liquids (sodium or potassium hydroxide) and sodium or potassium silicate. Then the mixture is subsequently mix and cure at a moderate temperature. The geopolymerization process increase when the alkaline activator used consists of soluble silicate; sodium or potassium silicate, rather than alkaline hydroxide alone (Palomo *et. al.*, 1999).

Numbers of research have been done in these past years by using geopolymer based such as metakaolin, fly ash and blast furnace slag in coating (Temuujin *et. al.*, 2012; Zhang *et. al.*, 2010; Cheng and Chiu, 2003). In 2003, Cheng & Chiu fabricate a granulated blast furnace slag based geopolymer for fire resistant application. The geopolymer panel made was exposed to a 1100<sup>0</sup> C flame, with the measured reverse-side temperature reaching less than 350<sup>0</sup> C after 35 min (Mustafa *et. al.*, 2011). This research show that geopolymer based material can withstand fire at high temperature thus allowing it to be made as coating material purpose by altering its chemical composition in the reaction system.

Metakaolin ( China National Materials Group Corp.) and granulated blast furnace slag ( Zhujiqiao cement plant, Anhui, China) were used as coating material for concrete structures which exposed to marine environment. These geopolymer used to inhibit the intrusion of corrosive ions (Zhang *et. al.*, 2010). While Temuujin used metakaolin prepared from Snobrite 65 kaolin from Unimin Corp. Australia (Cheng and Chiu, 2003) and fly ash from Collie thermal power station (Western Australia) (Temuujin *et. al.*, 2010) as a geopolymer based coating on metal substrates. The optimized coating formulation obtained show that these geopolymer have very promising fire resistant characteristics. However, the adhesion properties of metakaolin and fly ash based geopolymer to metal substrate depend on its chemical composition.

In 2012, vermiculite which has a high dehydroxylation temperature up to 800°C were added at 10 mass percent in fly ash based geopolymer coating as a fireproofing agent to geopolymer type composition to improve its thermal resistant properties. For comparison, fine and coarse-ground vermiculite powders sample from South Africa provided by Perlite and Vermiculite Factory (Perth, Western Australia) were prepared and added to the coating formulation. The addition of the coarse-ground vermiculite to the fly ash show greater improvement of fire resistant properties than the addition of the fine-ground vermiculite (Temuujin *et. al.*, 2012).

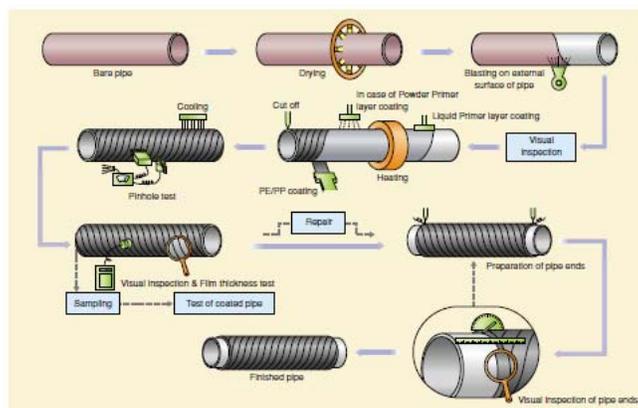
Davidovits suggested that by changing Si:Al ratio, it is possible to regulate the properties of geopolymers. Furthermore, by increasing the Si:Al ratio, the fire and heat resistant characteristics can be improved. The Si:Al composition optimum for geopolymers prepared from metakaolin and fly ash observed by Temuujin were 2.5 and 3.5 respectively. While Cheng mentioned for silica oxide/aluminium oxide,  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in the range of 3.16-3.46, the geopolymer material showed an optimum compressive strength characteristic. However, as the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio increase up to 3.85, the compressive strength decreased (Cheng and Chiu, 2003).

The chemical composition design is the basic key in gaining high compressive strength of geopolymer coating. It includes the NaOH molarity,  $\text{Na}_2\text{SiO}_3/\text{NaOH}$  ratio, geopolymer/alkaline activator ratio and curing temperature. Mustafa *et. al.* (2011) in his study revealed that a 12M NaOH solution and the combination of geopolymer/alkaline activator with  $\text{Na}_2\text{SiO}_3/\text{NaOH}$  of 2.0 and 2.5 respectively produced the compressive strength as high as 70 MPa (Mustafa *et. al.*, 2012). This indicate that the chemical composition plays an important role in obtaining desirable compressive strength as well as other properties.

There are several coating method that can be used such as dipping (Temuujin *et. al.*, 2009), spraying (Temuujin *et. al.*, 2010) and also painting (Balaguru *et. al.*, 2008). However, by spraying a strong uniform coating can be applied to a substrate and further increase the adhesive strength. The ease with which geopolymer can be applied onto substrate surfaces depend on the water content formulation. The water added into a starting mixture is to increase the flow ability. But, it decreased the geopolymerisation reaction and did not give beneficial thermal-resistant properties. For geopolymer coating preparation, it is important not to increase water content instead it may be better to use additives such as plasticizers to increase the flow ability of the coating material.

Another coating method that can be used is extrusion. For example, JFE Steel Corporation company [53] managed to develop a high quality polyethylene, PE or polypropylene, PP coated steel pipe for the transmission of gas, oil, water and other fluids with strong adhesion, excellent impact resistance, excellent bendability, easy repair and highly resistant to corrosion from moisture and chemicals. JFE external coating pipe is produced by a process of coating with a primer and PE or PP layer for small and medium diameter by extruded method and for large diameter line pipe by the spiral wrapping method. The tensile strength pipes coated with PE reaches 19 MPa and for PP reaches 33 MPa.

Figures below show an example of pipe coating method by extrusion process (JFE Steel Corporation company). The pipes coating involved two steps: First step is external coating (Figure 5, Figure 6) while the second step involve internal coating (Figure 7).



**Fig. 5:** External coating.

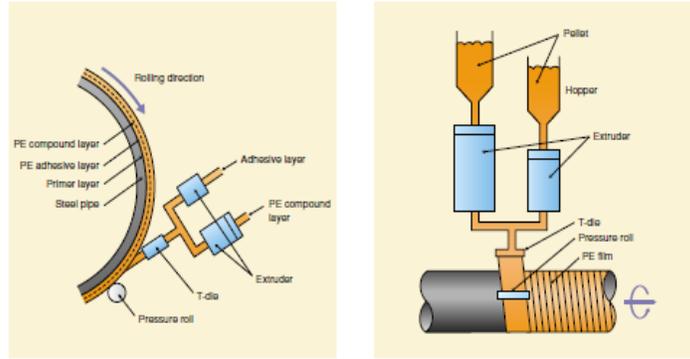


Fig. 6: External coating.

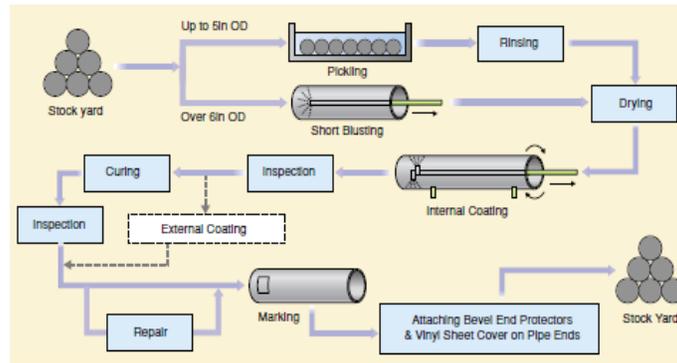


Fig. 7: Internal coating.

The testing method use in previous research was setting time test of fresh geopolymer paste by the Vicat method (ASTM C191) (Zhang *et. al.*, 2010). A Vicat needle was used to measure the geopolymer setting time. Both initial setting time and final testing time were tested. The crystalline phases were identified from X-ray diffraction (XRD) patterns obtained with a Bruker D8 Advance Diffractometer slipped with LynxEye detector using Cu-K $\alpha$  radiation. Diffraction patterns were collected from 10<sup>0</sup> to 80<sup>0</sup> 2 $\theta$ . The step size was 0.02<sup>0</sup> 2 $\theta$  with a scan rate of 0.6<sup>0</sup> 2 $\theta$  per minute. Automated phase identification software (EVA 2, Bruker) was used to analyse the diffraction patterns.

Geopolymer fracture surfaces were studied with a Zeiss EVO 40XVP scanning electron microscope with EDS X-ray detector (Energy Dispersive Spectroscopy, Oxford Instrument). The adhesive strength of the coated samples was measured with an Elcometer 106, adhesion tester according to ASTM D4541. Australian standard 1530.4 was used for measuring the heat insulating characteristics of the coatings. Using a custom made gas heating rig, the standard time/temperature curve (Eq. 3) was followed as closely as possible.

$$T = 345 \log_{10} (8t + 1) + 20 \tag{3}$$

Where T device temperature in <sup>0</sup>C at time t (min) form ignition of the heating rig.

Thermal expansion or shrinkage of geopolymer samples was measured with a DI-24 Adamel Lhomargy dilatometer (Roissy En Brie, France). In order to make the sample hard enough for cutting with a diamond-tipped blade, the cast sample were cured at 70<sup>0</sup>C over night. Measurement was conducted according to ASTM E831 over a temperature range of 20<sup>0</sup>C-900<sup>0</sup>C with a heating rate of 5<sup>0</sup>C/min. The average of the measurements was used as the representative dilatometric curves, and all results lay within a 15% standard deviation. The compressive strength of the geopolymer coating composition was measured by using an Instron-5500R testing machine

Given the stone-like property of geopolymer, permeability was measured by Darcy method, which is usually used to test the core in mining drill engineering. Sample of 3d aged was laid in pressure cabin and then distilled water was pressed to permeate through. The surrounding pressure was 3 MPa higher than the driven pressure to avoid water going through along the surface of sample. The permeated water over a period of time

was recorded till the permeation was steady. Permeability was calculated according to the following formula (API Production Department, 1988) :

$$k = 10^5 \cdot Q \cdot \mu \cdot L / (A \cdot \Delta p) \quad (4)$$

in which:

- k permeability coefficient ( $\mu\text{m}^2$ );
- Q velocity of permeated liquid (ml/s);
- $\mu$  viscosity of permeated liquid (Pas);
- L length of sample, fixed at  $3.50 \times 10^{-2}\text{m}$ ;
- A sample cross-section area,  $4.91 \times 10^{-4}\text{m}^2$ ;
- $\Delta p$  liquid pressure, set at  $2 \times 10^7$  Pa.

Anticorrosion was mainly evaluated by the variation of compressive strength under three different curing conditions at  $20 \pm 2$  °C: air (RH =  $90 \pm 5\%$ ), seawater and dry-wet cycle. Dry-wet cycle was carried out circularly by 12 h air curing and 12 h emerging in seawater. Concentrated Moclodon artificial seawater ( 3-fold concentration) was prepared as the reinforced corrosion medium. Specimens were tested on WHY-200 Auto Compressive Resistant Tester ( Shanghai Hualong, China) at different curing ages.

The testing formulas for physical property tests such as water adsorption rate and volumetric density were evaluated according to the Archimedes method. Water resistance of the coated samples were tested by a static immersion test (Wang *et. al.*, 2006) which comprises immersion of the coated samples in distilled water at 25°C and weighing after every 24 h after drying at 40°C for 1 h. Mass change versus immersion time was evaluated up to 72 h immersion.

For fire resistant tests, a 10mm thick geopolymer panel was exposed to an 1100°C flame. The reverse-side temperature of the panel was measured and recorded (Davidovits, 1999b). The thermogravimetric analyzer, TGA measurements were performed on thermogravimetric analyzer/differential scanning calorimetry, TGA/DSC1 Mettler Toledo equipment. Approximately, 20 mg of crushed powder was used for heating up to 1,000 °C using a heating rate and starting temperature at 10°C/min and 50°C, respectively. Measurements were performed in air.

The relative effects of mechanical bonding and chemical bonding of substrate coated with geopolymer. The substrates rods were embedded in the center of a mortar cylinder that was 38.1 mm tall and 57.2 mm in diameter. The mortar was prepared from a mixture of water, Type I cement, and sand in the proportions 0.485:1.0:2.75, respectively, following the ASTM C109 guidelines. Fresh mortar was poured around the steel rod to fill up the polypropylene container, and each container was tapped and vibrated to remove entrapped air from the mortar prior to consolidation.

Prior to testing, all samples were kept in a 100% humidity environment at room temperature ( 20°C ) and cured up to 97 days. After curing, each cylinder was removed from its container and the bond strengths were determined using the pin-pull testing configuration. The steel rod was pulled out of the mortar at a strain rate of 50mm per minute in displacement control. Both the applied load and the slip between the rod and mortar were monitored with a built-in load cell and a built-in linear variable differential transformer (LVDT).

These testing used to prove and measure the ability of geopolymer materials to be used as a protective coating on a different substrate.

#### ***Properties of Geopolymer Coating:***

For coating applications, the adhesive force of the geopolymer based coating to substrate is very important achieving the highest value in order to improve anticorrosion, fire and heat resistant, hardness as well as extending the service life of the material. This is believed to be strongly influenced by the formulation of the geopolymer (Temuujin *et. al.*, 2009) the coating formulation is calculate by taking note the content and composition of the amorphous part of the geopolymer used.

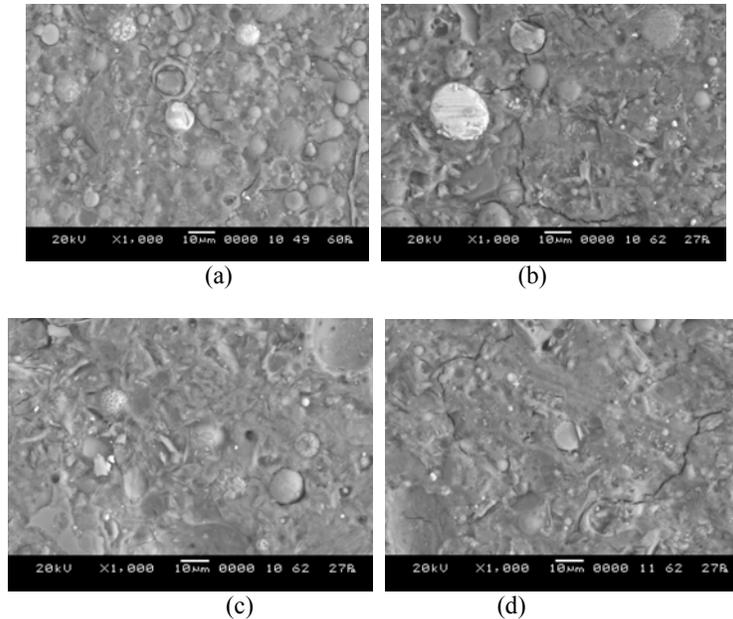
Scanning electron microscopy, SEM observations showed that the geopolymer bonding to steel was strong and likely to be physical adhesion. Heating these geopolymer compositions to 1000°C resulted in formation of sodium aluminosilicate or nepheline (Temuujin *et. al.*, 2009). The expansion of this geopolymer to temperature provided a level of matching with the thermal expansion of the substrate resulting in maintenance of the structural integrity of the coating. In order to achieve high adhesion strength between the substrate and coating material, the bonding needs to be chemical adhesion.

Temuujin *et. al.* (2010) showed that the best adhesive strength observed was for high silica containing composition (Si:Al = 3.5 ratio) which higher than 3.5 MPa and to achieve a greater fire insulating capacity the coating thicknesses should be increase. The substrate used also affect the adhesion strength of geopolymer coating material. The fly ash sample which is coated onto polished mild steel showed an adhesive strength of 2.7 MPa which is 0.5 MPa lower than non-polished mild steel substrate indicating that surface roughness

influences adhesion strength. Microstructure evolution and thermal properties of the optimized coating formulation show that they have very promising fire resistant characteristics.

Curing and sintering conditions also have a significant effect on the development mechanical strength in most cementitious systems. Mustafa et. al. (2013) studied on fly ash from Manjung power station in Lumut, Perak to produce as geopolymer coating paste. The geopolymer paste was sintered using temperature range from 600°C to 1500°C showed an increase in strength up to 40 MPa after 7 days.

According to SEM observation (Figure 8), the geopolymer coating at 600°C show sever damaged of fly ash particles while in the high temperature of sintering which is 1500°C shows an interaction between fly ash fine particles with the alkaline liquids. It is suggest that the coating represents a mixture of semi-reacted amorphous glassy phase and fly ash microsphere (Temuujin *et. al.*, 2011). Therefore, geopolymer materials is possible to be use as a coating in high temperature application as it can withstand a maximum temperature of approximately 1600°C (Cheng and Chiu, 2003).



**Fig. 8:** SEM image of geopolymer coating after sintering at certain temperature (a) 600°C, (b) 900°C, (c) 1200°C, (d) 1500°C, [56]

Geopolymer produced with fly ash/alkaline activator ratios in the range of 1.4-2.3 shows high compressive strengths, ranging from 42-52 MPa (Mustafa *et. al.*, 2011). The geopolymer system is exposed to high temperature (800°C) showed an increased in compressive strength up to 80 MPa. The strengths gain within 1-3 days. High compressive strength of 71.04 MPa is achieved for curing temperature of 60°C. While the porosity or permeability is less than 20% which is lower than OPC (Daniel *et. al.*, 2007).

The shrinkage of the geopolymer coating material to concrete structure was controlled by using PP fiber and self-prepared magnesium oxide, MgO expansion agent, later of which could produce a shrinkage compensating effect (Zhang *et. al.*, 2010). A previous research found that appropriate addition of PP fiber decreased not only the compressive modulus but also the large shrinkage of geopolymers (Zhang *et. al.*, 2009b).

In general, geopolymers intended for structural application with low Si:Al ratio, shrink with heating. However, the geopolymer-type coatings with high Si:Al ratio, expand with heating (Provis *et. al.*, 2009). In order to apply geopolymer as an innovative coating material, solving the volume shrinkage is the key work.

**Conclusion:**

As conclusion, geopolymer based materials exhibit an excellent properties which can be used as a protective coating material. This material also offers an innovative, sustainable solution for maintaining or extending the service life of an infrastructure at a moderate cost while reducing greenhouse emissions. However, there is lack of research on the geopolymer coating and it has not been popularize yet. It may still need additional engineering properties such as the use of new additives, processing and sintering temperature as well as geopolymer coating material in nanosize in order to improve properties of the coating material. On the other hand, the use of geopolymer as an inorganic and green material will lead the world towards sustainable environment with zero waste.

## ACKNOWLEDGMENTS

This study was supported by Center of Excellence Geopolymer and Green Technology UniMAP and School of Material Engineering, UniMAP. The authors of this research are very grateful to King Abdul Aziz City Science and Technology (KACST) for the financial support of this study.

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